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RESEARCH REVIEW 17

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FOREWORD

The Seventeenth Annual **Research Review** describes the ongoing research programme in the School of Biosystems Engineering at University College Dublin from over 74 researchers (10 academic staff, 2 technicians, 21 postdoctoral researchers and 41 postgraduates). The research programme covers three focal areas: Food and Process Engineering; Bioresource Systems; and Bioenvironmental Engineering. Each area is divided into sub-areas as outlined in the Table of Contents which also includes the name of the research scholar (in bold); the research supervisor(s); the title of the research; the nature* of the research programme; and the research sponsors. It also includes the noting of four awards for presentational excellence at the Seventeenth Annual **Biosystems Engineering Research Seminar** held in University College Dublin on **Thursday 15th March 2012**.

The four Appendices in the Review provide:

- a listing of research projects in progress which were not included in the Review;

- profiles of Postdoctoral Research Scholars;

- a photographic record of postgraduate students; and

- a photographic record of the full-time staff who assisted in project supervision and administration.

The Editors gratefully acknowledge the dedicated work of the individual research scholars, their research supervisors and the financial support of research sponsors. Suggestions as to how future editions might be improved in presentation, style or content would be greatly appreciated.

ENDA CUMMINS and TOM CURRAN   10 May 2012

*MEngSc1, MSc1, MAgrSc1 = Research Masters (Mode 1)
  MEngSc2, MSc2 = Taught Masters (Mode 2)

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APPENDICES

NON-DESTRUCTIVE EVALUATION OF APPLE QUALITY BY HYPERSPECTRAL IMAGING

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Abstract

A hyperspectral NIR imaging system was tested to evaluate the apple quality non-destructively. The study was carried out in the near infra-red (NIR) region (900- 1700 nm). Hyperspectral images were acquired for apple fruits and their spectral data were registered and analyzed. The acquired images were processed using the image processing software ENVI. Results indicated that the hyperspectral technique can be applied for the fast and non-destructive assessment of apply quality evaluation.

Introduction

During the past few decades a number of different techniques have been explored as possible instrumental methods for quality evaluation of food products. In recent years, hyperspectral imaging techniques have been regarded as a smart and promising analytical tool for analyses conducted in research, control, and industries. Hyperspectral imaging is a technique that generates a spatial map of spectral variation, making it a useful tool in many applications (ElMasry & Sun, 2010).
The use of hyperspectral imaging for both automatic target detection and recognizing its analytical composition is relatively new and is an amazing area of research. A hyperspectral system integrates both spectroscopic and imaging techniques to enable direct identification of different components and their spatial distribution in the tested sample. A hyperspectral imaging system produces a two dimensional spatial array vectors which represents the spectrum at each pixel location. The resulting three-dimensional dataset containing the two spatial dimensions and one spectral dimension is known as the datacube or hypercube (Chen et al., 2002; Kim et al., 2002; Mehl et al., 2004; Schweizer& Moura, 2001). The advantages of hyperspectral imaging over the traditional methods include minimal sample preparation, nondestructive nature, fast acquisition times, and visualizing spatial distribution of numerous chemical compositions simultaneously. The hyperspectral imaging technique is currently tackling many challenges to be accepted as the most preferable analytical tool in identifying compositional fingerprints of food products and their authentication. The need for fast and reliable methods of authenticity and object identification has increased the interest in the application of hyperspectral imaging for quality control in the agricultural, pharmaceutical, and food industries. Moreover, enhancement in instrumental developments, the availability of high-speed computers, and the development of appropriate chemometric procedures will allow this technique to be dominant in the future.
The objective of this study is to evaluate different apply quality traits non-destructively using hyperspectral imaging.

Materials and Methods

NIR hyperspectral imaging system
A laboratory hyperspectral imaging system in the NIR range (900–1700 nm) was used to acquire images of the apple sample in the reflectance mode. The system consisted of a 12-bit CCD camera, along with a standard C-mount lens, a spectrograph, an illumination unit of two 500-W tungsten halogen lamps, a translation stage and a computer supported with a data acquisition and control software.
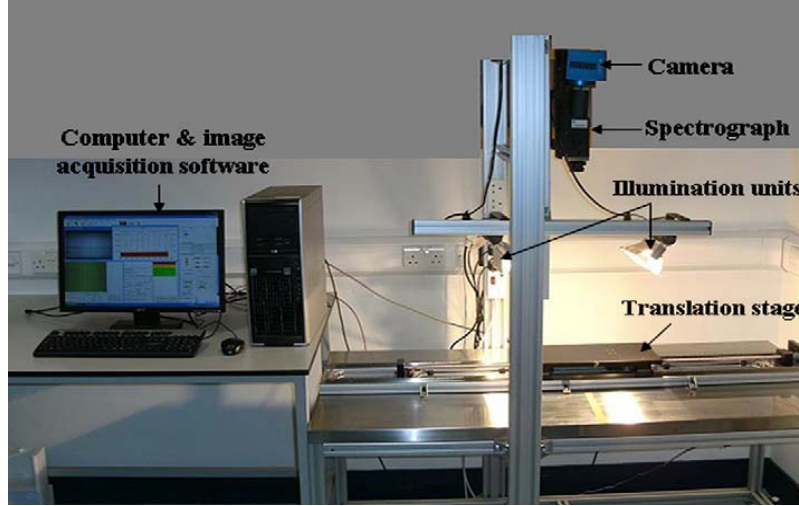
Figure 1: Hyperspectral Imaging System setup

Image acquisition and reflectance calibration
The image was acquired at room temperature where the sample was placed on the translation stage and the limits for scanning were adjusted using software controls. Upon adjusting the limits and scanning the object, the hyperspectral images of the sample was acquired. The captured images were calibrated and optimized due to the dark effect of the camera and to obtain the required reflectance by applying the equation

$$R= (R_o-D)/ (W-D) \tag{1}$$

Where R is the required reflectance corrected image, R_o is the raw image of the apple sample, D is the dark image and W is the white reference image. The dark image of 0% reflectance was acquired with camera lens covered and the light was entirely off, and the white image of 99% reflectance was acquired for a standard white Teflon tile.

Image segmentation and spectral data extraction

Following the image calibration, the image was segmented to separate the apple fruit from the background. First, the background was isolated from the sample by subtracting a low–reflectance band from a high-reflectance band, after which a thresholding was done with a value of 0.12. This step resulted in the image being segmented from its background. Then a region of interest (ROI) was chosen in order to obtain the spectral data from the sample.
The spectral data was obtained from the region of interest, by using the active region (white pixels) from the sample and the spectral profile was observed.

Results and Discussion

As shown in figure 2, the hyperspectral image of apple samples exhibited different intensities at different wavebands.The substantial data residing in each image require a deep investigation and analysis to extract the most valuable information from the images.
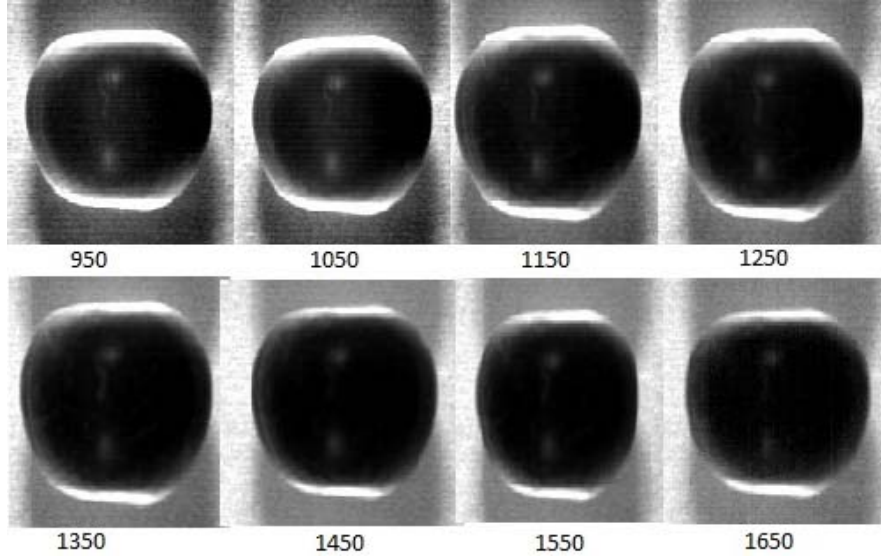
Figure 2. Hyperspectral image of the apple samples at different wavelengths.

Image segmentation and data extraction
To start processing the image, apple was isolated and segmented from its background and the spectral data were then extracted from the main region of interest (ROI) of the image as shown in Figure 3.
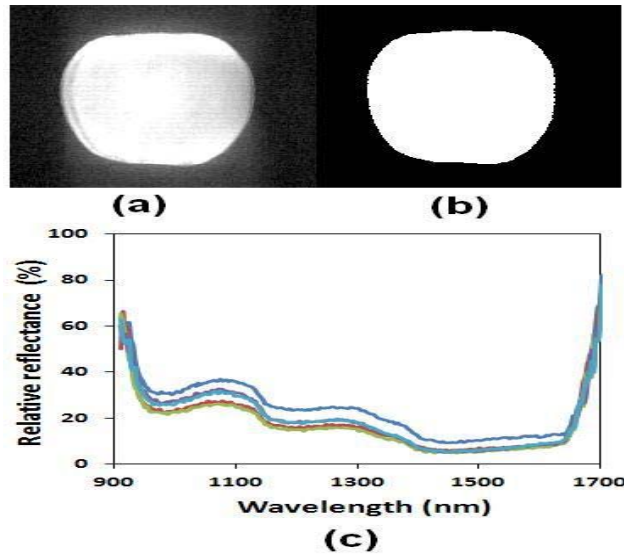
Figure 3. Processing of hyperspectral image (a) subtraction step between high and low reflectance bands,(b) segmentation step of the image to isolate apple sample from the background and (c)extracted spectral data from ROI.

Conclusions

This study has showed the application of NIR hyperspectral imaging system for quick and non-destructive evaluation of the sample. Industries can adopt this technique for quickly evaluating the food items without much of effort, before the food is being distributed to retail stores or super-markets.

References

Barbin, D.F.; ElMasry, G.; Sun,D-W. and Allen, P. (2011). Prediction of Pork Sensory Attributes Using NIR Hyperspectral Imaging Technique, *Biosystems Engineering*, 16, 9-12.

Chen, Y.-R.; Chao, K.; Kim and M. S. (2002). Machine vision technology for agricultural applications. *Computers and Electronics in Agriculture, 36(2), 173–191.*

Elmasry, G. & Sun, D.-W. (2010). Principle of Hyperspectral Imaging Technology, *Hyperspectral Imaging for Food Quality Analysis and Control, pp. 3-43,* Academic Press, Elsevier.

Gowen, A.A.; O'Donnell, C.P.; Cullen, P.J.; Downey, G. and Frias, J. (2007). Hyperspectral Imaging- an emerging process analytical tool for food quality and safety control, *Trends in Food Science & Technology, 18, 590-598.*

Kamruzzaman, M.; Elmasry, G.; Sun,D-W. and Allen, P. (2012) Prediction of some Quality Attributes of lamb meat using near-infrared hyperspectral imaging and multivariate analysis, *Analytica Chimica Acta, 714(2012), 57-67*

Kim, M. S.; Chen, Y. R.; Mehl and P. M. (2001). Hyperspectral reflectance and fluorescence imaging system for food quality and safety. *Transactions of the ASAE, 44(3), 721–729.*

Mehl, P. M.; Chen, Y. R.; Kim, M. S. and Chan, D. E. (2004). Development of hyperspectral imaging technique for the detection of apple surface defects and contaminations, *Journal of Food Engineering, 61, 67–81.*

Nicolai, B.M.; Lotze, E.; Peirs, E.; Scheerlinck, N. and Theron, K.I(2006)Non-destructive measurement of bitter pit in apple fruit using NIR hyperspectral imaging, *Postharvest Biology & Technology, 40(2006) 1-6*

Schweizer, S. M. and Moura, J. M. F. (2001). Efficient detection in hyperspectral imagery. *IEEE Transactions on Image Processing, 10, 584–597.*

APPLICATION OF HYPERSPECTRAL IMAGING TECHNIQUE FOR NON-DESTRUCTIVE PH PREDICTION IN SALMON FILLETS

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Abstract

Hyperspectral imaging (HSI) techniques in the wavelength of 400−1000 nm was applied for rapid and non-destructive measurement of pH value in salmon fillets. Spectral signatures were extracted and analyzed by partial least-squares regression (PLSR) to correlate spectral data of fillet samples with its pH values estimated by using a pH meter. Important wavelengths were selected by analyzing loading weights of PLSR model to build a simple PLSR model. The new PLSR model led to a correlation coefficient (R_{CV}) of 0.852 and root-mean-square error estimated by cross-validation (RMSECV) of 0.050. The results showed that hyperspectral imaging technique was suitable for rapid and non-destructive assessment of pH value in salmon fillets.

Introduction

Hyperspectral imaging (HSI), which integrates two well-known techniques of spectroscopy and imaging in one system, enables simultaneous acquisition of both spectral and spatial information from an object (Grahn & Geladi, 2007; Elmarsry & Sun, 2010). With the advancement of instrument and computing power, HSI has emerged as a novel, rapid and non-destructive tool for quality and safety evaluation of food and food products. (Elmasry *et al.*, 2008; Taghizadeh *et al.*, 2009; Elmasry & Sun, 2010; Wold *et al.*, 2011). Salmon is among the highest-value aquatic food product categories in global markets. Salmon products with high quality and safety are always expected and demanded by consumers. With such increased expectations, the need for accurate, rapid, and objective quality determination of quality attributes continues to grow (Sigurgisladottir *et al.*, 1997). However, the lack of rapid, reliable and non-destructive methods for determining quality characteristics in the salmon fillets has been one of the main obstacles for the development of quality control in the salmon industry. Conventional analysis methods involving manual and instrumental performance have some disadvantages with the procedure being either subjective or destructive. As an important quality characteristic of fish, pH value closely relates with protein, fat and other quality attributes. Generally, pH is measured by using a pH meter, which is however invasive and time consuming, and not suitable for the situation when large amounts of samples are required to be measured. Moreover, the pH measurement using a pH meter cannot visualize the pH distribution within salmon fillets, which is critical and necessary for the quality and safety inspection and control of salmon products for the Irish salmon industry. Therefore, the development of rapid and accurate quality inspection techniques with the function of visualizing attribute distribution is important for the Irish salmon industry to ensure the quality assurance of salmon products.

Recent years, HIS has been emerged and considered as a powerful alternative to pH meter for the quality measurement of salmon and other fish. Some applications in the use of HSI for the quality evaluation of fish have been investigated (Wold et al., 2006; Heia et al., 2007; Elmasry & Wold, 2008; Segtnan et al., 2009; Sivertsen et al., 2011). Given the limited information on the usefulness of hyperspectral imaging systems to predict pH of fish products, **the main aim of this study was to investigate the potential of using HSI technique as a rapid and non-invasive tool for predicting pH of salmon fillets. Quantitative models are established between hyperspectral images and reference pH values measured by using a pH meter.**

Materials and Methods

Samples preparation
Eighteen fresh salmon fillets without bone were collected from several local supermarkets in Dublin, Ireland, which included four salmon fillets (farmed in Scottish), six organic salmon (*Salmo salar*) fillets (farmed in Inishfarnard, Ireland) and eight Atlantic salmon (*Salmo salar*) fillets (farmed in Norway)

Hyperspectral imaging system
The system used for acquiring hyperspectral images consisted of Specim V10E spectrograph (Spectral Imaging Ltd., Oulu, Finland) covering the spectral range of 400–1000 nm (spectroscopic resolution of 5 nm), a CCD camera (Basler A312f, effective resolution of 580×580 pixels by 12 bits), objective lens (25mm focal length), illumination source (150W halogen lamp source attached to a fiber optic line light positioned at an angle of 48° to the moving table), mirror, a moving table, acquisition software (SpectralScanner, DV Optics, Padua, Italy) and PC.

Reflectance Calibration and Images Acquisition
Before image acquisition, reflectance calibration was carried out to account for the background spectral response of both the instrument ("W") and the "Dark" camera. The corrected reflectance value ("R") was calculated from the determined signal ("I") in a pixel-by-pixel basis as indicated by:

$$R_i = \frac{I_i - Dark_i}{W_i - Dark_i}$$

where *i* is the pixel index, i.e. *i*=1,2,3…,n and n is the total number of pixels within the region of interests (ROIs).
Eighteen hyperspectral images of salmon fillets were acquired with the system (room temperature 20℃ and relative humidity 50%), and data were recorded in units of reflectance and saved in computer.

pH Measurement
After image acquisition, each fillet was cut into rectangular shapes with dimensions of $2 \times 2 \times 1.5$ cm at different locations for pH measurement, resulting in a total of 157 subsamples available. Reference pH value of each subsample was measured using a portable pH meter (model 1212000, Thermo Orion, U.S.A.) at room temperature. The reference values of pH measured at different locations of salmon fillets are varied between 6.29 and 6.73 with a mean value of 6.43 and standard deviation of 0.10.

Data analysis
Average spectra of each cubed subsample were extracted from the same position within its corresponding hyperspectral image using the Region of Interests Function (ROI) of ENVI v4.6 software. Partial least-squares regression (PLSR) was used to establish the quantitative relationship between the extracted spectral data and the reference pH values measured by the pH meter.

Results and Discussion

Prediction of pH by PLSR and wavelength selection
PLSR model was first established for predicting pH valve in salmon fillets by using the full spectral range of 400-1000 nm with the variable number of 121 (Fig. 1). After full-cross validation, a good result was obtained with regression coefficient (R) of 0.894 for calibration process (R_C) and of 0.870 for validation process (R_V). Low RMSEC of 0.043 and RMSECV of

0.047 were also achieved and their small difference shows the established PLSR model was not overfitted.

Indeed, because the contiguous variables (wavelengths) contain a great degree of dimensionality with redundancy, optimal wavelengths/variables that carry the most useful information should be selected for simplifying the model calibration process. Moreover, on the basis of the selected wavelengths/variables, an optimized multispectral imaging system could be developed, which would have a lower price and higher speed than a hyperspectral imaging system.

By analyzing loading weights of the above established PLSR model, six individual wavelengths (440, 605, 685, 735, 795, and 850 nm) were identified as optimal wavelengths for the pH determination of salmon fillets. A new PLSR model was then established based on the selected variables. Compared to the result of the PLSR model which was established using the spectra within the full range wavelength, similar result was achieved by the new PLSR model with R_C and R_V of 0.863 and 0.852, respectively. The new PLSR model also had a small difference between RMSEC and RMSECV of 0.002, showing the model was not overfitted too. Moreover, more than 95% of variables were eliminated (6 vs 121) and the performance of new PLSR model was similar to full spectral model, showing that the analysis of loading weights for the optimal variable selection was efficient in this study.
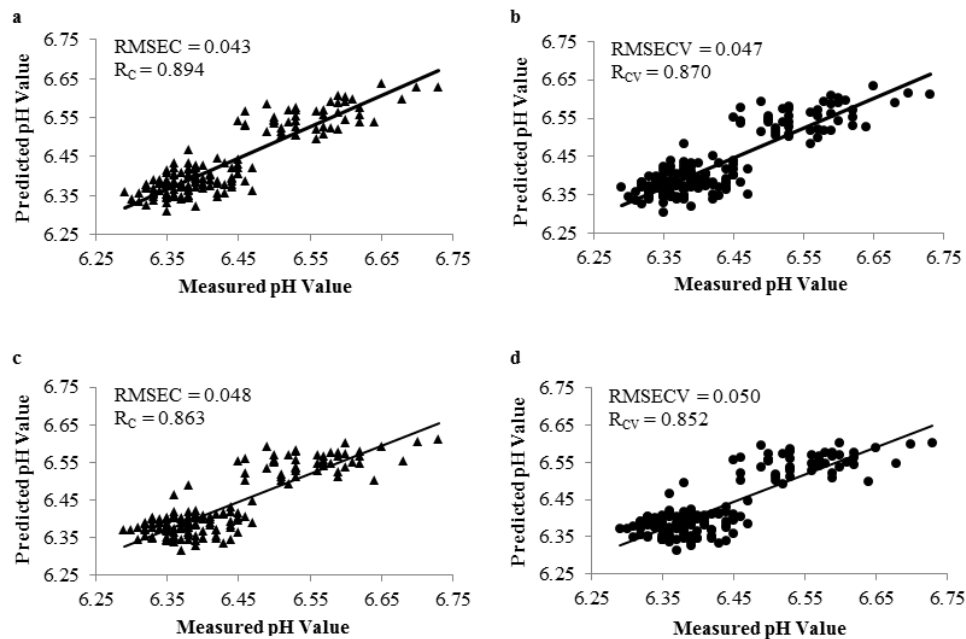
Figure 1. PLSR model for predicting pH value in salmon fillets. (a) Calibration model with full spectral range, (b) Cross validation model with full spectral range, (c) Calibration model with important wavelengths, (d) Cross validation model with important wavelengths.

Conclusions

A hyperspectral imaging system in the visible and NIR region of 400-1000 nm was developed to predict pH value in salmon fillets. Out of 121 wavelengths, only six wavelengths were selected by analyzing loading weights. The PLSR models were established for predicting pH values based on either full range spectra or spectra at optimal wavelengths. The overall results show a potential of applying hyperspectral imaging technique for rapidly and non-destructively predicting pH of salmon fillets.

References

ElMasry, G., Wang, N., Vigneault, C., Qiaoa, J., & ElSayed, A. (2008). Early detection of apple bruises on different background colors using hyperspectral imaging. LWT. 41: 337–345.

Elmarsry, Gamal, & Sun, D. W. (2010). Meat quality assessment using a hyperspectral imaging system. In: Hyperspectal Imaging for Food Quality Analysis and Control.(chapter 6) (pp.175−240). Academic Press/Elsevier, San Diego, California, USA.

Elmarsry, Gamal, & Sun, D. W. (2010). Principles of Hyperspectral Imaging Technology. In: Hyperspectal Imaging for Food Quality Analysis and Control.(chapter 6) (pp.3−43). Academic Press/Elsevier, San Diego, California, USA.

Elmasry G., & Wold, J. P. (2008). High-speed assessment of fat and water content distribution in fish fillets using online imaging spectroscopy. J. Agric. Food Chem., 56: 7672–7677.

Grahn, H. and Geladi, P. (2007) Techniques and Applications of Hyperspectral Image Analysis (John Wiley and Sons, Chichester, 2007), 1st ed.

Heia, K., Sivertsen, A., Stormo, S., Elvevoll, E., Wold, J., & Nilsen, H. (2007). Detection of nematodes in Cod (Gadus morhua) fillets by imaging spectroscopy. Journal of Food Science. 72(1): E011−E015.

Segtnan, V. H., Høy, M., Lundby, F., Narum, B., & Wold, J. P. (2009). Fat distribution analysis in salmon using non-contact near infrared interactance imaging: a sampling and calibration strategy. J. Near Infrared Spectrosc, 17: 247–253.

Sigurgisladottira, S., ØTorrissen, O., Lie, Ø., Thomassen, M., & Hafsteinsson, H. (1997). Salmon quality: Methods to determine the quality parameters. Reviews in Fisheries Science. 5(3): 223–25

Sivertsen, A. H., Heia, K., Stormo, S. K., Elvevoll, E., & Nilsen, H. (2011). Automatic nematode detection in Cod Fillets(Gadus Morhua) by tTransillumination hyperspectral imaging. Journal of Food Science, 76(1): S77–S83.

Taghizadeh, M., Gowen, A., & O'Donnell, C. P. (2009). Prediction of white button mushroom (Agaricus bisporus) moisture content using hyperspectral imaging. Sens. & Instrumen. Food Qual. 3: 219–226.

Wold, J. P., O'Farrell, M., Høy, M., & Tschudi, J. (2011). On-line determination and control of fat content in batches of beef trimmings by NIR imaging spectroscopy. Meat Science, 89: 317–324.

Wold, J. P., Johansen, I. R., Haugholt, K. H., Tschudi, J., Thielemann, J., Segtnan, V. H., Narum, B., & Wold, E. (2006). Non-contact transflectance near infrared imaging for representative on-line sampling of dried salted coalfish (bacalao). J. Near Infrared Spectrosc, 14: 59–66.

DETERMINATION OF ENTEROBACTERIACEAE IN CHICKEN FILLETS USING NIR HYPERSPECTRAL IMAGING AND MULTIVARIATE DATA ANALYSIS

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Abstract

Hyperspectral imaging was investigated for fast and direct determination of Enterobacteriaceae loads on chicken fillets. The spectral range of 930-1450 nm was utilized to establish full wavelength partial least squares regression (PLSR) models. The good performance, i.e., coefficients of determination $R^2 \geq 0.82$ and root mean squared errors (RMSEs) ≤ 0.47 $\log_{10}$ CFU g^{-1}, suggested great precision and stability of the PLSR model. Simplified PLSR models were also developed by utilizing only three wavelengths (930, 1121 and 1345 nm) selected from the PLS regression coefficients (BW) plot produced from the optimal full wavelength model, and the obtained R^2 were as high as 0.89, 0.86 and 0.87 with corresponding RMSEs of 0.33, 0.40 and 0.45 log10 CFU g^{-1} for calibration, cross validation and prediction, respectively. It was demonstrated that hyperspectral imaging is a potential tool for determining food sanitation and detecting bacterial pathogens on food matrix without using complicated laboratory regimes. In the future, multispectral imaging systems can be developed to conduct on-line detection of Enterobacteriaceae in the food industry.

Introduction

Detection of Enterobacteriaceae bacteria is of significant importance because food-borne illnesses caused by its member pathogens can result in substantial negative influence to the public. Traditional methods, including culture and colony counting methods, polymerase chain reaction (PCR) as well as immunology-based approaches, are available for precise determination of these microorganisms. However, these methods can be tedious or expensive and require well-trained personnel to carry out experiments due to technical complexity (Velusamy et al. 2010) and require 24-72 hours to obtain a completed result. Therefore, it is urgently necessary to develop a simple, fast, accurate and non-destructive method for determination of Enterobacteriaceae.

Hyperspectral imaging (HSI) is an emerging technology that makes full use of both spectral and spatial information to account for physical, chemical and biological attributes of the samples (ElMasry and Sun 2010). It has been widely used in food quality and safety control (Feng and Sun 2011; Gowen et al. 2007). With respects to bacterial detection, Dubois et al. (2005) proved that HSI was a potential tool for high throughput assay of presence or absence of pathogens in the food matrix by processing the images of isolated microbes. Some other researchers utilized this technology for determination of microbiological spoilage of meat (Grau et al. 2011; Peng et al. 2011).

Researchers in USDA succeeded in transferring this technique from preliminary laboratory investigations to recent on-line applications in industrial level for detecting faecal contamination and wholesomeness of chicken carcasses (Chao et al. 2010; Kim et al. 2001; Lawrence et al. 2006; Park et al. 2005). However, to be in accordance with relevant microbiological safety standards and regulations, it is necessary to investigate the potential of hyperspectral imaging for its effectiveness in sensing bacteria especially the pathogenic groups on food matrix. **Therefore, the main objective of the current study was to detect the total Enterobacteriaceae loads in raw chicken breast fillets with the aid of near-infrared hyperspectral imaging and chemometric methods.**

Materials and Methods

Samples and microbiological tests
Chicken fillets bought from a local supermarket were transferred to laboratory, prepared, stored and subjected to image acquisition by a hyperspectral imaging system and traditional tests using microbiological protocols, as described by Feng et al., (2012). In microbiological tests, standard pour plate method was applied. Briefly, violet red bile glucose (VRBG) agar was used to facilitate the selective growth of Enterobacteriaceae bacteria and plates were incubated at 30 ^{o}C for 48 h before typical colonies were counted.

Hyperspectral imaging system
The constitutional components of the pushbroom hyperspectral imaging system utilized in this study are shown in Figure 1. There are mainly five elements, i.e., a translation stage, illumination units, a spectrograph, a CCD camera and a personal computer installed with image acquisition software. This system worked in reflectance mode and covered a wavelength range of 900-1700 nm. More details about this system can be found elsewhere (Feng et al., 2012).
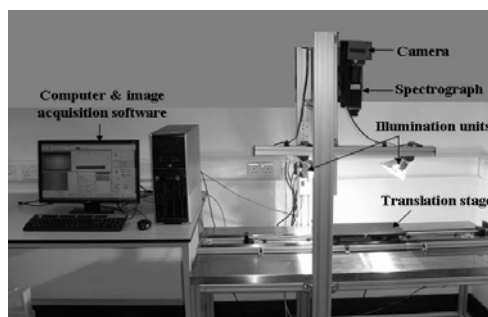
Figure 1. Set-up of the hyperspectral imaging utilized in this study. (ElMasry and Sun, 2010)

Data analyses
The original meat sample images (R_o) were first calibrated in to corresponding reflectance images (R_c) using two reference images, one (~100% reflectance) taken on a white tile and the other (R_d, ~0% reflectance) for dark current. The following equation was used:

$R_c = (R_o - R_d)/(R_w - R_d)$

To ensure the quality of spectra to be extracted from the image, regions of interest (ROIs) were manually chosen from the calibrated images in the form of ellipse. Average spectra (930-1450 nm) from these ROIs were then correlated with the measured bacterial loads of the corresponding meat samples using partial least squares (PLS) regression. The established models were then evaluated by calculating coefficients of determination (R^2) and root mean squared errors (RMSEs) for calibration, cross validation and prediction. Based on the regression coefficients (B) produced by the optimal full wavelength model, important wavelengths were chosen at peaks and valleys of the B-plot. The selected wavelengths were then utilized to build a new simplified model, which could facilitate the development of multispectral imaging systems for detection of bacteria.

Results and Discussion

Spectra
Figure 2 shows a typical chicken fillet spectrum in the wavelength range of 930-1450 nm. It should be noted that in the whole wavelength range 900-1700 nm, the wavelength ranges other than the determined band (930-1450 nm) were either of low signal-to-noise ratio or of limited information therefore discarded. In Figure 2, three main absorption peaks are present at 971 nm, 1191 nm and 1415 nm, which are due to the presence of O-H, C-H and O-H in

meat, respectively (Ortiz-Somovilla et al. 2007). Specifically, 971 nm and 1415 nm can be attributed to water content, with 1191 nm to fatty acid moieties (Ritthiruangdej et al. 2011).
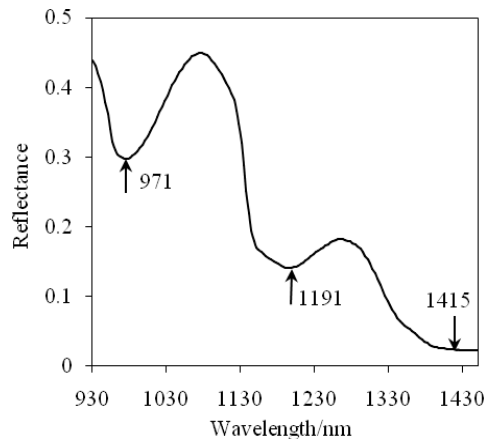
Figure 2. A typical spectrum of chicken meat in the wavelength range of 930-1450 nm.

Full wavelength PLSR models

A very good full wavelength calibration model was established where the coefficients of determination (R^2) for calibration, cross validation and external prediction were 0.88, 0.82 and 0.85, with corresponding RMSEs of 0.35, 0.45 and 0.47 $\log_{10}$ CFU g^{-1}, respectively. Since R^2_c and R^2_{cv} were very high and RMSEC and RMSECV were quite low and close, the established model was of great precision and stability. The power of this model was further proved by the good R^2_p and RMSEP values in predicting the unknown samples in the prediction set. Besides, four latent variables were used in developing the PLSR model where the lowest RMSECV (0.45 $\log_{10}$ CFU g^{-1}) was gained.

Simplified PLSR model

Three dominant peaks and/or extremes were identified in the regression coefficients plot (figure not shown) produced during the establishment of the optimal full wavelength model. The corresponding wavelengths, i.e., 930, 1121 and 1345 nm were then considered as important wavelengths for detecting Enterobacteriaceae in raw chicken fillets. Utilizing these three wavelengths, simplified models were then developed, where R^2 of 0.89, 0.86 and 0.87 with RMSEs of 0.33, 0.40 and 0.45 $\log_{10}$ CFU g^{-1} were obtained for calibration, cross validation and prediction, respectively (Figure 3). The results indicated that the three important wavelengths were powerful in the development of PLSR models. Moreover, a simplified multispectral imaging system that is much cheaper than HSI system could also be developed.
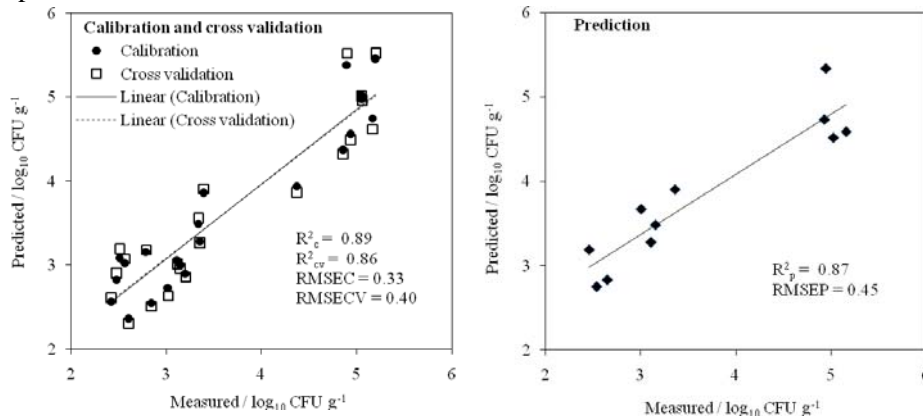
Figure 3. The performance of the full wavelength PLS regression model. RMSEs are in $\log_{10}$ CFU g^{-1}.

Conclusion

Hyperspectral imaging technique was employed in fast detection of Enterobacteriaceae in chicken breast fillets. Precise and stable PLSR models were built based on full wavelengths with $R^2 \geq 0.82$ and RMSEs ≤ 0.47 $\log_{10}$ CFU g^{-1}. The bacterial loads could also be accurately predicted by utilizing the three wavelengths (930, 1121 and 1345 nm) selected from the PLS regression coefficients. It was demonstrated that hyperspectral imaging is powerful in direct, fast and reagentless detection of Enterobacteriaceae in chicken fillets. Multispectal imaging systems based on suggested wavelengths in this study can be developed and enhanced in the future to meet the requirements of the food industry.

Acknowledgements

References

Chao, K., Yang, C.-C., Kim, M.S., 2010. Spectral line-scan imaging system for high-speed non-destructive wholesomeness inspection of broilers. Trends in Food Science & Technology 21(3), 129-137.

Dubois, J., Neil Lewis, E., Fry, J.F.S., Calvey, E.M., 2005. Bacterial identification by near-infrared chemical imaging of food-specific cards. Food Microbiology 22(6), 577-583.

ElMasry, G., Sun, D.-W., 2010. Principles of Hyperspectral Imaging Technology. In: Sun, D.-W. (Ed.), Hyperspectral Imaging for Food Quality Analysis and Control, pp. 3-43. Academic Press, San Diego.

Feng, Y.-Z. and Sun, D.-W., 2011. Application of hyperspectral imaging in food safety inspection and control: a review. Critical Reviews in Food Science and Nutrition Accepted Manuscript.

Feng, Y.-Z, ElMasry G, Sun, D.-W., Walsh, D., Morcy, N., 2012. Near-infrared hyperspectral imaging and partial least squares regression for rapid and reagentless determination of Enterobacteriaceae on chicken fillets, submitted.

Gowen, A.A., O'Donnell, C.P., Cullen, P.J., Downey, G., Frias, J.M., 2007. Hyperspectral imaging - an emerging process analytical tool for food quality and safety control. Trends in Food Science & Technology 18(12), 590-598.

Grau, R., Sánchez, A.J., Girón, J., Iborra, E., Fuentes, A., Barat, J.M., 2011. Nondestructive assessment of freshness in packaged sliced chicken breasts using SW-NIR spectroscopy. Food Research International 44(1), 331-337.

Kim, M., Chen, Y., Mehl, P., 2001. Hyperspectral reflectance and fluorescence imaging system for food quality and safety. Transactions of ASAE 44(3), 721-729.

Lawrence, K.C., Windham, W.R., Park, B., Heitschmidt, G.W., Smith, D.P., Feldner, P., 2006. Partial least squares regression of hyperspectral images for contaminant detection on poultry carcasses. Journal of Near Infrared Spectroscopy 14(4), 223-230.

Ortiz-Somovilla, V., España-España, F., Gaitán-Jurado, A.J., Pérez-Aparicio, J., De Pedro-Sanz, E.J., 2007. Proximate analysis of homogenized and minced mass of pork sausages by NIRS. Food Chemistry 101(3), 1031-1040.

Park, B., Lawrence, K., Windham, W., Smith, D., 2005. Detection of cecal contaminants in visceral cavity of broiler carcasses using hyperspectral imaging. Applied Engineering in Agriculture 21(4), 627-635.

Peng, Y., Zhang, J., Wang, W., Li, Y., Wu, J., Huang, H., Gao, X., Jiang, W., 2011. Potential prediction of the microbial spoilage of beef using spatially resolved hyperspectral scattering profiles. Journal of Food Engineering 102(2), 163-169.

Ritthiruangdej, P., Ritthiron, R., Shinzawa, H., Ozaki, Y., 2011. Non-destructive and rapid analysis of chemical compositions in Thai steamed pork sausages by near-infrared spectroscopy. Food Chemistry 129(2), 684-692.

Velusamy, V., Arshak, K., Korostynska, O., Oliwa, K., Adley, C., 2010. An overview of foodborne pathogen detection: In the perspective of biosensors. Biotechnology Advances 28(2), 232-254.

PREDICTION OF FAT AND MOISTURE CONTENT IN PORK USING NIR HYPERSPECTRAL IMAGING TECHNIQUE

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Abstract

Hyperspectral imaging based technique was investigated for objective determination of moisture and fat contents in pork. Near-infrared (NIR) hyperspectral images (900-1700 nm) were acquired for both intact and minced pork samples and representative spectra were extracted by automatic segmentation. Moisture and fat contents were determined by traditional methods and then related with the spectral information by partial least-squares regression (PLSR) models. The coefficient of determination obtained indicated that the NIR spectral range had an excellent ability to predict the content of moisture ($R^2_{cv} = 0.86$) and fat ($R^2_{cv} = 0.95$) in pork. Results indicated the potential use of NIR hyperspectral imaging technique for rapid assessment of pork composition.

Introduction

Considering the prominence of meat constitution regarding economical or health related aspects, it is crucial to analyze the chemical composition of fresh and minced meat to ensure that the consumers and processors get the right quality of meats from their suppliers. Chemical analyses of meat and meat products have traditionally been performed by conventional analytical methods. However, these methods usually require lengthy preparation, and sometimes are healthy and environmentally harmful (Prevolnik et al., 2011).
One of the alternatives to the conventional methods is based on near infrared spectroscopy (NIRS) (Wold et al., 2011). In spectroscopic techniques, the major drawback in obtaining representative NIR spectra is the way of presenting the samples to the instrument. The importance of avoiding the tedious task of milling samples is well recognised by the NIRS practitioners (Meza-Márquez et al., 2010). In contrast, previous investigations have revealed that the non-homogeneity of intact muscles provided poor results for moisture and intramuscular fat prediction models compared to homogenized samples, mainly due to different levels of fibres organization and physical and chemical characteristics of meat (Barlocco et al., 2006). Hence, it is indicated that chemical parameters in minced samples can be more accurately predicted than in intact tissue (Cozzolino and Murray, 2002).
The potential application of NIR hyperspectral imaging in this approach is still under investigation (Kobayashi et al., 2010). Hyperspectral images are created by combining hundreds of single band images at a certain wavelength, thus consisting of a NIR spectrum for each pixel in the image. Similar to conventional spectroscopy, chemometrics can be applied to extract relevant information from the spectra, allowing sample classifications or quantitative determinations. When additional reference information is available for comparison, partial least squares (PLS) and other regression models can be applied for prediction of the respective attributes (Burger and Geladi, 2006).
The main objective of the present study was to investigate the potential of using NIR hyperspectral imaging technique as a fast and non-destructive method to predict moisture and fat content in intact and minced pork.

Material and Methods

Sample preparation and compositional analysis

Fresh pork samples (n = 120) from four different muscles including *longissimus dorsi* (LD), *semimembranosus* (SM), *semitendinosus* (ST) and *biceps femoris* (BF) were cut into chops and imaged in the NIR hyperspectral imaging system. The samples were minced using a food processor (R-201E Ultra, Robot-Coupe, France) and hermetically stored in plastic containers to avoid moisture losses and image acquisition was performed for those samples.

Moisture and fat contents in minced samples were analysed using the Smart Trac (CEM Corporation, Matthews, North Carolina, USA), which utilizes microwave energy for estimating moisture content and Nuclear Magnetic Resonance (NMR) spectrometry to determine fat content (AOAC Official Method 2008.06). The moisture content was gravimetrically analyzed by determining the weight loss after drying. Then, the same dried samples were packed for fat content determination.

Hyperspectral imaging system
Pork samples were scanned in reflectance mode using a laboratory-based pushbroom NIR hyperspectral imaging system. The system consisted of a spectrograph (ImSpector, N17E, Spectral Imaging Ltd, Finland), a charged couple device (CCD) camera along with C-mount lens (Xeva 992, Xenics Infrared Solutions, Belgium), illumination unit comprising of two tungsten-halogen lamps (V-light, Lowel Light Inc, USA), a translation stage (MSA15R-N, AMT-Linearways, SuperSlides & Bushes Corp., India), a data acquisition software (SpectralCube, Spectral Imaging Ltd., Finland), and a computer. Spectral images were acquired in the wavelength range of 897-1752 nm with a spectral increment of about 3.34 nm between the contiguous bands producing a total of 256 bands.

Image acquisition and pre-processing
The images were reduced to the spectral range of 910-1700 with a total of 237 bands to avoid noisy information in the end of the spectra. The resized images were subsequently calibrated to obtain relative reflectance images using the following equation:

$$R = \frac{R_0 - D}{W - D} \tag{1}$$

where R was the relative reflectance of an image; R_0 was the original resized image; D was the minimum-reflectance image (~0% reflectance) acquired with the light source off and the camera lens completely covered, and W was the maximum-reflectance image (~100% reflectance) acquired from a white reference tile.

Prediction method
Partial least squares regression (PLSR) was applied to predict the amount of moisture and fat using the NIR spectral information extracted from the hyperspectral images of the pork samples (Burger and Geladi, 2006). The whole data set (120 samples) was divided into two groups, one for building the calibration model consisting of 80 samples (training set), and another group used for validation consisting of 40 samples (testing set). The PLSR models were built with the training set under full cross validation (leave-one-out cross-validation) method. The predictive ability of the regression model was evaluated by calculating the coefficient of determination in calibration R^2_C, standard error in calibration (SEC), coefficient of determination in cross-validation R^2_{CV} and standard error estimated by cross-validation (SECV). The ideal number of latent variables was identified at the minimum value of the prediction error sum of squares (PRESS) (ElMasry et al., 2011). PLSR models were performed using multivariate analysis software (Unscrambler 9.7, CAMO, Norway).

Results and Discussion

Chemical composition of the tested muscles
The mean, standard deviation (SD) and the range of each chemical component measured by conventional methods for each kind of the examined muscles are presented in Table 1. The overall moisture content varied from 68.98% to 75.67%, and fat varied from 0.30% to 8.96%. Fat composition was basically related to marbling since the external subcutaneous fat layer of

the LD was trimmed out before analysis. The BF muscle could be distinguished from the other muscles in terms of its moisture contents. In general, the obtained chemical assessments of the examined muscles are in accordance with those reported in other studies in pork (Kim et al., 2008).

Table 1. Moisture and fat content of the analysed pork samples

	Moisture (%)		Fat (%)	
	Mean±SD	min-max	Mean±SD	min-max
LD	72.72[ab]±1.06	69.12-75.08	1.96[a]±1.06	0.30-6.27
SM	73.32[a]±0.68	72.03-74.85	1.19[b]±0.48	0.37-2.45
ST	72.02[b]±2.11	68.98-74.62	4.83[c]±2.87	1.27-8.96
BF	74.36[c]±0.72	73.60-75.67	1.88[a]±0.69	1.10-3.50

* Different letters in each column represent statistically significant difference ($p<0.05$)

Spectral profiles
The main NIR spectral patterns of the pork samples originated from different muscles are shown in Figure 1.
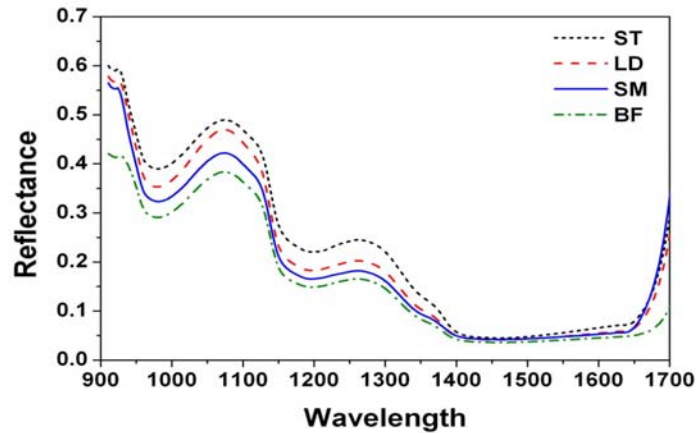
Figure 1. Average spectra for different pork muscles (ST: *semitendinosus*, LD: *longissimus dorsi*, SM: *semimembranosus*, BF: *biceps femoris*).

Spectral profiles of the four examined muscles exhibited similar pattern with differences in the magnitude of reflectance. The ST muscle had the highest reflectance, followed by LD and SM muscles, while the BF revealed the lowest reflectance in the NIR region. Variations observed in spectral reflectance among pork muscles could be related to differences in the sample properties.

PLSR models for predicting chemical composition
Table 2. Calibration statistics for predicting chemical composition with spectra extracted from intact (I) and minced (M) pork using the whole spectra from the PLSR models.

Component	LV	R^2_C	R^2_{CV}	R^2_P	SEC	SECV	SEP
Moisture (I)	10	0.81	0.70	0.58	0.49	0.62	0.92
Fat (I)	9	0.87	0.80	0.83	0.52	0.68	0.76
Moisture(M)	7	0.91	0.86	0.91	0.63	0.82	0.64
Fat (M)	8	0.96	0.95	0.95	0.30	0.37	0.37

As shown in Table 2, the developed PLSR models obtained for minced samples presented better coefficient of determination (R^2) values with less latent variables than models for intact samples. This is in accordance with previous results (Barlocco et al., 2006; Cozzolino and Murray, 2002). PLSR models for predicting chemical composition of minced pork samples under cross validation had a reasonable accuracy with coefficient of determination (R^2_{cv}) of 0.86 and 0.95 for moisture and fat respectively. The calibration models from minced samples

provided good accuracy when applied to an independent test set, with coefficients of prediction (R^2_P) of 0.91 and 0.95 for moisture and fat, respectively.

Conclusions

The results indicated that PLSR models had reasonable accuracy in predicting moisture and fat with coefficient of prediction (R^2_P) of 0.91 and 0.95, and SEP of 0.64 and 0.37 respectively, for minced pork. The results suggest that NIR spectral imaging could become a useful tool for quantifying the amount of important components such as water and fat. The technique can be implemented as a key component of computer-integrated systems and provide opportunities for several practical applications in meat quality inspection.

Acknowledgements

References

AOAC Official Method 2008.06. Moisture and Fat in Meats by Microwave and Nuclear Magnetic Resonance Analysis. June 23, 2008

Barlocco, N.; Vadell, A.; Ballesteros, F.; Galietta, G.; & Cozzolino, D. (2006). Predicting intramuscular fat, moisture and Warner-Bratzler shear force in pork muscle using near infrared reflectance spectroscopy. *Animal Science*, *82 (1)*, 111-116.

Burger, J; Geladi, P. (2006). Hyperspectral NIR imaging for calibration and prediction: A comparison between image and spectrometer data for studying organic and biological samples, *Analyst*, 131, 1152-1160.

Cozzolino, D., Murray, I. (2002). Effect of sample presentation and animal muscle species on the analysis of meat by near infrared reflectance spectroscopy. Journal of Near Infrared Spectroscopy, 10, 37–44.

ElMasry, G., et al., Non-destructive determination of water-holding capacity in fresh beef by using NIR hyperspectral imaging, Food Research International (2011), doi:10.1016/j.foodres.2011.05.001

Kim, J. H.; Seong, P. N.; Cho, S. H.; Park, B. Y.; Hah, K. H.; Yu, L. H.; Lim, D. G.; Hwang, I. H.; Kim, D. H.; Lee, J. M.; Ahn, C. N. Characterization of Nutritional Value for Twenty-one Pork Muscles. Asian-Aust. J. Anim. Sci. 21, (1): 138 – 143. 2008

Kobayashi, K.-I.; Yasunori Matsui, Y.; Yosuke Maebuchi, Y.; Toyota, T.; Nakauchi, S. (2010). Near infrared spectroscopy and hyperspectral imaging for prediction and visualisation of fat and fatty acid content in intact raw beef cuts. *Journal of Near Infrared Spectroscopy,* 18 (5). 301–315.

Meza-Márquez, O. G.; Gallardo-Velázquez, T.; Osorio-Revilla, G. (2010). Application of mid-infrared spectroscopy with multivariate analysis and soft independent modeling of class analogies (SIMCA) for the detection of adulterants in minced beef. *Meat Science*, 86, 2. 511-519.

Murray, I., Williams, P.C., 2001. Chemical principles of near-infrared technology. In: P. Williams and K. Norris. Near-infrared technology in the agricultural and food industries, second edition. St. Paul, Minn. American Association of Cereal Chemists.

Prevolnik, M. Škrlep, L. Janeš, Š. Velikonja-Bolta, D. Škorjanc, M. Čandek-Potokar. Accuracy of near infrared spectroscopy for prediction of chemical composition, salt content and free amino acids in dry-cured ham. Meat Science 88 (2011) 299–304.

Wold, J.P.; O'Farrell, M.; Høy, M.; Tschudi, J. 2011. On-line determination and control of fat content in batches of beef trimmings by NIR imaging spectroscopy. Meat Science 89 (2011) 317–324.

PREDICTION OF CHEMICAL COMPOSITION IN LAMB MEAT USING NIR HYPERSPECTRAL IMAGING

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Abstract

Emerging concerns about safety and quality and increased demands by the consumers, legislators and competition have promoted the meat industry migrating from its invasive testing methods yet practised in the meat industry to newer, non-destructive techniques. The main goal of this study was to investigate the potential of hyperspectral imaging in the near-infrared (NIR) range of 900-1700 nm for non-destructive prediction of chemical composition in lamb meat. Hyperspectral images were acquired for lamb samples originated from different breeds and different muscles. The mean spectra of the samples were extracted from the hyperspectral images and multivariate calibration models were built by using partial least squares (PLS) regression for predicting water, fat and protein contents. This study clearly illustrated that NIR hyperspectral imaging in tandem with PLSR modelling can be used for the non-destructive prediction of chemical compositions in lamb meat.

Introduction

There is a great interest in developing optical technologies that have the capability of predicting quality attributes in a real-time assessment. Recently, much progress has been made in developing hyperspectral imaging technique for non-destructive assessment tool for safety inspection and quality control of various food products. Although the technology is currently in an early development stage, its potential is tremendously promising. It has been introduced for the identification and quantification of chemical constituents as well as their location or spatial distribution simultaneously. However, major bottlenecks such as high costs and difficulties in high speed data acquisition and processing have limited the use of this technology in a real time assessment. But, hyperspectral imaging technology can be a very useful tool for selecting some important wavelengths for building a multispectral imaging system to meet the speed requirement of industrial production lines. If the high dimensionality of hyperspectral imaging data can be reduced properly by choosing some optimal wavelengths for certain applications, the technology would certainly be incomparable for process monitoring and real-time inspection.

Our previous work has shown the potential of using NIR hyperspectral imaging as a rapid method for discrimination of lamb muscles (Kamruzzaman, *et al*., 2011), prediction of quality attribute in lamb meat (Kamruzzaman *et al.,* 2012), quality classification of cooked, sliced turkey ham (ElMasry *et al*., 2011a), prediction of water holding capacity, pH, colour and tenderness of fresh beef (ElMasry *et al*., 2011b, ElMasry *et al*., 2012) classification, grading and prediction of quality and sensory attributes in pork (Barbin *et al*., 2012a, Barbin *et al*., 2012b). In the meat industry, routine chemical analysis still performed using laboratory analytical method, which is destructive, time consuming and unsuitable for on-line application. Therefore, the development of fast, non-destructive, accurate and online analytical methods is highly desired. According, a rapid, reliable and more accurate technique based on hyperspectral imaging could be established for routine chemical analysis of fresh meat which ultimately would bring some economical benefits compared to off-line or at-line analysis by increasing consumer confidence in the quality of the supplied meat.

The objective of the study was to evaluate the potential of non-destructive prediction and visualization of chemical composition in lamb meat using NIR hyperspectral imaging.

2. Material and methods

2.1. Sample preparation and reference analysis

Lamb samples for this study were collected from Ashtown Food Research Centre (AFRC), Teagasc, Dublin 15, Ireland. Three muscles i.e. *M. semimembranosis* (SM), *M. semitendinosus* (ST) and *M. longissimus dorsi* (LD) were taken for the experiment in order to obtain a wide range of chemical compositions. Each Muscle was cut to slices of 1 inch in thickness using a scalpel and cutting machine. Each sample was individually vacuum packed and shipped to the laboratory in ice boxes and then kept at 2°C. Each intact muscle was first scanned by the hyperspectral imaging system and then individually minced and homogenised after removing fat portion and again scanned in a circular cup and finally its reference water, fat and protein contents were determined using standard laboratory procedure.

Hyperspectral imaging system

The spectral images were acquired in the reflectance mode using a pushbroom hyperspectral imaging system in the spectral range of 900-1700 nm. The system includes a line-scan imaging spectrograph, a charged couple device (CCD) camera with C-mount lens, an illumination unit, a translation stage and a computer supported with image acquisition software for controlling the camera and acquiring images.

Image acquisition and pre-processing

The image acquisition was carried out at room temperature where lamb sample was put on the translation stage and upon entering the field of view, the acquisition of a hyperspectral image of the sample started. The captured images were calibrated due to dark current effect of camera, and to obtain relative reflectance using the equation:

$$R = \frac{R_0 - D}{W - D} \times 100$$

Where R is the relative-reflectance corrected image; R_0 is the original raw image; D is the dark image ($\sim$ 0 % reflectance) obtained by covering the lens with an opaque cap and W is the white reference image ($\sim$ 99 % reflectance).

Development of the calibration models

Partial least square regression (PLSR) is the most commonly used multivariate method for constructing calibration models to predict the constituent of interest. The purpose of developing regression models is to predict a sample property from the measured spectral data. In this study, three separate PLSR models were developed for each parameter using the PLS1 algorithm. The model was optimized by using cross-validation method. Instead of using leave one out cross validation (LOO-CV), leave-one-segment-out cross validation (LOSO-CV) was considered to validate the calibration models. The number of factors used in the model is determined at the minimum value of predicted residual error sum square (PRESS). The predictive capabilities of the models were evaluated by examining the statistical values obtained for the calibration. The main calibration statistics are such as the standard error of calibration (SEC), the coefficient of determination in calibration (R^2_c), the standard error estimated by cross validation (SECV), the coefficient of determination in cross-validation (R^2_{CV}) and the ratio of prediction to deviation (RPD).

Image visualization

In addition to accurate determination of major constituents in the food samples, another essential benefit of hyperspectral imaging techniques is to display the spatial distribution of food composition and the concentration gradients of different constituents in the food sample with the aid of image processing. In this study, PLSR model was used to visualize and map each pixel of the hyperspectral images in the form of chemical image to predict constituent concentration in the tested muscles at the pixel level.

Results and discussion

Calibration models and Prediction maps

The critical step for an accurate PLSR model is to select the correct number of latent variables (LVs) needed to obtain the best prediction. The ideal number of LVs for predicting water, fat and protein identified from PRESS plot. The performance of the calibration models for each constituent was validated by cross validation. The PLSR analyses showed a strong performance with measured water (R^2_{cv}=0.89, R^2_{cv}=0.86, SECV=0.50% and RPD=2.68) and fat (R^2_c=0.93, R^2_{cv}=0.91, SECV=0.38% and RPD=3.50) content and reasonable performance with protein (R^2_c=0.67, R^2_{cv}=0.58, SECV=0.30% and RPD=1.97) content in the full spectral range. The most important wavelengths (937, 964, 1050, 1141, 1211, 1304 and 1391 nm) were identified for both water and fat determination using regression coefficients resulting from the PLSR analyses. Table 1 summarises the prediction statistics and the performance of the PLSR models developed with full and selected important wavelengths. The performance models on this reduced set of important wavelengths (7 wavelengths) were almost similar to the model developed using the whole wavelengths range (237 wavelengths).

Table 1. Performance of PLSR model developed with full and some important wavelengths (no important wavelengths were identified for protein).

Model for	No of wavelengths	LVs	Calibration		Cross-validation		
			R^2_c	SEC (%)	R^2_{cv}	SECV (%)	RPD
Water	237	9	0.89	0.44	0.86	0.50	2.68
	7	6	0.87	0.48	0.86	0.51	2.63
Fat	237	9	0.93	0.32	0.91	0.38	3.50
	7	6	0.92	0.36	0.90	0.38	3.50
Protein	237	8	0.67	0.34	0.58	0.30	1.97

The PLS regression models developed using feature wavelengths were applied to each pixel of the individual hyperspectral image to predict water and fat in all surface of the sample. Figure 1 shows examples of chemical images for the water and fat of some examined samples. Although it was impossible to differentiate the water and fat distribution in the muscle, the spatial distribution of water and fat could be easily distinguished by the NIR hyperspectral imaging.
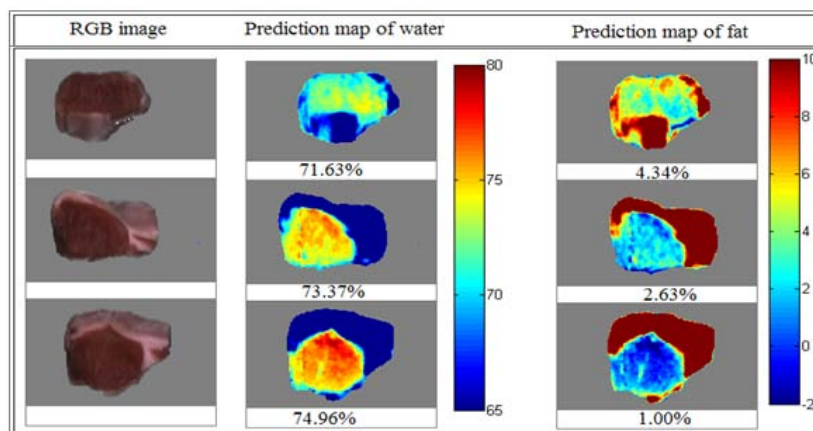
Figure 1. Prediction maps of water and fat of some representative samples. The values in the bottom of the chemical image represent the average percentage of water or fat of the muscle. RGB images were constructed by concatenating three spectral images at 950, 1250 and 1300 nm.

Conclusions

This is the first reported study to utilize NIR hyperspectral imaging for the prediction of chemical composition in lamb meat. This study has shown that NIR hyperspectral imaging offers an alternative to analytical methods for rapid and non-destructive prediction of water, fat and protein contents on lamb meat. The aptitude of the hyperspectral imaging technique to visualize the prediction of constituent concentration in a pixel-wise manner can be especially useful for enhancing the visual appearance of meat quality traits that cannot be visualized with either imaging or conventional spectroscopy.

Acknowledgements

References

Barbin, D., ElMasry, G., Sun, D-W., & Allen, P. (2012a). Near-infrared hyperspectral imaging for grading and classification of pork, *Meat Science*, 90, 259-268.

Barbin, D., ElMasry, G., Sun, D-W., & Allen, P. (2012b). Non-destructive determination of water-holding capacity in fresh beef by using NIR hyperspectral imaging. *Analytica Chemica Acta.* 719, 30-42.

ElMasry, G., Iqbal, A., Sun, D-W., Allen, P., & Ward, P. (2011a). Quality classification of cooked, sliced turkey hams using NIR hyperspectral imaging system. *Journal of Food Engineering*, 103, 333-344.

ElMasry, G., Sun, D-W., & Allen, P. (2011b). Non-destructive determination of water-holding capacity in fresh beef by using NIR hyperspectral imaging, *Food Research International.* 44, 2624-2633.

ElMasry, G., Sun, D-W., & Allen, P. (2012). Near-infrared hyperspectral imaging for predicting colour, pH and tenderness of fresh beef. *Journal of Food Engineering.* 110, 127-140.

Kamruzzaman, M., ElMasry, G., Sun, D-W., & Allen, P. (2011). Application of NIR hyperspectral imaging for discrimination of lamb muscles. *Journal of Food Engineering.* 104, 332-340.

Kamruzzaman, M., ElMasry, G., Sun, D-W., & Allen, P. (2012). Prediction of some quality attributes of lamb meat using near infrared hyperspectral imaging and multivariate analysis. *Analytica Chemica Acta.* 714, 57-67.

PHYTOCHEMICAL EXPOSURE ASSESSMENT IN FRUIT SMOOTHIES

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Abstract

Phytochemicals are important naturally occurring bioactive compounds in fruit and vegetables widely recognised for their potential health benefits to humans e.g. prevention of cancer. Frequent consumption of fruit and vegetables as fresh or smoothies increase the intake of phytochemical content. A model will be developed to investigate various processing stages of smoothies and its influence on the level of phytochemicals such as total phenols and flavonoids respectively. This study will evaluate the impact of different fruit and vegetable combinations on the phytochemicals presence in smoothies with subsequent human exposure.

Introduction

Fruit and vegetables are normally consumed by humans as salad, juice or smoothies. Fruit and vegetables remain an essential part and an important source of nutrients in many parts of the world, and also offer advantages over dietary supplements because of their low cost and wide availability. In particular, they are rich in water soluble vitamins (vitamin C and group B vitamins), provitamin A, phytosterols and high variety of minerals and phytochemicals depending on the plant species. Phytochemicals of fruit and vegetable have been associated with health benefits for centuries. Epidemiological studies have noted a consistent association between the consumption of diets rich in fruits and vegetables and a lower risk for chronic diseases including cancer and cardiovascular disease. There is accumulating evidence that much of the health-promoting potential of these plant foods may come from phytochemicals, bioactive compounds not designated as traditional nutrients. (Hannum, SM, 2004). The effect of various processing steps on the shelf-life of smoothies was elucidated (Walkling-Ribeiro et al, 2010). The Health Promotion Agency in Northern Ireland (NI) and the Department of Health and Children in ROI currently advising that smoothies count as one portion of fresh fruit, (Safe food, 2009). Fruit and vegetable are normally consumed by human as salad, juice or smoothies.

The main objective of this study is to assess the level of phytochemicals present in the selected fruit and vegetables and its impact on the phytochemical level during processing of smoothies and subsequent human exposure assessment.

Materials and Methods

Data on different fruit and vegetable combinations were collated from various scientific literature sources. The selection of fruit and vegetable are based on its level of phytochemical present for example total phenolic content in apples ranged from 0.92 to 1.41 mg CTE/g of fresh weight (Carbone et al., 2011). Similarly total flavonoid content of the grape ranged from 29 to 41 mg/kg of berry (González at al, 2011).

Formulation of smoothies combination
Five different smoothies combinations were formulated inorder to balance the selected phytochemical content (total phenolic and total flavonoid) in each combinations. Table 1 details the list of smoothies combinations used in preliminary modelling. Each combinations vary with ratio of fruit or vegetable inclusion thus totalling to 100 percent.

Table 1. Different smoothie combinations used in preliminary modeling

Combination 1	Combination 2	Combination 3	Combination 4	Combination 5
Carrot	Water melon	Banana	Mango	Blueberry
40 %	30 %	35 %	35 %	45 %
Apple	Pear	Grape	Peach	Banana
30 %	45 %	40 %	35 %	25 %
Orange juice	Apple juice	Orange juice	Orange juice 30	Pineapple juice
30 %	25 %	25 %	%	20 %

Smoothies process

The effect of processing on the final phytochemical concentration and texture within the smoothie will be determined by existing scientific literature (Kenny, O and O'Beirne, D., 2010). The processing steps involved in the production of smoothies and consumption by human Irish male and female consumption are illustrated in Figure 1.
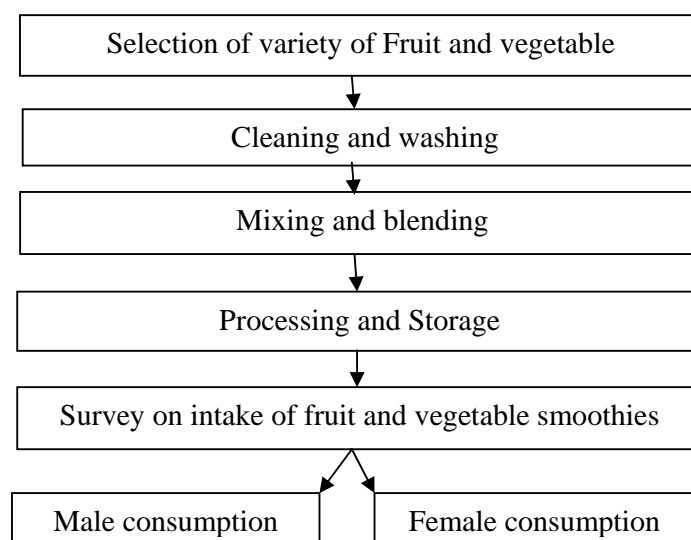
Figure 1. Flow diagram of smoothies processing.

Numerous processing steps including washing, mixing and blending steps may reduce the amount of phytochemical present in smoothies. As the effects of these steps are yet to be confirmed, recent studies (Safe food, 2009) on fruit smoothies showing that one regular 200 ml glass of smoothie during its processing stages a 2 – 5% drop in phytochemical concentration was observed. By following the same mathematical calculation the amount of total phenol and flavonoid content was calculated and presented in Table 2. A smoothie consumption study (Safe food, 2009) on citizens of the Republic of Ireland and Northern Ireland was conducted to determine the volume of smoothies being consumed by Irish human population, allowing for the estimation of daily or weekly phytochemical exposure due to smoothies. Studies are under examination on the total percentage of smoothies being consumed by male, female and children population in Ireland.

Model of simulation

Monte Carlo simulation is a complex stochastic technique used to solve a wide range of mathematical problems. Monte Carlo methods randomly select values from given distributions to create multiple scenarios of a problem. Each time a value is randomly selected, it forms one possible scenario and solution to the problem (Kane, H., et al 2010). Monte Carlo methods give a range of possible solutions, some of which are more probable and some less probable, resulting in a probability distribution for the solution parameter.

Results and Discussion

This study is ongoing and the model is being developed. A literature review reveiled the most frequent quantity of smoothie consumed per drinking occasion was regular glass (200 ml), small bottle/container (250 ml) and dome container (400 ml) according to a survey conducted by (Safe food, 2009) in island of Ireland. The survey indicated that one third of people consume roughly between 2 -5 smoothies in a week. The table 2 indicating an example from each combination on the consumption of a 200 ml standard size glass and assuming a 2 – 5% loss due to processing, an average value for the total number of phenolics and flavonoids consumed per week per person. As can be seen in table 2, if a person consumes a 200 ml glass of smoothie combination 1, two to five times a week their total phenolics consumption would be between 4.381g - 11.299g. If the same person was to consume the same amount of smoothie combination 2 their total phenolic intake per week would be between 0.53g - 1.36g. This same analysis will be applied to calculate percentage of Flavonoids in combination 1 would be 0.52 g - 1.35g per week. This same method will be applied to all other smoothie combinations.

Table 2: Total Phenolic and Flavonoids concentrations within each smoothie combination**.**

Smoothie	Total Phenolic g /100 ml		Total Flavonoids g /100 ml	
Combinations 1	1.153		0.137	
Combinations 2	0.139		0.640	
Combinations 3	0.527			
Combinations 4	0.478		0.164	
Combinations 5	2.514		0.420	
% Loss (2 to 5 % assumption)	2% Loss	5% Loss	2% Loss	5% Loss
Combinations 1	1.130	1.095	0.135	0.131
Combinations 2	0.136	0.132	0.627	0.608
Combinations 3	0.516	0.500		
Combinations 4	0.468	0.454	0.161	0.156
Combinations 5	2.463	2.388	0.412	0.399
Total Consumed in one week (Regular glass – 200 ml)	Total Phenolic (g)		Total flavonoids (g)	
	2 Times	5 Times	.2 Times	5 Times
Combinations 1	4.381-4.520	10.954-11.299	0.522-0.538	1.305-1.346
Combinations 2	0.529-0.545	1.322-1.364	2.433-2.510	6.082-6.274
Combinations 3	2.001-2.064	5.002-5.160		
Combinations 4	1.816-1.873	4.539-4.683	0.625-0.644	1.561-1.611
Combinations 5	9.552-9.853	23.879-24.633	1.598-1.648	3.995-4.121

Conclusions

This study represents a preliminary effort to model various fruit and vegetable combinations and the effect of phytochemical content of the smoothie produced. The model also takes into account the various smoothie combinations and their beneficial effects on human health. Additional studies will be required for the extension of the phytochemical subgroups, and the improvement of a better understanding on the loss of phytochemical content on processing and storage. Monte Carlo stimulation will be applied to analyse the variability of results.

References

Hannum, SM. (2004). Potential impact of strawberries on human health: a review of the *science critical reviews in food science and nutrition*, 44, 1-17.

Walkling-Ribeiro, M., Noci, F., Cronin, D.A., Lyng, J.G., Morgan, D.J. (2010). Shelf life and sensory attributes of a fruit smoothie-type beverage processed with moderate heat and pulsed electric fields. LWT-*Food Science and Technology.*

Muller, L., Gnoyke, S., Popken, A.M., Böhm, V. (2010). Antioxidant capacity and related parameters of different fruit formulations. LWT- *Food Science and Technology* 43, 992-999.

Kenny, O., O'Beirne, D. (2010). Antioxidant phytochemicals in fresh-cut carrot disks as affected by peeling method, *Postharvest Biology and Technology*, 58247–253.

Kane, H., Cummins, E., Tiwari, U. (2010). Assessment of phytochemical exposure from smoothie consumption using Monte Carlo simulation modeling, Biosystem engineering research review, Agriculture, Food Science Centre, University College Dublin.

Safe food. (2009) Smoothies: Consumer knowledge, attitudes and beliefs around the nutritional content of smoothies, Ireland, safe food.

Carbone, K., Giannini, B., Picchi, V., Lo Scalzo, R., Cecchini, F. (2011). Phenolic composition and free radical scavenging activity of different apple varieties in relation to the cultivar, tissue type and storage, *Food Chemistry* 127, 493–500, ScienceDirect.

Figueiredo-González, M., Martínez-Carballo, E., Cancho-Grande, B., Santiago, J.L., Martínez, M.C., Simal-Gándara, J. (2012). Pattern recognition of three Vitis vinifera L. red grapes varieties based on anthocyanin and flavonol profiles, with correlations between their biosynthesis pathways, *Food Chemistry* 130, 9–19, ScienceDirect.

SIMULATION MODEL FOR CAMPYLOBACTER IN PROCESSED CHICKEN

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Abstract

Broiler meat is regarded as the most common source of *Campylobacter* infection and risk management measures are required to reduce broiler meat contamination. Among the quantitative risk assessments for *Campylobacter* in broiler meat, evaluation of the poultry processing stage is particularly important for predicting the contamination level of broiler meat and the effects of control measures. In this study, a simulation model is built to evaluate *Campylobacter* contamination at the individual carcass level during different industrial stages. Using this model, we examined changes in the prevalence of contaminated carcasses, the number of *Campylobacter* per carcass after processing and compare the efficacy of different microbial decontamination treatments at washing, chilling and packaging.

Introduction

Campylobacter spp. is one of the main causative agents of gastroenteritis in Western countries. In Ireland, 1,808 cases of campylobacteriosis were reported to the Health Protection Surveillance Centre (HPSC) in 2009, corresponding to a crude incidence rate (CIR) of 42.6 per 100,000 population (Food Safety Authority of Ireland, 2011). Broiler chickens are generally regarded as one of the main sources of campylobacreriosis. Therefore, appropriate measures to reduce broiler meat contamination are required to lower the risk of *Campylobacter* infection in humans. To help establish effective control measures, risk assessments for *Campylobacter* in poultry meat are performed in many countries by international bodies, including international organizations such as the Food and Agriculture Organization of the United Nations and World Health Organization (Hayama et al., 2011).

There are five main stages during industrial process, they are: (1) scalding (transport through a warm water tank), (2) defeathering (removal of the feathers), (3) evisceration (extraction of intestines), (4) washing (spraying with water), and (5) chilling and packaging. Defeathering and evisceration during poultry processing could reduce or remove *Campylobacter* in the feathers or gastrointestinal tracts, while washing and chilling could wash off *Campylobacter* from the carcass. However, defeathering and evisceration with poor handling methods could lead to contamination of the carcass with *Campylobacter* from its own feathers or feces. Moreover, it could cause cross-contamination with other carcasses, either directly or indirectly, *via* equipment or human hands during processing (Hinton et al., 1996; Hayama et al., 2011). For *Campylobacter jejuni*, acetic acid treatment yielded reductions between 1.2-1.4 orders of magnitude. By lactic acid treatment, *C. jejuni* were reduced by 0.2–1.7 orders of magnitude. Compared to air chilling, immersion chilling carcasses will gain between 12 and 15% of their weight during the process. Freezing was more effective in reducing *Campylobacter* than air chilling. Many of the published studies originate from European countries, showed that reductions of *Campylobacter* on naturally contaminated poultry carcasses mainly ranged from 1.3 to 2.2 orders of magnitude (Boysen & Rosenquist, 2009).

The objective of this study was to develop a simulation model to evaluate how *Campylobacter* levels change during industrial process stages and to evaluate the effectiveness of decomtainiation treatments on the levels of *Campylobacter* .

Materials and Methods

Model

The model generally consists of two parts. The first one focuses on the cross-contamination including scalding, defeathering and evisceration. The second part assesses the efficacy of microbial decontamination treatment at washing, chilling and packaging. (Figure 1)
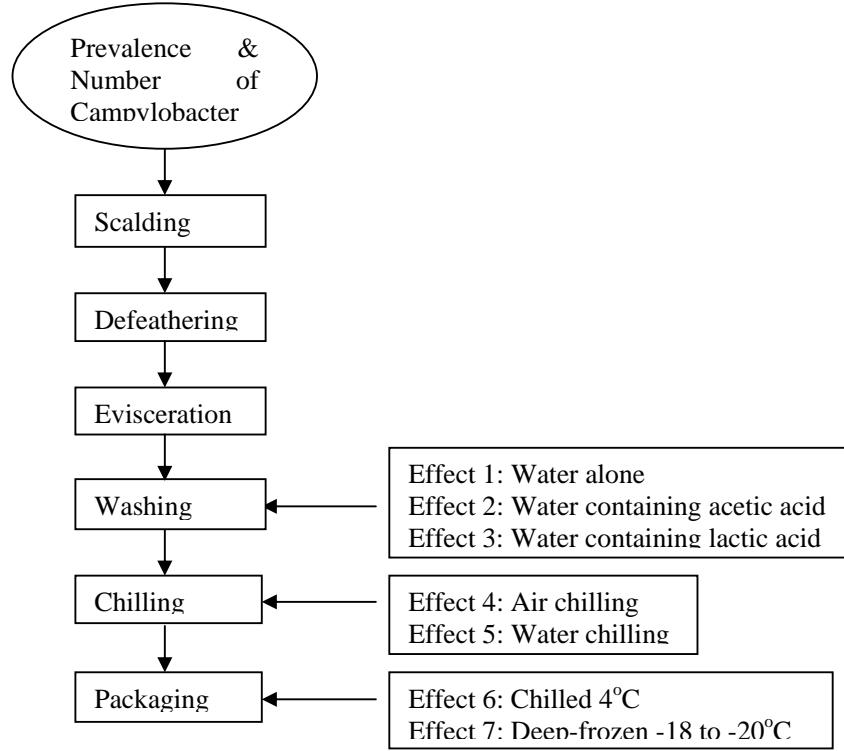
Figure 1. Flow diagram of simulation model.

Cross-contamination

The carcasses are processed in line, and move through a specific environment that may cause cross-contamination between carcasses. The "inactivation and removal" factors in the model include anything that may reduce the number of *campylobacter* during processing, that is, heat, dryness, wash off, wipe off, etc. Also, physical changes of the carcass as a consequence of processing (such as by defeathering) are incorporated in these factors.

Consider a line of poultry processed. At any of the consecutive processing stages (scalding, defeathering, evisceration), a carcass i entering stage S is contaminated with $N_{ext,S-1}(i)$ colony-forming units (cfu) of *campylobacter* on the exterior (skin and, if present, feathers). Here, if S is the scalding stage, S-1 refers to the input value, if S is defeathering, S-1 refers to the values after scalding, etc. At stage S, $N_{fec,S}(i)$ cfu *campylobacter* leak from carcass i with the feces (interior). There is a direct environment of the carcass that gets contaminated, either from the exterior, or in feces leaking from the carcass. This environment can also transfer back to the carcass. It holds $N_{env,S}(i)$ cfu *campylobacter* after the passage of carcass i. (Figure 2)

This yields the following model equations per stage S and carcass i:

$$N_{ext,S}(i) = (1 - a_{ext,S})(1 - c_{ext,S})N_{ext,S-1}(i) + b_{env,S}N_{env,S}(i-1)$$
$$+ (1 - a_{fec,S})N_{fec,S}(i)$$
$$N_{env,S}(i) = a_{ext,S}N_{ext,S-1}(i) + (1 - b_{env,S})(1 - c_{env,S})N_{env,S}(i-1) + a_{fec,S}N_{fec,S}(i)$$

Where $a_{ext,S}$ is the probability per cfu *campylobacter* on the exterior (skin and feathers) to move from the carcass exterior to the environment; $b_{env,S,}$ probability per cfu *campylobacter* in the environment to move from the environment to the carcass exterior; $1-a_{fec,S}$, probability per cfu *campylobacter* move from the interior to the exterior of the carcass directly; $c_{env,S}$, probability of inactivation or removal per cfu *campylobacter* in the environment, that is not transferred to the carcass exterior; $c_{ext,S}$, probability of inactivation or removal per cfu *campylobacter* on the carcass exterior that is not transferred to the environment.
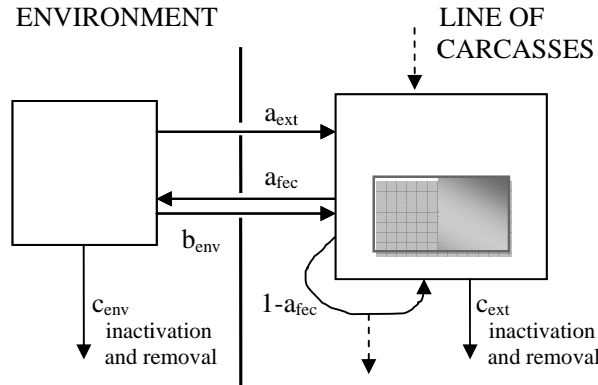
Figure 2. At stage S, the cross-contamination, inactivation, and removal occured.

Results and Discussion

The results of the processing model up to packaging are shown in Figure 3. On average, the model predicts a steady decrease of the numbers of *Campylobacter* on the carcasses during processing. The mean value of log (N_{ext}) for contaminated flocks decreases from 7.27 (SD 0.56) per bird at the entrance of the processing plant to 3.56 per carcass after packaging in colonized flocks. The variability between flocks and carcasses is large. Occasionally, individual carcasses and mean values per flock show an increase in the level during defeathering due to leaking feces with a relatively high concentration of *Campylobacter*. Moreover, the mean reduction of effect 1 to 7 during washing, chilling and packaging were -0.25, -0.51, -1.03, -0.83, -0.965, -0.175, -1.385 separately.
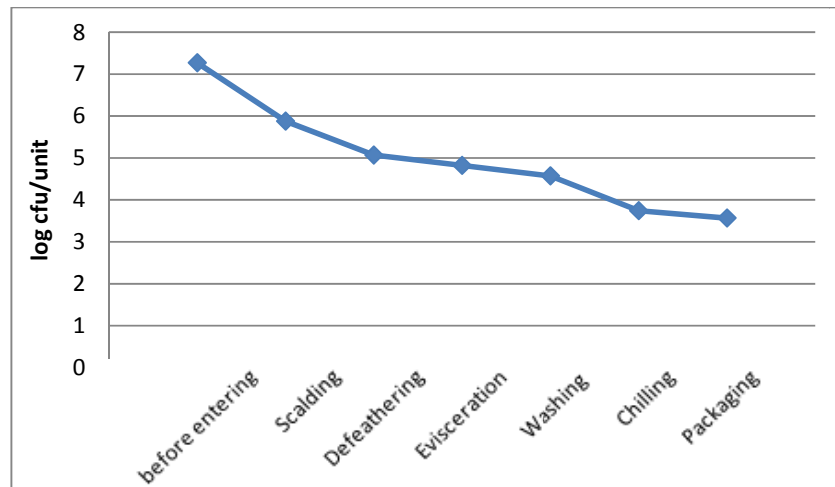
Figure 3: Numbers of *Campylobacter* per carcass [log (N_{ext})] are given for the consecutive stages of processing.

The distribution of *Campylobacter* after packaging is shown in Figure 4. The effect of animal prevalence can be seen, as the animal prevalence gets smaller, the distribution moves to the left.
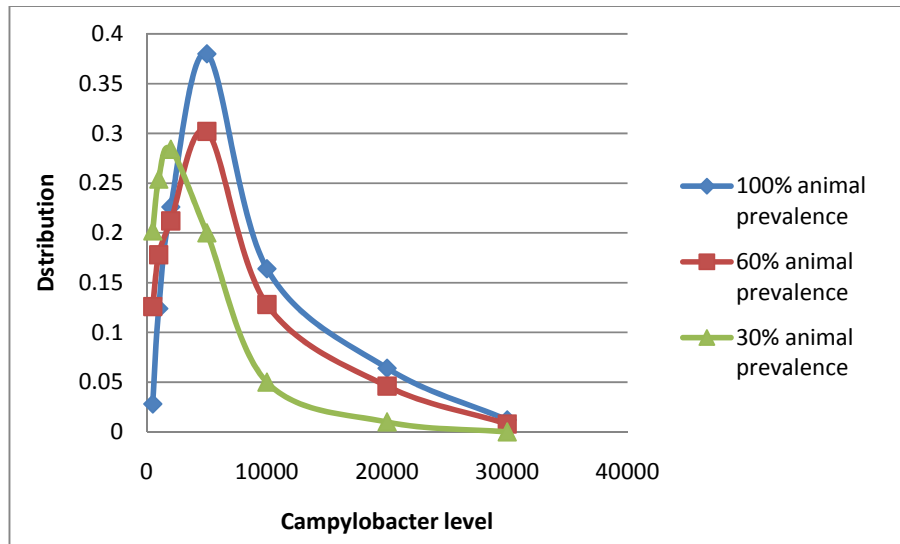
Figure 4. Distribution of *Campylobacter* after industrial process for different animal prevalence.

Conclusions

The individual-based simulation model developed in this study took into account the spread of within-flock contamination, reflecting *Campylobacter* contamination at the individual carcass level. The routes by which *Campylobacter* enters farms are not clear, but once present it can spread throughout the farm within 1 week. Therefore, risk mitigation measures during processing at slaughterhouses could be of importance in controlling *Campylobacter* contamination. These include reducing opportunities for self- or cross-contamination from feathers or leaking feces.

References

Boysen, L., & Rosenquist, H. (2009). Reduction of thermotolerant *Campylobacter* species on broiler carcasses following physical decontamination at slaughter. *Journal of Food Protection.* 72, 497–502.

Berrang, M.E., Bailey, J.S., Altekruse, S.F., Patel, B., Shaw Jr, W.K., Meinersmann, R.J. & Fedorka-Cray, P.J. (2007). Prevalence and numbers of *Campylobacter* on broiler carcasses collected at rehang and postchill in 20 U.S. processing plants. *J. Food Prot.* 70, 1556–1560.

Food Safety Authority of Ireland. (2011). Microbial Factsheet Series *Campylobacter* species.

Hayama, Y., Yamamoto, T., Kasuga, F. & Tsutsui, T. (2011). Simulation Model for *Campylobacter* Cross-Contamination During Poultry Processing at Slaughterhouses. *Zoonoses Public Health.* 58, 399–406.

Hinton, M.H., Allen, V.M., Tinker, D.B., Gibson, C. & Wathes, C.M. (1996). The dispersal of bacteria during the defeathering of poultry. *Factors affecting the microbial quality of meat, concerted action CT94-1456. Slaughter and dressing.* 2, 113–123.

EVALUATION OF QUATERNARY AMMONIUM COMPOUNDS RESIDUES IN FOOD PLANTS SURFACES: METHOD VALIDATION AND RESIDUE PERSISTENCE

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Abstract

A simple and accurate UV spectrophotometric method was validated and applied for the quantification of QACs (Quaternary Ammonium Compounds) residues on stainless steel surfaces in food processing environments. Different analytical performance parameters such as selectivity, linearity, precision, accuracy, limit of detection (LOD), and limit of quantitation (LOQ), as well as the changes of residues concentration within 6 days were studied. Selectivity studies showed that cleaning agents containing no QACs, as active substance, would not interfere with the determination of the residues. The calibration curve was linear in the range of 0.5-10 ppm ($r^2 > 0.99$). The LOD and LOQ were 0.53 µg/ ml and 1.77µg/ml, respectively. The accuracy of the method was 94.5 % and relative standard deviation (% RSD) for precision studies was less than 3 %. The percentage recovery of swabbing procedure over 3 days was acceptable (89%). The percentage RSD of the swabbing technique for inter-day studies was lower than 8.8%. The results approved the appropriateness of the method for daily routine analysis of residues deposited on the stainless steel surfaces in food plants. Residue studies revealed that the residues remained stable within 6 days which may be a potential risk of chemical contamination of the final product and the emergence of microbial resistance.

Introduction

Quaternary ammonium compounds as important industrial sanitizers, widely used in food processing plants, are generally sprayed or fogged on surfaces and equipment and may remain stable within time. The persistence of these chemicals may result in a risk of chemical contamination of the final product and the emergence of resistant mutant (Bridier et al., 2011). Therefore, reliable analytical method for monitoring of quaternary ammonium compounds residues is required. Different techniques for the analysis of QACs have been studied (Heinig et al., 1997; Liu and Ding, 2004; Núñez et al., 2002; Wulf et al., 2010). Despite of the good precision and accuracy of the mentioned method, these techniques require expensive instruments and well trained technicians, limiting their wide application as a routine analysis method in food factories. It should be noticed that no method has been validated for residue monitoring of QACs built in food processing environments.
The objective of this study is to validate and apply a simple but accurate spectrophotometric method for routine analysis of quaternary ammonium compounds allowing recovery and determination of low level residues deposited on stainless steel surfaces.

Materials and Methods

Preparation of standard and sample solutions
Working standard solutions (0.5-10 ppm) were prepared by diluting a stock solution of Dimethyl tetradecyl benzalkonium chloride (Sigma Aldrich, Germany). 0.9 µg/ml Eosin Y and 0.025% v/v Triton X-100 solutions ((Sigma Aldrich, Germany) were added to all the prepared solutions before reading their absorbance in the spectrophotometer (Unicam, UV-3 spectrophotometer,UK) at 535 nm. The calibration graph was obtained by plotting the absorbances versus concentrations.

Analysis of active substance in commercial samples
Different volumes of working standard solutions (1, 2, 3, 4, 5 ppm) were added to 1% commercial samples (Quadtet Clear and Triquart). The adsorbance was plotted versus the corresponding amounts added to obtain a standard addition calibration graph. The *x*-intercept, was then used for calculating the content of active substance in the commercial samples analysed.

Spray and recovery procedure
A series of 100 ml standard solutions (480, 560, 686, 753 and 960 ppm) were sprayed on 10×10 cm stainless steel plates (2B finish, 0.9 mm thickness, AMARI Ireland) by means of an adjustable spray gun operated with compressed air (Radionics, Ireland).The stainless steel sheets were weighted before and after spraying using a high precision scale (Sartorius, BP161P, Germany) to evaluate the weight of solution sprayed. The formula for calculating the net weight of the QACs on surfaces is:

$$\text{Concentration of residue} = \frac{W_s}{V_b} \times C_i \qquad (1)$$

where:
W_s= Weight of sprayed solution
V_b= Volume of buffer in the tube (we used 10 ml)
C_i= Initial Concentration of solution

A cotton swab (ITW Text wipe, TX 775, Fisher Scientific, Ireland) was immersed into a tube containing 10 ml borate buffer to be sufficiently moistened. Then, the total surface of the stainless steel plates were successively wiped first in a horizontal and secondly in a vertical way, starting from the outside towards the centre, with the moistened swab. The cotton swab was returned to the tube and the swabbing process was repeated by another dry cotton swab. The tube containing cotton swabs were placed in the ultrasonic bath (CQBF-1025, China Shipping Company, China) for 15 min. The final solution was used to determine the level of QACs in the spectrophotometer at 535 nm.

Results and Discussion

Linearity, Limit of Detection and Limit of Quantitation (LOD and LOQ)
The linearity of the spectrophotometric measurement in the range of 0.5-10 µg/ml was satisfactory and the coefficient of determination (r^2) was 0.99.
According to the regression equation calculated from the calibration graph, LOD and LOD can be calculated using the following equations:

LOD=3.3σ/S   (2)
LOQ=10σ/S   (3)

where σ is the standard deviation of the y-intercept and S is the slope of the calibration curve. The LOD and LOQ were calculated to be approximately 0.53 µg/ ml and 1.77 µg/ ml, respectively. The results confirmed that the method was sufficiently sensitive.

Selectivity and method suitability
In order to investigate the interfering effect of other detergents without QACs as active substance in the determination of quaternary ammonium compounds, selectivity study was performed by comparing the maximum absorbance of standard Dimethyl tetradecyl benzalkonium chloride, the commercial biocides Quadtet Clear and Triquart containing QACs, and two other detergents without QACs (Divaushaum and RBS 25) in the spectrophotometer at 535 nm. The maximum absorbance of standard solutions, Quadtet Clear and Triquart was at 535 nm while RBS 25 and Divaushaum did not exhibit any absorbance within the selected wavelength range.

In order to validate the method suitability, the amount of active substance QACs available in commercial samples (Quadtet Clear and Triquart) was quantified by adding increasing known amounts of standard solutions (0, 1, 2 , 3, 4 µg/ml) to the commercial samples and the absorbance was read at 535nm. Typical regression lines obtained for the analysis of QACs in commercial samples were: y= 0.041x +0.284, r^2= 0.997 and y= 0.046x +0.1274, r^2= 0.9841 for Quadtet and Triquart, respectively. According to the regression lines, the slope of the two commercial solutions spiked with standard solutions is approximately similar, revealing that the method is reliable for other testing commercial sanitizers.

Accuracy and precision
The accuracy studied by means of assays of recovery in Dimethyl tetradecyl benzalkonium chloride standard solutions gave mean values of 94.5%. The mean precision evaluated in the standard solution as relative standard solution (RSD%), was about 1.6%. The results revealed that the method had a suitable accuracy and precision.
The accuracy and precision of swabbing method, as an important step in residue recovery, have also been undertaken over 3 days under different laboratory conditions to examine the % recovery, repeatability and intermediate precision of swabbing protocol. The mean % recovery over 3 days was acceptable (88.5). By comparing the % recovery results exhibited in Table 1 and 2, it can be concluded that swabbing procedure did not considerably decrease the residues recovery from the stainless steel sheets. In addition, repeatability (intraday reported as % RSD) of the method in the three different days was good (average of 8.5%) and %RSD for intermediate precision study of the assay was lower than % 7.82, confirming the suitability of the method for daily routine analysis.

Table 1. Results of recovery and repeatability of the spectrophotometric method for the determination of quaternary ammonium compounds in solutions

Amount added (ppm)	Amount found (ppm)*	Recovery (%)	Repeatability (RSD %)
0.90	0. 83±0.03	92.96±0.03	0.57
2.06	1.93±0.19	93.95±0.19	2.85
2.73	2.65±0.02	97.16±0.02	0.32
4.75	4.56±0.26	96.07±0.26	2.81

* Values are averages of 3 replications

Table 2. Accuracy and precision of swabbing technique

Day						
1	%RSD	5.80	7.43	15.52	5.88	9.44
	% recovery	81.01±4.70	88.43±7.43	89.66±8.2	101.76±5.98	93.16±8.79
2	%RSD	8.37	9.19	10.20	9.35	7.40
	% recovery	85.60±7.17	88.88±8.17	96.55±9.85	90.20±8.43	101.71±7.52
3	%RSD	2.81	1.57	9.29	9.91	3.26
	% recovery	77.26±2.17	79.13±1.24	82.54±7.67	90.36±8.95	95.28±3.10

Residues monitoring of commercial Quadtet Clear biocide and standard QAC
The suggested method was applied for residues measurement of Quadtet Clear built up on stainless steel sheets within 7 days. The highest recommended concentration for using Quadtet Clear was 1 %, in which 530 ppm quaternary ammonium compounds, as active substance, was measured by the aid of suggested protocol described in previous sections. As shown in Fig. 3, the highest decrease rate of the initial concentration of active substance in Quadtet Clear was 5% (26.5 ppm) which occurred after 6 days, and according to standard deviations, this decrease rate is not significant. Therefore, the results proved that the concentration of the QACs did not change during time and the QACs residues do not degrade

after spraying and remain stable on the stainless steel surface. Therefore, QACs may be deposited on the surfaces after several sprays and this can be a potential risk of chemical contamination of the final product and appearance of resistant pathogenic bacteria. It should be, however, noted that there are many different factors affecting the stability of QACs including relative humidity, surface properties and spraying conditions. It is recommended to develop similar experiments on different surfaces and different conditions as well as on processing plants.
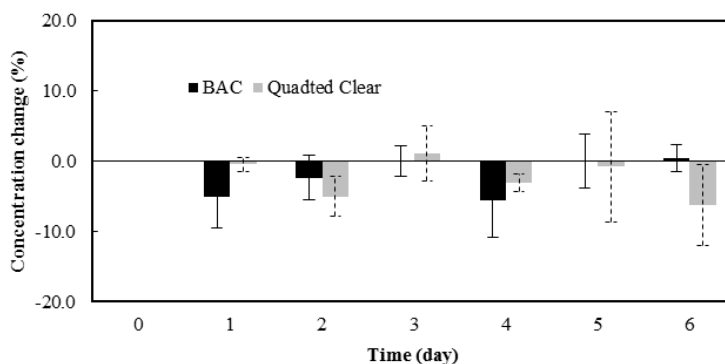
Figure 4. Changes of the concentration of standard benyzl dimethyl tetradecyl ammonium chloride and Quadted Clear within 6 days sprayed on the stainless steel sheet.

Conclusions

Results showed that the spectrophotometric method proposed for the quantification of QACs is a rapid and convenient method with a reasonable limit of detection and sensitivity for quantifying purposes that can be easily used as a routine method for residues analysis of quaternary ammonium compounds in food processing environments. Results also illustrated that QACs remained stable during time (up to 6 days) and may be accumulated on equipment after consecutive spraying for cleaning purposes which can be harmful in terms of chemical toxicity and microbial resistance. Therefore, more experiments are necessary to study the effect of different parameters on the stability of QACs and to evaluate the residues in real plant conditions.

References

Bridier, A., Briandet, R., Thomas, V., and Dubois-Brissonnet, F. (2011). Resistance of bacterial biofilms to disinfectants: a review. *Biofouling, 27*(9), 1017-1032.

Heinig, K., Vogt, C., and Werner, G. (1997). Determination of cationic surfactants by capillary electrophoresis with indirect photometric detection. *Journal of Chromatography A, 781*(1-2), 17-22.

Liu, H.-Y., and Ding, W.-H. (2004). Determination of homologues of quaternary ammonium surfactants by capillary electrophoresis using indirect UV detection. *Journal of Chromatography A, 1025*(2), 303-312.

Núñez, O., Moyano, E., and Galceran, M. T. (2002). Capillary electrophoresis-mass spectrometry for the analysis of quaternary ammonium herbicides. *Journal of Chromatography A, 974*(1-2), 243-255.

Wulf, V., Wienand, N., Wirtz, M., Kling, H.-W., Gäb, S., and Schmitz, O. J. (2010). Analysis of special surfactants by comprehensive two-dimensional gas chromatography coupled to time-of-flight mass spectrometry. *Journal of Chromatography A, 1217*(5), 749-754.

MIGRATION AND EXPOSURE ASSESSMENT OF ENGINEERED SILVER NANOPARTICLES FROM A PVC NANOCOMPOSITE

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Abstract

Nanotechnology is the manipulation of matter at the nanoscale, generally between 1 – 100 nm. The discovery of unique nanomaterial properties has lead to novel applications in the food industry, one of which is antimicrobial food packaging materials. Human exposure to nanomaterials may be influenced by the consumption of food subjected to such packaging conditions. The objective of this study was to evaluate likely migration of silver nanoparticles from a plasticised polyvinyl chloride (PVC) composite to a meat surface following varying storage time and temperature conditions. The resultant potential human exposure to the nanomaterials used in these nanocomposites was also investigated. The effect of nanoparticle size (diameter) and nanomaterial concentration (w/w) in the film (fill) were investigated in this experiment. Chicken breasts were packaged with the nanocomposites and stored at two different temperatures and two different storage times. The silver content of the chicken was subsequently quantified using inductively coupled plasma mass spectrometry (ICPMS). Migration was found to occur in trace amounts (with a range of 0.03 to 6.03 mg/kg). The factors; fill, time and temperature, were found to significantly impact the resulting silver levels in the chicken breasts in contact with the nanocomposites, with p values < 0.01, < 0.01 and < 0.05, respectively. An exposure assessment revealed that human exposure to silver is likely to be below a provisional toxicity limit (PIL); however it is acknowledged there is still considerable uncertainty about the toxicity of particles at the nanoscale.

Introduction

For the food industry, where competition is intense and innovation is vital, nanotechnologies have emerged to aid advancements in production, packaging and preservation of food. Nanotechnologies have been applied in the food sector from primary production to stock monitoring at the retail level (Cushen *et al.* 2011). One emerging and promising application of nanotechnologies in the food sector is food packaging. Antimicrobial effects, improved tensile properties, oxygen scavenging and improved light and gas barrier properties are some novel features that nanoparticulate fillers in food packaging materials can achieve (Avella *et al.* 2005, Bouwmeester *et al.* 2007, Rhim and Ng 2007). Perishable, high value food products are the most likely food category to benefit from these value-added innovations in packaging. In particular, nanosilver has emerged as a promising substance in food packaging because it is thought that the antimicrobial action is exhibited by the migration of silver cations from the particles (Kumar and Münstedt 2005, Busolo *et al.* 2010), which are nontoxic to model organisms (Asharani *et al.* 2008). It also has the additional novelty of being a long lasting antimicrobial, which can endure high temperatures and has low volatility (Kumar and Münstedt 2005). However, when silver nanoparticles are used in commercial packaging materials (which generate antimicrobially active cations through oxidation), it has recently been shown that they migrate out of packaging (polyethylene) in nanoparticulate form (Huang *et al.* 2011) and unlike the active silver cations, silver nanoparticles have been shown to exhibit toxicity (Asharani *et al.* 2008).

The objective of this study is to evaluate the potential for nanoparticle migration from a nanocomposite (with varying nanoparticle size and percent fill) to food surfaces (chicken breast) under varying storage conditions and to estimate likely human exposure to nanoparticles following the consumption of meat subjected to such packaging conditions.

The European Food Safety Authority (EFSA) is required by article 10 of Regulation (EC) No. 1935/2004 to carry out risk assessments on the risks originating from the migration of substances from food contact materials into food. Real food matrices present quantitative challenges due to the variation and complexity associated with them. PVC has many features which make it a suitable material for food packaging; it is transparent, cheap to produce, easy to process and resistant to chemicals (Lefteri, 2008). The inclusion of engineered silver nanoparticles in a PVC matrix has been shown to exhibit an antimicrobial effect (personal communication, Moloney *et al.* 2011). For the food industry, the use of an antimicrobial PVC has the potential to prolong the shelf life of food, and thus reduce waste and broaden export boundaries. This supports the need to focus on emerging packaging materials with a view to obtaining a commercially viable end product.

Materials and Methods

Materials

Nanoparticles were synthesised and incorporated in a solvent/polymer/plasticiser solution which was cast into films which contained nanoparticles with a diameter of either 50 nm or 10 nm (with specific surface areas of 57.2 and 11.5 m^2/g respectively, assuming spherical formation), each of which were provided at two levels of fill; 5% w/w and 0.5% w/w.

Experimental Design

The experiment was set up as a multi-factorial design to allow for the examination of the multiple factor effects. This maximises statistical power and resources. Skinless, boneless chicken breasts (samples) were sourced from an Irish supplier and wrapped in 120 cm^2 of the prepared nanocomposite films on the breast bone side of the chicken. Tin foil was wrapped around these to eliminate any possible variation that light may impart (Cruz *et al.* 2008). Each sample, nanocomposite, foiled (unit) was then vacuum packed. Units were kept in constant temperature rooms for the duration of the experiment. Temperature probes were used to log the internal temperature of the samples at the various temperatures used. Air temperatures used in this experiment were 5˚C and 20˚C which gave rise to average internal temperatures of the units of 6.6˚C, 7.2˚C, 19.9˚C and 24.1˚C. All packaging was removed from the samples. Samples were analysed using (ICPMS) according to protocol assigned the ISO number: DIN EN ISO 17294-2-E29. Statistical analysis of the results was carried out using SAS 9.1.

Exposure assessment model design: probabilistic simulation

If migration occurs, potential exposure must be evaluated to determine if the level of migration is harmful to human health. A mathematical model was created to evaluate the likely human exposure to silver nanoparticles as a result of the consumption of chicken after contact with the nanosilver PVC nanocomposite used in the migration tests (equation 1).

$$E_X = (m_x \times c) / bw \tag{1}$$

Where E is exposure in mg/kg$_{bw}$/day, x = scenario (wcs or mls), m is migration in mg/kg, c is the consumption of the food in kg/day and bw refers to the body weight of an individual in kg.

From the migration results, two separate scenarios were evaluated for the exposure assessment. These were the worst case scenario (wcs) (10 nm diameter nps; 5% fill; 4 days; 6.59˚C) and the most likely scenario (mls) (50 nm diameter nps; 0.5% fill; 3.1 days; 7.24˚C). Probability distributions were used to represent inherent uncertainty and variability in the model inputs. Migration (m) was modelled using an empirical distribution based on observed experimental results, consumption and body weight were modelled as lognormal and normal distributions respectively based on data provided by IUNA (2011). The model was run for 10,000 iterations to create predicted human exposure curves for x = wcs and x = mls.

For this study the most applicable reference value available was a PIL value (0.482 mg of silver/kg(body weight)/day) which was generated using oral toxicity studies using a model organism, interspecies allometric distribution factors and specific surface area of given nanoparticles published by O'Brien & Cummins (2010). This limit was adapted for this migration study by taking the specific surface area of the particular nanoparticles used in the nanocomposites into account. For the 10 nm particles, a PIL of 0.084 mg of silver/kg_{bw}/day was calculated and for 50 nm, a PIL of 0.421 mg of silver/kg_{bw}/day was calculated. Exposure curves were generated for wcs and mls and their respective 95th percentiles were compared to their respective PILs.
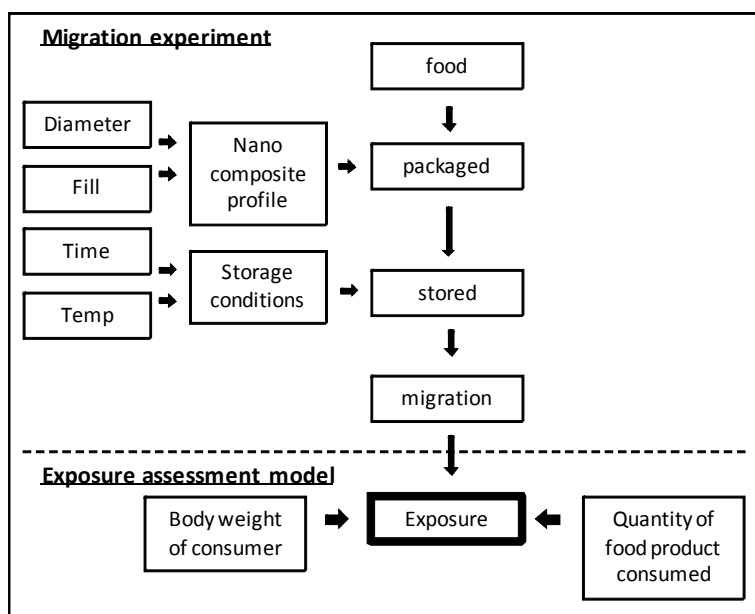
Figure 1. Flow chart of the migration experiment and the exposure assessment model.

Results and Discussion

The factors analysed were diameter, fill, time and temperature. The quantity of silver found in the samples did not differ significantly with increasing size of the silver nanoparticles (diameter) incorporated into the films ($p > 0.1$). The quantity of silver initially incorporated into the film (fill) proved to be a factor that significantly ($p < 0.01$) impacted on the quantity of silver found in samples. Samples in contact with films at the 5% fill level had higher silver quantities (mean = 3.93 mg/kg) than samples in contact with films at the 0.5% fill level (mean = 0.28 mg/kg). Results showed that the quantities of silver in samples increased with increasing storage time ($p < 0.01$). The exposure assessment showed that for the wcs, the 95th percentile of exposure amounts to 16.02% of the PIL for the particular size nanoparticle considered in the scenario (10 nm). For the mls, the 95th percentile of exposure was 0.16% of the PIL for 50 nm nanoparticles.

Conclusions

Nanomaterials are novel substances and as with all new substances, their use should be approached with caution. Thorough risk assessment in the area of nanotechnology in the food sector should clarify potential risks. It was shown that many factors influence the quantity of silver that migrates from the nanocomposite (fill, time and temperature) and that the size of nanoparticle did not significantly influence the migration. However, using limited toxicity information, results from this experiment show that eating foods packaged with PVCP which incorporates silver nanoparticles is not likely to lead to human exposure levels which exceed the PIL with the wcs and mls being 16.02% and 0.16% of the PIL adapted

to the particle size in the respective scenarios. The lack of knowledge in relation to nanotoxicity is recognised and is an area where further work is required and risk assessments refined as more results become available

Acknowledgements

References

Asharani, P. V., Lian Wu, Y., Gong, Z. & Valiyaveettil, S. (2008). Toxicity of silver nanoparticles in zebrafish models. *Nanotechnology* 19(25), 1-8.

Avella, M., De Vlieger, J. J. Errico, M. E., Fischer, S., Vacca, P. & Volpe. M. J. (2005). Biodegradable starch/clay nanocomposite films for food packaging applications. *Food Chemistry*, 93(3), 467-474.

Bouwmeester, H., Dekkers, S., Noordam, M., Hagens, W., Bulder, A., de Heer, C., ten Voorde, S., Wijnhoven S. & Sips A. (2007). Health risks of application of nanotechnologies and nanoparticles within the food production chain. Health impact of nanotechnologies in food production. RIKILT Institute of Food Safety and RIVM National Institute for Public Health and the Environment.

Busolo, M. A., Fernandez, P., Ocio, M. J. & Lagaron, J. M. (2010). Novel silver-based nanoclay as an antimicrobial in polylactic acid food packaging coatings. *Food Additives & Contaminants: Part A* 27(11),1617-1626.

Huang, Y., Chen, S., Bing, X., Gao, C., Wang, T. & Yuan. B. (2011). Nanosilver Migrated into Food-Simulating Solutions from Commercially Available Food Fresh Containers. *Packaging Technology and Science* 24(5), 291-297.

Kumar, R. & Münstedt. H, (2005). Silver ion release from antimicrobial polyamide/silver composites. *Biomaterials* 26(14), 2081-2088.

Lefteri, C. (2008). The plastics handbook. Mies; Hove: RotoVision.

Cushen, M., Kerry, J., Morris, M., Cruz-Romero, M. and Cummins, E. (2011). Nanotechnologies in the food industry - Recent developments, risks and regulation. *Trends in Food Science & Technology* (In Press).

Rhim, J. & Ng, P. K. W. (2007). Natural Biopolymer-Based Nanocomposite Films for Packaging Applications. *Critical Reviews in Food Science and Nutrition* 47(4), 411 - 433.

Cruz, J. M., Sanches Silva, A., Sendón García, R., Franz, R. & Paseiro Losada, P. (2008). Studies of mass transport of model chemicals from packaging into and within cheeses. *Journal of Food Engineering* 87(1),107-115.

O'Brien, N. & Cummins, E. (2010). Ranking initial environmental and human health risk resulting from environmentally relevant nanomaterials. *Journal of Environmental Science and Health, Part A: Toxic/Hazardous Substances and Environmental Engineering* 45(8), 992 - 1007.

COMPARISON OF OZONE AND CHLORINE FOR REDUCING MICROBIAL LOAD ON LETTUCE LEAVES

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Abstract

Minimal processing of lettuce (*Lactuca sativa*) and other fruits and vegetables make it difficult to ensure that these fresh produce are safe for consumers. Chlorine-based agents in water applied during processing operations have often been used to sanitize produce and reduce microbial populations. However, the production of chlorinated organic compounds with potential carcinogenic action during chlorine water treatment of lettuce and the limited antimicrobial efficacy beyond pH range 6 to 7.5 has created the need to investigate the effectiveness of alternative decontamination techniques. In this study, the ability of ozone to reduce microbial populations in lettuce leaves in consumer-sized bags preserved at $4^{o}C$ in a refrigerator was evaluated. The lettuce leaves were treated in A. ozone-in-water B. Water and C. chlorinated water. A comparative study of the microbial count was performed using the viable plate count method of enumerating microbes.

Introduction

Vegetables are often supplied pre-cut to manufacturers of ready-made meals and pre-prepared salads manufactures where they are stored under refrigerated conditions and used as needed. These pre-cut raw ingredients can have high microbial loads. For this reason, they are often treated (usually in chlorinated water) prior to their incorporation into the final product by the processing company. Delays in supply to the processing company after harvesting, often means that the vegetable is supplied with a relatively high microbial count to the producer. In this respect, products such as pre-prepared salad vegetables, that may not be washed or cooked before consumption, can put the consumer at risk if the food is not microbially safe (Sagoo et al., 2003)). Fresh products are responsible for a growing number of food borne diseases outbreaks each year (Beuchat, 2002). Sources of microbial contamination on vegetables during production include animal and human faeces, contaminated manure, inorganic amendments, irrigation water; water used for pesticide application or other agricultural purposes and contaminated dust (Beuchat and Ryu, 1997). The minimal processing of these products make it difficult to ensure that fresh produce is safe for the consumer. Moreover, tissue damage during processing and subsequent release of nutrients in fresh-cut produce enhances microbial development (Harris et al., 2003). Salad vegetables have been traditionally washed in chlorine solutions to reduce microbial levels. However, chlorine's health concerns regarding its by-products (Xu, 1999) are leading to a search for alternative sanitizers.

The main objective of this project was to carry out a comparative study of the microbial load of lettuce leaves treated separately with water, ozone in water and chlorinated water.

Materials and methods

Sample selection

The first three layers of the lettuce head were removed manually and discarded. The leaves were then chopped into 2-3 cm sizes on a plastic board using a stainless steel kitchen knife.

Sample treatment

The chopped lettuce was separated into 4 groups weighing 25 g each. The first group of lettuce sample was rinsed in 5 litres of tap water in an ultrasound cleaning bath (turn- off) (BRANSON 5210 MTH ultrasound cleaner) (fig. 1) and excess water drained. The second group of sample was treated in ozonated water for 10 minutes. In the experimental set-up, gaseous ozone was bubbled into 5 litres of tap water for 10 minutes, and then the lettuce was rinsed in the ozonated water (ozone generator turn-off) for 5 minutes. Excess water was drained from the leaves by centrifuging. The third group of lettuce sample was treated in ozonated water for 20 minutes. In the experimental set-up gaseous ozone was bubbled into 5 litres of tap water using an ozone injection system (Fig.1) (OzoneLabTM OL80 Desktop Line (90° panel series)), for 10 minutes, and then the lettuce was rinsed in the ozonated water for 5 minutes (ozone generator turn-on) and excess water drained from the lettuce. The fourth group of lettuce was treated with chlorinated water (100 ppm) for 5 minutes. The treated samples where packaged separately in plastic bags (weighing 25 g each) and stored in a refrigerator at 4°C prior to microbiological analysis.

Figure 1. Diagram of an ozone injection

Table 1: Different sample treatments

Sample	Treatment	Treatment time
I	Water only	5
II	Ozonated water	15
III	Ozonated water	20
IV	Chlorinated water	5

Microbiological analysis

Each of the lettuce replicate samples (25 g) was weighed into sterile stomacher bags containing 5 ml of ringer solution (¼ strength). The lettuce was homogenized in a stomacher blender for 5 minutes. 1 ml of the blended lettuce was serial diluted into 9 ml of ringer solution (¼ strength) (Fig. 2). 0.1 ml of the dilutions was pour-plated in a selective and total plate count agar and incubated for 48 hours at 36 ℃ under aerobic conditions. The number of colony forming units per gram of sample was calculated and expressed in CFU/g.

From the number of CFU in each plate, the concentration of the target microbe in the original lettuce was estimated using the formula:

Total CFU in original sample = Number of CFU/ Volume plated (ml) x total dilution used
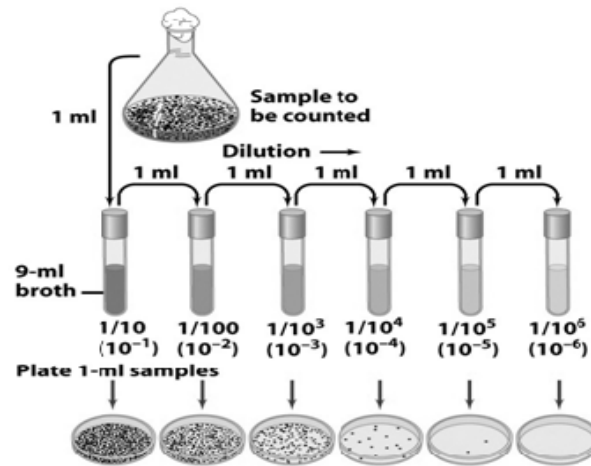
Figure 2. Serial dilution and plating

Results and Discussion

The project is ongoing, for this reason only expected results are discussed. As shown by Garcia et al. (2003), lettuce treated with 2.5, 5 and 7.5 mg/l of ozone had a 0.6 to 0.8-log reduction in the aerobic plate count compared with rinsing with distilled water (P< 0.05); however there was no significant difference among the concentration of ozone tested. Chlorine (100 to 200 mg/l) caused approximate 0.9-log to 1.2-log decrease in the aerobic plate count. Ozone has been seen by many as a natural replacement for chlorine for the

washing of produce (Graham, 2007; Khadre et al., 2001; Kim et al., 1999; Xu, 1999), since the break down of ozone to oxygen does not leave any residuals itself, and any by-products of ozone treatment are considered to be less of a health risk than those caused by chlorine treatment (Graham, 1997). Vegetables have the advantage of having smooth intact surfaces with low ozone demand (Khadre et al., 2001) making them particularly suitable for aqueous ozone treatments. Hülya et al. (2009) found out that the application of 2 ppm ozonated water treatment for 2 minutes was the optimum processing condition for ozone disinfection for leaf lettuce, in terms of reducing the microbial load and maintaining the sensory quality.

Conclusion

The purpose of this study was to look at the effect of water, aqueous ozone, and chlorinated water treatment on the microbial population in lettuce leaves. Previous research on this subject matter showed that the use of 2 ppm ozone concentration for 2 minutes was the optimum processing condition for ozone disinfection in leaf lettuce, in terms of microbial load and maintaining sensory quality. A 1 log unit reduction in total aerobic mesophilic bacteria in lettuce was obtained during the treatment of lettuce leaves with ozone water. The use of aqueous ozone is a better alternative to chlorinated water in the treatment of vegetables; however delays between harvesting and treatment of vegetables should be reduced as much as possible. This may reduce the chances of microbes migrating into deeper tissues of the leaves and this may reduce the effectiveness of the treatment.

Acknowledgement

References

Beuchat, L.R., & Ryu, J.H. (1997). Produce handling and processing practices: special issue Emerging Infectious Diseases, 3: 459–465

Beuchat, L.R. (2002). Ecological factors influencing survival and growth of human pathogens on raw fruits and vegetables. Microbes and Infection, 4(4):413-423

Garcia,A., Mount, J.R., Davidson, P.M.(2003). Ozone and chlorine treatment of minimally processed lettuce. J Food Science, 68 (9):1750-3841

Graham, D.M. (1997). Use of ozone for food processing. International Journal of Food and Technology, 51 (6):72–75

Kim, J.G., Yousef, Dave, A.E. S. (1999). Application of ozone for enhancing the microbiological safety and quality of foods. Journal of Food Protection, 62: 1071–1087

Khadre, M.A., Yousef, A.E., & Kim, J.G. (2001). Microbiological aspects of ozone applications in food− A review Journal of Food Science, 66:1242–1252

Sagoo, S.K., Little, C.L., Ward, L., Gillespie, I.A., Mitchell, R.T. (2003). Microbiological study of ready-to-eat salad vegetables from retail establishments uncovers a national outbreak of Salmonellosis. Journal of Food Protection, 66:403–409

Xu, Liangji. (1999). Use of ozone to improve the safety of fresh fruits and vegetables. Food Technology, 53 (10)

INVESTIGATION OF EFFECT OF PRESSURE REDUCTION RATE ON THE IMMERSION VACUUM COOLING OF COOKED HAMS

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Abstract

Immersion vacuum cooling is a good method to compensate the mass loss of vacuum cooling. In order to further understand immersion vacuum cooling, two pressure reduction rates, namely, 60 mbar/min and 100 mbar/min, were compared for their effect on cooling time, weight loss and quality of large cooked ham product during immersion vacuum cooling. Samples were cooled from a core temperature of 72 ^{o}C to 4 ^{o}C in a laboratory scale vacuum cooler. The first experiment results indicated that cooling time was shorter for a pressure reduction rate 100 mbar/min. But more replications need to be conducted for statistical significant results.

Introduction

There is currently a wide range of ready to eat meat products available to customer. The meat industry require a more rapid and safer cooling method to meet the increasing market demand. Rapid cooling of meat after cooking can preserve its nutritional quality and improve microbiological safety. In recent years, vacuum cooling has been proposed as a rapid cooling method for certain foods including cooked meats (Burfoot et al., 1990; Sun, 1999; Mc Donald et al. 2000; Desmond et al. 2000). However, vacuum cooling relies entirely on evaporation of moisture of the product for its cooling effect, which leads to high product mass (moisture) losses (8-12%) and this high moisture loss has been associated to some adverse effects on product quality (Burfoot et al., 1990; McDonald et al., 2000; Desmond et al., 2000). Compared to vacuum cooling (VC), immersion vacuum cooling (IVC) causes lower cooling losses and higher quality properties, which are generally comparable to those by air blast cooling (AB). The cooling times of IVC were slower than VC, but faster than AB (Drummond et al., 2009).

During the procedure of IVC, samples were transferred together with enough cooling solution covering the sample into a specially designed vessel equipped with a secure lid (Cheng & Sun, 2006). The lid allows the generated vapor from foods to escape, while it can prevent the boil-over of the solution from the vessel. Then the ham and solution in the container experience vacuum in a vacuum cooler. In order to control the boiling of both the water and moisture from the ham, during immersion vacuum cooling, the pressure inside the chamber is reduced in a controlled manner. Drummond et al. (2009) manually controlled the pressure with reference of the saturated vapor pressure at the instantaneous cooking solution temperature.

The objective of the present study is to investigate the effect of different pressure reduction rates, which are precisely controlled by a computer, on IVC cooling time for large cooked hams and their qualities.

Materials and methods

Preparation of samples

Log hams in perforated bags, about 4 kg, with similar size and weight, were prepared in the same batch by a supplier (MCCARREN & COMPANY LTD. Cavan, Ireland). They were stored below 0 $^{\circ}$C and thawed at approximate 4 $^{\circ}$C about 4 days before usage.

Cooking and cooling

After being weighed, a ham was vacuum-packed using a cooling bag and then cooked in an oven (FCV6, Zanussi, Sweden) at 82 $^{\circ}$C until the core temperature reached 72 $^{\circ}$C for 2 min. After cooking, the cooling bag was removed, and the cooked sample with the perforated bag was weighed, followed by moving the sample into a tank with a certain amount of water. The cooked sample in the water was cooled in a laboratory scale vacuum cooler, as shown in Figure 1. The time spent between removal of the product from the oven and start of IVC was as short as possible. The pressure reduction rate was set in a computer and achieved with the assistance of a pressure controller and a control valve between the chamber and the pumps, as shown in Fig. 1. After cooling, the sample and the perforated bag were weighed individually, and then the sample was vacuum-packed and stored at 4 $^{\circ}$C until further analysis.
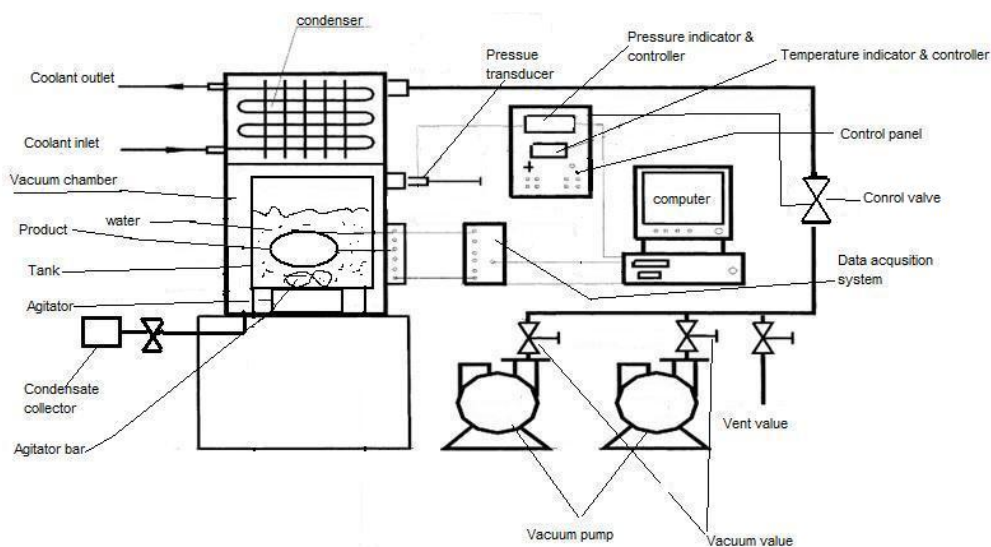
Figure 1. Schematic representation of a laboratory scale vacuum cooler.

Physical analysis

Cooling losses

The weight of each ham sample was recorded before and after cooling step. Cooling loss was calculated as the percentage weight loss between cooked and cooled beef sample.

Cooling loss (%)=(W_{ck}-W_{cl}) / W_{ck} × 100%　　　　　　　　　　　　(1)

where W_{ck} is the net weight of cooked ham and W_{cl} is the net weight after cooling.

Water holding capacity (WHC)

The water holding capacity (WHC) of each ham sample was determined by a modified centrifuge method (Desmond et al., 2000). A sample was evenly cut into 3 pieces along its longitudinal axis. Three cores were obtained from each piece, representing the whole piece. The cores were wrapped in cotton cloth and centrifuged for 10 minutes at 10,000 rpm (Model J2-HS,

Beckman Instruments, USA). The WHC of the sample (mean value of all cores) was expressed as the percentage weight retained after centrifugation (m_a), based on initial sample weight (m_b).

WHC (%) = m_a / m_b × 100%   (2)

Moisture analysis

Moisture content of each ham was measured by drying the sample about 5 g at 105 °C overnight.

Instrumental texture profile analysis (TPA)

An Instron Universal testing machine (Model 5544, Instron Corporation, UK) was employed and the texture profile analysis (TPA) was used to obtain an objective measurement of the hardness, springiness, gumminess and chewiness of ham samples.

Color analysis

The color of the cooked hams was measured by the chroma meter (Chroma CR300, Minolta Ltd. Osaka, Japan). Each sample took twelve replications and got the mean data used for analysis.

Results and discussion

Results of effect of different pressure reduction rates during IVC were shown in Table 1. The experimental results indicated that cooling time for 60 mbar/min was a little longer than that for 100 mbar/min (Figure 2). However, the cooling loss for pressure reduction rate at 60 mbar/min was less than 100 mbar/min. The former pressure reduction rate also caused darker color and less moisture of the cooled product, but its texture was similar to that for the latter pressure reduction rate. However, only one replicate has been carried out up to now. More replications are needed before statistic conclusions can be drawn.

Table 1 : The results for different pressure reduction rates.

| | | Pressure | reduction rate |
		60 mbar/min	100 mbar/min
Cooling time (min)		177.6	172.8
Cooling loss (%)		2.1	3.8
Moisture (%)		71.78	73.97
Color	L*	56.62	62.34
	a*	16.05	13.65
	b*	2.28	1.77
TPA	Hardness (N)	98.94	97.49
	Springiness(mm)	6.99	6.68
	Gumminess (N)	37.77	41.07
	Chewiness(N/mm)	262.75	276.07

| (a) | (b) |
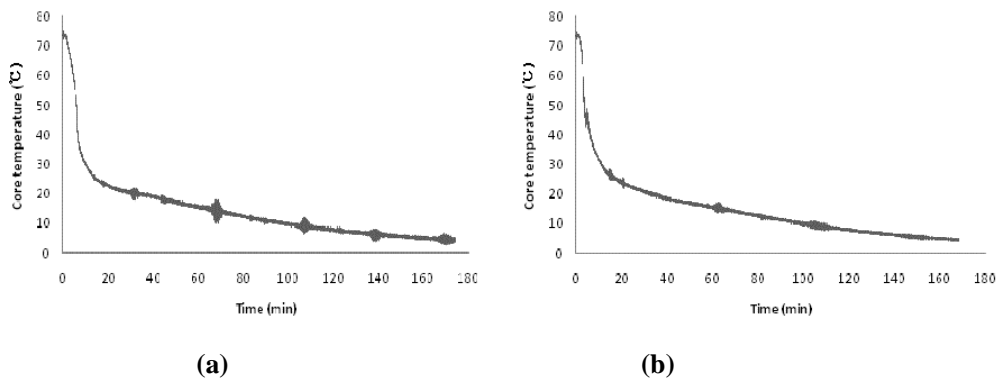
Figure 2. The core temperature curves for pressure reduction rates at 60 mbar/min (a) and 100 mbar/min (b)

Conclusions

The cooling time for pressure reduction rate of 100 mbar/min was shorter than 60 mbar/min. The different pressure reduction rates did not affect the quality of ham much. However, more experiments are required to obtain more statistically significant conclusions.

References

Burfoot, D., Self, K. P., Hudson, W. R., Wilkins, T. J., & James, S. J. (1990). Effect of cooking and cooling method on the processing times, mass losses and bacterial condition of large meat joints. *International Journal of Food Science and Technology*, 25, 657-667.

Cheng, Q., & Sun, D.-W. (2006). Feasibility assessment of vacuum cooling of cooked pork ham with water compared to that without water and with air blast cooling. *International Journal of Food Science and Technology*, 41(8), 938–945.

Desmond, E. M., Kenny, T. A., Ward, P., & Sun, D. W. (2000). Effect of rapid and conventional cooling methods on the quality of cooked ham joints. *Meat Science*, 56, 271-279.

Drummond, L., Sun, D.-W., Talens, Vila, C.T.,G.M. Scannell, A. G. M.(2009). Application of immersion vacuum cooling to water-cooked beef joint-Quality and safety assessment. *Food Science and Technology* 42, 332-337.

Mc Donald, K., Sun, D. W., & Kenny, T. (2000). Comparison of the quality of cooked beef products cooled by vacuum cooling and by conventional cooling. *Lebensmittel Wissenschaft und Technologie* .

Mc Donald, K., & Sun, D. W. (2000). Vacuum cooling technology for the food processing industry: a review. *Journal of Food Engineering*, 45, 55-65.

Sun, D. W. (1999). Effect of chilling methods on rapid cooling of cooked ham. *20th International Congress of Refrigeration*, 19--24 September, Sydney, Australia.

OZONE-INDUCED CHANGES OF CHEMICAL ATTRIBUTES OF LETTUCE

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Abstract

In this project, ozone was used to pre-wash fresh-cut lettuce. It was compared with samples washed with water and chlorinated water, to find out the effect on lettuce in terms of antioxidant activity, total phenol and ascorbic acid content. Expected experimental results are outlined and will be compared to known literature results.

Introduction

More emerging technologies are being used in the food industry such as UV irradiation, pulsed electricity, magnetic technology, ultrasound, high hydrostatic pressure, high intensity pulsed light and of course ozone technology (Alothman et al., 2010). These technologies contribute to preserve the antioxidants status, ascorbic acid content, storage stability and food safety. Compared with other emerging technologies, ozone technology has certain advantages in food pre-treatment, food preservation and food storage processing. Ozone as a clean technology is widely used in industry such as in the surface decontamination of vegetables, disinfection of drinking water and waste water treatment. Both the aqueous form and gaseous form of ozone is used to decrease the pathogenic and spoilage microorganisms in fruits and vegetables (Tiwari & Muthukumarappan, 2012). One of the biggest advantages of ozone is that it decomposes rapidly to produce oxygen, with no residues left on the food. However, sometimes ozone can react with organic compounds leading to chemical reactions that can cause new oxidized compounds to be generated which may remain on the food.

Ozone treatment has also been effective in extending the shelf-life of fruit and vegetables. Ozone is a powerful broad-spectrum antimicrobial agent against viruses, fungi, and bacteria. In 2001, the U.S. Food and Drug Administration approved the use of ozone as an antimicrobial agent in the treatment, storage, and processing of food. Apart from the use of microbial inactivation, ozone can also kill storage pests.

The objective of this study was to analyze the changes in chemical attributes including the antioxidant activity, total phenol and ascorbic acid induced by ozone pre-wash of fresh lettuce.

Material and Methods

Selection of lettuce
The first three layers of the lettuce head were removed manually and discarded. The leaves were then chopped into 2-3 cm sizes on a plastic board using a stainless steel kitchen knife.

Washing
In this experiment, four methods are used to wash the lettuce for comparison:

a) Water wash
    Water wash the lettuce for 2 minutes, keep the temperature at room temperature,

(20±0.5℃). This is a control sample used for comparison.
b) Pre-ozonated water wash
   Experiment is carried out in an ultrasound bath (BRANSON 5210) with a built-in diffuser. Ozone is generated using an ozone generator (YANCO INDUSTRIES LTD). Ozone is generated in the column firstly for nearly 10 min to form the pre-ozonated water used for lettuce washing. The treatment is performed at room temperature (20±0.5℃) for 10 min.
c) Simultaneous ozonated water wash
   This processing is carried out in the same device as above. The flow gas is a mixture of ozone and oxygen. Oxygen flow rate is controlled by a gas flow regulator and ozone concentration in the gas supply is varied (1-4.8% w/w of oxygen). An ozone gas analyzer is used to record the result.
d) Chlorinated water wash
   This part is also carried out at room temperature (20±0.5℃) using chlorinated water (100ppm) to wash the lettuce for 10 min.

Packaging and storage
The lettuce samples are dried after treatment and packed into small sealed bags and chilled for chemical analysis.

Measurement of total antioxidant activity
The test is carried out as follows: Firstly, bring the lettuce back to room temperature, and chop them into pieces. Take 1.25g as a sample, add in 25ml HPLC grade methanol. Secondly, homogenize using a homogenizer for 1 min at 24000 rpm. The tube utilizes a rotor stator dispersing element, with the 19mm diameter stator and 12.7 mm diameter rotor. Between them, a gap of 0.3mm exists with a 19.2cm shaft used. Thirdly, vortex the samples in a multitude Vortexer for 20 min at 800 g and then centrifuge for 15min at 2000g. Finally, filter the samples after centrifugal processing and store in the refrigerator for chemical analysis.

DPPH assay measuring antioxidant activity
Total antioxidant activity was measured using the DPPH assay as described by Goupy et al. (1999). The test is carried out as follows: Mix 500 µl dilute sample and 500 µl DPPH (0.238 mg/ml) solution in a microcentrifuge tube. Use a spectrophotometer to measure the absorbance against methanol at 515 nm. Calculate the relative decrease in absorbance (PI), which is used to calculate the related antioxidant activity (IC50) using the equations below (Patras et al., 2010).

$$VC = \frac{(C_1 - C_2) \times (PI_1 - 50)}{PI_1 - PI_2}$$ Equation 1

$$IC_{50} = C_1 - VC$$ Equation 2

$$ARP = \frac{1}{IC_{50}}$$ Equation 3

Measurement of total phenol content
According to the method of Singelton et al. (1999), the Folin-Ciocalteu reagent is used to determine the total phenol in vegetable samples. The test is carried out as follows: Firstly, add 100uL methanolic extract, 100uL MeOH, 100uL Folin-Ciocalteau reagent (FC) and 700 µl of Na2CO3 to 15 mL microcentrifuge tubes. Leave the tubes in a dark atmosphere for 20 min at room temperature. Secondly, centrifuge the samples at 10000g for 3 min. The last step, using aqueous Gallic acid (10-400 mg/L) as a standard, is to read the absorbance of samples. The results are expressed as mg of Gallic acid equal per 100 g of dry weight of samples.

Measurement of vitamin C content

Vitamin C was extracted using the method modified by Luximon-Ramma et al. (2003). The processing is as below: Firstly, homogenize 10g of chopped lettuce with 100mL of extraction solution for 1min. Secondly, stir for 15min using a magnetic stirrer. The last step, centrifuge the extracts got from stirring processing at 2300g for 10min, collect the supernatant for the analysis of vitamin C content. Vitamin C content of extract iss determined using the 2,6-dichloroindophenol (DCIP) titrimetric method. Results are expressed on a fresh weight basis as mg ascorbic acid equivalent/ 1g sample.

Results and discussion

Ozonation is expected to lead to the loss of antioxidant constituents, because of its strong oxidizing activity. But it is not expected that ozone washing treatment will have an effect on the final total phenol content of fresh lettuce. Some other researchers have shown that the ascorbic acid varies depending on different conditions, and vitamin C content will slightly decrease.

Conclusion

During this study, the expected result is that different treatments and preservation methods have an effect on the antioxidant activity, total phenols and ascorbic acid values of lettuce. The objective of the study is trying to figure out whether these effects are positive or negative; if positive, they are beneficial in food processing, if negative, more work has to be done to search for new methods to improve the processing.

Acknowledgement

Reference

Patras, A., Tiwari, B., Brunton, N. 2010. Influence of blanching and low temperature preservation strategies on antioxidant activity and phytochemical content of carrots, green beans and broccoli. *LWT-Food Science and Technology*, 44, 299-306.

Tiwari, B., Muthukumarappan, K. 2012. *Ozone in Fruit and Vegetable Processing*. Dublin: Blackwell Publishing Ltd.

Goupy, A. 1999. Antioxidant composition and activity of barley and malts extracts and of isolated phenolic compounds. *Science of Food and Agriculture*, 79, 1625-1934.

Luximon-Ramma, A., Bahorun, T., Crozier, A. 2003. Antioxidant actions and phenolic and vitamin C contents of common Mauritian exotic fruits. *Science of Food and Agriculture*, 83, 496-502.

Alothman, M. 2010. Ozone-induced changes of antioxidant capacity of fresh-cut tropical fruits. *Innovative Food Science and Emerging Technologies*, 11, 666-671.

Singelton, V. 1999. Analysis of total phenols and other oxidation substrates and antioxidants by means of Folin-Ciocalteu reagent. *Methods in Enzymology*, 299, 152-178.

SHELF LIFE ASSESSMENT OF PANINI BREAD USING MODIFIED ATMOSPHERE PACKAGING TECHNIQUES

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Abstract

The shelf life of a food product is a key attribute for both the manufacturer and the consumer alike. For the manufacturer it means access to bigger markets further away, a less intense more cost effective supply chain, reduced waste from out of life product and a more attractive proposition for retailers to list products in the first place. For the consumer it means flexibility, not having to go to the shop as often for the goods, having the option of buying in more volume on the weekly shop, allowing them to store the product at home and spread out the eating occasions. The consumer can also benefit from the more cost effective supply chain through reduced purchase price. For manufacturers, the goal is to get the longest life possible without affecting the key attributes of the product for the consumer. The technology for both equipment and packaging material is ever changing as both industry and academics alike, continuously increase their understanding of materials, equipment and products. The area of MAP materials and processes are of key importance as these have been well researched and proven in industry over many years.

Introduction

Bakery products are an important part of a balanced diet and, today, a wide variety of such products can be found on supermarket shelves. However, bakery products, like many processed foods, are subject to physical, chemical and microbiological spoilage (Smith et al., 2004). Packing equipment and packaging technology are constantly changing and improving with time. Food manufacturing facilities become outdated quickly in terms of their processes and equipment. This can result in a product becoming irrelevant in the marketplace and therefore reduced sales can occur. In order to keep up with improvements to process and technology, capital investment is usually required. With this in mind every time an investment has to be made on a particular process it is critical that the proposed changes are properly assessed and evaluated such that the return on investment can be realised. In order to completely assess the potential of a particular capital investment there are at least three headings that need to be critically analysed. Firstly there is the consumer and one has to ask a number of questions. Will the proposed change result in increased consumer interest in the product and therefore increased sales. Will the proposed change bring the product in line with the competition or will it allow the product to become a market leader? Are there any consumer technical or legislative issues with the proposed changes to process and equipment? Secondly there is the current process and equipment and its shortcomings. What is pushing the need for the changes? Are customers asking for the change or are the competitors in the market place making the changes? Apart from shelf life, what else is wrong with the current set up? What affect will the new process and equipment have on existing customers and product? Will the investment compliment what is already in place? Is the proposal adding complexity to the process and will it require additional expertise and staff? Finally there is the proposed process and its perceived benefits. What are the objectives and expected outcomes for this investment? What affect will the proposed investment have on the product?

The objective of this study is to look specifically at various packaging options and evaluate which ones give the longest shelf life without affecting key product attributes for the customer.

Materials and Methods

Experimental design for effectiveness of packaging on shelf life
Panini bread and time are the key ingredients in this study, while the chosen packaging materials and equipment are also essential. It is envisaged that much of the study will be carried out in conjunction with equipment suppliers together with the engagement of plastic packaging material suppliers and the suppliers of gas for MAP. The option for changing the product or its ingredients to improve shelf life is not available in this study because it focuses purely on the packing application.

The current packing process and packaging materials is shown in Fig. 1 to help understand limitations. The current process to assess the shelf life of the packed products is to take sufficient samples from the production run and monitor over a 15 day period at ambient temperature. Visually check the packs each day for evidence of mould growth and document the day at which initial growth is noted. See Figure 2.

Panini Simple Process Flow

	Raw Material Intake	--->	Ingredient Preparation for both	--->	Mixing "mother dough"	v
	specifications			"mother dough"	ingredient &	
	bulk flour, oils and water			only part of	temperature control	
	yeast, improvers, grains		v	overall dough mix		v
v	Fermentation of dough	<---	Mixing of "mother" with fresh dough	<---	Fermentation of "Mother Dough"	<---
	controlled		ingredient &		controlled	
	time, humidity		temperature		time, humidity	
	& Temperature		control		& Temperature	
v						
--->	Sheet and Cut Dough	--->	Prooving of Dough	--->	Baking	v
	working the		controlled		controlled	
	dough and		time, humidity		temperature	
	marking it		& Temperature		and time	
BAKERY						
PACKING						v
v	Bulk packing bags in cases	<---	Freezing	<---	Cooling	<---
	e.g. 2 bags of 40		controlled		controlled	
	pieces of bread		temperature		temperature	
			and time		and time	
v						
--->	Frozen Storage if required	--->	Decanting from Bulk to order	--->	Gas Flush Packing to order	v
	can sometimes		order receipt to		produce exact	
	bypass this step		packing < 24		quantity ordered	
			hours		by the retailer	v
	Consume within 8 days	<---	Despatch to Retailers	<---	Ambient Storage	<---
	short time		at ambient		this means	
	to sell and		temperatures.		product is	
	consume		limited shelf life		tempering up	

Figure 1. Current process

One of the main concerns against the current process is the total elimination of air which represents a serious hurdle in modified atmosphere packaging of bakery products, due both to the high spin-rates of the packaging lines and, particularly, to the typical texture of bakery products which retain large quantities of air inside their porous structure. Also baking time was shown to

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have, to a different extent, some measurable effects on the rate of oxygen substitution and hence, its optimization as well as the choice of gas mixture can contribute to improve modified atmosphere packaging of bakery products (Piergiovanni et al., 1997).

While there is little evidence of a risk to public health from mould-spoiled breads; indeed, the absence of evidence of risk in industrialised countries shows that in practice the risk in these countries is very slight. Mould growth in bread can be reduced by a range of techniques including the following: attention to hygiene within the bakery to reduce the opportunities for mould spores to gain access to the product (Legan, 1993). Regardless of consequence, mould growth is undesirable and needs to be prevented.

The main focus is that there are available three main categories of MAP machinery for bakery products distinguished according to the applied technique; these are thermoforming systems, pre-formed container machines and horizontal or vertical form-fill-seal machine systems. The choice of packaging machine will be dependent upon many factors, determined by the characteristics of the bakery product and the food market requirements (Kotsianis et al., 2002).

Some comparison testing will be carried out on similar competitor samples where shelf life is much longer than existing. Note that packaging requirements for fresh bakery goods are often minimal as many of the products are for immediate consumption. However, packaging can be an important factor in extending the shelf life of other cereal-based goods. Some amount of the texture changes and flavour loss manifest over the shelf life of a soft-baked good can usually be minimized or delayed by effective use of packaging materials. The gains in the extension of shelf life will be application specific (Galic et al., 2009).

Results and Discussion

Tests are currently underway studying the effects of the freezing process and the line speed on shelf life. Figures 2 gives an example of work done to date.
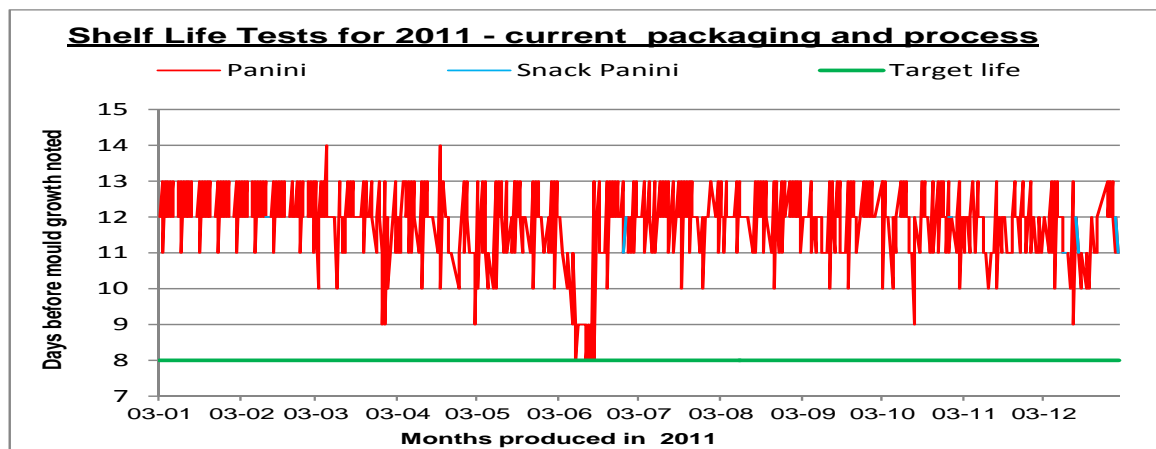
Figure 2. Shelf Life tests using the onset of mould growth as an indicator from bread out of current process

Note result of previous research where; affects of modified atmosphere packaging (MAP) and potassium sorbate (PS) on total viable count (TVC) and yeast and mould counts (YMC) in sliced bread during storage were investigated. Gas combinations of air (control), 100% N_2 (A), 70% N_2:30% CO_2 (B), 50% N_2:50% CO_2 (C), 30% N_2:70% CO_2 (D) and 100% CO_2 (E)

and PS concentrations of 0, 0.15 and 0.30% were tested during 21 days of storage at ambient conditions (20 ± 2 degrees C and $60 \pm 2\%$ RH). At the end of 21 days in all samples both with and without PS, the lowest YMC were in E. In air packed control without PS and with 0.15% PS, mould developed after 14 days storage. In addition to this, none of samples in all MAP treatments presented signs of mould at the end of the storage period (21 days). Similarly, E was the most effective treatment for the inhibition of bacteria. Also, it is concluded that 100 CO(2) atmospheres in MAP treatments and 0.15% PS addition to bread dough were sufficient for YM growth inhibition in sliced bread, in terms of human health. However, TVC was under 3 log cfu/g in only sample packaged with E and containing 0.30% PS until day 14. (Nurcan et al., 2011)

Conclusions

There are packing processes and packaging materials available that can help provide longer shelf life to the product without adversely affecting the important attributes on delivery to the consumer. Some competitors are already well ahead with these packaging materials and processes and are realising the benefits from them. They have shown that the consumer is not put off by such packaging and that there is a market out there for them.

Acknowledgements

References

Galic K.; Curic D.; Gabric D. Shelf Life of Packaged Bakery Goods - A Review. Critical Reviews in Food Science and Nutrition 49 (5) 405-426

Smith, JP, Daifas, DP, El-Khoury, W. 2004. Shelf life and safety concerns of bakery products - A review. Critical Reviews in Food Science and Nutrition 44 (1) 19-55

Legan, JD. 1993. Mold spoilage of bread – the problem and some solutions. International Biodeterioration & Biodegradation 32 (1-3) 33-53

Piergiovanni, L, Fava P. 1997. Minimizing the residual oxygen in modified atmosphere packaging of bakery products. Food Additives and Contaminants 14 (6-7) 765-773.

Kotsianis, IS, Giannou, V., Tzia, C. 2002. Production and packaging of bakery products using MAP technology. Trends in Food Science & Technology

Nurcan, D., Duygu, G., Neslihan, I., 2011. Influence of modified atmosphere packaging and potassium sorbate on microbiological characteristics of sliced bread. Journal of Food Science and Technology 48 (2) 236-241

EFFECTS OF IMMERSION VACUUM COOLING OF SAUSAGES WITH DIFFERENT WATER LEVELS

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Abstract

Three different water levels (distance from the top of sausage to water surface) were employed during immersion vacuum cooling of sausage, namely: high (HWL: 17 cm), middle (MWL: 7 cm) and low water level (LWL: 0.8 cm). Results revealed that the average final core sausage temperature achieved at HWL was just about 8^oC, while sausages cooled at MWL and LWL reached approximately 6^oC and 4^oC, respectively. This may be due to the poor heat transfer from water bottom to surface and between the sausage and water at bottom in high and middle water level. The average cooling time (to 8^oC) was found to be significantly different ($P<0.01$) between the three water levels: 47.32, 33.97 and 24.39 min for HWL, MWL and LWL, respectively. Total cooling times for MWL (to 6^oC) and LWL (to 4^oC) were 38.52 and 34.06 min, respectively. In terms of mass losses, TPA and moisture analysis, they were not statistically significantly affected ($P>0.05$) by the water levels. It could be concluded that IVC of sausages using LWL accomplishes the shortest cooling time, achieves the necessary final temperature and yields a product of acceptable quality.

Introduction

Numerous papers have addressed the application of vacuum cooling for various fields such as cooling of fruits (McDonald and Sun, 2000), vegetables (Ozturk and Ozturk, 2009), ready meals (Zhang and Sun, 2006), bakery products (Primo-Martín et al., 2008), fish, and large meat joints (Drummond and Sun, 2008). Based on its evaporative mechanism where the latent heat is extracted from the product for the phase change, vacuum cooling has several advantages over traditional methods which mainly rely on thermal conduction and convection during the cooling procedure (Wang and Sun, 2004). However, high cooling loss after vacuum cooling hinders its widespread employment.

Recently, immersion vacuum cooling (IVC) seems to show a potential to meet the demands of high cooling rate with comparatively lower cooling loss for cooked meat products (Feng et al., 2011). However, research on further improvements of IVC technology is still necessary. The total mass of water evaporated during the procedure will markedly affect the design of the cooling system, and therefore an evaluation of the optimal level of surrounding liquid is pertinent. Moreover, the cooling of sausages is usually accomplished using forced air cooling or immersion cooling and the IVC of sausage has as yet not been reported in the literatures.

The objective of the current work was thus to experimentally study the effects of different water levels on immersion vacuum cooling of sausage.

Materials and Methods

Samples preparation

Regular sausages were bought from a local butcher (Fenelons Butchers, Stillorgan, Co. Dublin, Ireland). Every two linked sections were considered as one experimental unit. The average weight, diameter and length of each section were 64.68 g, 3.08 cm, and 9.39 cm, respectively.

Cooking and cooling procedures

Each experimental unit was steam-cooked at 83^oC in a convective oven (Model FCV6, Zanussi, Italy) until sausage core temperature reached 72^oC for 2 minutes. In order to

eliminate the effect of water volume to the experiment, different diameter beakers (6.04 cm for HWL, 10.9 cm for MWL, 16.5 cm for LWL) were employed to achieve the different water level with the same water volume (690 ml). Shortly after cooking, samples were transferred into the transparent beakers and completely covered with hot water (80°C). A wired mesh with large holes was used to keep the sausages at the bottom of the beaker, preventing them from floating during IVC. A special design lid, suspended a certain distance above the beaker, was used to minimise water splashing out of the beaker, concurrently giving enough space for vapour escape. The pressure drop inside the vacuum chamber was carefully controlled by adjusting the main and bleeding values, to control the rate of pressure drop and avoid too serious boiling of water and burst of sausage during IVC. The minimum chamber pressure was controlled at approximately 7 mBar, to prevent freezing. For each water level, 6 replications were carried out, and all the samples after the cooling procedure were vacuum-packaged and stored at 4°C cold room for further analysis.

Data acquisition during cooling
The core temperature of each unit and the water temperature during cooling were measured using thermocouples (T-Type, Radionics, Ireland). In order to determine water temperature distribution at different heights during cooling processing with HWL and MWL, water temperatures were measured using thermocouples fixed to a vertical stick every 4 cm from the bottom of the beaker to the water surface. The chamber pressure was measured by a pressure transducer (PR4000, MKS, Germany). Data acquisition systems (SCXI1000, National Instrument, USA) and programs based on Labview (v4.2, National Instrument, USA) were used to record the temperatures and measured pressure in the vacuum chamber. All the data was collected at an acquisition interval of 1 s.

Weight loss
In order to minimize variation of sample's initial temperature before cooling, samples after cooking were moved directly into the vacuum chamber to begin the cooling immediately. The overall weight loss was estimated as the cooling loss, as the same cooking procedure should generate similar cooking loss for each unit. Weights before and after processing were measured, and the overall mass loss was calculated with the following equation:
Error! Reference source not found. (1)
where W1 was the weight of the raw sample (before cooking) and W2 was the weight of the cooled sample.

Physical property analysis
Five meat cores (25 mm in diameter × 20 mm in height) from each section of the cooled sausage were obtained to represent a whole unit for the colour and texture profile analysis (TPA). Each meat core colour was measured by tristimulus colorimeter (Chroma CR300; Minolta Ltd, Osaka, Japan). CIE L*a*b system was applied to exemplify the colour of the cooled sausage. As for TPA, two cycles of 50 % compression with 500 N load cell (50 mm/min crosshead speed) were employed to each meat core using Instron universal testing machine (Model No. 5544; Instron Corporation, High Wycombe, UK). The hardness, springiness, cohesion, gumminess and chewiness were recorded. The averages from the 5 replications were regarded as the values for the measured physical properties.

Moisture Analysis
Sausage moisture was determined by drying the batter content in an oven at 105°C overnight in triplicate.

Statistical analysis
One-way ANOVA program was applied to analyze the experimental data. Software SPSS (v11.5, USA) was used in the statistic analysis.

Results and Discussion

Cooling profile of sausage for different water levels

Table 1 displays for each water level tested: the achieved final sausage temperature, average water temperature at different heights in the beaker towards the end stage of IVC, cooling time to intermediate and final temperatures, and temperature differences between surrounding chilling water and sausage at the end stage of cooling. Results illustrated that final core temperature of sausage at HWL (8°C) was much higher than that at MWL (6°C) and LWL (4°C), respectively. This is probably due to the reduced water evaporation and poor water convection towards the end of cooling. It is known that a higher water level generates a higher hydrostatic pressure at the bottom. The water in the sausages would stop boiling when the hydrostatic pressure plus the remaining chamber pressure were higher than saturated water pressure, and subsequently cooling procedure was predominated by thermal conduction and heat exchange with the surrounding water. However, water evaporation was reduced and water convection became poor towards the end of cooling.

Analysis of water temperature at different heights for HWL revealed that the average water temperature at bottom could merely achieve 9.35^{o}C, compared to 6.31^{o}C in the middle and 3.88^{o}C at the water surface. In terms of the water temperature in MWL, the achievable average water temperature was -1.26^{o}C (at the surface), 0.86^{o}C (in the middle), and 6.77^{o}C (at the bottom). The large temperature difference between the surface and the bottom attributed to the long distances at HWL and MWL and the poor convection. Previous document has demonstrated that conduction and convection between water and products play an increasingly important roles in the later stage of immersion vacuum cooling (Cheng and Sun 2006; Feng et al. 2011). As the chilling water surrounding sausage could only reach approximately 9.35^{o}C (HWL) and 6.77^{o}C (MWL), it is comparatively difficult to chill down the sausage below 4°C in HWL and MWL at later stage of IVC procedure which mainly depends on conduction and heat exchange.

In terms of cooling time, the cooling time to 10°C for the HWL (35.54 min) was much longer than MWL (24.97 min) and LWL (21.39 min) (*P<0.01*). Poor conduction inside the sausage and reducing heat exchange between sausage and cooling medium (water) at the later stage of IVC could probably contribute to this phenomenon. As for temperature differences between the sausage and surrounding chilling water (when the sausage temperature spanned from 10°C to 8°C (Table 1)), the differences in LWL (6.79^{o}C) was significantly larger than in MWL (2.77^{o}C) and HWL (1.23^{o}C) (*P<0.01*), which enhanced the heat transfer, promoted the chilling procedure at the later stage of IVC, and hence finally shortened the cooling time.

Table 1. Parameters during immersion vacuum cooling with different water level

Water level	Final sausage temperature (°C)	Water temperature (°C)			Cooling time (min)				Temperature differences between sausage and water (°C)*
		surface	middle	bottom	10°C	8°C	6°C	4°C	
HWL	8	3.88[A]	6.31[A]	9.35[a]	34.54 A	47.32 A	---	---	1.23[a]
MWL	6	-1.26[B]	0.86[B]	6.77[b]	24.97 B	33.97 B	38.52 A	---	2.77[b]
LWL	4	---	---	---	21.39 C	24.39 C	29.14 B	34.06	6.79[A]

Note: *Average temperature differences based on sausage and water temperature from 10°C to 8°C; Means with different upper case letters within a column are significantly different (*P<0.01*); Means with different lower case letters within a column are significantly different (*P<0.05*)

Weight loss and physical profile of sausage

The results for the sausage weight loss and TPA cooled with different water levels are displayed in Table 2. There was no significantly statistic difference between each water levels

in weight loss (*P>0.05*). This might result from the surrounding chilling water during the whole cooling procedure.

Hardness, springiness, gumminess, chewiness and colour of the sausages were analyzed after cooling. There were no substantial distinctions in texture profile among IVC with different water levels. As all the sausages were immersed in the chilling water, the moisture did not differ from each other, which probably led to the comparatively TPA parameters which affected by products water content. As for colour, samples cooled with LWL presented significantly higher a* values (red) than MWL (*P<0.05*). This might be due to concentration of the pigment as a result of the substantial water evaporation, which is consistent with the high mass loss of LWL.

Table 2. Mass loss and TPA of sausage with different water levels

Water level	Weight loss (%)	TPA				Moisture (%)	CIE Colour		
		Ha	Sp (mm)	Gu (N)	Ch (N mm)		L*	a*	b*
HWL	1.18[a]	41.64[a]	6.18[a]	20.74[a]	129.38[a]	50.58[a]	68.91[a]	6.41[a]	9.11[a]
MWL	1.96[a]	44.41[a]	6.31[a]	18.87[a]	119.77[a]	52.28[a]	70.22[a]	6.16[a]	9.06[a]
LWL	2.83[a]	40.69[a]	6.12[a]	19.35[a]	120.37[a]	51.83[a]	69.15[a]	7.15[b]	8.68[a]

Note: Means with different lower case letters within a column are significantly different (*P<0.05*). Ha, hardness; Sp, Springiness; Gu, gumminess; Ch, chewiness; L*, lightness; a*, red/green; b*, yellow/blue.

Conclusions

It was found that in relation to the effects of different water levels on IVC, LWL could achieve the highest cooling rate, necessary final product temperature, and yield a product of acceptable quality. It was concluded that immersion vacuum cooling with LWL is the most potentially method to reduce the cooling time of IVC.

References

Cheng, Q. F. & Sun, D.-W. (2006). Feasibility assessment of vacuum cooling of cooked pork ham with water compared to that without water and with air blast cooling. *International Journal of Food Science & Technology,* 41, 938-945.

Drummond, L. & Sun, D.-W. (2008). Immersion vacuum cooling of cooked beef - Safety and process considerations regarding beef joint size. *Meat Science,* 80, 738-743.

Feng, C. H., Drummond, L., Zhang, Z. H., & Sun, D.-W. (2011). Vacuum Cooling of Meat Products: Current State-of-the Art Research Advances. *Critical Reviews in Food Science and Nutrition,* **in press**.

McDonald, K. & Sun, D.-W. (2000). Vacuum cooling technology for the food processing industry: a review. *Journal of Food Engineering,* 45, 55-65.

Ozturk, H. M., & Ozturk, H. K. (2009). Effect of pressure on the vacuum cooling of iceberg lettuce. International Journal of Refrigeration, 32, 402-410.

Primo-Martín, C., de Beukelaer, H., Hamer, R. J., & van Vliet, T. (2008). Fracture behaviour of bread crust: Effect of bread cooling conditions. Journal of Food Engineering, 89, 285-290.

Wang, L. & Sun, D.-W. (2004). Effect of operating conditions of a vacuum cooler on cooling performance for large cooked meat joints. *Journal of Food Engineering***,** 61, 231-240.

Zhang, Z. H. & Sun, D.-W. (2006). Effects of cooling methods on the cooling efficiency and quality of cooked rice. *Journal of Food Engineering* **77**, 269-274.

MODELLING FOOD PROCESSES ENHANCED BY ULTRASOUND

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Abstract

In food processing, the applications of ultrasound can be divided into two categories, namely replacing traditional technologies and assisting traditional technologies. In the latter case, the processing efficiency is enhanced and the disadvantages of traditional technologies during processing are improved. Among the processes enhanced by ultrasound, non-parametric simulative models can be employed to model the extraction and oxidation processes. With regard to ultrasound-enhanced freezing, thawing, brining and drying processes, it is better to use the models which can express the physical meaning of these processes. In the meantime, several empirical models can be considered to model the drying process in the presence of ultrasound.

Introduction

Ultrasonic technology has been widely used in food processing area. Generally speaking, its applications are based on several ultrasonic theories, including the generation of cavitation phenomenon, simultaneous formation of microstreaming, the compression and rarefaction induced by ultrasound and thermal effects of ultrasound (Mason, 1998). In the applications of ultrasound to food processing, the main purpose of utilization of ultrasonic technology could be broadly divided into two main categories. The first one is to replace the traditional processing techniques by the ultrasonic one. The other category is to assist or accelerate the traditional techniques so that processing can be completed more efficiently and rapidly. In this latter case, the whole process is enhanced by ultrasound, and disadvantages of traditional techniques during processing are improved. These ultrasonic effects can be defined as ultrasonic enhancement of food processes. These food processes include extraction, freezing, thawing, brining, oxidation and drying/ dehydration.

The objective of this article is to review the strategies of modelling food processes enhanced by ultrasound.

Materials and methods

Mathematical modelling of ultrasonic enhancement of extraction and oxidation process
When it comes to model the processes enhanced by ultrasound, both non-parametric simulative models and the models which can express the physical meaning of the process can be considered. During extraction and oxidation processes, it is difficult to confirm how the reactions enhanced by ultrasound occur exactly. Therefore, the most straightforward way is using non-parametric simulative models, which do not need to express the physical meaning of the process.

Response surface methodology (RSM) is the most popular tool for modelling. In RSM, a second-order polynomial equation below is always employed to build the relationship between the response variables and independent variables (Zhang et al., 2009):

$$Y = \beta_0 + \sum_{i=1} \beta_i X_i + \sum_{i=1} \beta_{ii} X_i^2 + \sum_{i=1} \sum_{j=i+1} \beta_{ij} X_i X_j \qquad (1)$$

where X_i and X_j are the independent variables, Y is the response variable, β_0, β_i, β_{ii} and β_{ij} are the constant, linear, quadratic and cross product coefficients, respectively. Up to now, RSM has been successfully used to model various extraction processes assisted by ultrasound.

On the other hand, artificial neutral network (ANN) is another choice to model the extraction and oxidation processes enhanced by ultrasound. ANN does not require a prior knowledge about the relationship between the input and output parameters (Plumb et al., 2005). Instead, it can train and learn itself to recognize the patterns in a systematic way.

Mathematical modelling of ultrasonic enhancement of freezing process
Food freezing is a complicated process, involving initial ice nucleation and subsequent crystal growth within the unfrozen aqueous phase, as well as the heat and mass transfer phenomena. Therefore, it is a difficult task to use mathematics to describe the whole freezing process enhanced by ultrasound. To our best knowledge, only Saclier et al. (2010) developed a theoretical model for ice primary nucleation induced by ultrasound. In this model, the relationship between the nucleation rate and ultrasound-generated pressure and temperature can be written as:

$$J(T) = \left(\frac{\mathscr{R} T \rho_{sol}}{M_{sol} h} \right) \exp\left(\frac{-\Delta G_D(T)}{\mathscr{R} T} \right) \exp\left(\frac{-\Delta G(T)}{\mathscr{R} T} \right) \qquad (2)$$

where J is the nucleation rate, T is time, h is the Planck constant, $\mathscr{R}$ is the perfect gas constant, ΔG is the critical free energy at the point of formation of a nucleus of critical size, ΔG_D is the activation energy for the water molecules diffusion across the water/ice interface, M_{sol} is the molar weight of the solution and ρ_{sol} is its density. Considering the high pressure produced during the collapse of cavitation bubble, ΔG can be expressed as:

$$\Delta G(T, p) = \frac{16\pi}{3} \frac{\sigma_{sl}^3(T, p)}{\rho_s^2(T, p) L^2(p) \left(\frac{T_m(p) - T}{T_m(p)} \right)^2} \qquad (3)$$

where L is the latent heat of melting, σ_{sl} is the crystal-solution interface energy, T_m is the solidification temperature, T is temperature, ρ_s is the solid phase density and p is the liquid pressure.

Mathematical modelling of ultrasonic enhancement of thawing process
Thawing is the reverse process of food freezing. When ultrasonic waves travel through the frozen samples, the temperature of thawed region rises since the acoustic energy is absorbed and dissipated as heat. Therefore, the thawing rate is enhanced. A differential equation below can be employed to describe the heat conduction in unfrozen region for slab geometry (Miles et al., 1999):

$$\lambda \frac{\partial^2 \theta}{\partial x^2} + 2\mu I_0 e^{-2\mu x} = \rho c \frac{\partial \theta}{\partial t} \qquad (4)$$

where λ is the thermal conductivity, θ is the increased temperature, μ is the amplitude attenuation coefficient, x is unfrozen region, I_0 is intensity per unit area at x=0, c is the specific heat capacity of sample and ρ is the density of the sample.

Furthermore, the thermal conduction and absorption of ultrasound at the position of frozen/thawed boundary can be described by:

$$\rho L \frac{dX}{dt} = I_0 e^{-2\mu x} - \lambda (\frac{\partial \theta}{\partial x})_{x = x}$$

(5)

where L is the absorption of latent heat of fusion of ice. By solving Equations (4) and (5), the ultrasonic thawing time and temperature in the thawed region can be calculated.

Mathematical modelling of ultrasonic enhancement of brining process

Brining process is a common step during the manufacturing of food products, particularly for meat and cheese products. In this operation, samples are salted by immersion in a brine solution, inside which the counter-current mass transport of salt and water takes place. Either external or internal mass transfer during brining process can be accelerated by ultrasound.

For modelling the cheese brining process enhanced by ultrasound, the equations based on the combination of microscopic mass transfer balance with Fick's law can be employed (Sánchez et al., 1999). The governing equation for parallelepiped shapes can be written below:

$$\frac{\partial X}{\partial t} = D(\frac{\partial^2 X}{\partial x^2} + \frac{\partial^2 X}{\partial y^2} + \frac{\partial^2 X}{\partial z^2})$$

(6)

where X is the local concentration of either moisture or NaCl in the cheese, D is the effective diffusional coefficients for either water or salt, t is the time and x,y,z are the characteristic coordinates of each geometry. By solving Equation (6), the influence of ultrasound on mass transfer during brining process can be elucidated.

Mathematical modelling of ultrasonic enhancement of drying process

Ultrasound irradiation is an efficient way to enhance the convective air drying. For modelling the ultrasound-enhanced drying process, the constant-rate period is usually not taken into account since it rarely appears. In this case, both the diffusional models based on the Fick's law with different degrees of complexity and several empirical models can be considered.

For the diffusion models, the governing equation for cube geometry is shown below:

$$\frac{\partial W_p(x, y, z, t)}{\partial t} = De(\frac{\partial^2 W_p(x, y, z, t)}{\partial x^2} + \frac{\partial^2 W_p(x, y, z, t)}{\partial y^2} + \frac{\partial^2 W_p(x, y, z, t)}{\partial z^2})$$

(7)

where De is the average effective moisture diffusivity, W_p is the local moisture content, t is the time, and x,y,z are the characteristic coordinates of each geometry.

To solve Equation (7), the strategies of either neglecting or considering the external resistance can be taken into account. Neglecting the external resistance is the simplest way for modelling. In this case, only water diffusion controls the water transfer during drying (García-Pérez et al., 2011).bFurthermore, both the external resistance and shrinkage should be considered to develop a more precise diffusion model. The main difficulty in finishing this modelling is that the boundary condition is moving due to the shrinkage whereas the dry matters are not affected (García-Pérez et al., 2011). The implicit finite difference method and the same boundary equations as models only considering external resistance can be used to solve the governing equations (García-Pérez et al., 2011). In addition, there is another way to correct models that ignore product shrinkage by multiplying a volume changing factor with De without shrinkage effect. The relationship between the rectified De and De without shrinkage effect is shown below (Schössler et al., 2012):

$$\frac{De - unrectified}{De - rectified} = (\frac{V_0}{V_f})^{2/d}$$

(8)

where V_0 and V_f are the initial and final sample volumes, d is the power exponent.

Another modelling strategy is to use the empirical models such as the Page model and Weibull model (García-Pérez et al., 2011). Compared to the diffusion models, the computation of empirical models is much easier. Therefore, both empirical and diffusion models should be taken into account to model the ultrasound-enhanced drying process.

Conclusions

In food processing area, the ultrasonic technology can be either used to replace traditional technologies or assist traditional technologies. For the processes assisted by ultrasound, the processing rate and efficiency is enhanced. To model ultrasound-enhanced processes, non-parametric simulative models are suitable for the extraction and oxidation processes. As for modelling other processes including freezing, thawing, brining and drying processes, it is better to employ the models which can express the physical meaning of these processes. In addition, several empirical models can be used for modelling ultrasound-enhanced drying process.

Acknowledgements

References

García-Pérez, J.V., Ozuna, C., Ortuño, C., Cárcel, J.A., Mulet, A. (2011). Modeling ultrasonically assisted convective drying of eggplant. *Drying Technology*, 29, 1499-1509.

Mason, T.J. (1998). Power ultrasound in food processing - the way forward. In Povey, M.J.W., & Mason, T.J. (Ed.). Ultrasound in food processing (1st ed.). London: Thomson Science, pp. 105-126.

Miles, C.A., Morley, M.J., Rendell, M. (1999). High power ultrasonic thawing of frozen foods. *Journal of Food Engineering*, 39, 151-159.

Plumb, A.P., Rowe, R.C., York, P., Brown, M. (2005). Optimisation of the predictive ability of artificial neural network (ANN) models: A comparison of three ANN programs and four classes of training algorithm. *European Journal of Pharmaceutical Sciences*, 25, 395-405.

Saclier, M., Peczalski, R., Andrieu, J. (2010). A theoretical model for ice primary nucleation induced by acoustic cavitation. *Ultrasonic Sonochemistry*, 17, 98-105.

Sánchez, E.S., Simal, S., Femenia, A., Benedito, J., Rosselló, C. (1999). Influence of ultrasound on mass transport during cheese bring. *European Food Research and Technology*, 209, 215-219.

Schössler, K., Jäger, H., Knorr, D. (2012). Effect of continuous and intermittent ultrasound on drying time and effective diffusivity during convective drying of apple and red bell pepper. *Journal of Food Engineering*, 108, 103-110.

Zhang, Q.A., Zhang, Z.Q., Yue, X.F., Fan, X.H., Li, T., Chen, S.F. (2009). Ultrasound-assisted extraction of flaxseed oil using immobilized enzymes. *Food Chemistry*, 2009, 513-518.

ULTRASOUND-ASSISTED FREEZING OF PROBIOTIC BACTERIA: THE FREEZING PROCESS AND CELL VIABILITY

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Abstract

Maintaining highly viable probiotic lactic acid bacteria cells in frozen products is quite important. Power ultrasound has been considered recently as a novel technique for improving the freezing process. In this paper, the effects of power ultrasound on the freezing process and the viability of *Lactobacillus plantarum* subsp. *plantarum* after freezing were assessed. The bacteria were grown in MRS broth and transferred into 1.2 ml tubing vials with or without DMSO. Freezing was performed in an ultrasonic bath system (25 kHz). Ultrasound irradiation (3 s, 0.25 W cm^{-2}) at different supercooled temperatures caused nucleation to occur close to the irradiation temperature. Lower nucleation temperatures resulted in a shorter phase change stage and reduced cell viability. Ultrasound-assisted irradiation at higher temperatures (-2 and -4 ^{0}C), on the other hand, increased the viability of the cells significantly. Ultrasound irradiation during the phase change stage of the freezing process (4 min) led to a further increase in the viability of the cells while reducing the freezing time. The higher mass transfer rate of water molecules achieved by ultrasound irradiation might have caused the improved viability and faster freezing process. Our results revealed that ultrasound irradiation during the nucleation stage or phase change step of the freezing process holds promise as a tool to ensure the higher viability of frozen suspended cells.

Introduction

Probiotic lactic acid bacteria have been a centre of focus recently for their beneficial properties (Mousavi et al., 2011). These bacteria are produced commercially as cultures and are stored in a frozen or freeze-dried state. They may also incorporate frozen or freeze-dried foods. The freezing process damages the cells. However, it is crucial to maintain the viability of the cells at a high level. Power ultrasound has been addressed recently as a novel technique to improve the freezing and crystallization processes (Kiani and Sun, 2011; Kiani et al., 2012; Kiani et al., 2011). It has been demonstrated that the nucleation phenomenon in different solutions can be controlled by ultrasound irradiation (Kiani and Sun, 2011). Ultrasound can also induce secondary nucleation and affect the crystal growth by fracturing the ice crystals (Chow et al., 2005) or increasing the mass transfer rate. It is valuable to investigate the effect of ultrasound assisted freezing on the viability of living cells, especially probiotic bacteria that their viability in cultures and products is very important.

This research studied the effect of ultrasound irradiation during the nucleation and phase change step of the freezing process on the process parameters and viability of probiotic bacterium, *Lactobacillus plantarum* subsp. *plantarum*.

Materials and Methods

Freezing experiments
L. plantarum subsp. plantarum, (DSM 20174) was cultured in de Man–Rogosa–Sharpe (MRS). The harvested cells were frozen with or without DMSO (5 %) (Simga-Aldrich, Ireland). The suspension of the cells was transferred into 1.2 ml vials. The vials were sealed and then frozen in the ultrasonic freezing equipment operating at 25 kHz (CQBF-1025, China Shipping Company, China). The temperature of the coolant was set at -20°C. Ultrasound intensities delivered into the vials at different points at the bottom of the bath were evaluated

as described by, and 4 locations with similar ultrasound intensities at each level setting in the generator were finally chosen for the freezing experiments. The ultrasound intensity as described by Kiani et al. (Kiani et al., 2011) was adjusted at 0.07, 0.25 or 0.42 W cm^{-2}. Temperature was measured by inserting a T-type thermocouple (Radionics Ltd., Ireland) into the center of a control vial logged using a data logger (OM 2040, OMEGA Engineering Inc., UK). The frozen vials were transferred to a freezer immediately after freezing and were stored at -20 ^{0}C before the viability of the cells was measured.

Determination of bacterial viability
In order to evaluate the viability of the bacteria the PCA method was used after 10, 20 and 30 days. Cryo-vials were thawed (10 min at 30 ºC), centrifuged at (4000 rpm) and re-suspended in Ringer's solution. Serial dilutions were obtained from and 0.1 ml aliquots were plated in triplicate on MRS agar and incubated at 30 ºC for 48 h. The number of colonies grew on the plates were counted as CFU ml^{-1}.

Ultrasound treatment
The effect of short ultrasound irradiation (3 s, at 0.25 W cm^{-2}) at the supercooling stage on the nucleation, freezing process, and viability of the probiotic bacteria was studied. The effect of ultrasound intensity (0.07, 0.25, 0.42 W cm^{-2}) irradiated for 4 min during the phase change stage was also studied. To study the effect of irradiation during the phase change step, the vials were exposed to irradiation after reaching the temperature to -2 ^{0}C for MRS broth and -4 ^{0}C for MRS broth containing 5% DMSO. If needed, the data were analyzed statistically using Minitab software (Version 14, Minitab Inc. USA). At least three replications were performed and ANOVA and mean comparison tests were used for the analysis of the data.

Results and Discussion

Freezing process for probiotic bacteria
Figure 1 depicts the freezing curves of probiotic bacteria suspended in MRS broth. The control sample without irradiation reached temperatures much lower than its freezing temperature before solidification commenced. Irradiation of a supercooled suspension of bacteria with ultrasound led to nucleation close to the irradiation temperature. These observations implied that, like the results obtained for water, sucrose solution and agar gels (Kiani et al., 2012; Kiani et al., 2011), ultrasound provides a useful method for inducing nucleation in the suspension of bacteria.
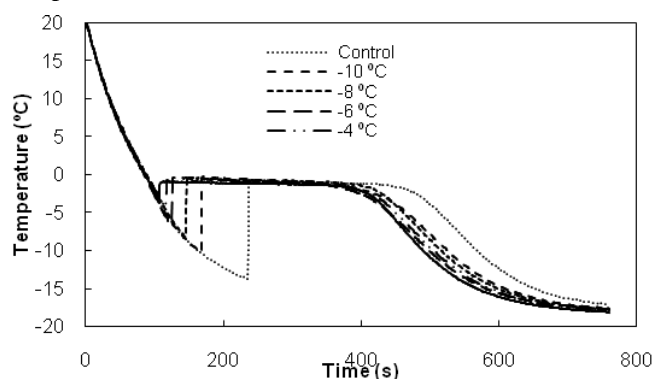
Figure 1. Effect of ultrasound irradiation (3s, 0.25 W cm^{-2}) at different temperatures to induce nucleation on the freezing curve during freezing of *L. plantarum* subsp. *Plantarum* in MRS broth.

Decreasing the nucleation temperature increased the freezing time from 0 to -7 ^{0}C. On the other hand, the freezing time from IFP to -7 ^{0}C decreased when the nucleation temperature was reduced. The presence of 5 % DMSO decreased the freezing point -1 ºC to -3 ºC.

However, the way that ultrasound irradiation affected the freezing curve of the solution containing DMSO was similar to how it affected the MRS broth suspension without DMSO. Increasing the intensity of ultrasound used during the phase change step decreased freezing times. Irradiation induces strong agitation as the bubbles collapse. This agitation has been shown to induce primary nucleation, break the ice crystals formed in liquids (Chow et al., 2005), and increase the rate of mass transfer which all can favor freezing rate.
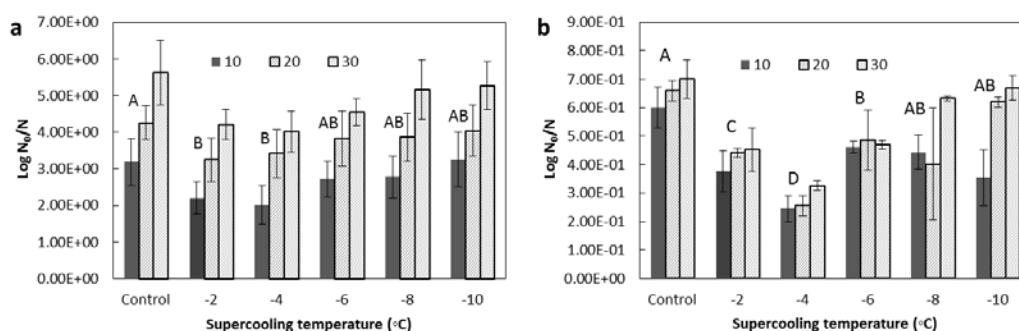
Figure 2. Effect of nucleation at different supercooling degrees induced by 3 s ultrasound irradiation (0.25 W cm^{-2}) on the viability of *L. plantarum* subsp. *Plantarum* after 10, 20 and 30 days. The bacteria suspended in MRS broth (a) or MRS broth containing 5 % DMSO (b) were transferred to 1.2 ml vials and were frozen in a cooled bath. Treatments with different assigned letters are significantly different.
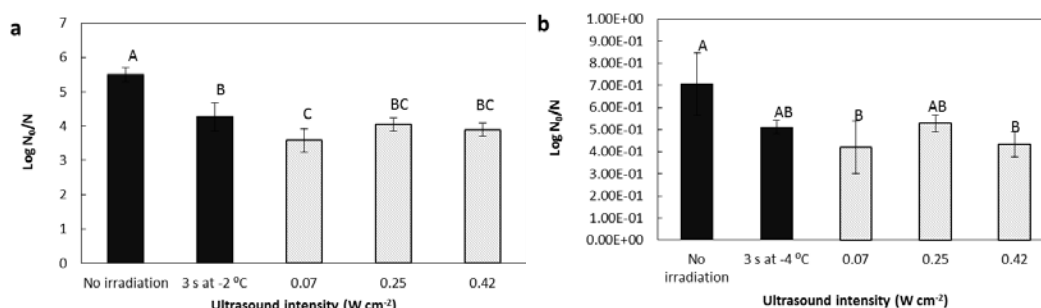
Figure 3. Effect of ultrasound irradiation at the phase change step (3 min) during freezing of *L. plantarum* subsp. *Plantarum* on the viability of the cells after 30 days. The bacteria suspended in MRS broth (a) or MRS broth containing 5 % DMSO (b) were transferred to 1.2 ml vials and were frozen in a cooled bath. Treatments with different assigned letters are significantly different.

Viability of probiotic bacteria
Different nucleation temperatures induced by ultrasound irradiation significantly affected the cell viability ($p < 0.05$) (Figure 2a). We observed a long supercooling step for the control sample, which resulted in lower cell viability. High degrees of supercooling can lead to higher freezing rates, and to the formation of smaller ice crystals. This phenomenon is known to be positive in food processing experiments (Li and Sun, 2002) as well as in tissue preservation leading to the introduction of novel supercooling formatin methods such as high-pressure freezing, antifreeze proteins, microwave irradiation and magnetic resonance freezing (Kiani and Sun, 2011). On the other hand, ultrasound irradiation at higher temperatures (-2 and -4 ^{0}C) significantly improved the viability of cells frozen in MRS (Figure 2a) due to the formation of fewer nuclei and larger crystals. The cells frozen in suspensions are believed to become damaged by higher rates of freezing. The main reason suggested for this phenomenon is intracellular ice formation. The cell suspensions could potentially achieve high

supercooling degrees even at high cooling rates. The lower cooling rates commonly employed in cell preservation procedures would augment the potential of supercooling (Kiani and Sun, 2011). According to both our the results and the literature (Mousavi et al., 2011), it is necessary to avoid high levels of supercooling when freezing cell suspensions. The results confirmed that ultrasound irradiation holds promise as a tool for ensuring the higher viability of cells. Similar results were obtained for the bacteria frozen in MRS broth containing 5 % DMSO (Figure 2b). Figure 3 shows the effect of ultrasound irradiation during phase change on the viability of *L. plantarum*. Ultrasound irradiation significantly enhanced the viability of the bacteria. The control sample with no irradiation experienced the highest number of cell death. Irradiation of ultrasound for 3 s improved cell viability, as already discussed. Ultrasound irradiation for 4 min at different ultrasound intensities during the phase change step resulted in even greater improvement of cell viability. Ultrasound irradiation during phase change shortened freezing times while improving the viability of the bacteria, which is a promising result. The reason for this remains unclear, but it could arise from different effects of ultrasound, such as mass transfer enhancement.

Conclusions

Ultrasound irradiation induced nucleation in the supercooled suspension of *L. plantarum*. Higher supercooling degrees lengthened overall freezing times but shortened phase change stages. Samples with higher supercooling degrees had shorter phase change steps. A quicker phase change is known to diminish ice crystal size, causing the formation of intracellular crystals which does not favor the viability of frozen suspended cells. Ultrasound-assisted irradiation at higher temperatures (-2 and -4 ^{0}C) increased the viability of the cells significantly. Ultrasound irradiation during the phase change stage of the freezing process further increased the viability of the cells while reducing the freezing time. The higher mass transfer rate of water molecules brought about by ultrasound irradiation might cause the improved viability and faster freezing process. Our results revealed that ultrasound irradiation during the nucleation stage or phase change step can be considered a promising tool to improve the viability of frozen suspended cells. We need more investigations into the mechanisms of ultrasound-assisted freezing of living cells and their relationship with water crystallization.

Acknowledgements

References

Chow, R., Blindt, R., Chivers, R., and Povey, M. (2005). A study on the primary and secondary nucleation of ice by power ultrasound. *Ultrasonics, 43*(4), 227-230.

Kiani, H., and Sun, D.-W. (2011). Water crystallization and its importance to freezing of foods: A review. *Trends in Food Science & Technology, 22*(8), 407-426.

Kiani, H., Sun, D.-W., Delgado, A., and Zhang, Z. (2012). Investigation of the effect of power ultrasound on the nucleation of water during freezing of agar gel samples in tubing vials. *Ultrasonics Sonochemistry, 19*(3), 576-581.

Kiani, H., Zhang, Z., Delgado, A., and Sun, D.-W. (2011). Ultrasound assisted nucleation of some liquid and solid model foods during freezing. *Food Research International, 44*(9), 2915-2921.

Li, B., and Sun, D. W. (2002). Novel methods for rapid freezing and thawing of foods - a review. *Journal of Food Engineering, 54*(3), 175-182.

Mousavi, Z., Mousavi, S., Razavi, S., Emam-Djomeh, Z., and Kiani, H. (2011). Fermentation of pomegranate juice by probiotic lactic acid bacteria. *World Journal of Microbiology and Biotechnology, 27*(1), 123-128.

IMPROVING ROUNDWOOD HAULAGE SUPPLY CHAINS THROUGH OPTIMISING VOLUME TRANSPORTED UNDER IRISH VEHICLE LEGAL DIMENSIONS AND WEIGHT RESTRICTIONS

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Abstract

Wood transportation cost can go up to 40% of the total supply chain costs, and this situation can be improved by optimising the delivered load. This paper presents the patterns on the use of volume and weight by trucks haulers (case study in Ireland) and the development of a methodology that can be used for wood transport companies in the forest in order to maximise the volume transported without incurring overweight penalties.

Introduction

In 2007, forests covered 10% of Ireland's surface, and this is projected to increase to 17% by 2030 (Department of the Environment, 2007). It is forecasted that roundwood volume will increase from 3.79 million m^3 in 2011 to 6.41 million m^3 in 2028 (Phillips, 2011); increasing at the same time the logistics involved in the wood supply chain. In the case of wood for energy purposes, biomass must be delivered to the energy plant or end user at the lowest cost possible. Several modes of transportation are used in the forestry sector and truck transportation constitutes an important part of the supply chain. Coillte (2003) stated that road transportation is and will remain the most important mode of timber transport in Ireland, forming a substantial part of the industry's raw material cost and having a major influence on the sector's overall economic performance and competitiveness. Nevertheless, wood transportation can count for 20 to 40% of the overall supply chain costs (Andersson et al., 2007).

All European countries imposed haulage regulations related to the restriction on dimensions and weight of the trucks. The weight restriction is more complex due to the relation between number of axles and the distance between them and how this changes the maximum permissible weight. As an example, the code of practice for the transport of round timber, presented by the Irish Forest Service in 2003 sets a maximum of 42,000 kg for trucks with 5 axles and 44,000 kg for trucks with 6 axles. This highlights the challenge facing truck operators of placing enough material in a truck (and trailer) of fixed dimensions. According to (Angus-Hankin et al., 1995) to carry less than the legal maximum weight is incurring opportunity costs. There are many areas where the truck transportation of fuelwood may be potentially improved; one of them is the maximisation of the delivered load up to the legal weight and dimension limits. The interactions between biomass Moisture Content (MC), dry matter, solid and bulk density and truck payloads constrains are complex but need to be evaluated in order to deliver the material cheaply and efficiently (OECD, 2004).

The objective of this study, based in Ireland, is to create a method that optimises log transportation by maximising the volume transported without incurring overweighs penalties (Figure 1).

Materials and Methods

This study was carried out in Medite Europe Ltd., located in Co. Tipperary.

Utilisation of volume and weight
To understand the pattern of utilisation of volume two cameras were positioned on both sides of the weighbridge, taking pictures of every truck entering the weighbridge carrying logs (pulpwood). A total of 100 trucks loaded with Sitka Spruce (*Picea sitchensis*) were photographed; images were then processed with Adobe Photoshop CS5 Extended ® software in order to measure and calculate the volume (Stack Volume). The Truck's Volume was estimated based on specifications of the different truck configurations. The Ireland Road Traffic Construction and use of Vehicles Regulations (2003) restrict the maximum weight of trucks. By comparing the Gross Vehicle Weight of each truck at the weighbridge to its legal maximum weight a pattern of weight utilisation was determined.

Bulk/Solid volume factor
The most commonly used unit for the measurement of wood biomass is the cubic metre solid volume (m^3), and in Ireland, this usually includes bark (expressed as over bark volume). A Solid/Bulk volume factor needed to be calculated in order to estimate the actual solid wood volume present in the trucks. The bulk volume determined by image processing does not accurately represent the amount of wood per m^3 since when logs are stacked there are air spaces between them (Kofman, 2010). Since density describes the relationship of weight to solid volume, and bulk density is the relationship between bulk weight and bulk volume. Therefore, the bulk density /solid density relationship should equate to the bulk volume /solid volume relationship. Moisture content has a confounding effect, as the total weight may be strongly influenced by the amount of water present in the wood. Because of this, moisture content was excluded by using the basic density of the logs and the bulk density (dry matter) of the woodchip.

The factor was determined as follows:
$$F = Dba/Dbu \qquad (1)$$

Where *F* is the Bulk/Solid factor, *Dba* basic density (kg/m^3) and *Dbu* bulk density (kg/m^3).

Optimisation of volume constrained by weight
Additional information was gathered in Medite's weightbridge related to GVW, tare weight, bulk weight, and wood Moisture Content (MC). The density of the wood was calculated since density is usually sufficiently accurate to permit proper utilization of wood products where weight is important, such as in this study. As moisture makes up part of the weight, density must reflect then this fact. This has resulted in the density of wood often being determined and reported on the basis on moisture content in use.

$$\rho = 1,000 * Gm * (1 + MC/100) \quad (kg/m^3) \qquad (2)$$

Where ρ is density, Gm is the specific gravity and MC is the moisture content of the wood.

After calculating the wood density (kg/m^3) at different MC, the amount of wood to fill the four types of truck volumes was determined: Type 1= 67.56 m^3, Type 2= 73.14 m^3, Type 3= 73.6 m3, Type 4= 78.2 m^3. In order to identify if the amount of wood loaded in the trucks was under the legal limit the average Legal Maximum Load was created. This maximum payload is the product of:
$$LML = L_{GVW} - x \quad T_w \qquad (kg) \qquad (3)$$

Where LML is the Legal Maximum Load, L_{GVW} is the legal gross vehicle weight established in the regulations and T_w is the average truck weight. Based on this LML and other truck configuration characteristics 5 Conditions were created:
The five conditions are:
1. *Condition 1* Truck rigid + Trailer with maximum legal weight of 44,000 kg (Truck type 2 and 3 and maximum payload of 24,503.72 kg).

2. *Condition 2* Truck articulated with maximum legal weight of 44,000 kg no crane (Truck type 1 and 4 and maximum payload of 28,274.78 kg).
3. *Condition 3* Truck articulated with maximum legal weight of 44,000 kg with crane (Truck type 1 and maximum payload of 25,855.71 kg).
4. *Condition 4* Truck articulated maximum legal weight of 40,000 kg no crane (Truck type 1 and 4 and maximum payload of 25,483.75 kg).
5. *Condition 5* Truck articulated maximum legal weight of 40,000 kg with crane (Truck type 1 and maximum payload of 22,815 kg).

Results and Discussion

Utilisation of volume and weight
The 100 trucks analysed in this study were loaded under the maximum truck capacity, with a average under utilisation of volume of 28.50 m^3 (39.24%). In contrast, 70% of the100 trucks were overloaded with an average excess weight of 2159.71 kg. The remaining 30% were under the legal weight by an average of 947.33 kg. Both situations represent an undesired scenario for the wood supply chain. Trucks overweight can face fines, or be rejected by the receiving industries, and in the long term increase the negative impact on road conditions. On the other hand, under weighted trucks incur opportunity costs, and decreases the wood transportation productivity.

Solid/Bulk volume factor
The average solid/factor was 0.68. This factor implies logs that are short, well delimbed, straight, and neatly stacked.

Optimisation of volume constrained by weight
After calculating the amount of wood at different MC that will fill the truck volume it was found that for condition 1, 2, 4 and 5 not even wood at 0% MC can fill the entire truck without exceeding the legal weight. Instead, in condition 3 the truck volume (67.56 m^3) can be loaded completely but with wood at MC of 0% which does not happen in the field. Due to these results it was needed to estimate the truck maximum volume that can be loaded under the weight restrictions. Since these results represent the amount of wood per solid volume, the bulk/solid factor should be considered to estimate the actual bulk volume to be loaded (this includes the air spaces between logs). Also, the achievement of this bulk volume will depend on the way the driver stacks the wood in the truck. Table 1 shows an example of optimisation on Condition 1 where it is highlighted the maximum weight that can be loaded into the trucks without exceeding the LML at different MC.

Table 1. Condition 1. Maximum amount of wood at different MC to be loaded at different volumes

MC	Legal Maximum Load (kg)	Weight (kg) at 60 m^3	Weight (kg) at 40 m^3	Weight (kg) at 35 m^3
6	24,504	24,168	16,112	14,098
60	24,504	36,480	24,320	21,280
84	24,504	41,952	27,968	24,472

Trucks in this condition can be loaded up to a maximum of 60 m^3 with wood at 6% MC (not a realistic scenario since in the forest wood MC cannot be less than 30% that is the Fibre Saturation Point). Next feasible scenario can be loading trucks at 40 m^3 with wood at up to 60% MC, and at a maximum MC of <84% the trucks can only be loaded up to 35m^3. Loading trucks at less than 35m^3 of their capacity implies lost in revenue. Moisture content was determined for twelve of the one hundred trucks dispatching to Medite. According to the

condition they represented, the optimum volume at which the trucks should be loaded without exceeding the legal weight was calculated (Table 2).

Table 2. Optimisation of loading volume restricted by weight

Truck no	MC (w)	Condition	Legal Maximum Load (kg)	Optimal payload (kg)	Vol. (m^3) at Opt. Payload
1	67.77	C4	25,484	24,866	39
2	65.72	C5	22,815	22,671	36
3	56.40	C3	25,856	25,556	43
4	52.54	C1	24,504	24,345	42
5...	56.96	C2	28,275	28,033	47
12	67.47	C4	25,484	24,819	39

Conclusions

The volume transported cannot be 100% optimised since none of the trucks can be fully loaded without being weight restricted even with wood at 0% MC. Even though, the maximum volume to be transported at its maximum legal weight can be determined and even tabulated and distributed to haulage companies in Ireland, providing a tool that will increase their efficiency. Even a small optimisation of the transport efficiency can translate into significant cost reduction.

Acknowledgements

References

Andersson G., Flisberg P., Lidén B., & Ronnqvist M. 2007. RuttOpt - A Decision Support System for Routing of Logging Trucks. Bergen, Norwegian School of Economic and Business Administration

Angus-Hankin C., Stokes B., & Twaddle A. 1995. *The transportation of fuelwood from forest to facility*. Biomass and Bioenergy, *9*(1-5), 191-203.

Department of the Environment, 2007. Ireland: National Climate Change Strategy 2007-2012. Dublin: Department of the Environment, Heritage and Local

Devlin G., McDonnell S., & Ward S. 2008. *Development of a Spatial Decision Support System (SDSS) for route costing calculation within the Irish timber haulage sector*. Transactions of the ASABE: American Society of Agricultural and Biological Engineers, 51(2), 273-279.

Forest Products Laboratory. 2010. Centennial edition: Wood Handbook, Wood as an Engineering Material. Wisconsin, United States Department of Agriculture Forest Service.

Kent T., Kofman P., Coates, E. 2011. Harvesting wood for energy: cost effective woodfuel supply chains in the Irish industry. Dublin, Council for Forest Research and Development (COFORD).

Kofman P. 2010. Units, conversion factors and formulae for wood for energy. Dublin, Council for Forest Research and Development (COFORD).

Minister for Transport, Tourism and Sport. 2003. Road Traffic (Construction and Use of Vehicles) Regulation. S.I. No. 5/2003.

Organisation for Economic Co-operation and Development (OECD). 2004. Biomass and Agriculture: sustainability, markets and policies. Paris, OECD.

Phillips H. 2011. All Ireland roundwood production forecast 2011 - 2028. Dublin: COFORD.

CALIBRATION AND VALIDATION OF MULTISPECTRAL MULTIPLATFORM BASED CHANGE DETECTION ON IRISH PEATLANDS

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Abstract

A lack of globally consistent, temporally frequent peatland maps results in uncertainty when assessing the role of peatlands in the global carbon and water cycles. In this study an image difference based change detection protocol was created and tested a five peatland sites in Ireland. The system utilised a standard deviation spectral threshold and a 9 pixel spatial threshold to mask out radiometric anomalies and mis-registration. Results showed <5% disturbance on all sites with <80% Kappa accuracy. This study has shown that a simple multispectral multiplatform change detection system can be implemented for national scale peatland disturbance monitoring.

Introduction

Change detection is the process of identifying differences in the state of an object or phenomenon by observing it at different times (Singh, 1989), and has now become one of the principle applications in environmental remote sensing (Mas, 1999; Lillesand et al. 2004). Approaches range in complexity from image difference (Coppin and Bauer 1994) and image ratio's (Gupta, 1998), which are easy to apply, to more complex procedures, such as vector analysis (Lambin and Strahler 1994) that can provide dynamic results (Lu et al. 2003). It is generally accepted that no one process is suitable for all change detection scenarios (Coppin et al. 2004). For national scale monitoring vegetation indices (VI) offer the advantage that they are robust because there is usually a strong correlation between upwelling radiance and the vegetation cover (Coppin et al. 2004), and they compress multispectral data to a single image (O Connell et al. 2012). Enhanced Vegetation Index 2 (EVI2) has been found to accurately depict vegetation communities on Irish peatlands (O Connell et al. 2012) and overcomes soil background contamination by having additional weighting on red reflectance data (Rocha and Shaver 2009).

The objective of this study was to calibrate and validate a multispectral, multiplatform change detection methodology for identifying disturbance to peatland.

Materials and Methods

Data
Satellite data (70 images) were acquired from various platforms via the Centre National d'Etudes Spatiale programme Image Incentive for the Scientific use of Images from the Spot System (ISIS), a European Space Agency (ESA) Category 1 Proposal and the US Geological Survey Global Visualization Viewer (http://glovis.usgs.gov/). The multispectral data were pre-processed using procedures detailed in O Connell et al. (In Press).

Accuracy Assessment
The change detection method was calibrated and verified using five contrasting sites in Ireland. They were chosen for accessibility, geographical spread, proximity of disturbed and undisturbed areas and the availability of auxiliary data (1 m Aerial photography (Ordnance Survey Ireland); Commonage Framework Plans (NPWS 2011); Habitat maps/ surveys (NPWS 2007); disturbance records and high resolution (1-5 m) satellite data obtained through the Category 1 Proposal. The sites chosen were Kerryhead (N 52.4545°, W 9.4075°),

Moanveanagh (N 52.4545°, W 9.4075°), Clara (N 53.3211°, W 7.6272°), Slieve Bloom Mountains (N 53.0928°, W 7.5793°), and the Wicklow Mountains (N 53.116°, W 6.356°).

Change Detection

Change detection was automated using Erdas Imagine Spatial Modeller (Lecia 2006) as a difference image between consecutive images processed as above. The model incorporated a mean ± SD threshold and spatial threshold. The SD threshold removed subtle change between master and slave due to atmospheric inconsistencies, sun illumination differences and minor pixel mis-registration (Mas 1999, Lu et al. 2003). The spatial threshold eliminated any "salt and pepper" effect due to localized topographical or atmospheric anomalies (Coppin et al. 2004). The process used a rolling master image, i.e. the slave from the last iteration became the master for the next. This simplified change detection to only negative values. A fixed master approach produces a complex array of negative and positive values that can be attributed to change in both the master and slave images.

Results and Discussion

Accuracy Assessment

The different accuracy measures show that 1.5 SD achieved the best User, Producer Overall and Kappa accuracy. Consistent across all sites was a high level of omission indicated by a low User change accuracy for thresholds below 1.5SD and high level of commission indicated by a low Producer change accuracy for thresholds above 1.5SD. Moanveanagh (89%), Clara (97%), Slieve Bloom Mountains (85%) and the Wicklow Mountains (95%) all achieved very high Kappa accuracy, while Kerryhead had the lowest at 80% (Figure 1).
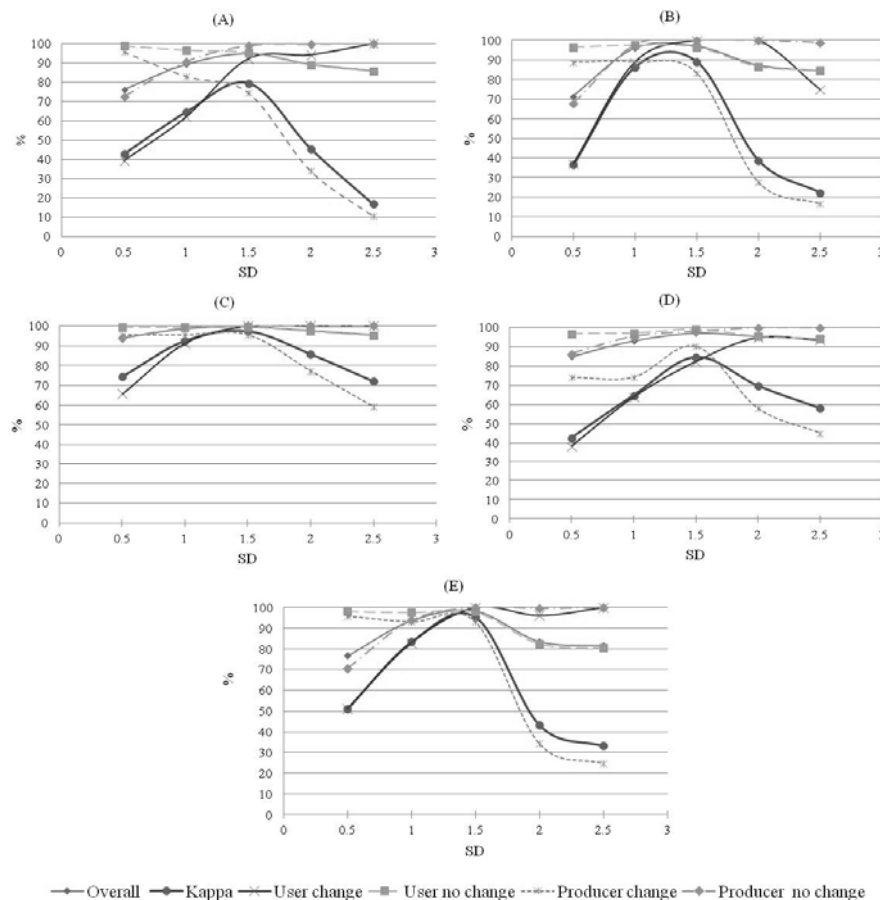
Figure 1. Accuracy assessment curves, expressed as percentage values, for Kerryhead (A), Moanveanagh (B), Clara (C), Slieve Bloom Mountains (D) and Wicklow Mountains (E).

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Change Detection

Using the calibrated threshold of 1.5SD, percentage change at each site between 2001 and 2010 showed very different trends (Figure 2). The time series graphs represent increments of change since the previous observation rather than change from an arbitrary anniversary date. At Kerryhead (Figure 2A) a maximum change of 4.6% was seen in May 2001 and minimum of 1.3% in September 2002. Between 2004 and 2007 disturbance was consistently >2% of total area, with sudden peaks occurred March 2004 (5.8%) and September 2010 (2.9%). At Moanveanagh bog (Figure 2B) there was a peak in disturbance of 7.2% in October 2003. A further disturbance event was identified in July 2007 (3.9%), but overall there was little change. Clara bog (Figure 2C), was difficult to analyse even with multiplatform data and had the shorted temporal range. There were two large disturbance events, one in April 2007 (4.0%) and the other in May 2008 (7.2%). Two peak disturbance events were identified in the Slieve Bloom Mountains (Figure 2D) in July 2006 (6.0%) and May 2010 (5.5%), with period little change from November 2007 to September 2009. In the Wicklow Mountains (Figure 2E) there was an extended period of little disturbance (<0.7%) from September 2001 to April 2006, but from July 2006 to September 2009 a period of relatively high (>3.9%) disturbance occurred.
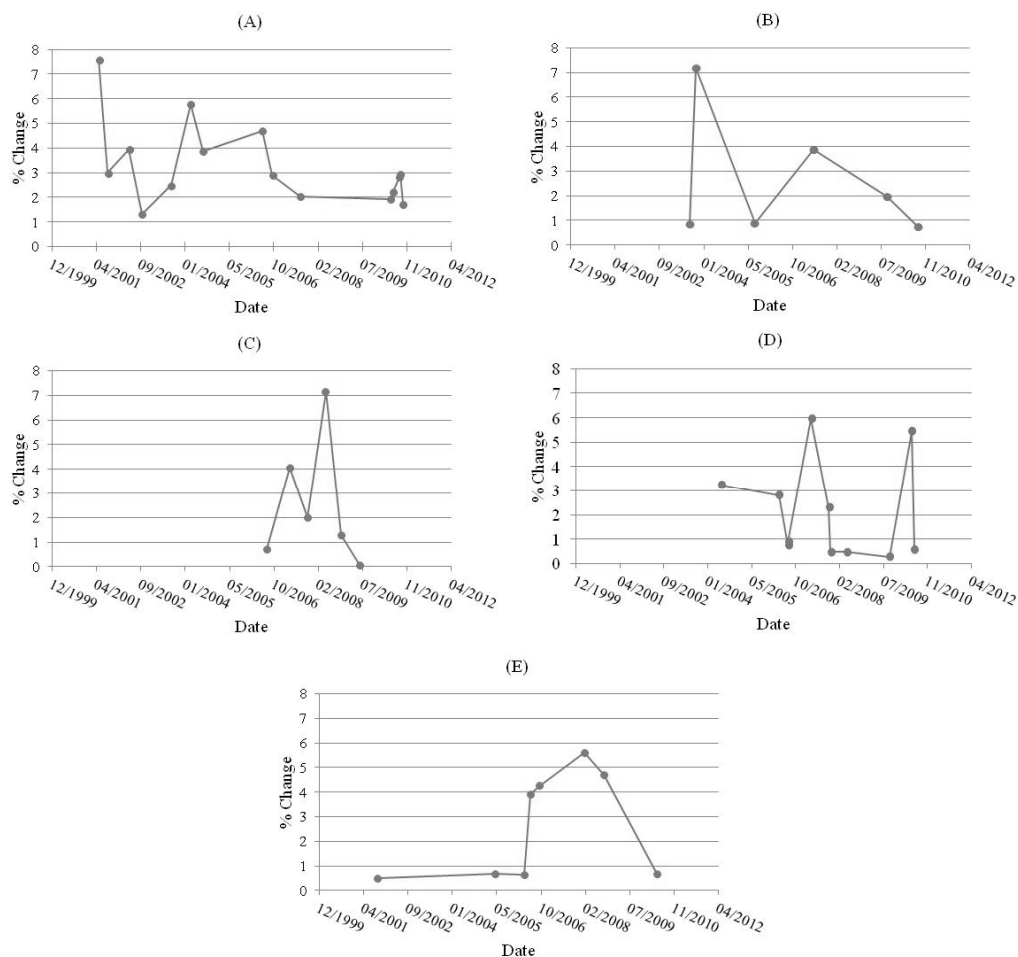
Figure 2. Percentage change (relative to overall area) for Kerryhead (A), Moanveanagh (B), Clara (C), Slieve Bloom Mountains (D) and Wicklow Mountains (E).

Conclusions

It can be concluded from this study that a simple multispectral multiplatform change detection system can be implemented for national scale peatland disturbance monitoring. The system can deploy readily available medium resolution data (up to 30 m pixel resolution), conversion to EVI2 for difference calculations and 1.5SD threshold to filter out unwanted noise. The system would have sufficient accuracy (Kappa >80%) for routine national scale monitoring.

Acknowledgements

References

Coppin, P., Jonckheere, I., Nackaerts, K. and Muys, B., 2004, Digital change detection methods in ecosystem monitoring: a review. *International Journal of Remote Sensing,* 25, 32.

Coppin, P.R. and Bauer, M.E., 1994, Processing of multitemporal Landsat TM imagery to optimizeextraction of forest cover change features. *Geoscience and Remote Sensing, IEEE Transactions on,* 32, 918-927.

Gupta, A.P.R.P., 1998, Land-use mapping and change detection in a coal mining area-a case study in the Jharia coalfield, India. *International Journal of Remote Sensing,* 19, 391-410.

Lambin, E. and Strahler, A., 1994, Indicators of land-cover change for change-vector analysis in multitemporal space at coarse spatial scales. *International Journal of Remote Sensing,* 15, 2099-2119.

Lecia, G., 2006, Erdas Imagine IN IMAGING, G. Ed 9.3 ed.

Lillesand, T.M., Kiefer, R.W. and Chipman, J.W., 5 2004, *Remote sensing and image interpretation*, John Wiley & Sons Ltd Chichester, UK.

Lu, D., Mauselm, P., Brondizio, E. and Moran, E., 2003, Change detection techniques. *International Journal of Remote Sensing,* 25, 44.

Mas, J.F., 1999, Monitoring land-cover changes: a comparison of change detection techniques. *International Journal of Remote Sensing,* 20, 139-152.

NPWS, 2007, Vegetation and habitat survey of Wicklow Upland SAC. IN CONSULTING, R. Ed. Malvern, UK, National Parks and Wildlife Service.

NPWS, 2011, Commonage Framework Plans. IN MARINE, D. O. A. A. F. A. T. Ed. Dublin.

O Connell, J., Vermote, E.F., Connolly, J. and Holden, N.M., 2012, Radiometric normalisation of a multispectral database of satellite imagery of peatlands for change detection monitoring. *International Journal of Remote Sensing,* In review.

Rocha, A. and Shaver, G., 2009, Advantages of a two band EVI calculated from solar and photosynthetically active radiation fluxes. *Agricultural and Forest Meteorology,* 149, 1560-1563.

Singh, A., 1989, Review Article Digital change detection techniques using remotely-sensed data. *International Journal of Remote Sensing,* 10, 989-1003.

DETECTION OF SLURRY ON SOIL

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Abstract

Monitoring of slurry spreading is often expensive and time consuming for local authorities. EU regulations require this process as a vital part of ensuring sustainable environmental utilisation. Remote sensing offers a unique and accessible means of overcoming some of the limits associated with manual monitoring of large areas of farmland. To make remote sensing a reliable tool it is important to ascertain the spectral reflectance signature of slurry that has been spread on grasslands with exposed soil. The reflectance signature of slurry on soil may have a distorting effect on the image produced. After experimental analysis in the field, imagery obtained from satellites can be calibrated with ground data to limit any errors.

Introduction

Agriculture in Ireland is primarily a grass-based industry and grass is the most important agricultural crop in Ireland (Holden and Brereton, 2002). Grassland farming and, in particular, cattle rearing and dairying accounts for more than 90% of farming activity (Hyde et al., 2003). Among the many legislative requirements farms in Ireland must adhere to the Nitrates Directive (91/676/EEC) has a profound impact on how farms are managed. Under this directive Ireland must protect its waters against pollution caused by nitrates from agricultural land. One of the main sources of nitrates on a farm is slurry (Jordan and Smith, 2005). It is a valuable natural fertilizer that farmers can use to reduce their dependence on artificial fertilizers. The high concentration of nitrates in slurry makes it exemplary for helping grasslands grow. Grass has great potential to absorb excess nitrogen as it has a long growing season and it requires more nitrogen to initiate growth (McGechan and Wu, 1998). However nitrates can be leeched from the soil or become runoff that collects in nearby water courses (Holden et al., 2004). For this reason there are strict guidelines when and where slurry can be spread. The closed period for spreading slurry in Ireland is generally in the winter months with specific regions having different starting and ending dates depending on soil types. Lack of storage for slurry is the main cause of spreading slurry when conditions are unsuitable (Holden et al., 2004). During the spreading season slurry cannot be spread when weather conditions are not suitable such as periods of drought or precipitation. Rainfall is a major restriction for when slurry can be spread, should not be excessive on the day of spreading (Holden et al., 2004). Slurry that is thick and viscous and will remain on vegetation were as thin slurry has properties like water and can easily move towards the base of the vegetation (Rodhe, 2003).

Slurry is spread on pastures that have been grazed or have been cut for the production of silage. After either of these events has occurred on a pasture there will be a large amount of exposed soil. Splash plate is the most common way of spreading slurry. It spreads the slurry over the surface of the grass and soil. It is an easy way of applying slurry but also has more wastage involved. Injection of slurry decreases the loss of slurry due to evaporation but is more costly and is not beneficial in economic terms if done on a small scale (McGechan and Wu, 1998). In order for monitoring of slurry spreading events to become more efficient the use of remote sensing may offer a cost effective means to do this. Due to slurry been spread on bare soil as well as grass it is important to be able to account for a difference in the spectral reflectance value. **The objective of this experiment was to determine spectral reflectance of slurry spread on grass and soil.**

Materials and Methods

Selection of field site

The experiment was established at Lyons Farm in Co. Kildare (Latitude 53.306416, Longitude – 6.539612). This farm is used for teaching and research by University College Dublin. The farm consists of 234 hectares that is predominately used for beef and dairy production. A field within the farm that had recently been grazed was selected. The farm was able to provide sufficient slurry and farmyard runoff for use in the experiment.

Experimental design

One strip of grassland was divided into 5 plots each measuring 1 m². Each m² plot was pegged out with a buffer between plots. In preparation for the experiment each plot was cut to the same grass height. A sample of biomass was taken to determine the amount of vegetation and to monitor any changes in growth that occur.

The experiment consisted of five plots that each received a different treatment. The treatments were as follows.

1. Nothing sprayed to act as a control
2. 5000 ml of slurry
3. A mixture of 2500 ml of slurry and 2500 ml of water
4. 5000 ml of water
5. 5000 ml of dirty water (farm yard runoff)

The treatments were all sprayed onto the plots using a watering can and were spread evenly over the surface of the grass. The treatment with water was added as an extra control to rule out any initial difference caused by the water content of the slurry mixtures.

These plots were replicated 12 times to give a total of 60 plots. The strips of plots were placed at random around the field. Within each strip the treatment order was randomly selected so that each treatment would not negatively impact each other (randomised block design). The weather conditions needed to start this experiment were a clear sunny day. Any precipitation would have negative effects on the setup and recording of results as well as breaking with regulations.

The spectral reflectance of each plot was then taken using a CROPSCAN multispectral radiometer. The radiometer was attached to a pole and positioned over the plot. The diameter of field of view is half the height of the radiometer above the plot (See Fig 1). A scan of the plot takes a few seconds. To distinguish between the grass, soil and slurry the radiometer uses narrow band interference filters to select certain bands in the visible and near infrared regions of the electromagnetic spectrum. All recordings are stored in the Data Log Controller that accompanies the radiometer. This process was repeated each day to gather multiple readings and to monitor changes in the treatments with time.
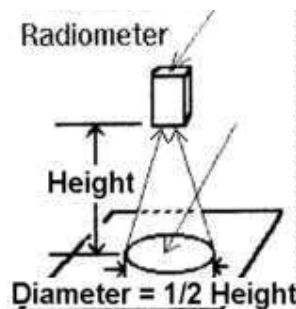
Figure 1. CROPSCAN in operation (Cropscan, 2012)

Results and Discussion

The experiment is currently been conducted and results are still pending. The mean and standard deviation of each treatment will be calculated across plots. Statistical analysis of the results will reveal any significant differences between the treatments. To illustrate this difference the spectral reflectance signature of each treatment will be plotted.

The spectral reflectance of vegetation, soil and water is simplified in figure 2. This is an ideal representation of the three main elements that will be found in the experiment. The resulting diagrams for each treatment will differ considerably from this example but is useful to show where the difference will most likely occur. The spectral reflectance signature of dry soil and wet soil is noticeably different. This is due to presence of water. The spectral signature of water can be identified as it absorbs energy in the near infrared (NIR) wavelength and beyond. When water is present in soil the reflectance will decrease in all wavelengths of the visible to the middle IR. The spectral reflectance of grass within a pasture that has recently been grazed or cut for the production of silage will have a different appearance than that of a healthy non-grazed pasture. Apart from the decrease in biomass the remaining grass will be short and will have a lower amount of chlorophyll. There will also be a large increase in exposed soil surface. The combination of both of these factors will result in considerably different outcome in reflectance values for the same pasture.
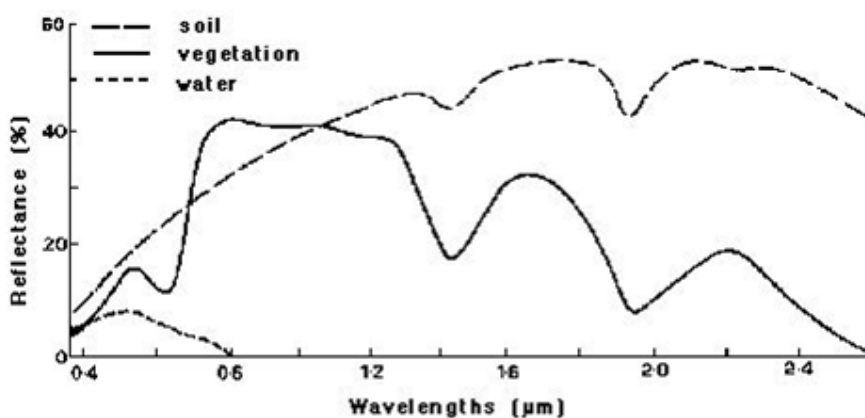
Figure 2. Typical spectral reflectance curves for vegetation , soil and water (Lillesand and Kiefer, 1979)

Conclusions
Remote sensing has a unique advantage to offer in the monitoring of slurry spreading events. The spectral reflectance response of all matter differs depending on a number of conditions. In order for local authorities to benefit from remote sensing then determining for certain that the imagery obtained from satellites can show spreading events is of importance. Imagery that can account for a difference in expected spectral response of slurry on grasslands and exposed soil will help advance remote sensing as a monitoring tool.

Acknowledgements

References

CROPSCAN (2012). Retrieved February 01, 2012 from http://www.cropscan.com

HOLDEN, N. M., FITZGERALD, D., RYAN, D., TIERNEY, H. & MURPHY, F. (2004) Rainfall climate limitation to slurry spreading in Ireland. *Agricultural and Forest Meteorology,* 122**,** 207-214.

HOLDEN, N. M. BRERETON, A. J. (2002) An Assessment of the Potential Impact of Climate Change on Grass Yield in Ireland over the Next 100 Years. *Irish Journal of Agricultural and Food Research,* 41**,** 213 - 226.

HYDE, B. P., CARTON, O. T., O'TOOLE, P. & MISSELBROOK, T. H. (2003) A new inventory of ammonia emissions from Irish agriculture. *Atmospheric Environment,* 37**,** 55-62.

JORDAN, C. & SMITH, R. V. (2005) Methods to predict the agricultural contribution to catchment nitrate loads: designation of nitrate vulnerable zones in Northern Ireland. *Journal of Hydrology,* 304**,** 316-329.

LILLESAND, T. M. & KIEFER, R. W. (1979) *Remote sensing and image interpretation*, Wiley.

MCGECHAN, M. B. & WU, L. (1998) Environmental and Economic Implications of some Slurry Management Options. *Journal of Agricultural Engineering Research,* 71**,** 273-283.

RODHE, L. (2003) Methods for determining the presence of slurry on the crop and in the upper soil layer after application to grassland. *Bioresource Technology,* 90**,** 81-88.

RISK RANKING OF ANTIMICROBIALS IN THE ENVIRONMENT

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Abstract

Extensive pharmaceutical use has led to an increase in antimicrobial levels in the environment. Such antimicrobial prevalence poses a potential risk for environmental toxicity and resistance formation. A mechanistic model is being developed from which the degree of antimicrobial presence in the environment will be determined. The six main groups of antimicrobials consumed in Europe; penicillins (PEN), β-lactams (BET), tetracyclines (TET), macrolides (MAC), quinolone/fluoroquinolones (Q/F) and sulfonamides/trimethoprim (S/T) were identified and are to be used in the model. The model is to simulate the release of antimicrobials into the environment by integrating the effects of antimicrobial use, metabolism, degradation, and dilution; all processes within the cycle chain. Each of these input variables is to be assigned a probability density to represent inherent uncertainty and variability in the parameter. Monte Carlo simulation models are to be used to give a resulting probability distribution of the predicted environmental concentrations (PECs) for each antimicrobial group. The resulting PECs are then to be ranked using the risk estimates of Hazard Quotient (HQ) for toxicity and Minimum Inhibitory Concentration (MIC) for resistance formation. PECs of the antimicrobials will be compared to HQ guidelines and MIC estimates, and conclusions and recommendations shall be made from these comparisons. Risk estimates may be made for each antimicrobial group for comparing years for the purpose of comparing the prevalence of antimicrobials in the environment both before and after annual European Antibiotic Awareness dates. The inputs which have the highest impact on the model results shall be identified and from this possible mitigation strategies shall be constructed.

Introduction

Antimicrobial presence can lead to the formation of antibiotic resistance amongst environmental bacteria populations. Antimicrobial resistant bacteria are biological hazards and are associated with increased human morbidity and mortality and are a public health concern (EFSA 2008). Such is the importance of the issue, the European Centre of Disease Prevention and Control (ECDC) has created an annual European Antibiotic Awareness Day (EAAD) to help raise awareness of the threat to public health that antibiotic resistance poses and to encourage prudent antibiotic use; whilst a national campaign has been initiated to reduce unnecessary antibiotic use in Ireland in 2012 (ECDC 2012a). Such activity reflects the inherent risk that antimicrobials pose to non-target organisms. It is therefore the job of environmental modellers to identify the main contributing factors which lead to antimicrobial residues in the environment and to identify which antimicrobial groups pose the greatest risk.

This project aims to develop a model which is to simulate the release of antimicrobials into the environment. Parameters used in our model shall integrate the effects of antimicrobial usage, metabolism, degradation, and dilution; all processes within the antimicrobial environmental release cycle chain. The model shall help us to critically identify the contributing factors which lead to antimicrobials in the environment and identify antimicrobial groups which pose the greatest risk to toxicity and resistance formation. Such information is critical to the formation of risk mitigation strategies with which policy makers may utilize to help effectively mitigate risk.

The objective of this study is to evaluate the likely predicted environmental concentrations (PEC) of the most significant antimicrobial groups through determining

the leading factors influencing the presence of antimicrobial residues in the environment and to develop a risk ranking model based on our findings.

Materials and Methods

Monte Carlo simulation is to be used to model and estimate the distribution (prevalence in the environment) for each input factor of our chosen antimicrobials; PEN, BET, TET, MAC, Q/F and S/T. Input factors are usage, metabolism, degradation and dilution effects. Probability density distributions are to be used to characterise any inherent uncertainty and variability in these parameters and to evaluate the likely effect of the different process (input factors) within the framework of the life-cycle chain of antimicrobials. From such distributions the likely PECs of each antimicrobial group and their residues will be conducted using simulation models in EXCEL. From the PECs a quantitative risk ranking of antimicrobial groups will be conducted to test our hypothesis that predicted environmental concentrations of selected antimicrobials may pose a toxicity treat and be conducive to bacteria resistance formation. A risk based ranking approach is to be used as it can account for probability of exposure from different antimicrobial groups and the subsequent effect of active substances on non-target organisms (Benford 2008), such as to the environment and human health. Sensitivity analysis shall be carried out to identify the relationship between the variables through calculating a correlation coefficient (Le and Boen 1995). Correlation is the degree to which one variable is dependent on another (Vose 2008).

Foremost data concerning antibiotic consumption and antimicrobial prevalence and toxicity in the environment throughout Ireland and Europe are to be sourced from relevant ESAC databases (ESAC 2010). Literature is to be examined to find the most accurate and concurrent data concerning human metabolism effects on antimicrobials, degradation effects of antimicrobials in the environment and dilution effects of waste water treatment plants (WWTP) in Ireland and Europe. Risk ranking models of antimicrobials for both before and after annual European Antibiotic Awareness dates may be complied so as to demonstrate the possible effects of reduction methods being implemented throughout Europe on these annual dates (ECDC 2012b). Risk estimates will be assigned to PEC values. Hazard quotient (HQ) values (for toxicity) and Minimum Inhibitory Concentration (MIC) (for resistance formation) shall represent our risk estimates. The evidence for a cut off concentration to which no resistance can form is nonexistent (Harris and Cummins 2011). Therefore MIC values will have to be interpreted. These estimates will use antimicrobial resistance potential values for resistance formation values and effect concentration (EC_{50}) and lethal concentration (LC_{50}) values for toxicity values. From such analysis an understanding of the environmental stability of antimicrobials in the environment and the classification of antimicrobials which pose the greatest risk will be created. PECs will also be compared to regulatory environmental requirements.

Results and Discussion

This study is ongoing. Previous studies in this area (Harris and Cummins 2011) have found that PEC values for the same microbial groups did not in fact exceed levels where toxicity to non-endpoint bodies was exceeded; though worryingly the PEC values predicted that such levels in the environment may in fact lead to resistance formation for these antimicrobial groups, with BET and Q/F having the highest resistance formation potentials. Risk ranking values are to be used for each microbial group to further research these claims and to compare how well the risk ranking findings faired in identifying the leading contributing factors contributing to antimicrobial residues in the environment. It is also hoped that these risk ranking values will allow for the identification of possible relationships between our identified variables and give us a more robust understanding of the nature of antimicrobials in the environment and how best antimicrobial prevalence in the environment is to be tackled. Also, the contributing factors and leading mechanisms of resistance formation are presently

uncertain (Harris and Cummins 2011). Perhaps our research into the relationships between our identified variables will give us a better understanding of what limit of exposure initiates resistance formation.

Conclusions

The calculated PEC values shall be compared to HQ guidelines and MIC estimates to investigate if there is any difference between the recommended environmental regulatory requirements and the calculated values. The main input variables which impact on the model shall be identified and with such information recommendations for possible risk mitigation strategies which will help tackle the issue of antimicrobial resistance formation and environmental toxicity may be constructed. Monitoring of antimicrobial prevalence is essential if we are to keep our present and future environment safe. Comparisons of PECs for both before and after annual European Antibiotic Awareness dates shall be undertaken. Such comparisons may possibly reveal that current efforts by the ECDC to reduce antimicrobial prevalence in the environment have been successful, or have not. Such findings may be presented to the ECDC. Findings from this study may highlight the stages of the model of environmental antimicrobial release which have the highest impact and which deserve the greatest amount of attention from policy makers and environmental scientists alike, and may assist policy makers in the construction of mitigation strategies. Results from this study may also highlight the need for further research into antimicrobials in the environment.

References

Benford, D. 2008. Risk—What is it? *Toxicology Letters,* 180**,** 68-71.
ECDC. 2012a. Campaign in Ireland. Available at:
        <http://ecdc.europa.eu/en/eaad/Pages/campaign_Ireland.aspx> [Accessed 18/03/2012]
        --- 2012b. European Antibiotic Awareness Day. Available at:
        <http://ecdc.europa.eu/en/EAAD/Pages/Home.aspx/> [Accessed 25/04/2012]
ESFA. 2008. Report of the Public Consultation on the EFSA Draft. Available at:
        <http://www.efsa.europa.eu/en/efsajournal/doc/749.pdf> [Accessed 25/03/2012]
Harris, S., E. Cummins. 2011. RISK RANKING ANTIMICROBIAL PRESENCE IN THE
        ENVIRONMENT. In *Biosystems Engineering, UCD School of Agriculture, Food
        Science and Veterinary Medicine*. University College Dublin: UNIVERSITY
        COLLEGE DUBLIN.
Le C., Boen J. 1995. Health and numbers: basic biostatistical methods. New York, John
        Wiley.
Vose D. 2008. Risk analysis: a quantitative guide, John Wiley & Sons Inc.

EVALUATION OF PESTICIDE GUIDELINE VALUES IN DRINKING WATER BY USING PROBABILISTIC APPROACH

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Abstract

The use of pesticides to control crop pests can to lead drinking water contamination and constitute a threat to human health. This paper describes a probabilistic approach to assess the health risk level of pesticide in drinking water. A framework for calculation of a pesticide guideline is presented with the most important factors that need to be considered when estimating human toxicity from animal studies. The model can be used to assess chemical compliance in terms of their potential risk to public health during monitoring.

Introduction

Pesticides are used worldwide in agriculture to control pests, vectors of plant, human disease and livestock disease (Cooper and Dobson, 2007). However, they can potentially be toxic to non-target living organisms or can alter the quality of food and different environmental components such as soil and water. Pesticide residues in drinking water can result from surface water or groundwater contamination due to leaching through tile drains, surface runoff, spray drift, careless disposal of empty containers and equipment washing (Konstantinou *et al.*, 2006; Huber *et al.*, 2000).

To ensure good quality status of water intended for human consumption, the European Union Directive 98/83 drinking water directive has set an upper limit of 0.1 µg/l for individual pesticide in drinking water and 0.5 µg/l for total pesticides (CEC 1980; Fava *et al.* 2010). The Irish Environmental Protection Agency (EPA 2009, 2010) revealed that some pesticides were detected above the drinking water standard (0.1 µg/l). These were: MCPA, Triazine, Atrazine, Dichlorobenzine, Isoproturon, etc. (EPAa 2009, EPAb 2010). It is noted that the approach of comparing the level of pesticide in drinking water to the maximum admissible concentration (0.1 µg/l) is very conservative, and somewhat tenuous as the drinking water standard is not based on any toxicological studies (but in some cases reflects technical limits) and the exceedance of this value does not necessarily indicate a high risk (Hamilton *et al.*, 2003). This makes the interpretation of monitoring results difficult in terms of human health implications.

At the international level, the WHO introduced the concept of guideline values to address toxicological and public concern. The guideline value of a chemical is defined as "*the concentration of a constituent that does not result in any significant risk to health over a life time of consumption*" (WHO, 2008). Based on that approach, Younes (2000) calculated the statutory guideline values of 32 chemicals. The main limitation of the WHO guideline value for chemicals is that all the inputs were fixed values based on the general consensus of the experts of the member states which include daily water consumption, body weight of an adult and the contribution of drinking water to the total exposure to a chemical. Although it has limitations, the WHO guideline value concept has merit in giving the first indication of the threshold level of a chemical and it is recommended to the member states to make adjustments by taking into account local circumstances while deriving their guideline values (Fawel 2007).

The objective of this study is to determine the guideline values of pesticides and to assess their health impacts by evaluating the health status of monitoring results.

Materials and Methods

Work to date

A flow diagram of the model is given in **Figure 1**. The WHO has suggested a simple algorithm as described (in **equation 1**) to calculate the guideline values of chemical (WHO, 2008). Instead of WHO which recommended a generic uncertainty for the extrapolation of animal toxicity to human, this study will capture the uncertainty of extrapolation animal toxicity to human by considering animal test used, study design and sample size during animal testing, animal body weight and size. In addition, a distribution function will be applied to all the inputs of the **equation 1**.

$$GV = \frac{TDI \times BW \times P}{C}$$ (Equation 1)

Where
GV   Guideline value
TDI   Threshold daily intake (mg/kg)
Body weight   Body weight (mg/kg)
C   Daily water consumption (l)
P   fraction of the TDI allocated to the drinking water

Chemical selection

In Ireland, a recent study (Labite and Cummins 2011) assessed the risk of pesticides used in agriculture. Out of 34 active substances evaluated, MCPA, Terbuthylazine, Atrazine, 2,4-D, Simazine, Mecoprop, Mecoprop-P and Metribuzin were highlighted as compounds which required the most vigilance based on their leaching potential and toxicity. The selection of chemicals included in this study were based on those which pose the greatest threat to groundwater and human health (Labite and Cummins 2011) and those detected above 0.1 µg/l in a recent EPA monitoring survey (EPA 2009).

Guideline value for pesticides

Pesticides are a group of Chemicals that can cause harmful effects and are classified in two groups: carcinogenic and no carcinogenic chemicals (WHO 2008). The carcinogenic chemicals represent a group of chemicals that can be ingested up to below a threshold dose at which no health adverse effects occurs in contrast to carcinogenic chemicals which can cause cancer effects in humans or animals at any dose (Vermeire and van der Zandt. 1995). The latter are beyond the scope of this study.

The Tolerable daily intake (TDI) is based on the NOAEL or LOAEL if the former is not available. The NOAEL is the "*highest experimental level in a toxicological study that did not result in a statistically and biologically significant effect*" (WHO 2008). There are several issues associated with its use: the uncertainty in the data is not considered, the value of NOAEL relies on the number and the sample size of each treatment group and is limited to the experimental doses as well (Oberg 2010). To overcome the limitations of the NOAEL, the approach of Benchmark Dose (BMD) is preferred to assess the safe dose. The BMD is "*the lower confidence limit of the dose that produces a small increase in the level of adverse effect*" (WHO, 2008). In contrast to the NOAEL which is derived from single dose, the use of BMD has the advantage of including data from the entire dose-response curve of the effect under consideration and it is not limited to experimental doses (Oberg 2010; Murri 2009). The results are presented in term of the lower confidence and encompassed the variability and uncertainty of the data. The use of the BMD approach has numerous limitations which

include the harmonization of the model to be used, relatively complex (i.e. specially to inexperienced investigators), lack of consensus in terms of the lower confidence bound
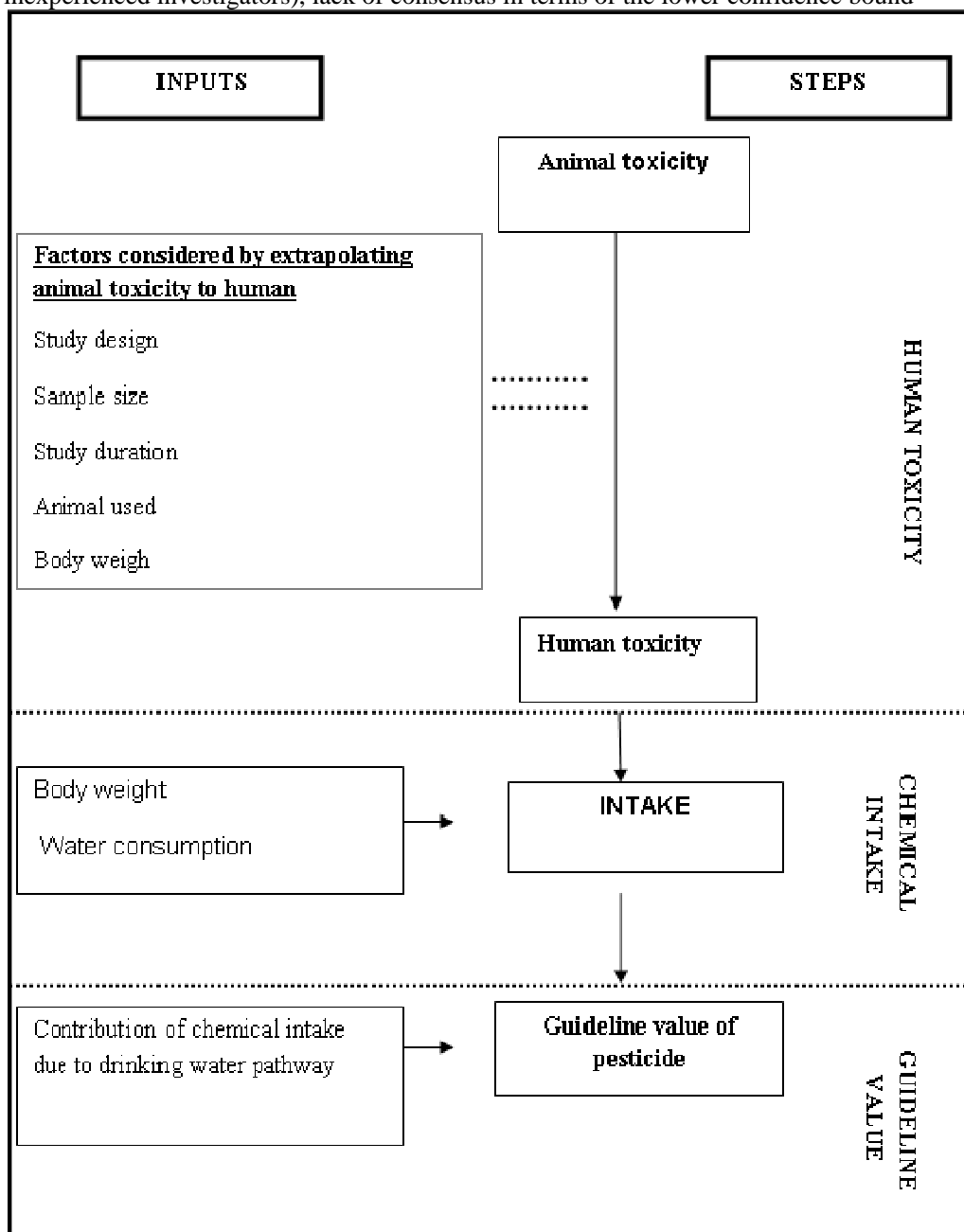
Figure 1. Framework of guideline value calculation

(BMDL), the benchmark response (BMR) and BMDL, model fitting, etc (Oberg 2010; Murri 2009). In addition, there is the issue of data availability as the use of the BMD approach requires the raw data of the toxicity studies from where the NOAEL has been determined. Based on these limitations, the calculation of the TDI based on the NOEAL (despite its weakness) is still used to date. Dourson and Parker (2007) suggested the use of distribution to capture the uncertainty of the tolerable dose.

This study will use a novel approach to capture the uncertainty of NOEAL from different studies by encompassing a range of parameters (such as species selection, sample size, body weight) based on data availability. To capture the uncertainty of NOAEL from different

studies, the approach will be based on a weight of each parameter and the NOAELs will be retrieved from articles which include the following criteria: species, sample size and study length, body weight, animal size.

Results and Discussion

For each pesticide, the model (Figure 1) will produce an uncertainty distribution about the threshold level of chemical in drinking water and the results will be analyze to estimate to predict the number of people that could be potentially affected within exposed population.

Conclusions

Pesticides monitoring despite its relevance is not sufficient to indicate the probable health risk upon their detection above the drinking water standard (0.1 μg/l). This project will help to establish a guideline values for commonly used pesticides in Ireland.

Acknowledgements

References

Cooper, J., Dobson, H. (2007).The benefits of pesticides to mankind and the environment.*Crop Prot*, 26, 1337-1348.

Dourson, M.L., Parker A.L. (2007). Past and future use of default assumptions and uncertainty factors: default assumptions, misunderstandings, and new concepts. *HERA*. 13, 82-87.

EPAa. (Environmental Protection Agency). (2009). The provision and quality of drinking water in Ireland. A Report for the years 2007-2008. Available at: www.epa.ie. Accessed data: 02/05/12.

EPAb. (2010). The provision and quality of drinking water in Ireland. A Report for the years 2008-2009. Available at: www.epa.ie. Accessed data: 02/05/12.

Fawell, M.B.E. (2007). Drinking water standards and guidelines. Available at:www.fwr.org.

Hamilton, D.J., Ambrus, A., Dieterle, R.M., Felsot, A.S., Harris, C.A., Holland' P.T., Katayama, A., Kurihara, N., Linders, J., Unsworth, J., Wong, S-S. (2010). Regulatory limits for pesticide residue in water (IUPAC Technical Report) Pure *Appl. Chem,* 75, 8, 1123-1155.

Huber, A., Bach, M., Frede, H.G. (2000). Pollution of surface waters with pesticides in Germany: modeling non-point source inputs. *Agr ecosyst environ*, 80, 3, 191-204.

Konstantinou, I.K., Hela, D.G., Albanis ,T.A. (2006). The status of pesticide pollution in surface waters (rivers and lakes) of Greece. Part I. Review on occurrence and levels. *Environ Pollut* 141, 3, 555-570.

Labite, H., Cummins, E. (2012). A quantitative approach for ranking human health risks from pesticides in Irish groundwater. *HERA*, 11-29 (in press).

Vermeire,T., Van Der Zandt, E. (1995). In: Leeuwen, C.J., Hermens J.L.M. (eds), Risk Assessment of Chemicals: An Introduction procedures of hazard and risk assessment. Kluwer Academic Publishers, Dordrecht/Boston/London. pp. 293-337

Muri, S.D, Schlatter, J.R., Brüschweiler, B.J. (2009).The benchmark dose approach in food risk assessment: Is it applicable and worthwhile? *Food chem toxicol*, 47, 2906-2925.

Ober, M. (2010). Benchmark dose approaches in chemical health risk assessment in relation to number and distress of laboratory animals. *Regul Toxicol Pharm*, 58, 451-454.

WHO (World Health Organization) 2008: Guidelines for Drinking-water Quality. Third edition. Available http://www.who.int/water_sanitation_health/dwq/fulltext.pdf. Accessed date: 18 February 2012.

SIMULATION MODEL TO PREDICT THE FATE AND EFFECT OF CIPROFLOXACIN AFTER WASTEWATER TREATMENT

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Abstract

The extent to which hospital effluent contributes to antimicrobial presence in the environment and the impact it has on resistance dissemination remains unknown. To investigate the fate of the antimicrobial ciprofloxacin in hospital effluent, a Monte Carlo simulation model was developed to model ciprofloxacin levels from hospital use through to wastewater treatment plant (WWTP) effluent, in addition to modelling resistance formation potential. The mean predicted concentration (PC) of ciprofloxacin in hospital effluent, urban effluent, WWTP effluent and sludge was 579, 6.06, 2.59 and 3.48 mg/m^3, respectively. The mean PC of ciprofloxacin in WWTP effluent was less than the MIC and resulted in levels above an assumed lower limit for resistance formation. The probability of conditions in WWTP effluent being favorable for resistance at 20% and 80% of the MIC was 3% and 72%, respectively. The study concluded that release of hospital effluent into the wastewater system may lead to concentrations of ciprofloxacin which may be conducive to resistance formation.

Introduction

Antimicrobials are vital for the treatment of many terminal illnesses. They dramatically extend survival rates and without them life expectancy of both healthy individuals and patients suffering from life threatening diseases would be reduced. Antimicrobial residues are being released into the environment, *via* hospital effluent, following patient intake and subsequent excretion. These residues can have toxic effects on the environment and can contribute to the development and dissemination of resistance. Antimicrobial resistance significantly effects the successful treatment of infections and increases the risk of treatment complications and morbidity (Andersson and Hughes, 2010). Fluoroquinolones are among the most highly consumed antimicrobials in Europe (Vander Stichele *et al*., 2006) and are often detected in the environment (Heberer 2002; Alexy and Kümmerer, 2006). Ciprofloxacin is a broad spectrum fluoroquinolone which is active against both gram negative and gram positive bacteria and is often used to treat human and animal bacterial infections (Vasconcelos *et al*., 2009). The rate of ciprofloxacin resistance has been increasing since 2002 (HPSC 2009, 2011) in both the hospital and community environment (Vila, 2005). The MIC of ciprofloxacin to *E. coli* ranges between 4-15 mg/m^3 (EUCAST, 2010). Residues found in the environment below this level may lead to the development of resistance. **The objective of this study was to investigate the fate of the antimicrobial ciprofloxacin within the urban effluent system, originating from hospital effluent, and to determine the predicted concentration (PC) of ciprofloxacin in hospital, urban and WWTP effluent, thereby establishing potential for resistance formation.**

Methods

In order to study the fate of ciprofloxacin from hospital use to WWTP effluent a simulation model was created within EXCEL 2010 with the @Risk 5.0 add-on (Palisade, 2009). The following stages were identified to simulate the process which leads to ciprofloxacin presence in the environment; ciprofloxacin hospital use, excretion into hospital effluent, dilution within urban effluent and

separation from aqueous to solid effluent. Environmental systems are complex; thus, to account for the inherent variability and uncertainty (Cummins *et al*., 2010) each model input was assigned a probability density distribution (Table 1), as discussed below. Monte Carlo simulation techniques were applied to sample from the input distributions to create an output distribution. The simulation model was then used to draw inferences about the system.

Table 1. Inputs and equations for the simulation of ciprofloxacin in hospital effluent

Symbol	Description	Model	Units
Inputs			
C	Hospital ciprofloxacin use	Cumulative(min,max,(x),(fx))	mg/day
E_x	Excretion [a]	Triangular(0,65.4,100)	%
V_h	Hospital water use	Loglogistic(0,525.32,6.14)	m^3/day
V_w	WWTP water use (influent)	Loglogistic(32207,16215,2.59)	m^3/day/1000inh.
D_i	Dilution factor	$(V_w - V_h)/V_h$	-
pH	Urban effluent pH	Loglogistic(7.12,0.74,8.02)	pH
K_d	Sorption [b]	pH < 8, Normal(0.61,0.01), pH > 8 Normal(0.44,0.01)	%
Outputs			
PC_{he}	Hospital effluent PC	$(E_x / 100) \times C$	mg/day
PC_{hev}	Hospital effluent PC	PC_{he} / V_h	mg/m^3
PC_{ue}	Urban Effluent PC	PC_{hev} / Di	mg/m^3
PC_{we}	WWTP Effluent PC	$PC_{ue} - (PC_{ue} \times Kd)$	mg/m^3
PC_{sl}	Sludge PC	$PC_{ue} \times Kd$	mg/m^3
R_{pol}	Resistance formation potential	True if $PC_{we} / 1000 \leq$ MIC	%
R_{polB}	Bound R_{pol}	True if $PC_{we} /1000 <$ MIC and $PC_{we} >$ MIC_x	

Where PC is predicted concentration and MIC_x is the minimum inhibitory concentration with a lower limit of x (20, 40, 60 and 80%). [a] (Hoffken *et al*., 1985; Bergan *et al*., 1987; Lettieri *et al*., 1992; Wingender *et al*., 1984; Wagenlehner *et al*., 2006; Davis *et al*., 1987; Wise *et al*., 1984); [b] (Githinji *et al*., 2011).

Model Inputs

Ciprofloxacin hospital use (C)

Data was obtained from a case study general hospital documenting ciprofloxacin use. A continuous empirical distribution in the form of a cumulative probability density distribution was assigned to this data in to simulate ciprofloxacin usage within the model (Table 1).

Excretion into hospital effluent (E_x)

Scientific literature was examined to determine the rate of excretion of ciprofloxacin and, when documented, ciprofloxacin metabolites. A probability distribution was created using the following sources (Hoffken *et al*., 1985; Bergan *et al*., 1987; Lettieri *et al*., 1992; Wingender *et al*., 1984; Wagenlehner *et al*., 2006; Davis *et al*., 1987; Wise *et al*., 1984) (Table 1).

Dilution within urban effluent (D_i)

A WWTP associated with the hospital case study site provided influent data in terms of flow (V_w) and BOD (Kg/day) which was converted to create a standardised value of average influent (m^3) per 1000 inhabitants. The hospital also provided water usage data (V_h) which was used to create a probability density distribution to represent hospital effluent volume. A back-calculation was used to estimate the volume of water in the urban effluent system which dilutes the hospital effluent

Antimicrobial removal from effluent

Ciprofloxacin is highly hydrophobic and sorbs to particles and can be removed from the liquid to the solid particles in this manner. Ciprofloxacin sorption (K_d) is pH dependent. A log logistic distribution was used as the best-fit distribution to represent the pH of urban effluent based on data obtained from the WWTP. The sorption coefficient (K_d) determined by Githinji *et al*. (2011) at pH 7.5 was 0.609

±0.011 and at pH 8.5 was 0.4356 ±0.009. Monte Carlo simulation techniques were used to sample from the pH distribution. If the output was less than 8 a normal distribution with mean 0.61 and standard deviation 0.01 was used to represent the K_d of ciprofloxacin to particles and if the output was greater than 8 a normal distribution with mean 0.44 and standard deviation 0.01 was used (Table 1) in accordance with data by Githinji *et al*. (2011).

Human and Environmental Risk
To determine the potential for adverse effects to humans the environment resistance formation potential was examined (Table 1, outputs). Ciprofloxacin resistance formation (*E. coli*) potential was based on concentrations being released below the MIC (4-15 mg/m^3). The resistance formation potential was tested at 5 boundaries: 20, 40, 60, 80 and 100% of the MIC.

Results

The Monte Carlo simulation model produced probability density distributions of predicted ciprofloxacin concentrations for each sample point; hospital effluent, urban effluent, WWTP effluent. Table 2 shows the mean, 5th and 95th percentile of the PC for each sample point. The results seen in Table 2 suggest that ciprofloxacin residues are entering the environment at low concentrations (mean of 2.59 and 3.48 mg/m^3, for WWTP effluent and sludge, respectively) following release in hospital effluent. Concentrations are likely to be present at levels which are conducive to *E. coli* resistance formation (Table 3).

Table 2. Simulation model output results including uncertainty for predicted concentrations of ciprofloxacin (mg/m^3) in the municipal wastewater treatment and subsequent toxicity

Output	x	5th Per	95th Per
Hospital effluent PC	579.90	170.99	1062.61
Urban effluent PC	6.06	1.72	10.95
WWTP effluent PC	2.59	0.71	4.89
Sludge PC	3.48	0.97	6.44

Where PC is predicted concentration; Per is percentile;

Table 3. The probability of *E. coli* resistance formation from WWTP effluent, sludge and the receiving soil between assumed limits of the MIC

Resistance formation limit	Resistance formation potential (%)	
	Effluent	Sludge
0.2 of MIC	1.96	4.86
0.4 of MIC	7.63	15.63
0.6 of MIC	24.01	38.92
0.8 of MIC	65.66	75.76
1 of MIC	99.12	95.99

Where MIC is minimum inhibitory concentration

Discussion and Conclusions

As there are currently no antimicrobial residue monitoring programmes, government recommended testing methods or acceptable limits, simulation modelling can be useful to predict the risk antimicrobial residues may pose to human health or the environment. In this study, hospital usage and subsequent excretion of antimicrobials in the environment may be present at levels that are conducive to resistance formation. At the lowest examined range (20% of MIC) favourable conditions for *de novo* resistance formation remained for *E. coli* (i.e. occurred on 2% of occasions). It remains uncertain what, most significantly, influences antimicrobial dissemination and maintenance within the effluent

system and the environment. The release of hospital effluent into the municipal waste system appears to impact residue presence in the environment. There is a need for further investigation into antimicrobials in the environment and the development of antimicrobial resistant strains.

Acknowledgments

References

Alexy R,Kümmerer K 2006. Antibiotics for human use. In Organic pollutants in the water cycle (pp. 65-86): Wiley-VCH Verlag GmbH & Co. KGaA

Andersson DI,Hughes D 2010. Antibiotic resistance and its cost: Is it possible to reverse resistance? Nature Reviews Microbiology 8(4):260-71

Bergan T, Thorsteinsson S, Solberg R, *et al*. 1987. Pharmacokinetics of ciprofloxacin: Intravenous and increasing oral doses. The American journal of medicine 82(4A):97

Cummins E, Kennedy R,Cormican M 2010. Quantitative risk assessment of cryptosporidium in tap water in ireland. Science of The Total Environment 408(4):740-53

Davis RL, Koup JR, Williams-Warren J, *et al*. 1987. Pharmacokinetics of ciprofloxacin in cystic fibrosis. Antimicrob. Agents Chemother. 31(6):915-9

EUCAST 2010. Tables of qc targets and ranges v1.3. (pp. 2)

Githinji L, Musey M,Ankumah R 2011. Evaluation of the fate of ciprofloxacin and amoxicillin in domestic wastewater. Water, Air, & Soil Pollution 219:1-11

Heberer T 2002. Occurrence, fate, and removal of pharmaceutical residues in the aquatic environment: A review of recent research data. Toxicology Letters 131(1-2):5-17

Hoffken G, Lode H, Prinzing C, *et al*. 1985. Pharmacokinetics of ciprofloxacin after oral and parenteral administration. Antimicrobial agents and chemotherapy 27(3):375

HPSC 2009. Antimicrobial consumption and resistance. (pp. 102-9)

HPSC 2011. Ears-net report for quarter 1 2011

Lettieri JT, Rogge MC, Kaiser L, *et al*. 1992. Pharmacokinetic profiles of ciprofloxacin after single intravenous and oral doses. Antimicrob. Agents Chemother. 36(5):993-6

Palisade 2009. @risk 5.0.

Vander Stichele RH, Elseviers MM, Ferech M, *et al*. 2006. Hospital consumption of antibiotics in 15 european countries: Results of the esac retrospective data collection (1997–2002). Journal of Antimicrobial Chemotherapy 58(1):159-67

Vasconcelos TG, Henriques DM, König A, *et al*. 2009. Photo-degradation of the antimicrobial ciprofloxacin at high ph: Identification and biodegradability assessment of the primary by-products. Chemosphere 76(4):487-93

Vila J 2005. Fluoroquinolone resistance. Frontiers in Antimicrobial Resistance: A tribute to Stuart B. Levy, eds. DG White, MN Alekshun and PF McDermott:41–52

Wagenlehner FME, Kinzig-Schippers M, Tischmeyer U, *et al*. 2006. Pharmacokinetics of ciprofloxacin xr (1000 mg) versus levofloxacin (500 mg) in plasma and urine of male and female healthy volunteers receiving a single oral dose. International Journal of Antimicrobial Agents 27(1):7-14

Wingender W, Graefe KH, Gau W, *et al*. 1984. Pharmacokinetics of ciprofloxacin after oral and intravenous administration in healthy volunteers. European Journal of Clinical Microbiology & Infectious Diseases 3(4):355-9

Wise R, Lockley RM, Webberly M, *et al*. 1984. Pharmacokinetics of intravenously administered ciprofloxacin. Antimicrob. Agents Chemother. 26(2):208-10

THE CARBON FOOTPRINT OF PASTURE BASED MILK PRODUCTION: CAN WHITE CLOVER MAKE A DIFFERENCE?

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Abstract

The objective of this paper was to undertake a Carbon Footprint (CF) analysis based on life cycle assessment (LCA) methodology to estimate the change in greenhouse gas (GHG) emissions from Irish dairy production when mineral fertilizer N (FN) is replaced by biologically (white clover, WC) fixed N, evaluate the sensitivity of the CF model at the research farmlet scale, and the uncertainty of CF when up-scaling to national policy. The results showed that WC had 11 to 24% lower CF compared with FN (average CF = 0.87 and 1.05 kg CO2 eq per kg Energy Corrected Milk, 91% economic allocation). Ratio sensitivity analysis indicated that the difference was probably not caused by error due to modelling assumptions. The upscaling of CF from research farmlet to national scale was assessed in terms of the likely differences between management of research farmlets and commercial farms where milk production per cow is likely to be more variable and suboptimum management more frequent. It was found that introducing white clover to commercial farms may not have as great an influence on CF as estimated at the research farmlet scale. The suitability of CF as a national scale policy support tool for agricultural greenhouse gas (GHG) emissions management was assessed and it was concluded that at present too many knowledge gaps exist for CF to be reliable when estimated from farmlet data, including lack of knowledge of sward type specific emissions (from field, animal and slurry management), active clover management on dairy farms, production system efficiency, productivity and profitability interactions at commercial farm scale and uncertainty about carbon leakage due to displacement of fertilizer in the system.

Introduction

There is an established concern about the effect of greenhouse gas (GHG) emissions on global climate change. In Ireland agriculture is the single largest contributor to overall emissions at 26% (EPA, 2010). The Intergovernmental Panel on Climate Change (IPCC) has provided methodologies for inventorying GHG from agricultural sector at national scale. However, those methodologies do not fully capture the GHG profile of agricultural products along the production chain. A holistic method, Life Cycle Assessment (LCA), can better reveal the environmental impacts of an agricultural system. A recent study by the Joint Research Centre (JRC) of European Commission evaluated livestock contribution to the EU GHG (GGELS, 2010) and found that compared to the LCA results, the 'agriculture' sector defined by IPCC guidelines estimates only 57% of total GHG emissions caused by EU-27 livestock production up to the farm gate. This finding highlighted the importance of the life cycle view-point when addressing the environmental impact of agricultural production. The main GHG from agricultural production are CO_2, CH_4 and N_2O. Nearly 80% of the N_2O emissions due to agriculture are related to the use of fertilizers. As a result of the increasing price of fertilizers and the more stringent regulation on N losses from intensively managed grassland, white clover (*Trifolium repens* L.) has received attention for its capacity to fix atmospheric N and make it available for pasture production. Research based on two farms in the Netherlands (Schils et al., 2005) found that white clover had a marked effect (22% lower per kg milk) on the GHG emissions.

The objective of this paper was to develop a LCA model of two contrasting dairy systems at research farmlets (with and without white clover), to evaluate change in GHG emissions as result of introducing white clover, and to evaluate the uncertainty of CF when upscaling to national strategy.

Materials and Methods

The four parts of LCA methodology were implemented according to ISO standards (ISO, 2006)

Goal and Scope
The goal was to develop a LCA model of two contrasting management strategies for a dairy system in Ireland (with and without white clover) to evaluate changes in GHG emissions as result of introducing white clover.

The production system evaluated was low-cost, grass-based rotational grazing as implemented as research trials at the Teagasc Solohead Research Farm, Co Tipperary, Ireland (52°51' N, 08°21' W) between 2001 and 2006 (Humphreys *et al*., 2008, 2009; Table 1). All cows were Holstein-Friesian. The soil was a clay-loam and the ten-year average rainfall was 1005 mm (Humphreys *et al*., 2009). The functional unit (FU) was defined as 1 kg energy corrected milk (ECM, Casey and Holden, 2005), defined as:

$$kg\ ECM = kg\ milk * (0.25 + 0.122 * Fat\% + 0.077 * Protein\%) \qquad (1)$$

The system boundary was set as cradle-to-gate and involved the foreground processes of milk production on the farm and the background processes extended to include production and transportation of synthetic fertilizers; cultivation, processing and transportation of concentrate feed (except citrus pulp and minerals because of lack of data); production and use of electricity and diesel fuels; and clover seeds for over-sowing. Infrastructure and machinery were excluded as they were assumed to be the same for both systems. Disposal of dead animals, medicines, pesticides, soil carbon sequestration, small consumables such as transmission oil and disposal of plastic for bailed silage were not included. Economic allocation between sale of milk and sale of surplus calves and culled cows (on average both 91% for FN and WC) was applied using average market prices between 2000 and 2006 (www.cso.ie, http://epp.eurostat.ec.europa.eu). Economic allocation between co-products for concentrate feed was applied to soybean hulls and maize gluten meal.

Table 1. System characteristics at Solohead averaged over 2001 to 2006

Classification [1]	WC	FN		FN	WC
Stocking rate[2] (LU ha^{-1})	1.75	2.10	2.50	2.50	2.00; 2.20	2.00; 2.20
Synthetic fertilizer N (kg ha^{-1})	80	180	248	353	226	90
Concentrate feed (kg cow^{-1} yr^{-1})	536	536	536	536	531	520
Milk delivered at farm gate (kg cow^{-1})	6550	6275	6242	6375	6526	6521
Milk fat (%)	4.1	4.2	4.1	4.2	4.2	4.2
Milk protein (%)	3.5	3.6	3.5	3.6	3.6	3.5
Biological-N fixation (kg ha^{-1} yr^{-1})	87.4	9.1	3.2	0.1	12.2	112.5

[1]The stocking rate (LU = livestock unit) were 2 in 2003 and 2.2 during 2004-2006

Life Cycle Inventory and Impact Assessment
The foreground, primary data describing the variations in low-cost, grass-based, rotational grazing were obtained from research records from the Teagasc Solohead Farm (Table 1. See also Humphreys et al, 2008; 2009). A few assumptions had to be made to translate the research trial data into a workable farming system (data not shown). The GHG inventory was made by multiplying life cycle activity data by emission factors (EF) from literature. In the on-farm sector, enteric CH_4 from cows was estimated according to IPCC Tier 2 (O'Mara *et al*., 2006). All livestock were calculated in terms of a calendar year. CH_4 emissions for manure management and soils were estimated using relevant EFs derived from literature. N_2O emissions from manure management and soils were estimated with IPCC Tier 2 (EPA, 2010). No appropriate EF was found for CH_4 or N_2O emission from dirty water storage and spreading so it was not included in the LCA model. Indirect N_2O emissions from atmospheric

deposition and leaching were estimated using IPCC Tier 2 (EPA, 2010). Diesel combustion due to the field work on-farm was included in the on-farm sector as was estimated from Kramer (1999). In the pre-farm sector, GHG emissions from fertilizer production and ingredients of concentrate production were taken from relevant Ecoinvent v 2.1 datasets in SimaPro 7.3. Emission from electricity production was taken from report on energy in Ireland during 1990-2007 (Howley et al., 2008). Emissions form diesel production, road and water transportation were taken from Casey and Holden (2005). Fertilizer was assumed to be transported from Germany and concentrates from their origin to Ireland.

Life Cycle Impact Assessment (LCIA) was restricted to Global Warming Potential assuming CO_2 equivalence of 25 for CH_4 and 310 for N_2O.

Interpretation
Comparison between the two systems was made as emissions per kg ECM, i.e. GHG/FU.

Results and Discussion

The CF of WC was 11 to 24% lower than FN across the range of fertilizer N input. With physical allocation (85% to milk) the average CF for WC was 0.81 kg CO2 eq kg ECM-1 and significantly lower than FN, which was 0.98 kg CO2 eq kg ECM[-1] (P < 0.001). With economic allocation (91% to milk) the difference was also significant, with 0.87 and 1.05 kg CO2 eq kg ECM[-1] respectively. The majority of GHGs were within Ireland and contributed more to WC (85%) than to FN (80%). The contributors that accumulated c. 95% of GHGs were enteric CH4 (WC: 51% and FN: 43%), excreta deposition (WC: 13%, FN: 11%), fertilizer spreading (WC: 6%, FN: 12%), fertilizer production (FN: 10%), electricity production (WC: 8%, FN: 6%), indirect N2O (both 6%), slurry storage (WC: 4%, FN: 3%), concentrate production (WC: 4%, FN: 3%), and slurry spreading (WC: 3%). Significant correlation was found between surplus N per kg ECM and CF (R^2 = 0.66, P < 0.001), which indicated that a 1 g reduction of on-farm surplus N could reduce CF by 26 g CO2 eq. A similar relationship (29 g CO2 eq) was reported by Schils et al. (2006). The ratio sensitivity analysis revealed that to reverse the priority of WC and FN, changes to EFs and assumptions had to be much greater than the uncertainty range found in the literature, thus the benefit of WC in reducing CF of milk production at this scale is likely to be real.

However, scaling up from experimental scale to national policy raises issues of limitations that need to be considered. The LCA model for CF did not properly capture the difference between research farmlets and commercial farms where milk production per cow is more variable and suboptimum management more likely. Also effects of stocking density, soil carbon sequestration and nitrate leaching were perhaps not properly captured in the CF model for use at national scale. From a policy perspective the role of carbon leackage arising from national accounting and cost-effectiveness of clover also need to be considered.

Conclusions

The carbon footprint (CF) of milk production from WC was 11 to 24% lower than from compared with FN swards. Sensitivity analysis showed the model on research farmlets was robust and white clover could reduce greenhouse gas emissions. CF model requires further research on system efficiency, productivity and profitability to translate effects to the national scale.

Acknowledgements

References

Casey, J. W. and Holden, N. M. (2005). The relationship between greenhouse gas emissions and the intensity of milk production in Ireland. Journal of Environmental Quality 34: 429-436.

EPA (Environment Protection Agency) (2010). Ireland's national inventory report for 2010. EPA, Johnstown Castle, Wexford, Ireland

GGELS (Evaluation of the livestock sector's contribution to the EU greenhouse gas emissions), 2010. Joint Research Centre, European Commission. Available online at:

Grass and Forage Science 63(4): 467-480.

http://ec.europa.eu/agriculture/analysis/external/livestock-gas/index_en.htm

Humphreys, J., Casey, I. A., Laidlaw, A. S. (2009): Comparison of milk production from clover-based and fertilizer N-based grassland on a clay-loam soil under moist temperate climatic conditions. Irish Journal of Agricultural and Food Research, 48, pp. 189-207.

Humphreys, J., O'Connell, K., Casey, I. A. (2008). Nitrogen flows and balances in four grassland-based systems of dairy production on a clay-loam soil in a moist temperate climate.

ISO (2006). Environment management -- Life cycle assessment -- Principles and framework. EN ISO 14040: 2006, ISO, Geneva, Switzerland.

Kramer, K. J., H. C. Moll, and S. Nonhebel. 1999. Total greenhouse gas emissions related to the Dutch crop production system. Agricultural Ecosystem Environment, 72: 9–16.

Schils, R.L.M., Verhagen, A., Aarts, H.F.M., Kuikman, P.J., Šebek, L.B.J., 2006. Effect of improved nitrogen management on greenhouse gas emissions from intensive dairy systems in the Netherlands. Global Change Biology 12, 382-391.

LIFE CYCLE ANALYSIS OF PELLET PRODUCTION FROM MISCANTHUS SINENSIS X GIGANTEUS ENERGY CROP

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Abstract

The demand for biomass pellets has increased in recent years in line with EU renewable energy targets. This demand is likely to continue rising, putting pressure on traditional raw materials for biomass pellets such as sawdust. As such, alternative raw materials including energy crops must be sourced. This paper presents a life cycle assessment study of biomass pellet production from the energy crop Miscanthus. The overall process chain from Miscanthus sowing, through cultivation, to pelleting was modelled using Simapro 7.3 software. CML 2001 and CED methodologies were used to determine the acidification, eutrophication and global warming potentials, along with the cumulative energy demand for each stage of the life cycle. Sensitivity analysis was performed by varying the crop yield and the application of alternative fertiliser. The LCA study showed that the energy consumption in the pelleting process results in the highest contribution to each of the impact categories.

Introduction

In Ireland, there is an increasing awareness of the need to reduce greenhouse gas (GHG) emissions in line with Kyoto commitments and to develop alternative energy sources to reduce dependence on finite fossil fuel resources. The Government has adopted the European Union's (EU) Renewable Energy Directive (RED) target of 20% of overall gross energy consumption by renewables by 2020, further driving the need to develop bioenergy resources (EU, 2009). Biomass pellets represent a valuable source of bioenergy. Focus has primarily been on the use of wood for pellets, however, prices of these raw materials are increasing. In addition, the increased demand for pellets for heating is causing shortages of the traditional raw materials, sawdust and wood shavings. As a result of these two factors attention has turned to using alternative sources of biomass such as dedicated energy crops (Miscanthus, reed canary grass and hemp) and agricultural residues as raw material. The use of biomass for energy offers many environmental benefits, however it can lead to negative environmental consequences. Large-scale increases in biomass cultivation can pose risks to natural ecosystems by impacting on soil and water resources (Fantozzi and Buratti, 2010). As a result of these concerns, there have been many questions regarding the sustainability of bioenergy and the rate at which national governments, and the EU, are encouraging bioenergy development (McManus, 2010). Life cycle assessment (LCA) is a tool which can be used to assess the sustainability of energy product systems in terms of energy balance and environmental impacts. Both the emission and the energy use of wood pellet have been analyzed in previous studies (Pa et al., 2011, Mani et al., 2005, Petersen Raymer, 2006, Hagberg et al., 2009, Chen, 2009, Magelli et al., 2009). A number of studies have dealt with alternative raw materials for pellet production. Fantozzi and Buratti (2010), carried out a LCA of wood pellets from short rotation coppice (Poplar). The study assessed the environmental impacts of Poplar cultivation through to pelleting. Sultana and Kumar (2011) analysed the energy usage and GHG emissions associated with the use of agricultural residue (straw) for pellet production in over a range of scenarios.
The aim of this paper is to analyse pellet production from Miscanthus, with regard to emissions and energy requirements throughout the life cycle.

Materials and Methods

Goal and scope

The aim of this study is to evaluate the environmental impacts associated with pellet production from Miscanthus. The reference functional unit is 1 tonne of pellets produced at the pellet plant. All of the energy and mass flows in the system are normalized to this unit. The boundaries of the system are illustrated in Figure 1. The system encompasses all aspects of the pelleting system; raw material acquisition (crop cultivation and harvesting), feedstock processing, transport to the pelleting plant, and pelleting at the plant.
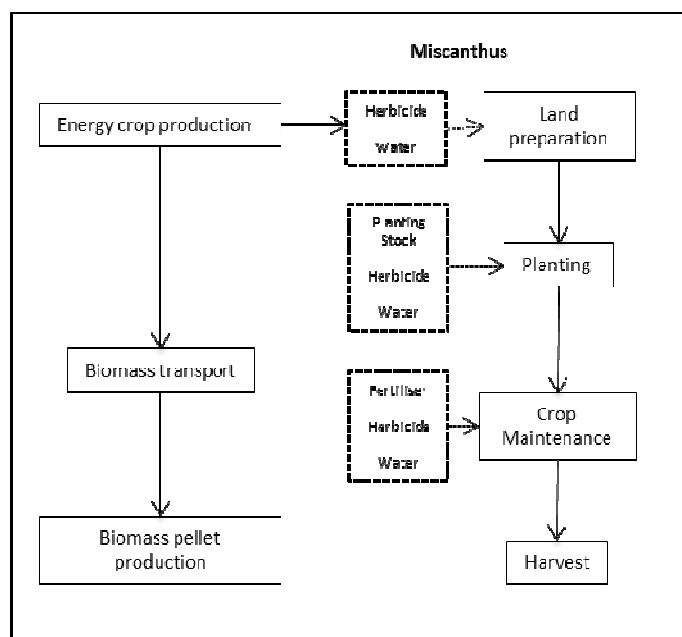
Figure 1. System diagram

Life cycle inventory

The LCA was conducted in Simapro 7.3 (PRé Consultants bv, the Netherlands). The data for the pelleting plant was obtained from trials in the UCD research laboratory. This data was combined with pelleting infrastructure data from the ecoinvent database (ecoinvent, 2007). Secondary data on Miscanthus production was obtained from published literature. The gathered data was supplemented with data from the Simapro databases.

Life cycle impact assessment

Four categories are considered in this LCA; acidification potential (AP), eutrophication potential (EP), global warming potential (GWP) and cumulative energy demand (CED).

Interpretation

The energy demand and environmental impacts are compared for each process in the life cycle. The effects of changes in yield and the use of alternative fertilisers are explored.

Results and Discussion

Table 1 gives the results of the impact assessment for the Miscanthus pellet chain. The table gives the impacts per stage of the life cycle. The production of 1 tonne of Miscanthus pellets requires 4,104 MJ of energy and results in the emission of 296 kg CO_2-eq. In addition to this, 1.655 kg SO_2-eq and 0.502 kg PO_4-eq. An analysis of the results depicted in figure 2 shows that the largest contributor to all 4 impact categories is the pelleting process. This step utilises a large quantity of delivered energy in the form of electricity. The production of this

electricity results in the largest degree of emissions in the life cycle. When considering the life cycle of the energy crops in isolation, it is clear that the maintenance step results in the most emissions. This is due to the production and application of synthetic fertilisers.

Table 1. Results of the impact assessment of the Miscanthus pellet chain

Impact category	Unit	Total	Land Preparation	Planting	Maintenance	Harvest	Crop Removal	Pelleting
AP	kg SO2 eq	1.655	0.008	0.008	0.395	0.150	0.005	1.089
EP	kg PO4- eq	0.502	0.003	0.009	0.278	0.044	0.002	0.167
GWP	kg CO2 eq	296.35	1.30	1.31	55.13	26.63	0.80	211.19
CED	MJ	4104	21	113	410	446	13	3100

The energy ratio of the system can be calculated by comparing cumulative energy demand in table 4 to the energy content of the Miscanthus pellets (17.57 MJ/kg). The energy ratio can be described by the equation:

ER = Eo / Ei, where Eo - energy output, Ei - energy input, ER - energy ratio.

As such the energy ratio of this system can be expressed as:

ER = 17,570 MJ/kg ÷ 4,104 MJ/kg

ER = 4.28

Sensitivity analysis - yield

The yields for the low, average and high scenarios were assumed to be 10, 11.5 and 13 tonnes/ha respectively for Miscanthus. The results are shown in figure 2. As expected, impacts are reduced with increased yields. This highlights the importance of achieving the highest possible yield while maintaining the same resource use in the cropping cycle.
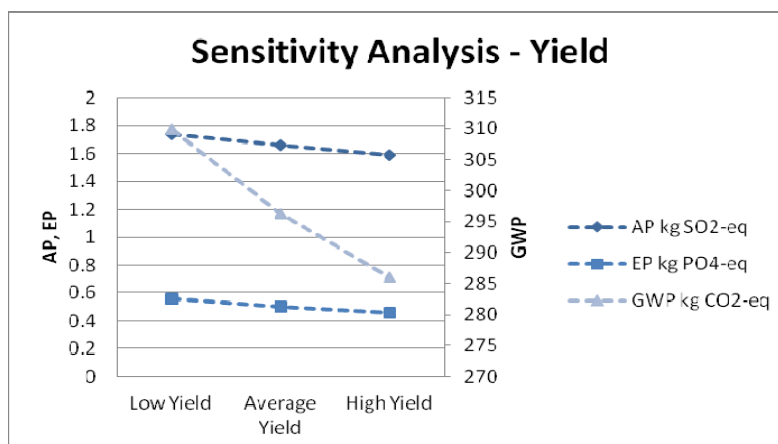
Figure 2. Graph of environmental impacts versus yield

Sensitivity analysis – alternative fertiliser

As shown by the results, the production of synthetic fertilisers makes a large contribution to each of the impact categories studied due to the energy and resources used to produce them. The application of biosolids to the crop as an alternative fertiliser has the potential to reduce these impacts through the utilisation of a waste product to meet the crops nutrient requirements. Sensitivity analysis was carried out on substituting biosolids for synthetic fertilisers. The results show that using biosolids in place of synthetic fertiliser increases both acidification and eutrophication potential by 58% and 45% respectively. However, global warming potential and cumulative energy demand are reduced by 17% and 8.6% respectively.

Conclusions

The results from the LCA study show that the largest contributor to all four impact categories is the pelleting process. This step utilises a large quantity of energy in the form of electricity. The production of this electricity results in the largest degree of emissions in the life cycle. The second largest contributor to each of the impact categories is the maintenance of the Miscanthus crop. This is due to the production and application of synthetic fertilisers. The production of synthetic fertilisers is an energy intensive process and utilises non-renewable fossil fuels. Sensitivity analysis indicates that the use of biosolids in place of synthetic fertilisers reduces the global warming potential and energy requirement of the system. However, the application of biosolids increases the acidification and eutrophication potential. As such, the decision to apply biosolids or synthetic fertiliser would require a careful analysis of both positive and negative effects. Sensitivity analysis indicates that varying yield has an effect on the environmental impact of the pelleting system. High yielding crops result in the lowest impacts per tonne of pellets produced.

Acknowledgements

References

Chen, S. 2009. *Life Cycle Assessment of Wood Pellet.* Master of Science, Chalmers University of Technology.

Ecoinvent, C. 2007. ecoinvent data v2.0 ecoinvent reports No. 1-25. *In:* INVENTORIES, S. C. F. L. C. (ed.). Dübendorf.

EU 2009. Directive 2009/28/EC of The European Parliament and of the Council of 23 April 2009 on the promotion of the use of energy from renewable sources and amending and subsequently repealing Directives 2001/77/EC and 2003/30/EC.

Fantozzi, F. & Buratti, C. 2010. Life cycle assessment of biomass chains: Wood pellet from short rotation coppice using data measured on a real plant. *Biomass and Bioenergy,* 34**,** 1796-1804.

Hagberg, L., Sarnholm, E., Code, J., Ekvall, T. & Rydberg, T. 2009. LCA calculations on Swedish wod pellet production chains - According to the renewable energy directive. Stockholm, Sweden: IVL Swedish Environmental Research Institute Ltd. .

Magelli, F., Boucher, K., Bi, H. T., Melin, S. & Bonoli, A. 2009. An environmental impact assessment of exported wood pellets from Canada to Europe. *Biomass and Bioenergy,* 33**,** 434-441.

Mani, S., Sokhansanj, S. & Bi, X. 2005. A streamlined life cycle of biomass densification process.

McManus, M. C. 2010. Life cycle impacts of waste wood biomass heating systems: A case study of three UK based systems. *Energy,* 35**,** 4064-4070.

Pa, A., Bi, X. T. & Sokhansanj, S. 2011. A life cycle evaluation of wood pellet gasification for district heating in British Columbia. *Bioresource Technology,* 102**,** 6167-6177.

Petersen A. K. 2006. A comparison of avoided greenhouse gas emissions when using different kinds of wood energy. *Biomass and Bioenergy,* 30**,** 605-617.

Sultana, A. & Kumar, A. 2011. Development of energy and emission parameters for densified form of lignocellulosic biomass. *Energy,* 36**,** 2716-2732.

FOOD CROPS VS. FUEL CROPS – IMPACT ON WATER QUALITY

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Abstract

It is widely acknowledged that intensive agriculture can have negative consequences in terms of the quality of surface water, increased greenhouse gas emissions and climate change. Producing energy from biomass is an alternative to fossil fuels which has positive benefits for the environment. In Ireland, the majority of crops produced are food crops (e.g. potatoes, barley, oats and wheat). Production of energy crops (e.g. miscanthus, oil seed rape and willow) has grown increasingly with the introduction of the EU energy crops scheme. Production systems and inputs for such crops are significantly different to those employed in the conventional tillage production. These variations in production highlight the need to examine and compare the effects of both systems on the natural environment. The present study will aim to assess the impacts on surface water quality from both food crop and energy crop production systems. The task will be carried out using the catchment model Soil Water Assessment tool (SWAT) which utilises geographic information systems (GIS) mapping data.This is a system of hardware and software used for storage, retrieval, mapping, and analysis of geographic data. This will ultimately highlight potential environmental risks associated with growing fuel crops rather than food crops and assist in addressing social and environmental concerns.

Introduction

By 2020, this country is obliged to meet 16% of its energy needs by using power from renewable sources (Department of Agriculture, 2009). The biomass to energy market is in a position to contribute to this. However the intensive use of herbicides, artificial fertilisers, fungicides and pesticides in production practices is a growing cause for concern (Tilman et al., 2002). According to Curley and Mc Donnell (2009) pollution from agriculture needs to be tackled if our waters are to remain uncontaminated from contaminants such as nitrogen. Nitrogen in soils occurs as organic or inorganic nitrogen. The inorganic forms include ammonium (NH_4^-), nitrite (NO_2^-), nitrate (NO_3^-), nitrous oxide (N_2O), and elemental nitrogen (N_2). The three most important forms, NH_4^-, NO_2^-, and NO_3^-, usually represent 2 to 5% of the total soil N. The source of NH_4^+ is from mineralization of organic N and from fertilizers. Some of NH_4^+ is converted to NO_2^-, which is toxic to plant roots by bacteria *Nitrosomonas* ($2NH_4^- + 3O_2 = 2NO_2^- + 2H_2O + 4H^+$), and then oxidized to NO_3^- by *Nitrobacter* ($2NO_2^- + O_2 = 2NO_3^-$). The NO_3^- anion is very mobile and subject to leaching losses (Tisdale et al., 1993). Nitrate in streams is derived from many anthropogenic and natural resources including chemical fertilizers, animal wastes, domestic sewage, legumes, mineralization of vegetation, soil organic matter, and from atmosphere through electrical, combustion and industrial processes. NO_3^- is a very soluble and mobile anion. It can be transported from agricultural fields in both overland flow and subsurface flow, and by volatilization into the atmosphere. Ammonium is absorbed by the soil colloids and moves very little until converted to NO_3^- In contrast to the overland transport in which nitrate takes minutes or hours to get to a stream, downward vertical leaching and the subsequent underground travel is a long process which takes months or years. The soil system has a strong memory with respect to nitrate production and leaching. **The objective of this study is to examine the impacts on surface water quality from both food crop and energy crop production systems.**

A wide range of environmental issues related to biofuels development have been identified. These include potential changes in air quality, water availability and quality changes. In each

of these areas there are potential benefits such as the protection of ecosystems in the future and risks to be considered. An important perspective for considering such risks and associated strategies to reduce them is weighing the environmental trade-offs between biofuels technologies and the fossil fuel technologies they supplant. A similar approach can also be applied to biofuels feedstock production in asking how dedicating land to feedstock production will alter impacts from current land use. There are three important considerations in making such an assessment:

1. The agronomic attributes of the bioenergy cropping system being considered, including specifically effects on soil and water quality;
2. The net effect of any differences between (1) and the land use system it replaces; and
3. The quality and quantity of energy that is produced from the feedstock per unit of energy expended and per unit of environmental cost of the fossil energy it replaces.

It is generally agreed that SWAT is the most suitable for Ireland. It is possible to apply SWAT to any river basin. It is used to measure the impact of land management practices on water quality over a specified period. A study was conducted by Coffey et al. in 2008, on the catchment area of the river Fergus in county Clare. The model constructed involved Arc SWAT, based on GIS model predictions showed a high level of correlation between observed areas. The authors concluded that model predictions could be improved with more reliable input information. Despite the shortcomings of the model, there is strong evidence that SWAT can play an important role in determining the transport of pollutants and pathogens in water catchments in Ireland. The review of SWAT peer reviewed literature by (Gassman et al (2010) describes a large number of SWAT studies incorporating GIS. High levels of correlation are reported. The authors conclude that the model is flexible and robust and can be used to simulate a variety of watershed variables. They conclude that this model is continuing to evolve.

Materials and Methods

The proposeed model structure is given in figure 1.
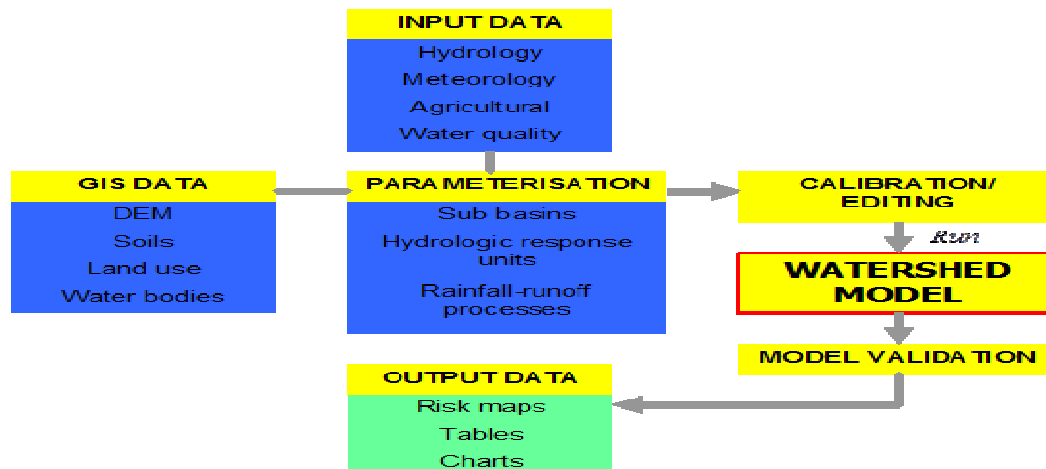
Figure 1: Methodology of the large scale modelling of agrichemical concentrations in rivers

The production chain is examined at each stage to establish the effects of the crop inputs in terms of contaminant pathways as highlighted in figure 2.

Crops grown in Ireland at present

Traditional Crops:
The principal crop grown in Ireland is potatoes. The second largest crop grown is barley (167,000 hectares, 403,100 tonnes) after this wheat (84,400 hectares, 801,800 tonnes). The

smallest crop grown is oats (19,700 hectares, 139,870 tonnes) (Department. of Agriculture, 2009).
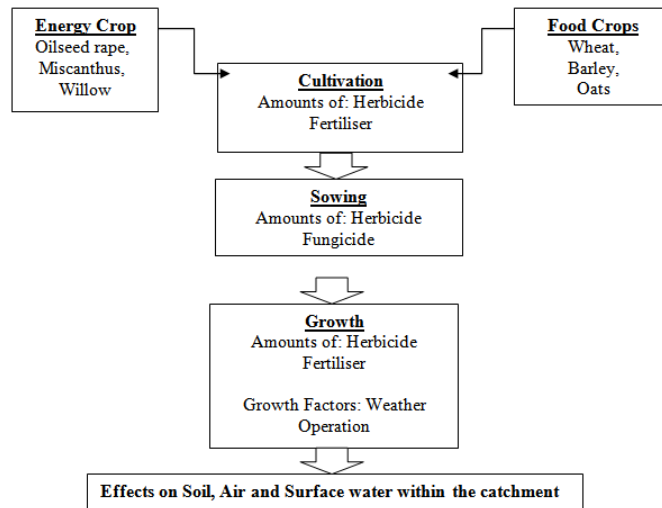
Figure 2. Production process of energy and food crops

Energy Crops:
The growth of oil seed rape has been carried out in Ireland for a number of years. It was traditionally deployed as an intermediate during the rotation of food crops. It contributes the largest energy crop grown in this country at present (Venendaal et al., 1997). The amount of Miscanthus grown in 2009 was 740 hectares and willow just 170 hectares (Department of Agriculture 2009). A summary of the areas of food crops and energy crops are given in Table 1 and 2 respectively.

Table 1 (Food Crops Grown In Ireland)

Crop Name	Year (2009)
Barley	167,000 hectares
Wheat	84,400 hectares
Oats	19,700 hectares

Table 2 (Energy Crops Grown In Ireland)

Crop Name	Year (2009)
Miscanthus	740 hectares
Willow	170heactres

(Department of Agriculture, 2009)

In producing any crop, the following factors have an impact on the surrounding environment; (a) the deployment of fertilisers, pesticides and herbicides. (b) The type of crop grown and (c) Soil structure etc.

SWAT Model
The Soil and Water Assessment Tool (SWAT) is a process-based continuous daily time-step model which evaluates land management decisions in large un-gauged rural watersheds. It is designed to predict long-term nonpoint source pollution impacts on water quality such as sediment, nutrient and pesticide loads (Arnold et al., 1994).

Model inputs

The model will be constructed considering physical characteristics of the watershed and its subbasins such as precipitation, temperature, soil type, land use and topography. The developed model will Include management inputs such as crop type, tillage operations, planting and harvest dates, fertilizer use. Either simulated or measured precipitation and temperature values may be used in SWAT. Measured stream flow will be statistically compared with model predictions.

Model processes

This includes calculations of water balance (i.e. surface runoff, return flow, percolation, evapotranspiration, and transmission losses), crop growth, nutrient cycling, and pesticide movement. Model outputs include sub-basin and watershed values for surface flow, ground water and lateral flow, crop yields, and sediment, nutrient and pesticide yields.

Results and discussion

The steps and nutrient inputs used in the production of an energy crop and a food crop will be assessed and simulated in the SWAT model. Results from SWAT will enable an assessment of whether food crops or fuel crops have a bigger impact on surface water quality in terms of nutrient impairment. Energy crops are perceived to have deeper roots which lessen contamination by absorbing fertilisers at lower levels in the soil. However, fuel crops require less fertiliser than traditional food crops.

Conclusion

Energy crop production is increasing steadily in Ireland. Due to the fact that crop production concerns are increasingly focused on risks posed to the environment, it has become timely to adopt risk modelling to study and assess the changes/interventions of all chemical hazards in the production system. By creating an improved understanding of surface water quality impacts, the model developed in this study will help to reduce the risk to the natural environment from contaminants originating from traditional and future crop production systems.

References

Arnold, J.G., J.R. Williams, R. Srinivasan, K.W. King, and R.H. Griggs, 1994. SWAT - Soil and Water Assessment Tool, USDA, Agricultural Research Service, Grassland, Soil and Water Research Laboratory, 808 East Blackland Road, Temple, TX 76502,

Central Statistics Office (2008). Cereals Supply Balance 2007/2008. Dept. Agriculture, Fisheries and. Food (2009). Non-food Crops in Ireland.

Curley, E., Mc Donnel K. (2009) Drinking water quality in Ireland, The Impact of Irish Agriculture. U.C.D

Coffey, R., Cummins E., Bhreathnach N., V.O. Flaherty b , M. Cormican c. (2009). Development of a pathogen transport model for Irish catchments using SWAT. Agricultural Water Management 97 (2010) 101–111. 1 (3), 1-110.

Gassnan Philip W., Manuel R. Reyes, Colleen H. Green. (2010). SWAT . A review on SWAT. 11 (3), 1-30.

Tilman, D., Cassman, K.G., Matson, P.A., Naylor, R., Polasky, S. (2002). Agricultural sustainability and intensive production practices. *Nature,* 418**,** 671-677.

Tisdale, S. L., Nelson, W. L., Beaton, J. D.,and Havlin, J. L., 1993 (1956). *Soil Fertility and Fertilizers*. (5th ed.) Macmillan, New York, 634 pp

Werf, H. M. G. v. d. (1996). Assessing the impact of pesticides on the environment. *Agriculture, Ecosystems & Environment,* 60.

PERFORMANCE MONITORING: SMART SYSTEMS INTEGRATION WITHIN BROILER PRODUCTION HOUSES

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Abstract

Research has shown that variations in the ambient conditions within a poultry house can cause stress in poultry, thus reducing growth performance due to a decrease in feed intake and high stress levels, and increased mortality. An array of sensors will be used to monitor conditions (temperature, humidity, etc.) in a broiler production facility. Noise monitoring (bird chirping) and thermal imaging may provide a good indication of stress in poultry. Work on analysing the chirping of chickens has already shown positive results, especially in predicting the onset of hatching in eggs. It is reasonable to conclude that noise analysis technology could be the critical factor in improving broiler production systems in the future. The optimisation of overall broiler performance will be accomplished through the detection of deficiencies and suitable modifications. Based on the analysis of this data, a 'Happiness Index' for poultry may be developed.

Introduction

With increased fuel prices, the introduction of new EU directives on animal and environmental welfare, and indirect pressure on farmers from the consumer to satisfy them that their food meets acceptable standards and is readily traceable has made a more challenging environment for broilers producers in recent years (Wathes, 2007; Hynes, 2011). The need for new technologies in the industry to enhance production systems is seen as the way forward. Precision livestock farming (PLF) involves the use of sensors to collect data, followed by data analyses with the objective of enhancing the understanding of the system interactions, and developing control systems. PLF is related to the optimal reduction of losses in the entire production process (Mollo et al., 2009). The three biggest factors affecting chicken performance, as stated by Yahav et al. (2001), are: ambient temperature, relative humidity and air speed (adequate ventilation), which influence poultry energy metabolism and body water balance (Yahav et al., 2005). As a result of undesirable conditions in poultry houses, reduced growth and performance of chickens due to a decrease in feed consumption and higher stress level can occur (Abu-Dieyeh, 2006), as well as high mortality rates (Ferreira et al., 2011). Factors which affect the animal's physiology such as temperature, humidity, air flow, light and carbon dioxide has been widely studied. A novel idea for investigating bird performance is by measuring and analyzing amplitude and frequency of bird vocalization in poultry houses (de Moura et al., 2008). The results of the experiments conducted showed a correlation between bird grouping pattern and vocalization during thermal stress exposure (Mollo et al., 2009). The idea of studying chicken noise is a relatively new idea, but further studies have been conducted on other animals, in particular pigs (Manteuffel et al., 2004; Schön et al., 2004; Moura et al., 2008). Woodcock et al. (2004) investigated effect of hen vocalization's on feeding behaviour of young chickens, resulting in improvement in body weight and feed conversion during periods. de Moura et al. (2008) used noise analysis to evaluate chick thermal comfort, finding correlations between frequency/amplitude and chick swarms/temperature variations. Exadaktylos et al. (2011) used frequency analysis techniques to identify the time at which eggs inside an incubator reached the internal pipping stage. An algorithm was developed with a 98 % success rate. The use of noise analysis has huge potential in this industry, and should be studied in greater depth.

The objective of this study is to use smart systems to monitor and enhance conditions within the poultry house, thus improving operational efficiency of the broiler production

systems, with specific focus on using bird noises (chirping) as a measure of broiler welfare.

Materials and Methods

Acoustic sensors
Initial bird chirping will be recorded using an OLYMPUS VN-8700PC Digital Voice Recorder, which features a built-in memory of 4GB, a frequency response of 70 Hz to 19 kHz at 192 kbps and records in WMA/MP3 format. The device will then be connected to PC via USB for analysis. The device will be place approximately 0.5m above ground level, and will provide continuous data over the course of the experiment (~ 6 weeks).

BOSCA Device
This project will use in-house sensors to collect data over a significant time period, using a single, integrated device (BOSCA). The device will consist of the following sensors, which will be located at poultry level (approximately 0.5-0.6 m above ground level):

Table 1. BOSCA sensor array specifications

Sensor	Functionality	Data frequency
Air speed	0-5 m/s	5 min
CO_2	0-5000 ppm	15 min
Humidity	10-90 %	15 min
Light	0-100 lux	1 h
Temperature	0-45 ^{o}C	15 min

The device will also include a data acquisition card and a GSM cellular network connection which will send daily readings via text to a mobile device. The device is being built in conjunction with external collaboration from Institute of Technology Tralee, and it is expected that at least four of these will be placed into different quadrants of the broiler houses.

Thermal & visual imaging
Thermal imaging will be recorded using an Electrophysics PV320T2 Camera, which has the advantage of seeing through dusty conditions. The camera will be connected via USB to a laptop and will provide continuous readings, which will provide adequate information in conjunction with the noise recording device. Visible light images will be captured using a Fuji 9500 digital camera. Both cameras will be placed at a suitable height (approximately 2.5-3 m above ground level) for optimal viewing of broilers. An example of a broiler captured using thermal imaging techniques is shown in Figure 1.
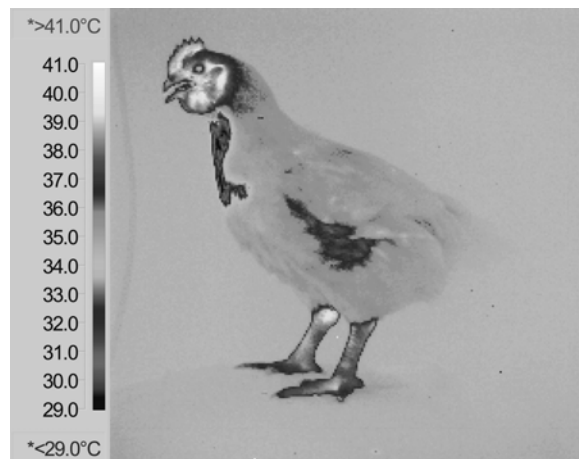
Figure 1. Example of thermal imaging of broiler chicken exposed to 35 ºC

Expected Results

Initial analysis of the birds will involve capturing sounds of the birds over a number of weeks and using the recorded data to analyze frequency and amplitude. The concept is to develop a baseline level at which the birds are in state of thermal comfort. Following the development of a baseline, the authors intend to identify peaks in which the birds experience discomfort. Having identified both the peaks and the baseline levels for the broilers, the authors can then attempt to identify a correlation between these levels and any undesirable conditions (data provided from *BOSCA*, thermal/visual imaging) that are occurring during these periods. The development of this correlation will enable the farmer/producer to make informed decisions on the correct adjustment/modification to the system.

Conclusions

This study will utilise monitoring techniques for the overall optimisation of a broiler production system. Failure to provide adequate monitoring systems within broiler production will reduce profitability resulting in poor feed conversion and increase of diseases. It is expected that noise analysis of poultry chirping will help determine periods of distress. Little research has been conducted in this area, either due to technological limitations, or reluctance on the part of the farmer. New, stricter regulations and higher costs are forcing broiler producers to look at novel technologies to produce a more efficient system. The research will develop correlations during periods of distress with changes in conditions which will demonstrate the potential of integrating these systems into broiler production houses. It will provide sophisticated smart monitoring techniques while at the same time minimising energy costs and maximising net returns.

Acknowledgements

References

Abu-dieyeh, Z. H. M. 2006. Effect of High Temperature *Per se* on Growth Performance of Broilers. *Internation Journal of Poultry Science,* 5**,** 19-21.

Berckmans, D. 2008. Precision livestock farming (PLF). *Computers and Electronics in Agriculture,* 62**,** 1.

De Moura, D. J.,Naas, I. D. A.,Alves, E.,DE Carvalho, T. M. R.,Do Vale, M. M. & DE Lima, K. A. O. 2008. Noise analysis to evaluate chick thermal comfort. *Scientia Agricola,* 65**,** 438-443.

Exadaktylos, V.,Silva, M. & Berckmans, D. 2011. Real-time analysis of chicken embryo sounds to monitor different incubation stages. *Computers and Electronics in Agriculture,* 75**,** 321-326.

Ferreira, V.,Francisco, N. S.,Belloni, M.,Aguirre, G. M. Z.,Caldara, F. R.,Naas, I. A.,Garcia, R. G.,Paz, I. & Polycarpo, G. V. 2011. Infrared Thermography Applied to the Evaluation of Metabolic Heat Loss of Chicks Fed with Different Energy Densities. *Brazilian Journal of Poultry Science,* 13**,** 113-118.

Hynes, B. 2011. Farm input costs set to increase. *Farmers Journal*.

Manteuffel, G.,Puppe, B. & Schön, P. C. 2004. Vocalization of farm animals as a measure of welfare. *Applied Animal Behaviour Science,* 88**,** 163-182.

Mollo, M. N.,Vendrametto, O. & Okano, M. T. 2009. Precision Livestock Tools to Improve Products and Processes in Broiler Production: A Review. *Brazilian Journal of Poultry Science,* 11**,** 211-218.

Moura, D. J.,Silva, W. T.,Naas, I. A.,Tolón, Y. A.,Lima, K. A. O. & Vale, M. M. 2008. Real time computer stress monitoring of piglets using vocalization analysis. *Computers and Electronics in Agriculture,* 64**,** 11-18.

Schön, P. C.,Puppe, B. & Manteuffel, G. 2004. Automated recording of stress vocalisations as a tool to document impaired welfare in pigs. *Animal Welfare,* 13**,** 105-110.

Wathes, C. 2007. Precision livestock farming for animal health, welfare and production. Tartu: Estonian University of Life Sciences, Jõgeva Plant Breeding Institute, Estonian Research Institute of Agriculture.

Woodcock, M. B.,Pajor, E. A. & Latour, M. A. 2004. The effects of hen vocalizations on chick feeding behavior. *Poultry Science,* 83**,** 1940-1943.

Yahav, S.,Shinder, D.,Tanny, J. & Cohen, S. 2005. Sensible heat loss: the broiler's paradox. *Worlds Poultry Science Journal,* 61**,** 419-434.

Yahav, S.,Straschnow, A.,Vax, E.,Razpakovski, V. & Shinder, D. 2001. Air velocity alters broiler performance under harsh environmental conditions. *Poultry Science,* 80**,** 724-726.

A COMPARISON OF GRID-BASED COMPUTATION METHODS OF TOPOGRAPHIC WETNESS INDEX DERIVED FROM DIGITAL ELEVATION MODEL DATA

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Abstract

A Decision Support System (DSS) is being developed to improve nutrient management which uses the Hybrid Soil Moisture Deficit (HSMD) model to assess when slurry spreading is 'safe' and will not pose a risk of pollution to surface water. The movement of water from high to low elevation under gravity plays an important role in the distribution of soil water accumulation within the landscape and can be described using the terrain analysis tool of Topographic Wetness Index (TWI). TWI has been calculated for two hydrological sub-catchments with a gridded Digital Elevation Model (DEM) using three different flow accumulation algorithms at two grid size resolutions. This paper compares variation and distribution of TWI values within the six grids computed in each catchment. Analysis has shown that the single-flow direction algorithm D8 is inappropriate for calculation of TWI due to lack of flow divergence isolating cells away from the accumulated flow path. A stream cut-off TWI value will be required to normalize TWI values between hydrological sub-catchments.

Introduction

Surface water in Ireland is at risk of eutrophication due to nutrient enrichment in the form of nitrates and phosphorus which is thought to have significant contributions from agricultural sources (Schulte et al., 2006). Reducing the potential for nutrient run-off occurring from agricultural land plays an important role in the development of sustainable agriculture. A farm-scale Decision Support System for sustainable nutrient management is being developed to provide farmers with advice on minimising nutrient loss from land spread organic and mineral fertilisers. Within the DSS, the Hybrid Soil Moisture Deficit (HSMD) model (Schulte et al., 2005) is used to assess the likelihood of a transport vector in the form of free-flowing water being available to move nutrients from land to surface water. 'Safe' spreading of slurry and mineral fertiliser will occur when there is a low likelihood of a transport vector being available, as predicted using the HSMD model.

In its current form, the HSMD model operates with a flat field assumption and does not account for the influence of slope on soil moisture. To overcome this model limitation it has been proposed that the use of a Topographic Wetness Index (TWI) derived from a DEM could be combined with the HSMD model to better predict the presence of gravity moveable water at any given time. TWI is a secondary/compound attribute of a DEM calculated using the formula:

$TWI = ln(a_s /tan\beta)$ where a_s = upslope contributing area and $tan\beta$ = local slope gradient (Wilson and Gallant, 2000). TWI assumes that slope has the greatest influence on soil hydraulic gradient and can therefore be used to predict areas of soil water accumulation within the landscape. A high TWI occurs on converging, flat terrain where soil water is most likely to accumulate. Conversely, low TWI values occur in landscape zones were soil water is likely to quickly drain away.

The objective of this paper is to compare the variation between TWI calculated using three different flow accumulation algorithms and two DEM resolutions.

Materials and Methods

Site Locations

The hydrological sub-catchments of Johnstown Castle (JTC), Wexford (52°17'52"N 6°30'20"W) and Lyon's Estate (LE), Dublin (53°17'52"N 6°32'08"W) were delineated and extracted from the DEM for TWI modelling. Johnstown Castle has a catchment area of approximately 180km² and Lyon's Estate has a smaller catchment area of 10km².

Data and GIS Modelling

The ISIS (Irish Soil Information System) 20 metre resolution DEM was resampled to 40 metres resolution to provide two DEMs of different resolution for the comparison of modelled TWI. The open source package System for Automated Geoscientific Analyses (SAGA) was used to model TWI. Figure 1 illustrates the modelling processes required to produce the data for input into the TWI formula. Pre-processing of the DEM involved resampling to 40 metre, filling sinks within the DEM to produce a hydrologically corrected land surface (Wang and Liu, 2006), and calculation of slope using the 'least squares fitted plane' method originated from (Horn, 1981)).
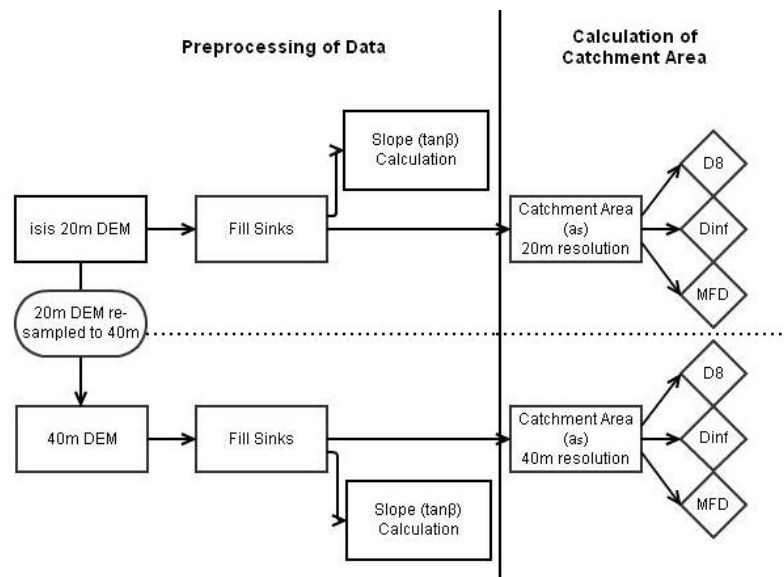
Figure 1. Flow diagram: Pre-processing and modelling of DEM for TWI calculation

Upslope contributing area (also referred to as catchment area) can be calculated using different flow accumulation algorithms. For this study, 3 flow algorithms were selected for analysis; D8 (O'Callaghan and Mark, 1984), Dinfinity (Tarboton, 1997), and Multiple Flow Direction (MFD) (Freeman, 1991; Quinn et al., 1991). The D8 method is the earliest and simplest method for calculating upslope contributing area and directs flow to only 1 of its 8 neighbouring cells in the direction of steepest decent. The MFD method is the most computationally intensive algorithm and directs a proportion of flow from centre cell to all of its 8 neighbouring cells proportional to the gradient of flow path; the steeper the gradient, the higher the proportion. Like D8, the Dinfinity algorithm calculates the steepest down slope direction, but instead of directing flow to one of the 8 cardinal and diagonal neighbouring cells, flow direction is based upon 8 triangular facets in a 3x3 cell window over the centre cell. Flow is directed proportionally to a maximum of 2 neighbouring cells to avoid the grid bias found with the D8 method. Produced are three upslope contributing area (a_s) data sets and slope ($tan\beta$) calculated for each DEM resolution to input into the formula $TWI = ln(a_s /tan\beta)$.

Results and Discussion

Maps of TWI (Figure 2) provided a visual comparison of the grid structure produced by the different flow algorithms and DEM resolutions. The higher resolution 20 metre DEM has more visually distinct TWI patterns due to the greater range of TWI values produced. This was exemplified by the MFD algorithm which produced a range of 10.1 TWI values at 40 metre resolution compared with a bigger 12.2 range at 20 metre resolution.
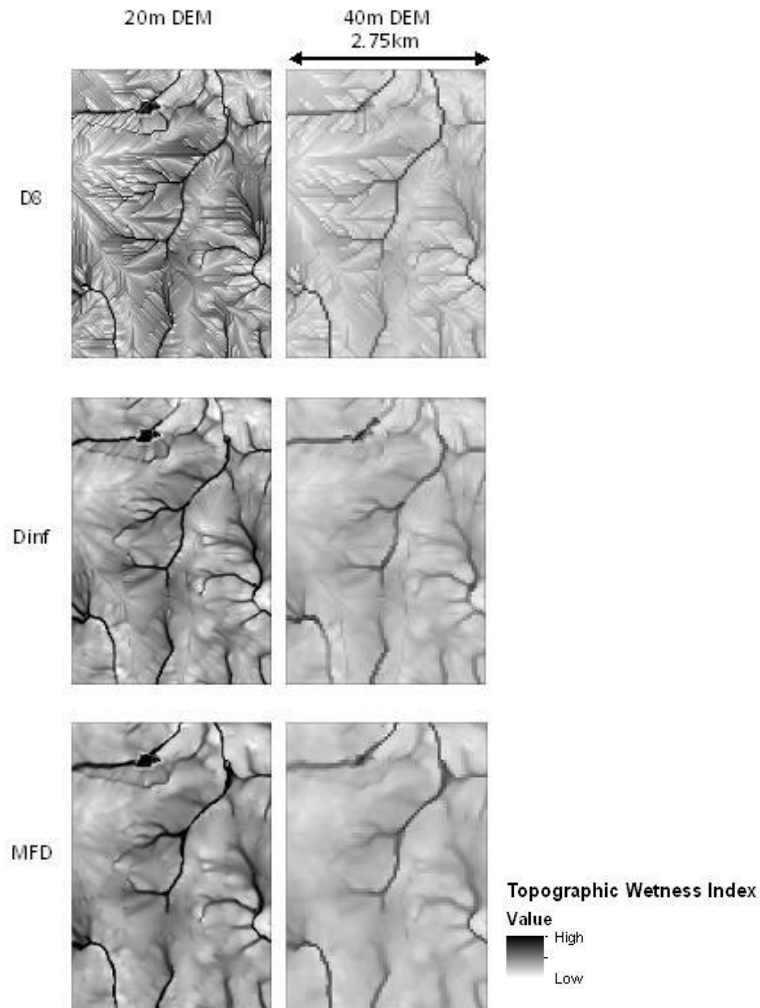
Figure 2. Maps of TWI computed at 2 resolutions using 3 different flow accumulation algorithms.

The most striking difference between the maps was the parallel flow lines produced by D8 which were less obvious with Dinfinity and MFD. This linear flow pattern produces neighbouring cells with significantly different TWI values due to the converging nature of the D8 flow algorithm. Unlike D8, the Dinfinity and MFD algorithms can diverge as well as converge flow. The lack of flow divergence associated with the D8 algorithm isolates cells away from accumulated flow paths. Another artefact of the D8 algorithm was evident following cumulative frequency analysis. The single flow direction method of D8 produced overall lower TWI values because catchment area flow paths were shorter than for the Dinfinity and MFD catchment area computation methods.

Standard Deviation (SD) of TWI values were highest when calculated using the 20 metre resolution DEM and the MFD flow algorithm producing SD values of 2 in the Lyon's Estate catchment and 2.1 in the Johnstown Castle catchment. The MFD algorithm produced the

highest SD value as a result of the diverging and converging nature of the algorithm. Over dispersion of flow can be seen on the MFD maps. Compared to the other flow algorithms, the MFD method produced larger areas of high (darker) TWI, which is evidence to suggest that there was over-dispersion of flow within the MFD algorithm.

Analysis of kurtosis between the six methods reveals that the larger Johnstown Castle catchment has a high kurtosis (2.9) compared to the smaller Lyon's Estate catchment (0.7). The larger the hydrological catchment area, the higher the flow accumulation figures produced which produces higher TWI values. A solution to this problem is the creation of a stream initiation cut-off value within the TWI values to create a more uniform distribution of TWI values between catchments regardless of catchment area.

Conclusions

The dispersive nature of the MFD method was of concern because of its inconsistency with the physical definition of upslope catchment area (a_s) (Tarboton, 1997). The Dinfinity method appeared to be the most appropriate when considering processing times, ability to converge and diverge flow without creating over dispersion or significant linear flow lines, and therefore its ability to produce a realistic model water accumulation within the landscape. This study has shown the importance of the use of a stream initiation cut-off value when working with TWI values computed from more than one hydrological catchment. Further research into the accuracy of each resolution and flow accumulation method at predicting soil moisture will be required through field reconnaissance and comparison with a higher resolution DEM in selected locations.

Acknowledgements

References

Freeman, T.G. (1991) Calculating catchment area with divergent flow based on a regular grid. Computers & Geosciences 17:413-422.

Horn, B.K.P. (1981) Hill shading and the reflectance map. Proceedings of the IEEE 69:14-47.

O'Callaghan, J.F., and D.M. Mark. (1984) The extraction of drainage networks from digital elevation data. Computer Vision, Graphics, and Image Processing 28:323-344.

Quinn, P., K. Beven, P. Chevallier, and O. Planchon. (1991) The prediction of hillslope flow paths for distributed hydrological modelling using digital terrain models. Hydrological Processes 5:59-79.

Schulte, R.P.O., J. Diamond, K. Finkele, N.M. Holden, and A.J. Brereton. (2005) Predicting the Soil Moisture Conditions of Irish Grasslands. Irish Journal of Agricultural and Food Research 44:95-110.

Schulte, R.P.O., K. Richards, K. Daly, I. Kurz, E.J. McDonald, and N.M. Holden. (2006) Agriculture, Meteorology and Water Quality in Ireland: a Regional Evaluation of Pressures and Pathways of Nutrient Loss to Water. Biology and Environment: Proceedings of the Royal Irish Academy 106B:117-133.

Tarboton, D.G. (1997) A new method for the determination of flow directions and upslope areas in grid digital elevation models. Water Resources Research 33:309-219.

Wang, L., and H. Liu. (2006) An efficient method for identifying and filling surface depressions in digital elevation models for hydrologic analysis and modelling. International Journal of Geographical Information Science 20:193-213.

Wilson, J.P., and J.C. Gallant. (2000) Secondary Topographic Attributes, in: J. P. Wilson and J. C. Gallant, (Eds.), Terrain Analysis: Principles and Applications, John Wiley & Sons. pp. 87-132.

EVALUATION OF OUTPUTS FROM A "SUSTAINABLE NUTRIENT MANAGEMENT DECISION SUPPORT SYSTEM" (SNM-DSS) COMPARED TO FARMER OPINION

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Abstract

A Sustainable Nutrient Management Decision Support System (SNM-DSS), which uses the Hybrid Soil Moisture Deficit (HSMD) model at its core, has been developed to predict optimum conditions for nutrient spreading. As part of the testing and validation of the SNM-DSS, the relationship between SMD predictions and farmer opinion on slurry spreading opportunities were investigated. Six farmers were involved in a survey where the question "can slurry be spread today?" was answered on a daily basis for the three HSMD model drainage classes (well-, moderately- and poorly-drained soils). Meteorological stations were installed on farmers land and recorded weather data required for daily SMD calculation. Daily SMD predictions were then compared to farmer perception of suitable conditions for slurry spreading. Opinions on field drainage quality differed between experts and farmers, for whom the perception was related to the type of soils they farm. Providing correct allocation of fields into a drainage class and recalibration of the moderately-drained class, the decision whether to spread slurry could be normalised with respect to SMD predictions for the national scale. It was also found that the decision whether to spread slurry could be determined by soil moisture conditions relative to field capacity. For instance spreading should not be allowed when SMD < 2 mm but could be advised when SMD > 5 mm on well-drained soils and SMD > 10 mm on moderately and poorly-drained soils. The HSMD model is a robust model that could be used as a core component in a decision support tool for daily farm management practices such as slurry spreading.

Introduction

Agriculture intensification caused notable increase of water pollution in Ireland through the 1980s and 1990s. While the level of water pollution has recently stabilised with annual variations in water quality probably explained by annual weather variations, water bodies are still pressurized (McGarrigle et al., 2010). In order to reduce the hazard associated with nutrient pollution, the Irish regulatory authorities have prohibited the spreading of fertilisers over the winter period with closed periods in 3 zones based on annual rainfall statistics. While this calendar approach is supported by scientific evidence, its justification has been debated by the farming community. An alternative lies in a Sustainable Nutrient Management Decision Support System (SNM-DSS), which has been developed to predict optimum conditions for nutrient spreading depending on real-time observations of soil and weather conditions. Recent scientific findings and developments such as the Hybrid Soil Moisture Deficit (HSMD) model (Schulte *et al.*, 2005) are assembled in the SNM-DSS to optimize nutrient utilization in Ireland. The Hybrid Soil Moisture Deficit (HSMD) model forms the basis of this system and is essential for defining the thresholds for optimum management. It is believed that agricultural community would welcome scientific support and would benefit from a decision support tool (Moore, 2007). Nevertheless it is important to test and evaluate the decision support system and to confirm that theoretical assumptions and user needs are met.

As part of the testing and validation of the SNM-DSS, the relationship between SMD predictions and farmers opinion on slurry spreading opportunities were investigated.

Materials and Methods

Survey and participants
Six farmers were involved in the survey for two and a half year (from September 2008 to March 2011). A diary was filled in every day where the question "can slurry be spread today?" was answered for three drainage classes (well-drained, moderately-drained and poorly drained soils). Three options ("Yes", "Only if necessary" and "No") were offered to the participants to answer the question. The 4 private and 2 research farms were representative of moderate to intensive grassland farms in Ireland with widespread geographical location and diverse management. The farms were located in counties Carlow, Cork, Kilkenny, Meath and Monaghan. General farm attributes are given in Table 1.

Weather data
Meteorological stations were installed on each farm and recorded weather data required for daily SMD calculation (temperature (T_{max} and T_{min} in °C), rainfall (mm), wind speed at 10m (m s^{-1}) and radiation (J cm^{-2}) on a hourly basis. The geographical location (latitude and longitude) was used as spatial co-ordinates for SMD calculation. In this paper, SMD data have been rounded to the nearest integer for data analysis purpose. Daily SMD were then compared to farmer perception of suitable conditions for slurry spreading.

Land drainage allocation
Farmers were asked to classify the field where the weather station was installed into a drainage class (well, moderately or poorly drained) based on their perception of drainage quality. This field was also allocated by the authors into a drainage class with respect to HSMD model definitions. A well-drained field would drain any water in excess of field capacity almost instantaneously. A moderately drained field could carry a water surplus up to around 24 hours but and would have no standing water 48 hours after rainfall at the very latest and a poorly drained field could carry a water surplus for a number of days.

Table 1. General farm attributes, farmer perception of natural land drainage and allocation into one HSMD model drainage class. R, P and N/A stand for Research, Private and Not Applicable respectively.

County	Field	Farm type	Production type	Livestock density (LU/ha)	Farmer drainage perception	HSMD model drainage class
Carlow	1	Research	Crop (main), beef and sheep	<1	Well	Well
	2				Well	Well
Cork	1	Research	Dairy	>2	N/A	Well
	2				N/A	Moderate
Kilkenny	1	Private	Beef and sheep	1 – 1.5	Well	Moderate - Poor
	2			>2	Well	Moderate
Meath	1	Private	Beef	1.5 - 2	Well	Moderate
	2				Well	Moderate
Monaghan	1	Private	Dairy and beef	>2	Well-Moderate	Moderate
	2	Private	Dairy	1.5 - 2	Poor	Poor

Statistics
In order to compare the three drainage classes, paired student's t-tests were used on the distribution of "Yes" answer percentage for calculated SMD (between SMD=-10mm and SMD=+10mm, where there is a risk of nutrient transport by gravity moveable water).

Results and Discussion

Land drainage perception
Opinions on field drainage quality differed between farmers and model users (Table 1). The drainage quality perception of a farmer for a given field was related to the heterogeneity and the type of soils they farm. In general farmers considered that the fastest field to drain water surpluses was a well-drained soil. This is sufficient for land management at the farm scale but this is not consistent with the definition of HSMD model drainage classes (Schulte et al., 2005). The allocation of a field into one of the three HSMD model drainage classes could normalise the perception of drainage quality at the national scale and probably reduce the hazard associated with nutrient management. The difference in farmer perception of a drainage class was also illustrated by large standard deviations, especially for the poorly-drained class (Figure 1).

Normalisation with respect to SMD predictions
While the p-values were approaching the significance level of 0.05, the poorly-drained class did not statistically differ from the well-drained ($p = 0.058$) and the moderately-drained ($p = 0.051$) classes when SMD < +10 mm. In contrast the distribution of "Yes" answers was found to be significantly different between well-drained and moderately-drained soils ($p < 0.001$). This difference may be attributed to the fact that model predictions for the well-drained and the moderately-drained classes did not physically differ at anytime (Kerebel et al., 2012). The latter have also shown that similar water contents were observed on moderately-drained soils for all values of SMD ≤ 0 mm. This is confirmed by the trends of farmer answers for the moderately-drained class where the percentage of "Yes" answers showed very little variations (for all values of SMD ≤ 0 mm, 4% < "Yes" answers < 19%) (Figure 1). The relationship between "Yes" answers and SMD predictions was more gradual for both well-drained and poorly-drained soils for -10 mm < SMD < +10 mm. Provided the moderately-drained class is re-calibrated, these results suggest that the allocation of fields to HSMD model drainage classes could potentially normalise the decision for nutrient spreading with respect to SMD predictions.

Slurry spreading opportunities
It was also found that the decision whether to spread slurry could be determined by soil moisture conditions relative to field capacity. The drier the soil was, the highest the agreement rate for slurry spreading was (Figure 1). According to farmer opinion, suitable conditions for slurry spreading were not met when the soil was at or wetter than field capacity (percentage of "Yes" answers < 41%). A 50% agreement rate was reached when SMD is 2 mm to 3 mm which suggests that some fields may be suitable for slurry spreading at water contents near field capacity (Figure 1). Farmers agreed 75% of the time or more that conditions were suitable for spreading when SMD was greater than 7 mm, 11 mm and 12 mm on well, moderately and poorly-drained soils respectively (trendlines, Figure 1). Since Kerebel et al. (2012) proved that 5 mm SMD intervals were more appropriate for practical purposes, thresholds for slurry spreading could be set at SMD = 5 mm for the well drained class and 10 mm for moderately and poorly-drained classes.
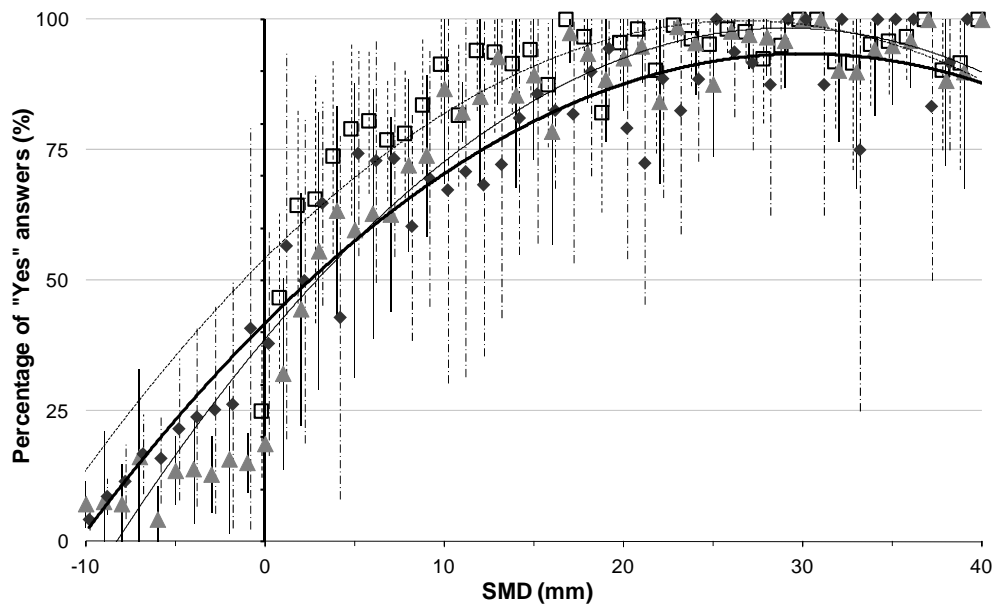
Figure 1. Percentage of "Yes" answers to the question "Can slurry be spread today?" related to the calculated SMD on a given day. Open squares with dashed trendline, gray triangles with regular trendline and black diamonds with bold trendline represent well, moderately and poorly drained classes respectively

Conclusions

The HSMD model showed potential for normalisation of farmers' perception of suitable conditions for slurry spreading with respect to SMD predictions at national scale. Thresholds for efficient and environmentally friendly spreading of fertilisers could be easily set using farmers' expert opinion. For instance spreading should not be allowed when SMD < 2 mm but could be advised when SMD > 5 mm on well-drained soils and SMD > 10 mm on moderately and poorly-drained soils. The HSMD model is a robust model that could be used as a core component in a decision support tool for daily farm management practices such as slurry spreading.

Acknowledgements

References

Kerebel A., Cassidy R., Jordan P. and Holden N.M. 2012. Field validation of the HSMD model and evaluation of its potential as the core component of the SNM-DSS. (In preparation)

McGarrigle, M., Lucey, J., Cinnéide, M. Ó. & Castle, J. 2010. water quality in Ireland 2007-2009.

Moore, A.D. 2007. Decicion support tools: keys to success. Making Science Work on the Farm. A Workshop on Decision Support Systems for Irish Agriculture. Agmet, Wexford.

Schulte, R., Diamond, J., Finkele, K., Holden, N. & Brereton, A. 2005. Predicting the soil moisture conditions of Irish grasslands. Irish Journal of Agricultural and Food Research, 44, 95-110.

VISUAL EVALUATION SOIL STRUCTURE AND GRASSLAND MANAGEMENTS

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Abstract

Assessments of soil structural quality under grassland managements in nationwide were processed using the method of VESS combined with some laboratory analysis. This study proved that the VESS method is reliable for grassland soils in Ireland and corresponding relationships were found among Sq values and other soil properties and managements. Sq values of the soils studied were in Sq1 and Sq3 scale. Soils in the fields with intensive grazing or permanent swards with more than 100 year ages were deteriorating with topsoil slightly compacted. We found there was no marked changes should be in operation according to these criteria. But some improvements and consideration should be paid attention for long-term sustainable productivity which include (1) controlling grazing intensity in high moisture fields; (2) shorten grazing season in rich rainfall areas or in fields with drainage problem and (3) applying regular plowing or fallow practice in permanent swards to recover soil resilience.

Introduction

Evaluation of soil structure which mainly includes measurements of bulk density and porosity in laboratory needs easier, feasible and reliable method in fields. Peerkamp method, named spade method as well created in 1959 (Peerlkamp) and has been developed after further revised versions by Batey and Ball (2007) and Ball et al. (2007). More diagnostic indicators related to soil physical, root morphology, soil microbes contribute to make this visible method more accurate, as the applicable conditions as well based on a series of fields experiments in Scotland, France (Rogre-Estrade et al., 2004), Germany (Beste, 2003; Muller, et al., 2009), Denmark (Munkholm, 2000), Canada and China (Muller, et al., 2009). In 2003, Ball and Douglas devised a semi-quantitative method with soil and root assessment procedure which allows ranking of the topsoil in terms of roots, soil structure and soil surface condition based on Munkholm (2000) and ranked according to a marking scheme similar to that of Beste (1999). Spaces for soil color, texture and internal surface features and decomposition of OM can be noted for additional information but not given in the "Soil Block Description". In 2011, a revised vision of VSSQA with a new name as VESS was developed based on studies above. Scoring of visual pores inside 1-1.5cm fraction and aggregate size and shape of 1-1.5cm fraction are added to score list (Guimarães and Ball, 2011). **This study assessed the application of VESS in Ireland and compare soil structure under different managements on grassland. Some laboratory work was done as complementary to the assessment result of the VESS method.**

Material and methods

Study sites

20 sites from 12 farms were chosen for nationwide sampling. Three sites were under grass for less than 20 yrs, ten sites were under grass for 40 to 100 yrs and the remaining seven sites were under grass for more than 100 years. Three sites were organic farms (G9, G10S1/S2) where no chemical fertilizer was applied.

Methods
Visual evaluation of soil structure
For each sample site, the environment around were observed carefully for further descriptive

Table 1. The location of study sites and general description

Sites	Location	Farm type	Age (yrs)	Since Last Reseeding (yrs)	Sand %	Silt %	Clay %	Organic fertilizer m³/ha	Chemical N input kg/ha	pH	SR (cow/ha)
G1S1	Co.Cork	Gd &S	>40	5	51	32	18	13.6	250	6.2	>2
G1S2	Co.Cork	Gd &S	>40	5	48	40	12	13.6	250	6.0	>3
G2S1	Co.Carlow	Gbs	>20	no	62	23	15	0	0	6.7	1-1.5
G3S1	Co.Monaghan	Gdb	12	12	63	24	14	6.8	150	6.1	>2
G4S1	Co.Monaghan	Gd &S	>40	6	66	20	14	22.5	327	5.1	>2
G5S1	Co.Kilkenny	Gdb &S	>40	10	47	31	22	9.1	200	5.0	>2
G6S1	Co.Kikenny	Gbs	>150	>30	40	33	27	9.1	33.8	6.1	1-1.5
G7S1	Co.Meath	Gb & S	15	5	35	39	27	22.5	G:100-135 S:135-200	5.7	1.5-2
G7S2	Co.Meath	Gb & S	>40	5	31	55	14	22.5	G:100-135 S:135-200	5.5	1.5-2
G8S1	Co.Dublin	Gbs	>40	5	34	35	31	9.1	100	5.6	1.5-2
G8S2	Co.Dublin	Gd&S	>40	no	29	38	33	11.4-13.6	70-100	5.9	1.5-2
G8S3	Co.Dublin	Gd&S	>40	1	31	41	28	11.4-13.6	70-100	6.1	1.5-2
G9S1	Co.Westmeath	Gb&S	>40	no	32	31	37	0	0	5.3	1-1.5
G10S1	Co.Offaly	Gb	12	12	27	48	25	8.4	0	5.3	1-1.5
G10S2	Co.Offaly	Gb	>200	no	23	59	17	8.4	0	6.7	1-1.5
G11S1	Co.Meath	Gb&S	>100	9	39	39	22	6.8	100	5.1	<1
G11S2	Co.Meath	Gb	>100	no	28	46	26	9.1	100	4.8	<1
G12S1	Co.Cavan	Gb	>100	no	35	33	31	13.6	33	4.8	<1
G12S2	Co.Cavan	Gb	>100	no	32	36	32	13.6	33	4.5	<1
G12S3	Co.Cavan	Gb&S	>100	8	31	39	29	13.6	67	5.8	<1

Gb means beef grazing; Gd means dairy grazing; S means silage harvest presented; Gbs means mixture of beef and sheep grazing while Gdb means mixture of dairy and beef grazing

information. A 30 m by 30 m plot was chosen for getting 5 subplots. Soil blocks (20cm by 20cm by 20cm) were extracted carefully and transferred into a tray for observation before being cut into two pieces according to the method from Bruce Ball, et al. (Guimarães and Ball, 2011).

Laboratory analysis
Soil samples were collected at each subplot after visual evaluation of soil structure and kept in labeled plastic bag for laboratory analysis. Water content was determined by oven drying. Soil texture was measured using the pipette method (Gee and OrD, 2002). soil porosity (φ) was estimated from bulk density (ρb) by assuming a constant particle density (ρp) of (2.65 g/cm3) using Eq. $\varphi = 1- (\rho b /\rho p)$. Soil total nitrogen and total carbon content were measured by CHN analyzer (LECO) using <2 mm air-dried soil.

Results and discussion

Of the 20 sites, soils at 3 sites (15%) were classified as Sq1 and 4 (20%) were Sq2, 4 sites (20%) were on the boundary of Sq1 and Sq2 with topsoil compacted lightly due to physical disturbance by animals. Soils from the remaining 8 sites (40%) were between Sq2 and Sq3 with 1 site (5%) was Sq3. Soil blocks from high livestock rate (G4S1, G7S1, G8S3) showed themselves slightly compact at topsoil due to animal physical perturbation, making the soil structure deterioration. Statistic analysis indicated that Sq had a negative relationship with organic fertilizer input, and a positive relationship with chemical N fertilizer input (r= 0.208). The application of organic fertilizer (i.e. manure or slurry) has found benefits to soil aggregates formation and stability (Alidad and Mehdi et al., 2012) thus making soil structure stabilized. We also found significant negative correlations between Sq with soil carbon content ($p<0.01$) and between Sq with soil nitrogen content ($p<0.05$) (Table 2)

Table 2. Correlation among Sq and fertilizer application and soil properties

		Sq	F_{org}	F_N	sand	silt	clay	BD	WC	Nc	Cc	SR
Sq	Pearson Correlation	1	-.196	.208	.326	-.437	.023	.272	-.133	-.517[*]	-.625[**]	.158
	Sig. (2-tailed)		.409	.378	.160	.054	.924	.245	.575	.020	.003	.505

*. Correlation is significant at the 0.05 level (2-tailed).   **. Correlation is significant at the 0.01 level (2-tailed). F_{org} means the application of organic fertilizer; F_N means the application of chemical N fertilizer; N_c and C_c mean soil total nitrogen and carbon content at 0-20 cm depth, respectively; SR is livestock rate.

The test was easily used and around 15-20 minutes needed to operate one block, mainly for detailed description of defining Sq classes in the VESS scoring slice. The using of the VESS scoring method in Irish soil was feasible and reproducible. The size of the most aggregates after first break up was one of the most reliable diagnose for scoring Irish soil. The score of size of aggregates was always corresponding to the final score. While the score of force used for breaking was unreliable in operation. Sampling time is important since water content would affect soil block extraction and soil scoring.

Table 3. Threshold Sq values for sustained agricultural productivity. (from Ball et al., 2007)

Sq score	Soil structural quality	Management needs
1-2	Good	No changes needed
2-3	Fair	Long-term improvements
3-5	Poor	Short-term improvements

According to the threshold values for managements proposed by Ball et al. (2007) (Table 3), it seems no marked changes should be operated urgently in Irish grassland soils, but some

consideration should be paid attention for maintaining sustainable soil structural quality and productivity in long-term. In permanent grasslands, regular plough or fallow rotation will benefit for preventing compaction of topsoil and controlled or shorted grazing seasons will be advantageous to avoid animal perturbation on soils especially in wet fields after intensive rainfall or with poor drainage.

Conclusion

This study has proved the VESS is reliable, quick and readily understood method. The size and shape of 1-1.5 cm fraction are reliable diagnostic indicators in the VESS method application in Ireland but the force needed to break up block and aggregate is subjective and not trustable. The threshold proposed by Ball (2007) suites to soils in grassland as well and some attentions and improvements should be considered for long-term sustainable soil productivity. They maybe: (1) controlling grazing intensity in wet fields preventing animal physical perturbation of soil structure; (2) shorten grazing season in rich rainfall areas or in fields with poor drainage status and (3) operation regular plowing or fallow rotation in permanent swards where topsoil has been compact or tends to be in compaction.

Acknowledgements

References

Alidad Karami, Mehdi Homaee et al., 2012. Organic resource management: Impacts on soil aggregate stability and other soil physico-chemical properties. Agriculture, Ecosystems & Environment, 148, 22-28

Ball, B.C., Batey, T. & Munkholm, L.J. 2007. Field assessment of soil structural quality - a development of the Peerlkamp test. Soil Use and Management, 23, 329–337

Ball, B.C., Watson, C.A. & Baddeley, J. 2007. Soil physical fertility, soil structure and rooting conditions after ploughing organically managed grass / clover swards. Soil Use and Management, 23, 20– 27

Beste, 1999. An applicable field method for the evaluation of some ecologically significant soil-function-parameters in science and agricultural consulting practice. International Soil Conservation Organisation (ISCO) - Conference 1999, West Lafayette, Indiana, USA

Gee G.W and Or D., 2002. Particle size analysis. In: Methods of soil analysis, part 4: physical methods. Dane J.H and Topp G.C. Number 5 in the Soil Science Society of America Book Series, SSSA, Madison, USA

Giarola, N.F.B., Silva, A.P., Tormena, C.A., Ball, B. & Rosa, J.A., 2010. Visual soil structure quality assessment on oxisols under notillage system. Scientia Agricola, 67, 479–482.

Mueller, L., Kay, B.D., Hu, C., Li, Y., Schindler, U., Behrendt, A., Shepherd, T.G. & Ball, B.C., 2009. Visual assessment of soil structure: evaluation of methodologies on sites in Canada, China and Germany Part I: comparing visual methods and linking them with soil physical data and grain yield of cereals. Soil & Tillage Research, 103, 178–187

Peerlkamp, P.K., 1959. A visual method of soil structure evaluation. Meded. v.d. Landbouwhogeschool en Opzoekingsstations van de Staat te Gent. XXIV No. 24, pp. 216–221.

Guimarães R. M. L., Ball B. C.., Tormena C. A. (2011). Improvements in the visual evaluation of soil structure. Soil Use and Management 27, 395-403.

Roger-Estrade, J., Richard, G., Caneill, J., Manichon, H., et al., 2004. Morphological characterization of soil structure in tilled fields. From a diagnosis method to the modeling of structural changes over time. Soil Tillage Res. 79, 33–49.

PREDICTION OF QUALITY PARAMETERS OF BIOMASS PELLETS BASED ON CHEMICAL COMPOSITION

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Abstract

Calorific value (CV) is the amount of energy released during combustion; knowledge of this value would allow for the more efficient operation of energy production systems. Mechanical durability (MD) is the ability of pellets to remain intact when handled. A high MD value reduces the amount of dust and fines that are created during handling. Multiple linear regression (MLR) was used to accurately predict the CV and MD of the biomass pellets in this study. The CV of the pellets was predicted with a coefficient of determination (R^2) value of 0.99 and a standard error of the estimate (SEE) of 0.082% (Range: 16.3895 to 18.9152MJ/kg). The MD of the pellets was predicted with an R^2 value of 0.94 and SEE of 0.492% (Range: 92.6 to 97.5%). This study demonstrates that MLR can be used to predict the additional information of CV and MD of biomass pellets from their chemical composition.

Introduction

Demand for sources of alternative energy is growing (Allison *et al.*, 2009). The use of pellets produced from biomass sources is one alternative. The majority of pellets produced globally utilise wood chips as a feedstock (Allison *et al.*, 2009). Due to realistic harvest yields and recovery rates, wood as a feedstock may not meet the growing demand for pellets (Nolan *et al.*, 2010). Alternative feedstocks will be required to meet this demand. For this reason specific energy crops (short rotation coppice willow and *Miscanthus*) and herbaceous energy grasses (Switchgrass, Reed Canary Grass (RCG) and Tall Fescue (TF)) are being employed to meet this demand. Biomass as a feedstock varies widely in its chemical composition (Obernberger & Thek, 2010). The varying components include moisture content (MC), carbon content (CC) and ash content (AC) which are due to varying harvest dates, weather conditions and soil composition. These chemical constituents have an effect on quality parameters i.e. calorific value (CV) and mechanical durability (MD), of the biomass pellets (Lewandowski & Kicherer, 1997). CV is the single most important property in solid biofuels, it is necessary for the design and operation of both small and large scale boilers to ensure biomass optimisation in energy production, as well as for the design of storage areas to increase the amount of time between pellet orders (Lewandowski & Kicherer, 1997; Obernberger & Thek, 2010). Storage capacity of pellet central heating systems should be big enough to store one to one and a half times the annual fuel demand, pellets with a lower CV will require a greater amount of space to meet this demand (Obernberger & Thek, 2010). MD is the ability of pellets to remain intact when handled. A high MD value reduces the amount of dust and fines that are created during the handling process, which both reduces the risk of dust explosions and fires and reduce the risk of respiratory illnesses to both operators and consumers (Obernberger & Thek, 2010). Under CEN/TC 335 the quality parameters of biomass pellets must comply with stringent limits (Obernberger & Thek, 2010). The prediction of these quality parameters from empirical compositional analysis would reduce the amount of time spent analysing the samples. Multiple linear regression (MLR) is a possible method for the prediction of these pellet quality parameters.

The objective of this study was to determine the CV and the MD of biomass pellet blends based on the chemical composition of the pellets using MLR.

Materials and Methods

Biomass pellet production
Pellet blends (N = 9) were produced from biomass (RCG, Pine, TF) obtained from the Teagasc Crops Research Centre (Oakpark, Co. Carlow). The pellets were produced using a Greenforce MZLP 250 kg hour^{-1} pellet mill in Lyons Research Farm, Co. Dublin. The biomass was blended to produce nine varieties of pellet (Table 1). The pelletising process involved movement through a 5 kW hammer mill with an 8 mm screen. The material was then forced through a 6 mm die to form the cylindrical pellets. A portion of the pellet samples were ground to a particle size of 1 mm for use in the laboratory analysis. The samples were stored in air tight containers prior to analysis.

Table 1. Percentages of each biomass used in the sample blends.

Biomass	RCG_{100}	$RCG_{75}P_{25}$	$RCG_{50}P_{50}$	$RCG_{25}P_{75}$	P_{100}	$TF_{25}P_{75}$	$TF_{50}P_{50}$	$TF_{75}P_{25}$	TF_{100}
RCG[1]	100	75	50	25	-	-	-	-	-
Pine	-	25	50	75	100	75	50	25	-
TF[2]	-	-	-	-	-	25	50	75	100

[1] Reed Canary Grass [2] Tall Fescue

Determination of quality indices
MC, CC, AC, CV and MD of the ground pellets were determined in duplicate according to International standards (British Standards, 2010; CEN/TC 335, 2009a, 2009b, 2009c, 2009d). CC was determined using a carbon analyser (Skalar, Breda, Holland). AC was determined using a furnace (Carbolite, Hope, England). CV was determined using a bomb calorimeter (Parr Instrument, Moline, IL, USA). MD of the samples was determined using a tumbling box in accordance with the standard method.

Data Analysis
MLR is an expansion of linear regression that aims to predict a single dependent or response variable (Y value) using several independent or predictor variables (X values) by fitting a hyperplane to the data. MLR was carried out to predict the dependent variables CV and MD from the independent variables MC, CC and AC using Sigmaplot software (V12, Systat Software Inc., London, United Kingdom). The AC value of 2.8846% for the RCG_{100} blend was extrapolated using the values for P_{100}, $P_{75}RCG_{25}$, $P_{50}RCG_{50}$ and $P_{25}RCG_{75}$.

Results & Discussion

Prediction of Calorific Value
The CV of the samples was accurately predicted with a coefficient of determination (R^2) value of 0.99 (Figure 1a) and a standard error of the estimate (SEE) of 0.082. The Predicted Residual Error Sum of Squares (PRESS) statistic was determined at 0.120. This statistical value is a gauge of how well a regression model predicts new data. The smaller the PRESS statistic, the better the predictive ability of the model.

The t-values shown in Figure 1b show the chemical components that are most important in developing the model. From this figure it can be seen that MC and AC are the most important components with t-values of -14.528 and -7.253, respectively. The MC affects the CV of the pellets as the O-H bonds of water contain less energy than C-C bonds (Lestander & Rhen, 2005). The AC also affects the CV values, Monti et al., (2008) reported that a 1% increase in the AC leads to a 0.2 MJ kg^{-1} decrease in the CV. The CC of the samples has very little effect on explaining the prediction of the CV of the samples compared with MC and AC. The ANOVA table shown in Table 2 shows that there is a significant relationship between the independent variables (MC, CC & AC) and the dependent variable (CV), p-value <0.001.
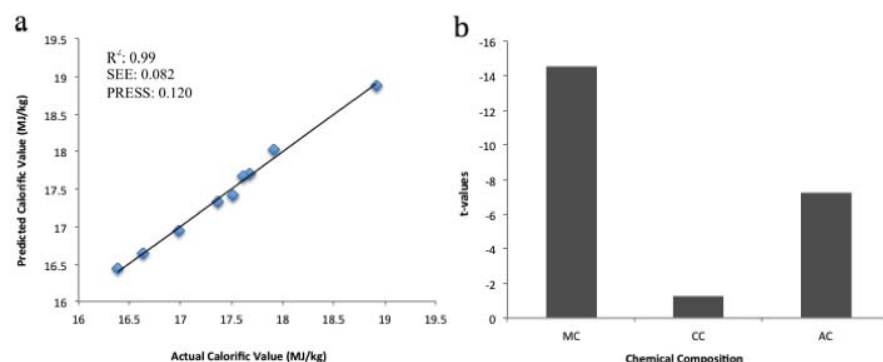
Figure 1. Results of the multiple linear regression model developed for the prediction of the calorific value showing (a) the linear regression plots of predicted versus actual values and (b) the t-values of the developed model.

Table 2. ANOVA table resulting from multiple linear regression models

	DF	SS	MS	F	P
Regression	3	4.413	1.471	217.37	<0.001
Residual	5	0.0338	0.00677		
Total	8	4.447	0.556		

DF=Degrees of Freedom, SS=Sum of Squares, MS=Mean Sum of Squares, F=F Ratio, P=P value

Equation 1 shows the model resulting from MLR for the prediction of the CV of the biomass samples;

$$CV = 22.726 – (0.237 \text{ x MC}) – (0.0372 \text{ x CC}) – (0.347 \text{ x AC}) \quad \textbf{[Eq. 1]}$$

Prediction of Mechanical Durability
The MD of the samples was accurately predicted with an R^2 value of 0.94 (Figure 2a) and a SEE of 0.492. The PRESS statistic for the MD was determined at 4.711.
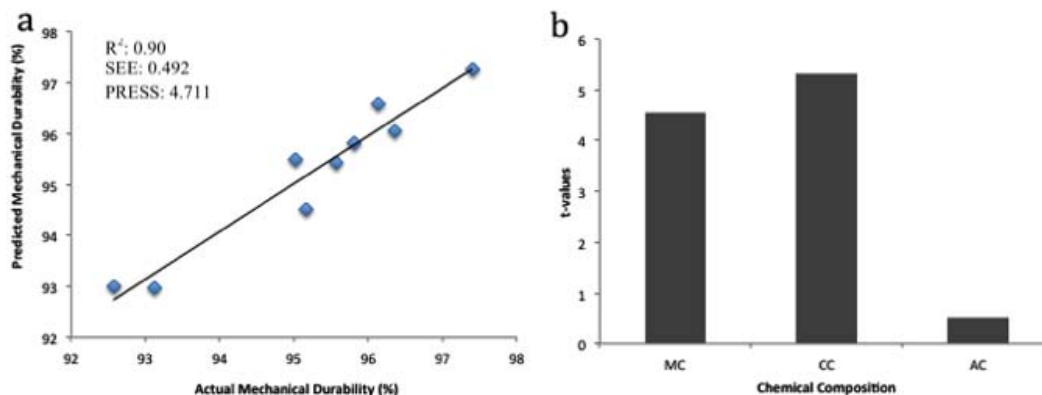
Figure 2: Results of the multiple linear regression model developed for the prediction of the mechanical durability, showing (a) the linear regression plots of predicted versus actual values and (b) the t-values of the developed model.

Table 3: ANOVA table resulting from multiple linear regression models

	DF	SS	MS	F	P
Regression	3	17.597	5.866	24.195	0.002
Residual	5	1.212	0.242		
Total	8	18.810	2.351		

DF=Degrees of Freedom, SS=Sum of Squares, MS=Mean Sum of Squares, F=F Ratio, P=P value

Figure 2b shows that the most important parameters for the prediction of the MD of the biomass pellets are the CC and the MC (t-values of 5.32 and 4.553, respectively). The CC affects the MD of the samples as higher levels of carbon may indicate the presence of greater amounts of lignin,

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which acts as a natural binding agent in the pellets (Obernberger & Thek, 2010). Filbakk et al., (2010) reported higher MD values of pellets that contained higher CC values. The MC affects the MD of the pellets as less stiff more ductile particles enter the pellet die leading to better binding of the particles. Moreover, the binding forces of the water molecules strengthens the bonds between the individual particles in the pellets (Filbakk *et al.*, 2011). The AC has little effect on the prediction of the MD. Table 3 shows that there is a significant relationship between the independent variables and the MD of the samples, p-value <0.01. Equation 2 shows the formula resulting from MLR for the prediction of the MD;

$$MD = 40.484 + (0.445 \text{ x } MC) + (0.946 \text{ x } CC) + (0.143 \text{ x } AC) \quad \textbf{[Eq. 2]}$$

Conclusions

MLR can be used to accurately predict both the calorific value and mechanical durability (R^2 values of 0.99 and 0.94, respectively). The standard error of the estimate for the models was estimated at 0.082 and 0.492 for the calorific value and the mechanical durability, respectively. The PRESS statistics (0.120 and 4.711, respectively) shows that both models developed can be used to accurately predict the reference values of the samples. MLR can be used to predict additional compositional information from the pellet samples chemical composition. Further studies investigating larger sample sets need to be conducted to allow for more robust models to be developed.

Acknowledgements

References

Allison, G., Morris, C., Hodgson, E., Jones, J., Kubacki, M., Barraclough, T., Yates, N., Shield, I., Bridgwater, A. & Donnison, I. (2009). Measurement of key compositional parameters in two species of energy grass by Fourier transform infrared spectroscopy. *Bioresource Technology, 100*, 6428-6433.

British Standards. (2010). Draft BSEN 15104 Solid Biofuels - Determination of Total Content of Carbon, Hydrogen and Nitrogen - Instrumental Methods. London.

CEN/TC 335. (2009a). EN 14774-2:2009 Solid Biofuels - Determination of Moisture Content - Oven Dry Method *Part 2: Total Moisture - Simplified Method*. London.

CEN/TC 335. (2009b). EN 14775 Solid Biofuels - Determination of Ash Content. London.

CEN/TC 335. (2009c). EN 14918 Solid Biofuels - Determination of Calorific Value. Brussels.

CEN/TC 335. (2009d). EN 15210-1:2009 Solid Biofuels - Determination of Mechanical Durability of Pellets and Briquettes, *Part 1: Pellets*. London.

Filbakk, T., Jirjis, R., Nurmi, J. & Heibe, O. (2010). The effect of bark content on quality parameters of Scots pine (Pinus sylvestris L.) pellets. *Biomass and Bioenergy, In Press, Corrected Proof.*

Filbakk, T., Skjevrak, G., Heibe, O., Dibdiakova, J. & Jirjis, R. (2011). The influence of storage and drying methods for Scots pine raw material on mechanical pellet properties and production parameters. *Fuel Processing Technology, 92*(5), 871-878.

Lestander, T. & Rhen, C. (2005). Multivariate NIR spectroscopy models for moisture, ash and calorific content in biofuels using bi-orthogonal partial least squares regression. *Analyst, 130*, 1182-1189.

Lewandowski, I. & Kicherer, A. (1997). Combustion quality of biomass: practical relevance and experiments to modify the biomass quality of Miscanthus x giganteus. *European Journal of Agronomy, 6*(3-4), 163-177.

Monti, A., Di Virgilio, N. & Venturi, G. (2008). Mineral composition and ash content of six major energy crops. *Biomass and Bioenergy, 32*(3), 216-223.

Nolan, A., McDonnell, K., Devlin, G. J., Carroll, J. P. & Finnan, J. (2010). Potential availability of non-woody biomass feedstock for pellet production within the Republic of Ireland. *International Journal of Agriculture & Biological Engineering, 3*(1), 63-73.

Obernberger, I. & Thek, G. (2010). *The Pellet Handbook - The Production and Thermal Utilisation of Pellets*. London: Earthscan.

EXAMINATION OF CELL BODIPY[505/515] UP-TAKE BY FOUR HIGH-LIPID MICROALGAE

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Abstract

Rapid assessment techniques for the screening of microalgae strains towards the yield optimisation of biofuel and extraction of valuable co-products are also aimed at providing real-time and reliable data for process pathway decisions. Attention has focused on *in situ* measurements of cellular lipids, notably, the use of lipophilic fluorescence methods (Nile red and BODIPY[505/515]) to monitor characteristics within individual cells using flow cytometry or fluorescence microscopy. The use of a BODIPY[505/515] fluorescence method has been suggested as an alternative to the widely-used Nile red fluorescence method for quantifying the total lipid content in microalgal cells. This paper was to study the response using flow cytometry of four algae species to staining with the lipid probe BODIPY[505/515] with the aim of enhancing the lipid staining method for potential application in biofuel-directed microalgae production. The study was based on four microalgae species (*Dunaliella teteriolecta, Tetraselmis suecica, Nannochloropsis oculata,* and *Nannochloris atomus*) selected because of their inherent high lipid content. An extended analysis was carried out with *N. oculata* due to the depressed fluorescence observed when compared with the other experimental strains. It was found that lipid fluorescence of thick cell-walled microalgae, such as *N. oculata,* are significantly enhanced by pre-treatment with a stain carrier such as DMSO. The lipid fluorescence enhancement method provides a quick and simple index for *in vivo* flow cytometry quantification of total lipid contents for purposes of species screening or whole culture monitoring in biofuel-directed microalgae production.

Introduction

Attention has been focused on *in situ* measurements of cellular lipids, notably the use of lipophilic fluorescence probes to monitor lipid changes within individual cells using flow cytometry. Principal applications of flow cytometry are in monitoring of cell growth by cell-counting and quantified characterisation of intrinsic cell fluorescence. This can be used to check for homogeneity of cell cultures, monitoring of cell lipid content to optimise harvesting, and monitoring lipid type to determine the optimum co-product, hence, the right processing pathway. The application of BODIPY[505/515] fluorescence method for estimation of lipid contents in microalgae has only recently been tested. Cooper et al. (2010) successfully applied BODIPY[505/515] (4,4-Difluoro-1,3,5,7-Tetramethyl-4-Bora-3a-Diaza-s-Indacene) to monitor oil storage within several microalgae species and their results suggested that the lipid probe can be useful for certain technical applications such as confocal imaging and high content screening of microalgae samples for valuable products. BODIPY[505/515] has a high oil/water coefficient, which allow it to easily cross cell membranes such that the lipid components of live cells can be distinctively labelled. It is easily excited by a blue 488 nm laser, with emission in the green spectrum at 515 nm, which is spectrally distinguishable from algal chloroplasts (Cooper et al., 2010).

The objective of this paper was to study the response using flow cytometry of four algae species to staining with the lipid probe BODIPY[505/515] with the aim of enhancing the lipid staining method for potential application in biofuel-directed microalgae production.

Materials and Methods

Experimental organisms and cultivation conditions
Four microalga cultures, selected for their known high lipid concentration, were obtained from the Culture Collection of Algae and Protozoa (CCAP, Dunstaffnage Marine Laboratory, Oban, Scotland). The cultures included one heterokont (Eustigmatophyceae) *Nannochloropsis oculata* (Droop) Hibberd (1981) (849/1), and three green algae (Chlorophyceae) *Dunaliella teteriolecta* Butcher (1959) (19/27), *Tetraselmis suecica* (Kylin) Butcher (1959) (66/4), and *Nannochloris atomus* Butcher (1952) (251/4A). Over the course of the experiment, the cultures were maintained axenically in f/2 medium (Guillard and Ryther, 1962) at 20 °C, under continuous illumination at a light intensity of 150 μmol s^{-1} m^{-2}.

Evaluation of BODIPY$^{505/515}$ lipid fluorescence characteristics
A 500 μM stock solution of BODIPY$^{505/515}$ (4,4-Difluoro-1,3,5,7-Tetramethyl-4-Bora-3a-Diaza-s-Indacene; Life Technologies, Dublin, Ireland) was made by dissolving the dye in anhydrous dimethyl sulfoxide (DMSO) according to Cooper et al. (2010). A baseline staining method was established whereby aliquots of the stock solution were added directly to algal suspensions to achieve a final staining concentration of 0.12 μg mL^{-1} and 2% DMSO, which was then shaken gently by hand for 10 seconds and analysed immediately. Each sample was analysed for its background autofluorescence, BODIPY$^{505/515}$ fluorescence, and chlorophyll fluorescence. Fluorescence measurements were taken before and after staining by excitation with a blue laser at 488 nm and emission measured in the range of 530 ±15 nm for BODIPY$^{505/515}$ and 670LP nm for chlorophyll. Each measurement duration was made for 60 seconds using a BD Accuri C6 Flow Cytometer (BD Accuri, Michigan, USA) while flow cytometry was initially used to isolate live algal cells from the measured chlorophyll fluorescence (i.e., cells with chlorophyll fluorescence were considered to be live (Marie et al. 1999), chlorophyll fluorescence > 1,000 mean fluorescence intensity (MFI)); these cells were subsequently analysed with CFlow and FCSExpress software to determine the cell concentration, autofluorescence, and BODIPY$^{505/515}$ fluorescence. All measurements were taken in triplicate.

Examination of BODIPY$^{505/515}$ up-take by algal cells
Dynamic measurement of BODIPY$^{505/515}$ up-take by algal cells was analysed using the "non-stop flow" method outlined by Vines et al. (2010). The "non-stop flow" method allows continuous data collection from an open sample tube with a time delay of less than 2 seconds between the addition of test reagent and laser intercept point. BODIPY$^{505/515}$ up-take by three algal strains (*D. teteriolecta*, *T. suecica* and *N. atomus*) was determined for samples without pre-treatment. In the case of *N. oculata*, BODIPY$^{505/515}$ up-take was determined for samples with and without pre-treatment. All samples were diluted to a defined cell concentration of 1 × 10^6 cells mL^{-1} with fluorescence measurements taken in triplicate. *N. oculata* pre-treatment involved the addition of 0.06 g mL^{-1} DMSO to the sample and incubating for five minutes at room temperature before analysis. All fluorescence measurements were recorded continuously over a 4 minute test period with stain addition occurring after 2 minutes to achieve a final staining concentration of 0.12 μg mL^{-1} and 2% DMSO. All compounds were added using a gel loading pipette tip (STARLAB, Switzerland), allowing the addition of test compounds and mixing of sample with ease.

Results and Discussion

From observations in this study using the "non-stop flow" method, all microalgae cells exhibited instantaneous uptake of stain with the BODIPY$^{505/515}$ staining method. Figure 1 shows that the BODIPY$^{505/515}$ stain rapidly permeated into the cells to enhance fluorescence of the lipid bodies within the cells. *D. teteriolecta* and *T. suecica* exhibit consistently narrow

fluorescence intensity band whereas *N. oculata* and *N. atomus* produces increasingly scattered fluorescence signals.
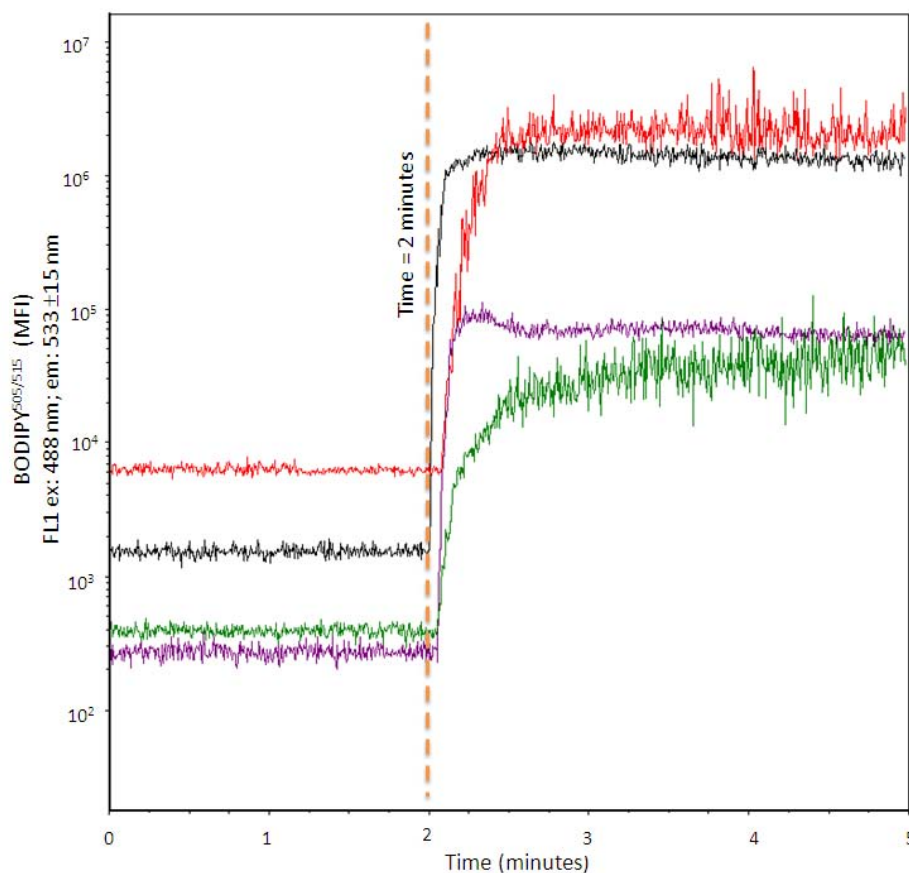
Figure. 1: BODIPY$^{505/515}$ stain up-take for *Nannochloropsis oculata* (——), *Dunaliella teteriolecta* (——), *Tetraselmis suecica* (——), and *Nannochloris atomus* (——). Cells were monitored for base autofluorescence and with the addition of BODIPY$^{505/515}$ (0.12 μg mL^{-1}) occurring at 2 minutes into the analysis.
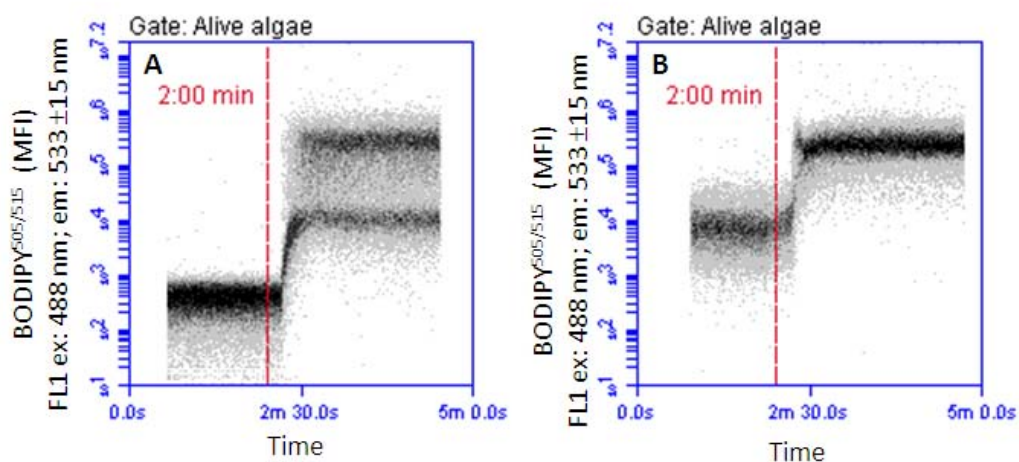
Figure. 2: Bivariate histograms of BODIPY$^{505/515}$ stained fluorescence for *N. oculata* for stain injection at 2 minutes into the analysis for (A) Staining (0.12 μg mL^{-1}) without pre-treatment, and (B) Staining (0.12 μg mL^{-1}) after 0.06 g mL^{-1} DMSO pre-treatment.

Further investigation revealed that for *N. oculata* without pre-treatment, the measured fluorescence was congregated in two distinct populations (Figure 2A) which was not the case for the other three strains (*D. teteriolecta*, *T. suecica*, and *N. atomus*). The unique response may be attributed to the thick cell wall of *N. oculata* which reduced the stain permeation rate. It is considered that the mechanics of this observation are similar to those highlighted by Doan and Obbard (2010) for Nile red staining of *Nannochloropsis* sp., who reported that, treatment with DMSO as stain carrier significantly enhanced the lipid staining efficacy. In this study the addition of 0.06 g mL^{-1} of DMSO to the working solution followed by an incubation period of five minutes at room temperature before staining resulted in a significant increase in fluorescence. It could therefore be argued that, with DMSO pre-treatment, the stain permeates into all cells uniformly, giving a consistent fluorescence emission as one distinct population such as that observed in Figure 3B.

Conclusion

From the examination of the stain up-take by *N. oculata* cells using the "non-stop flow" method, it was shown that without pre-treatment, the fluorescence characteristics was in two distinct populations (fully stained and partially stained cells, Figure 2A), arguably due to the low rate of stain permeation through the cell wall in the majority of cells. The observed non-uniform fluorescence distribution restricts the potential application of the staining method for applications such as high-throughput screening of biofuel-directed algae production. The staining efficacy of the BODIPY$^{505/515}$ lipid probe was enhanced with DMSO pre-treatment, thereby allowing it to effectively penetrate all the cells to exhibit a consistent BODIPY fluorescence (Figure 2B). The "non-stop flow" method provides an innovative method to monitoring of algae cell wall permeability; hence, verification of staining technique that could achieve consistent fluorescence emission.

Acknowledgements

References
Cooper, M.S., Hardin, W.R., Petersen, T.W., Cattolico, R.A. 2010. Visualizing "green oil" in live algal cells. Journal of Bioscience and Bioengineering, 109(2), 198-201.
Doan, T.-T., Obbard, J. 2010. Improved Nile Red staining of Nannochloropsis sp. Journal of Applied Phycology, 23(5), 895-901.
Marie, D., Partensky, F., Vaulot, D., Brussaard, C. 1999. Enumeration of Phytoplankton, Bacteria, and Viruses in Marine Samples. Current Protocols in Cytmoetry, 11.11.1 - 11.11.15.
Vines, A., McBean, G.J., Blanco-Fernández, A. 2010. A flow-cytometric method for continuous measurement of intracellular Ca2+ concentration. Cytometry Part A, 77A(11), 1091-1097.

EFFECT OF CARBON DIOXIDE CONCENTRATIONS ON THE CARBON MITIGATION POTENTIAL OF MICROALGAE

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Abstract

Biological carbon mitigation is a technique which utilises carbon dioxide (CO_2) from the flue gases of, for example, a power plant to cultivate photosynthetic autotrophic organisms such as microalgae. This aim of this study was to assess the feasibility of cultivating *Nannochloris atomus, Dunaliella tertiolecta, Tetraselmis suecica* and *Pavlova lutheri* using CO_2 enhanced air streams and to determine the rate of carbon mitigation. Three of the microalgal strains grew more effectively in the trials where air enhanced with 2% CO_2 was bubbled through the cultures. *Nannochloris atomus* demonstrated the greatest overall carbon mitigation at a rate of $0.313gC.L^{-1}.d^{-1}$. However, it proved most difficult to harvest *via* centrifugation due to the small cell size. *Dunaliella tertiolecta* and *Tetraselmis suecica* expressed high carbon mitigation potentials as they demonstrated good growth rates, biomass productivity, and ease of harvesting despite both having lower carbon contents than *Pavlova lutheri* and *Nannochloris atomus*.

Introduction

Concerns over global warming and carbon emissions have sparked interest in methods of sequestering carbon which has been released through the burning of fossil fuels. Human activity is already directly and indirectly affecting almost half of the terrestrial biological carbon cycle (Hughes & Benemann, 1997). If this cycle were properly managed, it could be a major contributor to the mitigation of CO_2 (Hughes & Benemann, 1997). A large fraction of the anthropogenic carbon dioxide (CO_2) emissions results from the combustion of fossil fuels for energy production. With energy needs increasing, especially in the emerging economies of the developing world, CO_2 emissions are expected to rise considerably in the coming years (Kessel, 2000). Meeting energy demands without high emissions will require stringent management of CO_2 including the use of post combustion carbon sequestration. Biological carbon mitigation (BCM) is the process whereby autotrophic organisms and plants convert this CO_2 into organic carbon through photosynthesis producing large amounts of biomass (Stephan et al., 2001). All biological media contain carbon and the major stores of carbon can be found in vegetation (e.g. forestry), soils (e.g. peat), as well as a large portion being sequestered over time naturally in the ocean (Lal, 2005; Raven & Falkowski, 1999; Worrall et al., 2010). Through photosynthesis and other metabolic pathways, carbon becomes incorporated into the cells of these organisms (Petela, 2008; Stephan et al., 2001). Careful management of the carbon cycle would ensure that biomass could be utilised for various commercial applications while ensuring sufficient carbon is stored in biological media, thereby maintaining safe levels of CO_2 in the atmosphere (IGBP Terrestial Carbon Working Group, 1998). Microalgae, with high photosynthetic efficiency and rapid growth rates, have shown great potential for this process of biological carbon mitigation. This study assessed the feasibility of cultivating micro-algae using CO_2 enhanced air streams to determine the rate of carbon mitigation. *Nannochloris atomus, Dunaliella tertiolecta, Tetraselmis suecica* and *Pavlova lutheri*, unicellular microalgal species, were selected and assessed for its potential to sequester carbon from a high concentration CO_2 source. Flue gases from point sources may contain up to 15% CO_2 and a direct relationship between CO_2 concentration and growth rate can be seen for many microalgal strains.

The objective of this study was to assess the feasibility of cultivating microalgae using CO_2 enhanced air streams and to assess the rate of carbon mitigation.

Materials and Methods

In this experiment microalgae were cultivated in 1L batch reactors (20cm x 10cm x 5cm, working volume 900ml) for a period of 9 days. A randomised single factorial experiment was employed with CO_2 concentration in the air stream (0%, 2%) as the independent variable. The strains of microalgae selected for this study were *Nannochloris atomus, Dunaliella tertiolecta, Tetraselmis suecica* and *Pavlova lutheri* which were sourced from the in the Scottish Association for Marine Science's culture collection (CCAP) (Argyll, Scotland). These were kept in 300ml stock cultures and were stored at $20^{o}C$ under constant illumination from fluorescent lights. At the start of the trials the 300ml stock culture of each strain was transferred to 600ml of f/2 medium in separate culture flasks. f/2 medium is a general enriched seawater medium created by Guillare, 1975. The flasks were positioned in a growth chamber with climate control (KBWF 240, Binder Gmbh, Germany). Using the APT-$COM^{TM}3$ (Binder Gmbh) data control system, the temperature was set at $23^{o}C$ while light provided by fluorescent lamps was set on an 18/6, light/dark photo period. Light intensity was approximately $200\mu mol.m^{-2}.s^{-1}$ at the surface of the culture flask. pH was monitored using an Orion 5 Star series pH meter. Air enhanced with CO_2 was bubbled through each of the 1L flasks at a rate of 0.45 $L.min^{-1}$. The various levels of CO_2 were achieved using a KM 20-2ME gas mixer (Witt-gasetcchnik, Germany) with which the desired output of CO_2 concentration may be selected by mixing compressed CO_2 and air sources. The CO_2 level in the air was verified using a CO_2 gas analyser (5200 Multipurpose, Servomex, UK). The algae were sampled 3 times daily and cell counts were taken using a haemocytometer to assess growth. The data collected from the cell counts was used to produce growth curves and calculate biomass production rates for each trial. The total biomass dry weight was also determined daily by extracting 5ml of sample and passing it through a 1.2µm retention glass microfiber filter. This is followed by 5ml of ammonium formate (0.5 M) to dissolve the salts in f/2 medium without damaging the cells. Ammonium formate does not leave any residues as it decomposes to volatile compounds during the drying process. The microfiber filters were then dried at $105^{o}C$ for 24hr in the oven and then reweighed to give the biomass dry weight. On day 9 each batch was centrifuged and washed to remove the seawater. The remaining pellet of biomass was then dried in the oven at $105^{o}C$ for 24hrs. The total carbon (TC) content of each culture was the assessed in triplicate at the end of the trial using a carbon analyser (Primacs[slc] TOC analyser (CS22) Skalar, Netherlands)

Results and Discussion

The dried algal mass was used to calculate total biomass production as well as biomass productivity (P) in the exponential phase of growth (Table 1). Comparing this with the carbon content (% carbon), the CO_2 mitigation rate of each strain in the exponential stage of growth may be calculated (Table 1).

The cell counts in the exponential phase of growth were used to calculate the specific growth rate, μ_{max} (d^{-1}). From this the doubling time (t_d) could also be calculated (Table 1). The CO_2 mitigation rate was calculated using the carbon content of the produced biomass and the dry biomass productivity in the exponential phase of growth. Three of the microalgal strains grew more effectively in the trials where air enhanced with CO_2 was bubbled through the cultures while the fourth, *Pavlova lutheri,* which has a long lag phase and low overall productivity, grew better in air (Figure 1). *Nannochloris atomus* achieved the highest biomass productivity while *Tetraselmis suecica* had a greater overall biomass production (Table 1).

Table 1: Carbon mitigation and growth productivity of selected microalgae bubbled with air containing 2% added CO_2

Microalgal strain	Specific growth rate $\mu_{max} (d^{-1})$	Biomass productivity (P) $(g.L^{-1}.day^{-1})$	Total biomass production $(g.L^{-1})$	Carbon content (%)	CO_2 mitigation rate $(g.L^{-1}.day^{-1})$
Nannochloris atomus	0.53	0.598	0.211	52.4	0.313
Dunaliella tertiolecta	0.43	0.579	0.312	43.9	0.254
Tetraselmis suecica	1.01	0.399	0.407	44.9	0.179
Pavlova lutheri	0.60	0.143	0.146	45.2	0.065

Nannochloris atomus has a high carbon content and a high biomass productivity which gave it the highest carbon mitigation rate (Table 1). However, it proved most difficult to harvest via centrifugation due to the small cell size. *Dunaliella tertiolecta* and *Tetraselmis suecica* expressed high carbon mitigation potentials as they demonstrated both good growth rates and biomass productivity despite having a lower carbon content than *Pavlova lutheri* and *Nannochloris atomus*.
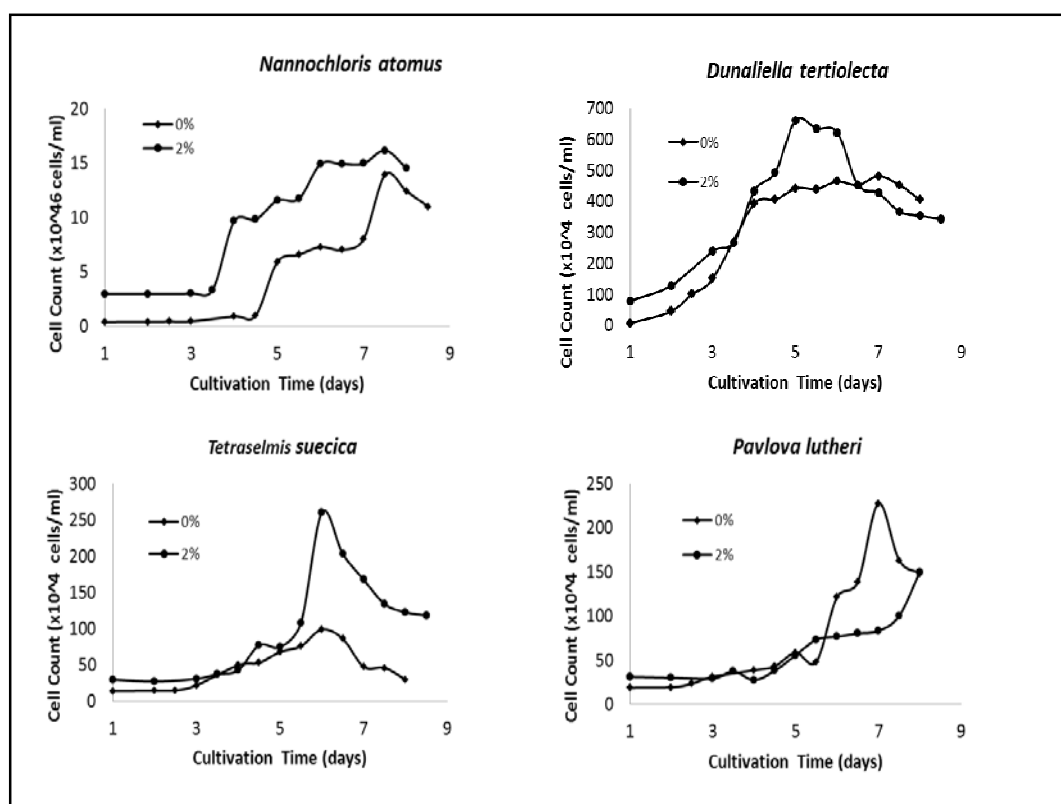
Figure 1: Growth of selected microalgae in a batch reactor

Conclusions

The results of this experiment support the use of microalgae for biological carbon mitigation of CO_2 from point sources. This has been established due to their proven ability to grow more effectively in elevated CO_2 air streams as well as their determined high carbon mitigation rates. Microalgae also demonstrate the potential to create valuable by-products from produced

biomass which may offset the cost of biological carbon mitigation. Following on from the findings in this research further testing may be carried out on the selected strains to determine optimum conditions for growth while maximising the CO_2 mitigation rate.

Acknowledgements

References

Hughes, E., Benemann, J.R. 1997. Biological fossil CO_2 mitigation. *Energy Conversion and Management*, **38**(Supplement 1), S467-S473.

IGBP Terrestial Carbon Working Group. 1998. The Terrestrial Carbon Cycle: Implications for the Kyoto Protocol. *Science*, **280**(5368), 1393-94.

Kessel, D.G. 2000. Global warming - facts, assessment, countermeasures. *Journal of Petroleum Science and Engineering*, **26**(1-4), 157-168.

Lal, R. 2005. Forest soils and carbon sequestration. *Forest Ecology and Management*, **220**(1-3), 242-258.

Petela, R. 2008. An approach to the exergy analysis of photosynthesis. *Solar Energy*, **82**(4), 311-328.

Raven, J.A., Falkowski, P.G. 1999. Oceanic sinks for atmospheric CO_2. *Plant, Cell and Environment*, **22**, 741-55.

Stephan, D.J., Shockey, R.E., Moe, T.A., Dorn, R. 2001. Carbon Dioxide Sequestering Using Microalgal Systems. US Department of Energy.

Worrall, F., Bell, M.J., Bhogal, A. 2010. Assessing the probability of carbon and greenhouse gas benefit from the management of peat soils. *Science of The Total Environment*, **408**(13), 2657-2666.

THE EFFECT OF HARVEST DATE ON THE COMBUSTION CHARACTERISTICS OF *MISCANTHUS GIGANTEUS*

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Abstract

The aim of this paper was to determine the effect of harvest time on the combustion quality of the biomass fuel. This research examines the effect of cutting date on the *Miscanthus* biomass. The *Miscanthus* samples were collected at different dates, namely January, February, March and April. The parameters examined in this experiment were GCV, NCV, ash, Cl, K, N S, C and H content. The range of values recorded for the various parameters from both aspects of this trial were as follows: GCV 18.18 – 18.51 MJ/kg; NCV 4.84 - 11.87 MJ/kg; ash 1.69 - 1.97%; Cl 0.07 - 0.27%; K 0.27 - 0.31%; N 0.32 - 0.39%; S 0.13 - 0.19%; C 47.56 - 50.00%; H 5.92 – 6.09%. Date of harvest affected the GCV, NCV, Cl and C content which all improved with later cutting dates. This proves choosing the correct harvest date impacts the biomass fuel quality.

Introduction

Increasing CO_2 levels in the atmosphere as a result of burning fossil fuels coupled with the depletion of fossil fuel reserves such as oil, coal and gas has led to an increase in popularity of biomass crops as a source of energy. *Miscanthus*, with its high yields of dry matter, possesses many of the attributes desired in an energy crop. These include high yields (10-25t/Ha) (Lewandowski et al., 2000), low moisture content (< 25 % mcwb) and favourable energy and chemical contents at harvest (Nolan et al., 2009).

Miscanthus harvesting previously took place in autumn however research has shown that delaying the harvest until spring results in a reduction in moisture content, ash and other chemical elements, improving the quality of the fuel (Lewandowski & Heinz, 2003). A low mineral content at harvest is desirable in biomass intended for thermal conversion because it minimises the impact on combustion efficiency and lowers stack emissions (Christian et al., 2008). Delaying the harvest of *Miscanthus* improves the combustion quality by reducing moisture content and by leaching undesirable biomass components. (Lewandowski & Heinz, 2003). The parameters under investigation in this research are gross calorific value (GCV), net calorific value (NCV), ash, chloride (Cl), potassium (K), nitrogen (N), sulphur (S), carbon (C) and hydrogen (H). These parameters effect the energy yield of the biomass (GCV and NCV), emissions (N, Cl and S) and ash melting point (K) and also lead to corrosion of boiler components if occurring in excessive concentrations (Lewandowski & Kicherer, 1997). This study aims to examine how the biomass quality varies over the course of the spring harvest window at different harvest dates.

The objective of this study was to determine the effect of harvest time on the energy, ash and chemical content of *Miscanthus giganteus* harvested during the spring harvest window.

Materials and Methods

Samples of *Miscanthus* used to determine the moisture content of the standing crop for a previous experiment in 2010 were used in this experiment. The dried *Miscanthus* samples were prepared for analysis as per CEN TS14780 (CEN, 2005a). The calorific value was determined using CEN TS14918 (CEN, 2005b). The C, H and S concentrations of the

Miscanthus samples were established using CEN TS15104 (CEN, 2005c). The content of ash in the *Miscanthus* was established as per CEN TS 14775 (CEN, 2004). Chloride concentrations of the *Miscanthus* samples were ascertained according to CEN TS 15289 (CEN, 2006). The N content of the *Miscanthus* was determined in accordance with the standard CEN TS 15104 (CEN, 2005c). The K concentration of the *Miscanthus* was ascertained by using atomic absorption spectrometry. The leaf and stem material were analysed separately. A combined value for all parameters was then determined by adjusting the results of the analysis to give a total composition relative to the overall harvested material combining leaf and stem.

The biomass material was taken from four different dates and analysed. The dates were January 14th (Group A), February 4th (Group B), March 4th (Group C) and April 8th (Group D).

Results and Discussion

No statistical difference ($p > 0.05$) was observed between cutting dates for ash content, K, N, S or H content. A mean ash content of 1.9% was observed for all cutting dates. Potassium content was also unaffected by cutting date where a mean K concentration of 0.3% was recorded. The mean N content for the duration of the trial was 0.35% while the mean H content was 6.0%. The parameters which were statistically different between treatments are summarised in table 1 below.

Table 1. Chemical properties of combined leaf and stem at four cutting dates in spring

			Group			
			A	**B**	**C**	**D**
	F stat	Sig.		Mean *(St. Dev.)*		
Date			*14 Jan*	*04 Feb*	*04 Mar*	*08 Apr*
M.C. (%)			62.2	60.4	40.9	27.7
GCV (MJ/Kg)	$F_{(3,15)} = 58.760$, p <0.001	***	18.18[A,B]	18.43[A,C,D]	18.27[D,E]	18.66[B,C,E]
			(±0.06)	(±0.05)	(±0.04)	(±0.07)
NCV (MJ/kg)	$F_{(3,15)} = 277.585$, p <0.001	***	4.84[A,B]	5.32[C,D]	9.00[A,C,E]	11.87[B,D,E]
			(±0.20)	(±0.36)	(±0.54)	(±0.42)
Cl (%)	$F_{(3,15)} = 71.087$, p <0.001	***	0.270[A,B,C]	0.225[A,D]	0.219[B,E]	0.072[C,D,E]
			(±0.03)	(±0.01)	(±0.03)	(±0.01)
C (%)	$F_{(3,15)} = 7.033$, p <0.01	***	49.63[A]	49.73[B]	50.00[C]	47.56[A,B,C]
			(±0.46)	(±0.80)	(±0.53)	(±1.32)

*Implies p-value >0.05, ** implies p-value >0.01, *** implies p-value >0.001, ns implies no significant difference between treatments. [A, B, C, D] implies significant difference between groups A, B, C and D.

A significant difference was observed between cutting dates for the following parameters: GCV, NCV, Cl, and C. Figure 1 shows the trend of each of these parameters over the course of the trial. The GCV of the material cut at different harvest dates was statistically different (p<0.001), delaying the harvest date was found to increase the GCV of the material. Material cut in January had a mean GCV of 18.18 MJ/kg.
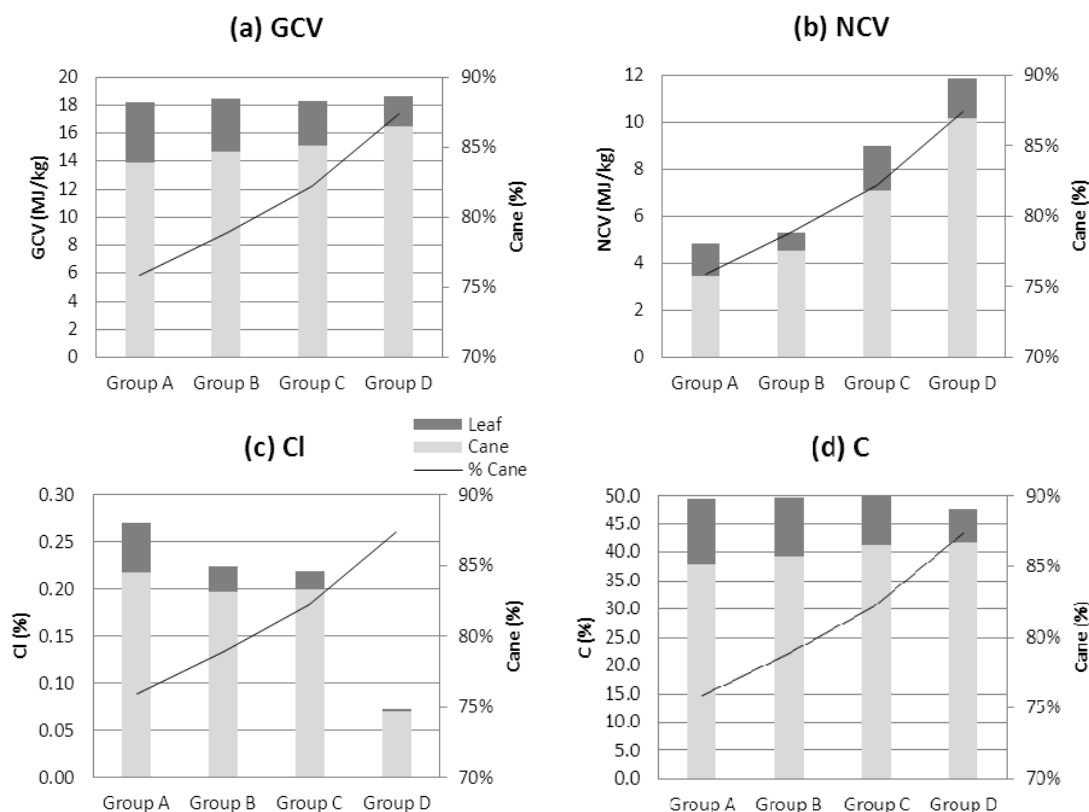
Figure 1. Influence of cutting date on GCV, NCV, Cl, and C trends and % leaf throughout the spring

Delaying the harvest date increased the GCV to the extent that the GCV of *Miscanthus* cut in April was 18.66 MJ/kg. This is illustrated in **Error! Reference source not found.**(a) GCV. The increase in GCV occurring over the course of the harvest window could be due to the reduction in the amount of leaf occurring in the sample. As leaf has a lower GCV than stem material, this leads to a higher proportion of stem material occurring per kg, therefore increasing the overall GCV of the sample.

Error! Reference source not found.(b) shows the increase in NCV over the course of the harvest window (p<0.001). An increase of 7 MJ/kg occurred in NCV between the months of January and April. This can be largely attributed to the reduction in moisture content which occurred over the same period, which reduced from 62% to 27%. This is of importance with respect to the quality of the fuel as it results in the fuel yielding more energy per tonne on a wet basis than fuel with a higher GCV which possesses a higher MC, therefore lowering the NCV of the fuel.

A considerable reduction in chloride content was also observed over the course of the trial (p<0.001). From an initial Cl content of 0.25%, the Cl content reduced to 0.22% after the first time interval (between Group A and Group B) and decreased further to 0.08% by the last cutting date (April 8th) as shown in **Error! Reference source not found.**(c). The reduction in Cl concentration occurring over the course of the harvest window could be attributed to leaching of Cl from the biomass material.

The carbon content of the biomass was also found to reduce over the course of the trial (p<0.001). A statistical difference was observed between Groups A and D, Groups B and D, and Groups C and D (p < 0.05). *Miscanthus* cut in April (Group D) had approximately 2%

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less C that material harvested at the earlier dates. An overall reduction in C content of approximately 2.5% occurred over this period as illustrated in Figure 1(d) C. Cutting the material earlier in the harvest window resulted in a higher biomass C content. There was no observed difference in the C content of *Miscanthus* harvested at the first three harvest dates, however all three harvest dates had a higher C content than material harvested at the last harvest interval.

Conclusion

It can be concluded from this study that the time at which the *Miscanthus* crop is harvested has a significant effect on biomass quality. While the reduction in moisture that is observed results in improving the storability of the material, it also increases the NCV of the biomass. An increase in GCV of the biomass results in an overall increase in energy obtained from the fuel. Reduced C and Cl content result in lower emissions from the material during the combustion process. Reducing the Cl content also reduces the risk of damage occurring to various components of the combustion equipment as a result of the formation of HCl during the combustion process. Therefore it can be determined that harvest time is of critical importance in terms of optimising biomass fuel quality.

Acknowledgements

References

CEN. 2004. CEN TS14775 Solid biofuels - Determination of ash content. Brussels.

CEN. 2005a. CEN TS14780 Solid biofuels - Methods for sample preparation. Brussels.

CEN. 2005b. CEN TS14918 Solid biofuels - Determination of calorific value. Brussels.

CEN. 2005c. CEN TS15104 Solid biofuels - Determination of total content of carbon, hydrogen and nitrogen - Instrumental methods. Brussels.

CEN. 2006. CEN TS 15289 Solid Biofuels - Determination of total content of sulphur and chlorine. Brussels.

Christian, D.G., Riche, A.B., Yates, N.E. 2008. Growth, yield and mineral content of Miscanthus × giganteus grown as a biofuel for 14 successive harvests. *Industrial Crops and Products*, **28**(3), 320-327.

Lewandowski, I., Clifton-Brown, J.C., Scurlock, J.M.O., Huisman, W. 2000. Miscanthus: European experience with a novel energy crop. *Biomass and Bioenergy*, **19**(4), 209-227.

Lewandowski, I., Heinz, A. 2003. Delayed harvest of miscanthus--influences on biomass quantity and quality and environmental impacts of energy production. *European Journal of Agronomy*, **19**(1), 45-63.

Lewandowski, I., Kicherer, A. 1997. Combustion quality of biomass: practical relevance and experiments to modify the biomass quality of Miscanthus x giganteus. *European Journal of Agronomy*, **6**(3-4), 163-177.

Nolan, A., Mc Donnell, K., Mc Siurtain, M., Carroll, J.P., Finnan, J., Rice, B. 2009. Conservation of miscanthus in bale form. *Biosystems Engineering*, **104**(3), 345-352.

FLUIDISED BED PYROLYSIS OF SPRUCE, *SALIX*, *MISCANTHUS*, AND WHEAT STRAW

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Abstract

Fast Pyrolysis is a thermal degradation process occurring in the absence of oxygen. The pyrolysis products of biomass are gas, char, and a liquid termed biooil. This paper describes fast pyrolysis of four Irish-grown biomasses on a continuously fed fluidised bed reactor (300g/h). Total biooil yields were 60.2 wt % (miscanthus), 64.9 wt % (Straw), 65.2 wt % (Salix), and 72.2 wt % (Spruce) on a dry feedstock basis. The water content of the biooils ranged between 14.94 % for spruce to 39.89 % for wheat straw, depending on the initial water content of the feedstock and the thermal decomposition pathways followed. The presence of alkali metals in the ash appeared to significantly decrease the amount of organic product in the biooil and increase the char yield and water content of the biooil. Chemical analysis via GC/MS indicated that the biomass constituents (cellulose, hemicellulose, and lignin) appeared to follow known decomposition pathways. Higher yields of acetic acid from the annual plants are likely to be due to relatively higher acetylation of the hemicellulose compared to softwoods and hardwoods. Preferential metal-catalysed carbonisation and dehydration reactions over depolymerisation was indicated by decreasing yields of levoglucosan and increasing yields of hydroxyacetaldehyde with increasing ash content.

Introduction

Fast Pyrolysis occurs under high temperature unpressurised conditions in the absence of oxygen. The traditional objective of the process has generally been to maximise the liquid biooil fraction. A typical fast pyrolysis product distribution from wood is 70 wt % biooil, 15% wt char and 15 wt % gas (on a dry basis), while biooil yields from agricultural residues are generally lower. On a commercial scale, it is generally envisaged that char and gas (or a fraction of the biooil) would be combusted to heat the reactor. It is recognised that temperatures ranging between 470-500°C maximise the biooil organic product for wood. A high heat transfer rate to the biomass is also critical for maximum biooil yields. Biooil can be directly combusted, or intensively upgraded to transport fuel-type liquids. Indeed, the pyrolysis reactions may be manipulated with catalysts and/or reactive gases (under high pressure) to produce a partially upgraded product. Fast pyrolysis has not yet been applied on a commercial scale, though several demonstration plants are operational. Upgrading technologies and modified fast pyrolysis processes are generally still at the laboratory scale (Butler et al., 2011b).

It is important to appreciate that the cell wall composition of biomass (lignin, cellulose and hemicelluloses) and the ash character have a significant influence on pyrolysis behaviour and composition of the biooil product.

The objective of this work is to compare the fast pyrolysis of Spruce, Short Rotation Willow Coppice, Miscanthus, and Wheat Straw and compare the composition of the biooil.

Materials and Methods

Feedstock preparation and preliminary analysis
Preliminary analysis of the various feedstocks included proximate and ultimate analysis, as well as cell wall composition. Knowledge of the cell wall composition is particularly useful as it facilitates tracing of the decomposition of the various components and how they relate to the composition of the pyrolysate. A description of the preliminary analysis employed here can be found in literature (Azeez et al., 2010).

Fluidised bed pyrolysis and biooil analysis
The fluidised bed pyrolysis system has previously been described (Butler et al., 2011a, Azeez et al., 2010). Approximately 250g of biomass (300-500µm) was fed over a one hour period and pyrolysed at a temperature of 470°C. After the experiment a partial mass balance was conducted. Three products were collected; char, biooil (collected from the first condenser at 0°C and the electrostatic precipitator) and a watery condensate fraction (collected from the second intensive condenser at -10°C). The biooil fraction was used for GC/MS analysis. A description of the method employed for GC/MS analysis and of the GC/MS system can be found in literature (Azeez et al., 2010).

Results and Discussion

Preliminary analysis of biomass
Tables 1 and 2 below illustrate the proximate and cell wall composition of the biomasses. The ash content is a critical parameter for the pyrolysis process and is highest in the annual plants (miscanthus and wheat straw). The lignin content of spruce is much higher than that of wheat straw.

Table 1: Proximate analysis of the four biomass feedstocks employed (mfb)

	spruce	willow	miscanthus	wheat straw
moisture	2.45	3.89	7.57	6.33
volatiles	76.6	84.1	70.0	69.3
ash	0.26	1.16	3.43	3.76
fixed carbon	23.1	14.7	24.2	26.9

Table 2 Macrocomposition of the four biomass feedstocks (mfb)

	spruce	willow	miscanthus	wheat straw
extractives	3.45	2.67	6.42	7.89
Klason lignin	27.73	22.5	21.4	15.96
hollocellulose	72.1	64.18	71.71	74
glucose	49.42	43.83	47.51	40.98
xylose	4.69	14.64	20.87	26.73
mannose	13.95	2.48	0.29	0.48
galactose	2.09	1.08	0.64	1.4
arabinose	1.34	0.9	1.86	3.68
rhamnose	0.11	0.38	0.13	0.29
cellibose	0.11	0.65	0.74	0.64
4-O-methyl-glucuronic acid	0.5	0.87	0.41	0.44

Pyrolysis Product Mass Balance and Basic Characterisation
The mass balance distribution is show in Table 3. Total biooil yield refers to the total amount of liquid collected, while the total dry organic yield refers to the biooil yield minus the water

content as measured by Karl Fischer Titration. Some general observations can be made on the product mass distributions, but it is difficult to attribute trends to one particular parameter since there are many variables in the system. Dry organic yields decreased and char generally increased with decreasing feedstock lignin content and increasing ash content. This trend has also been observed by other authors (Fahmi et al., 2008). Increased yields of pyrolysis water from spruce to straw may be attributed to catalytic cracking of pyrolysis vapour by alkali metals to char and gas. It is also important to note that the biooil from spruce and was much more homogenous than that of salix, miscanthus and wheat straw.

Table 3 Mass balance distribution and basic biooil characterisation [1]mfb [2]as % of dry biooil

	spruce	salix	miscanthus	straw
Char	11.4	16.2	21.8	21.5
Total liq. yield[1]	69.8	65.2	60.7	63.3
Total org. yield[1]	48.3	41.4	32.6	30,8
Biooil Fraction[2]				
Yield	49.0	48.9	42.4	38.7
Water content	15.3	25.8	34.7	36.1
Solids	0.12	0.34	0.38	na
Pyrolytic Lignin	17.5	15.1	15.7	7.0

Chemical analysis of the biooil

Taking into consideration the proximate analysis and cell wall composition of the biomasses, pyrolytic decomposition appears to follow known degradation pathways. The increasing concentration of acetic acid from spruce (softwood) to willow (hardwood) to miscanthus and straw (both annual plants) is likely to be due to the relatively higher portion of acetylation of the hemicellulose molecules. While the composition of the biomass lignin was not examined, the relative portions of phenols, guaiacols and syringols correspond to those generally known to be contained in the various biomass types. For example hardwood lignins typically contain Guaiacyl-Syringyl units, whereas Guaicyl units predominate in softwoods.

Table 4 Selection of 10 Major Compounds in the biooils. Values are reported as % of dry biooil.

	spruce	salix	miscanthus	straw
Acetic Acid	2.93	8.55	8.90	9.30
Acetaldehyde, hydroxy	12.82	9.70	8.04	9.35
Acetol	3.12	4.15	6.83	8.63
1-hydroxy-2, Butanone,	0.20	0.35	0.96	1.38
2-hydroxy-1-methyl-1,	0.87	1.42	2.85	3.11
Cyclopenten-3-one,				
2 (5H)-Furanone,	0.69	0.88	0.79	0.84
5-(hydroxymethyl)-Furaldehyde	0.39	0.10	0.08	0.07
4-vinyl Phenol	-	-	1.29	0.27
4-vinyl Guaiacol	0.28	0.13	0.66	0.77
Levoglucosan	4.95	2.13	1.33	1.12

No syringol compounds were detected in spruce biooil, while syringol compounds totalled 2.66 wt% in willow biooil. Syringol compounds amounted to slightly less in miscanthus (1.80 wt%) and wheat straw (1.45 wt%). Guaiacol compounds were maximum in spruce (4.14 wt%) followed by miscanthus (2.84 wt%), wheat straw (2.38 wt%) and least in willow biooil (2.84 wt%). Phenol compounds were maximum in miscanthus (2.57 wt%), mainly due to the

presence of 4-vinyl Phenol. Also observed here is the commonly observed inverse relationship between levoglucosan and hydroxyacetaldehyde, though to be due to preferential decomposition of cellulose to char and gas in the presence of alkali metals over depolymerisation to levoglucosan.

Conclusions

The yield of liquid organic product by fluidised bed pyrolysis ranged between 48.3 wt% for spruce to 30.8 wt% for wheat straw. The presence of ash appeared to have a significant effect on steering the decomposition pathway from levoglucosan to less desirable products like char, gas and water. The compound 4-vinyl phenol was present in a significant amount in the annual plants 1.29 wt% in miscanthus and 0.77 wt% in wheat straw, but not in spruce or willow biooil. The inhomogeneity of the oil from wheat straw may be a problem for further applications.

References

Azeez, A. M., Meier, D., O'Dermatt, J. & Willner, T. 2010. Fast Pyrolysis of African and European Lignocellulosic Biomasses Using Py-GC/MS and Fluidized Bed Reactor. *Energy & Fuels,* 24**,** 2078-2085.

Butler, E., Devlin, G., McDonnell, K. & Meier, D. 2011a. Fluidised bed pyrolysis of Irish biomasses for fuel and chemical production. *In:* Curran, T. & Cummins, E. (eds.) *Biosystems Engineering Research Review 15.* Dublin.

Butler, E., Devlin, G., Meier, D. & McDonnell, K. 2011b. A review of recent laboratory research and commercial developments in fast pyrolysis and upgrading. *Renewable and Sustainable Energy Reviews,* 15**,** 4171-4186.

Fahmi, R., Bridgwater, A. V., Donnison, I., Yates, N. & Jones, J. M. 2008. The effect of lignin and inorganic species in biomass on pyrolysis oil yields, quality and stability. *Fuel,* 87**,** 1230-1240.

THE INFLUENCE OF TYRE INFLATION PRESSURE OF HARVEST MACHINERY ON SOIL COMPACTION AND CROP RE-GROWTH IN MISCANTHUS

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Abstract

An experiment was conducted in April 2009 in which the stubble of a mature Miscanthus crop was trafficked twice with heavy axle loads at high tyre inflation pressure (HP) and low tyre inflation pressure (LP). The trial was then monitored in 2009, 2010 and 2011 in order to determine the effects of this once-off traffic event on soil compaction and crop re-growth. Soil penetration resistance (SPR) was measured to assess the level of soil compaction. Crop re-growth was assessed throughout each growing season by monitoring stem numbers and stem height. The crop was harvested in October and March each year to assess the trafficked zone biomass yield and overall stem yield respectively. SPR values were very high in all treatments, including the control, at all depths. Stem numbers, stem height, biomass yield and stem yield were all lower, though not statistically significant, in plots trafficked at high tyre inflation pressure when compared to plots trafficked at low tyre inflation pressure and the control plots (no experimental traffic).

Introduction

Miscanthus *x giganteus* is a woody rhizomatous C_4 grass species that yields high quality material for both energy and fibre production (Jones and Walsh, 2007). Harvesting can be done by using mowing, baling and chopping machines for some building material applications and for energy and paper pulp use (Venturi et al., 1998). Economic pressure favours the continuous increase of machinery power, vehicle weight and implement size (Alakukku et al., 2003) but as vehicles have become progressively larger, they have also increased in their ability to damage the very medium that is responsible for producing and supporting agricultural crops (Raper, 2005); soil compaction may be the most devastating effect of vehicle traffic. Alakukku (1996) reported that four passes on the same location compacted a clay soil to 0.5 m depth. Penetrometer resistance was 22% to 25% greater in the compacted plots when compared to control plots (no experimental traffic). Optimum crop yields are dependent upon root growth, which is highly affected by soil compaction (Abu-Hamdeh, 2003). Taylor, (1971) found that the ability of plant roots to penetrate soil is restricted as soil strength increases and ceases entirely at 2.5 megapascals (MPa). Forristal (2003) stated that crop response to soil compaction is variable and influenced by many factors, including crop type, soil type, degree of compaction and moisture status during the growing season. In a UK study that assessed the effects of Miscanthus harvest machinery, Nixon and Hilton (2006) reported that there was no significant effect on crop re-growth where land had been trafficked by tractor and machinery wheels, however, soil compaction was slightly higher.

The objective of this research was to investigate the influence of harvest traffic, operating at high tyre inflation pressure and at low tyre inflation pressure, on soil compaction and crop re-growth in a mature Miscanthus x *giganteus* crop in Ireland.

Materials and Methods

Experiments were conducted at the Teagasc Crops Research Centre, Oak Park. Co. Carlow in a mature (16 years established) Miscanthus crop. Experimental plots were arranged in a randomised, complete block design with four replications. Each plot measured 3.00 metres wide and 3.30 metres long. The equipment used in this experiment consisted of a tractor with a till-and-sow combination unit (power harrow and pneumatic seeder) mounted on the rear three-point-linkage. This gave an axle load of 8.310 tonne on the rear of the tractor. The experiment consisted of three treatments:

1.   Control – No traffic
2.   Trafficking (two passes) at High Tyre Inflation Pressure – 2.5 bar.
3.   Trafficking (two passes) at Low Tyre Inflation Pressure – 1.6 bar.

Electronic weighpads were used to measure the static axle loads of the tractor used in this experiment. Tyre inflation pressures were adjusted based on the tyre manufacturers' recommendations for the individual axle load at a road/transport speed of 40 kph (2.5 bar) and at a field/work speed of 10 kph (1.6 bar). Soil penetration resistance was measured using an Eijkelkamp Penetrologger in all plots. Crop re-growth was assessed on a weekly basis throughout the growing season by monitoring stem numbers and stem height in sample areas that had been trafficked in each plot. These sample areas were harvested in late October 2009-2011 in order to assess trafficked zone biomass yield. The remainder of the plots were harvested each Spring to assess overall stem yield. All data was analysed by means of a one-way analysis of variance (ANOVA) using MINITAB 15 (Minitab® Statistical Software). Significance was set at the 5% level.

Results and Discussion

There was very little difference in SPR values across all treatments including the control in the three years of assessment (Figures 1, 2 and 3). Values of 2 MPa were recorded at a depth of 10 cm, increasing to 3 MPa at 20 cm deep and 3.5 MPa at 30 cm deep. All these values are likely to impede or prevent root growth (Taylor, 1971)
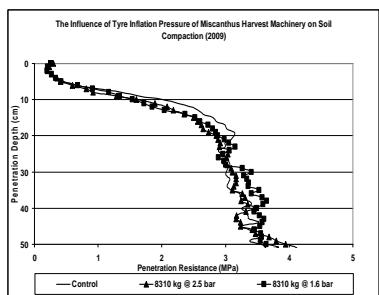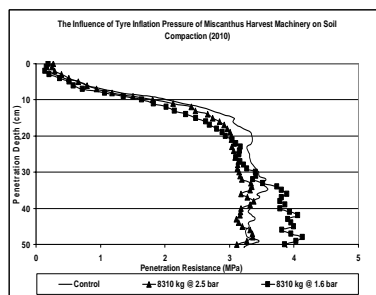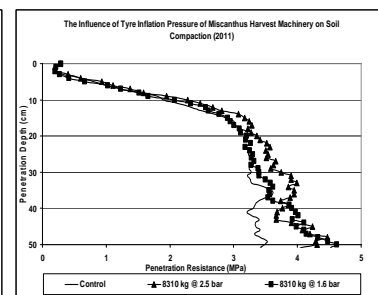

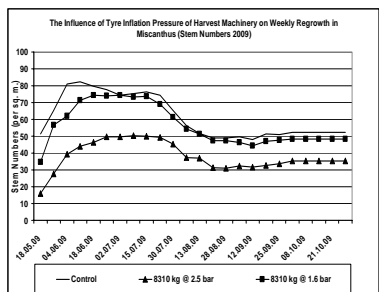**Figure 1:** SPR 2009   **Figure 2:** SPR 2010   **Figure 3:** SPR 2011
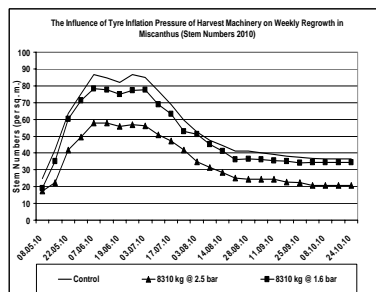
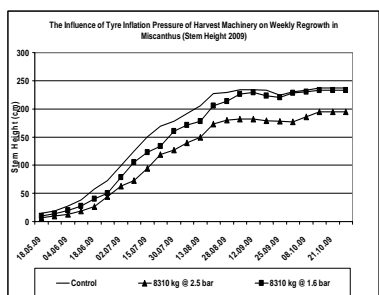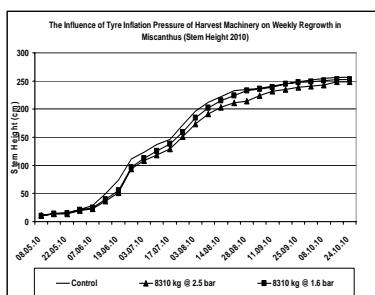**Figure 4:** St No. 2009   **Figure 5:** St No. 2010   **Figure 6:** St No. 2011

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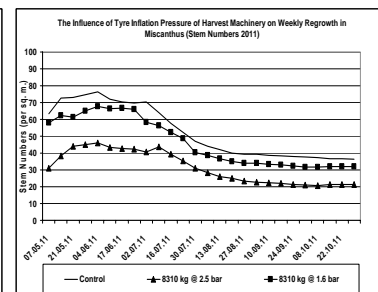
Figure 7: St Ht 2009   **Figure 8:** St Ht 2010   **Figure 9:** St Ht 2011
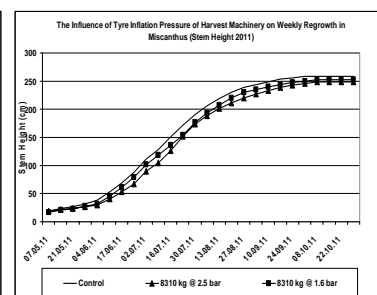
Crop re-growth results show (a) average stem numbers per square metre and (b) average stem height. Stem numbers (St No.) were substantially lower in HP plots when compared to LP plots and the untrafficked control (UC) plots in 2009, 2010 and 2011 (Figures. 4, 5 and 6). Similarly, stem heights (St Ht) were substantially lower in the HP plots when compared to the LP plots and the UC plots in 2009 (Figure 7). However, in 2010 and 2011 there was very little difference between all three treatments (Figures 8 and 9).

Crop yield results show (a) total biomass in the trafficked zones of plots at the end of the growing season and (b) overall stem yield at harvest. Trafficked zone biomass yield (TBY) was substantially lower in HP plots when compared to LP plots and the UC plots in 2009, 2010 and 2011 (Figures 10, 11 and 12). Similarly, overall stem yield (OSY) was substantially lower in HP plots when compared to LP plots and the UC plots in 2009, 2010 and 2011 (Figures 13, 14 and 15).
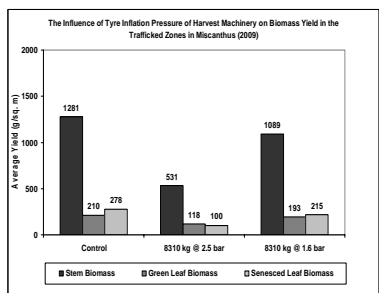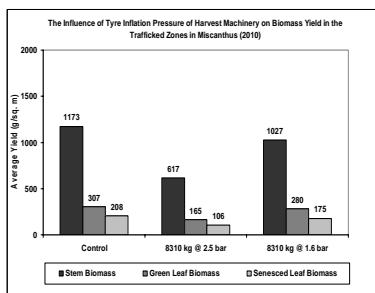
Figure 10: TBY 2009   **Figure 11:** TBY 2010   **Figure 12:** TBY 2011
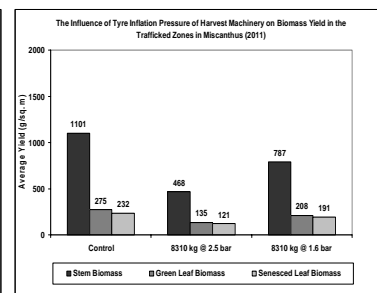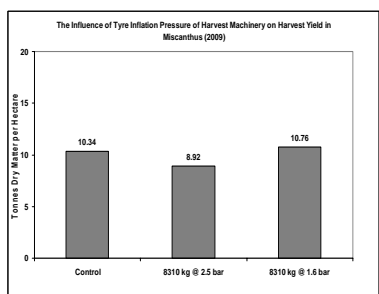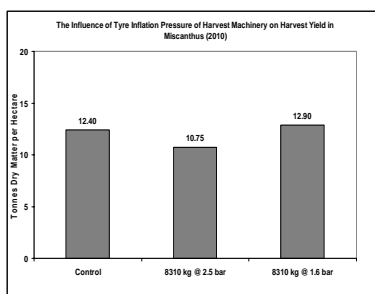
Figure 13: OSY 2009   **Figure 14:** OSY 2010   **Figure 15:** OSY 2011

Conclusions

Soil was very compact in all treatments including the control in 2009 when the trafficking took place and in subsequent years. With the untrafficked control plots showing very high SPR values it must be concluded that the soil was in a very compact condition in advance of conducting this

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experiment and the treatments applied did not increase compaction. The high SPR values were probably caused by natural consolidation and harvest traffic in the preceding years since the crop was sown in 1993. Re-growth results suggest that trafficking at high tyre inflation pressure negatively impacts stem numbers in the year of trafficking and in subsequent years with a consequent reduction in crop yield. Stem height was negatively impacted in the year of trafficking but this was not found in subsequent years. Trafficking at low tyre inflation pressure had very little impact on stem numbers and stem height and as a consequence crop yield showed no negative impact when compared to the control in any given year. Since machinery must be used to harvest the crop, it must then be logical to operate it with reduced tyre inflation pressure in order to prevent yield reductions. It should also be noted that even in a very compact soil condition, Miscanthus has an ability to grow and produce stem yields of approximately 15 tonne/ha dry matter in years when growing conditions are favourable.

Acknowledgements

References

Abu-Hamdeh NH, 2003. Soil compaction and root distribution for okra as affected by tillage and vehicle parameters. Soil and Tillage Research 74:25-35.

Alakukku L, 1996. Persistence of soil compaction due to high axle load traffic. I. Short-term effects on the properties of clay and organic soils. Soil and Tillage Research 37:211-222.

Alakukku L, Weisskopf P, Chamen WCT, Tijink FGJ, van der Linden JP, Pires S, Sommer C, Spoor G, 2003. Prevention strategies for field traffic-induced subsoil compaction: a review: Part 1. Machine/soil interactions. Soil and Tillage Research 73:145-160.
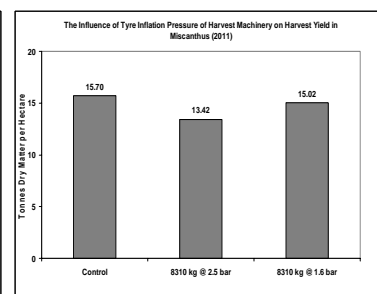
Forristal D, 2003. Machinery, Tyres and the Soil. In: National Tillage Conference (Ireland): Teagasc.

Jones MB, Walsh M, 2007. Miscanthus for Energy and Fibre. London: Earthscan.

Nixon P, Hilton B, 2006. Optimisation of Miscanthus Harvesting and Storage Strategies. Report for Future Energy Solutions: FES B/CR/00797/00/REP.

Raper RL, 2005. Agricultural traffic impacts on soil. Journal of Terramechanics 42:259-280.

Taylor HM, 1971. Effect of soil strength on seedling emergence, root growth and crop yield. In: Compaction of Agricultural Soils (Barnes KK, ed). St. Joseph, Michigan: ASAE; 292–305.

Venturi P, Huisman W, Molenaar J, 1998. Mechanization and Costs of Primary Production Chains for Miscanthus x giganteus in The Netherlands. Journal of Agricultural Engineering Research 69:209-215.

OPTIMISING POINT SOURCE CO_2 MITIGATION BY MICROALGAE USING NEAR-INFRARED SPECTROSCOPY

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Abstract

Climate change as a result of rising anthropogenic CO_2 levels is an issue of increasing concern. There are a number of mitigation options available, but the focus here is placed clearly on the use of microalgae to combat this problem. This study took 3 replicates of *Nannochloropsis oculata* from laboratory cultures for 3 trials at CO_2 levels of 2, 4 and 6% to determine any correlations between haemocytometric cell counts and near-infrared measurements for biomass density. Results indicate that the best partial least squares model for predicting cell counts was from NIR transmittance spectra pre-treated using standard normal variant and Savitsky-Golay 1st derivative. This model had a coefficient of determination (R^2) value of 0.79 and a root mean square error of cross validation of 434409, with a range of cell counts from 452,500 cells ml^{-1} to 3,710,000 cells ml^{-1}. The R^2 value between the colour measurements and the cell counts showed less promise, ranging from 0.01 to 0.08.

Introduction

In order to minimise the effects of climate change it is necessary to implement mitigation strategies such as increasing energy efficiency of existing and new technologies, increasing the use of CO_2 neutral renewable energies, and most importantly in the context of this study, increasing the use of CO_2 mitigation strategies for point source emitters (Bernard, 2011). Such strategies are underpinned by government and non-governmental organisation (NGO) policies, incentives and legislation to drive forward the adoption of clean energy technologies. For example, the Kyoto Protocol (1997), an international agreement, set out an agreed upon target to reduce CO_2 emissions by 5.2% based on the 1990 levels, through these methods discussed. The area of using microalgae for both carbon mitigation as well as a renewable energy source (through liquid biofuel conversion) has become a growing sector in recent decades as one such strategy to meet the above objectives (Bernard, 2011). Through photosynthesis, microalgae can incorporate inorganic carbon, primarily in the form of CO_2, thus have the potential to reduce or at a minimum impede the rise of the atmospheric levels of this greenhouse gas (Bernard, 2011). The purpose of this study was to assess the potential of a technique, near infrared (NIR) spectroscopy, to be employed as an on-line sensing technology during microalgal CO_2 mitigation and thus may provide further valuable information to this area. Hence, by investigating if there are any correlations between these NIR measurements and the traditional haemocytometric cell counts; it could be possible to verify the feasibility of this technique, which offers online, real-time information and a higher throughput of samples at a low cost (Bellon-Maurel & McBratney, 2011). Correlations between colour parameters and the cell counts were also investigated.

The aim of this study was to determine the potential of using near-infrared spectroscopy and colour parameters to predict the cell density of *Nannochloropsis oculata* cultures.

Materials and Methods

Experimental Design
The experimental design was to culture three replicates of *Nannochloropsis oculata* under laboratory conditions for a number of trials within a given trial time period of seven days. The

conditions undertaken were decided upon through the use of preliminary trials. Samples of these cultures were taken daily to measure the cell counts as well as the NIR transmittance, reflectance and colour data.

Sample Preparation
Samples of the species *Nannochloropsis oculata* were taken for use in the experimental trials. Cultures were grown at laboratory scale and established from a pure stock culture. For the maintenance and cultivation of the samples, f/2 medium (Guillard & Ryther, 1963) was used, consisting of sodium nitrate, sodium dihydrogen phosphate, trace metals and vitamin solutions. The media was added to 20 µm filtered and UV treated seawater. Each glass culture flask contained 700 ml of the f/2 medium which was then inoculated with 200 ml of concentrated algae (1 x 10^6 cells ml^{-1}). For the trials, inoculum of the *Nannochloropsis oculata* was acclimatized to the experimental conditions, including carbon dioxide, by maintaining them for 3 days under air mixed with carbon dioxide to the specified % (v/v) that was to be used in each given trial.

Reaction Vessels & Culture Conditions
Strains of the *Nannochloropsis oculata* were cultured in three 1 L clear glass culture flasks with three entry and exit tubes for air flow and sampling. All equipment was autoclaved before trials to sterilise it prior to inoculation with algae. The cultures were set up separately under environmentally controlled conditions in the laboratory growth chamber. All environmental parameters including light, temperature, pH and air flow rate were kept constant. The growth chamber used was a Binder GmbH KBWF 240 growth chamber, allowing program control of climate and illumination. Aeration was carried out via the use of a compressed CO_2 cylinder and air mixer connected to the vessels, with the effluent air being released externally from the growth chamber. Flow rate was set by a MR3000 flow meter at a rate of 0.5 L min^{-1} L^{-1} media. The air was filtered to 5 µm by sterile air filter units. The chamber was maintained at a constant temperature of 23°C, at which this mesophillic strain thrives, with a light/dark period of 18/6 hour intervals from fluorescent light tubes present in the growth chamber, placed at an approximate distance of 5 cm from the culture flasks. Lux was approximately 200 µmol m^{-2} s^{-1}, during the light period. pH was kept between 7.5 and 8 also for optimal growth conditions. Three different trials were carried out at controlled levels of CO_2 2, 4 and 6%, as a percentage of the influent air. Preliminary trials were carried out beforehand and found that a 3 day acclimatization period was sufficient, followed by the trials being run over a 5 day period.

Cell Counts
Triplicate samples (one from each culture vessel) were taken aseptically every 24 hours over the trial period and cell counts were determined by use of a microscope and haemocytometer. The haemocytometer was cleaned with ethanol and set up with the coverslip for each sample followed by 20 µl of the cell suspension then being placed on the slide to be observed. Viewed under the microscopes 10x objective lens, the cell counts were taken from the 4 corner 4 x 4 grids consecutively, using a hand tally counter. Necessary dilutions had to be made for some of the samples to ensure viable counts could be carried out. These dilutions were subsequently carried out with ethanol. The cell density of each of the samples was then determined by the following equation (Strober, 2001):

Cell Density / ml = Dilution Factor x 10^4 x (Count1 + Count2 + Count3 + Count4) / 4

NIR Measurements
NIR spectra were collected at the same time as the corresponding cell counts i.e. every 24 hours throughout the trial. A temperature controlled sample cell was designed and constructed at the University of Kentucky (Lexington, KY, USA) which allowed for the recording of sidescatter, reflection and transmission spectra (300 nm to 1100 nm). Light from a tungsten halogen light source was transmitted through a fibre optic cable into the sample cell. The side

scattered, reflected, and transmitted light responses were then collected and transmitted through fibre optic cables to a miniature spectrometer (model HR2000CG-UV-NIR, Ocean Optics B.V., Duiven, Netherlands). The sample cell was connected to a water bath to maintain a 35°C temperature. Spectral data and colour parameters were recorded using SpectraSuite software (v.6.1, Ocean Optics). 10 replicates of each sample were recorded using the SpectraSuite software and the means determined.

Data Analysis

Analysis of the spectral data was carried out with The Unscrambler software package (v.10, Camo, Norway). An average of 10 spectral scans was used in analysis. Spectral ranges were cut to a useful range of 350 to 1050 nm. The data set was subjected to a number of pre-treatments to reduce signal noise. These treatments included standard normal variant (SNV) and 1st and 2nd derivative steps. Combination treatments were also applied. Partial least squares regression was carried out on this data to develop prediction models. A full cross validation was carried out on the data set (n = 60). Root mean square error of cross validation (RMSECV) was determined for the validation models.

The accuracy of each of the models was then assessed using the coefficient of determination (R^2) and range error ratio (RER) between predicted and measured values (Williams, 2003). The RER is the value taken from dividing the RMSECV values by the range of the cell count values, in this instance. RER values less than 6 indicate poor classification status, 7 - 20 indicate poor to fair status and these models may be used in screening applications, while over 21 shows a good classification and are suitable in quality control operations (Fagan *et al*., 2007).

Results and Discussion

Intensity peaks for *Nannochloropsis oculata* were observed at 641 nm and 712 nm from both transmittance and reflectance measurements. All prediction models were tabularised and compared, with raw data model for reflectance NIR showing the best predictive results, giving an R^2 value of 0.79, shown above in Figure 1, and an RER of 7.89.
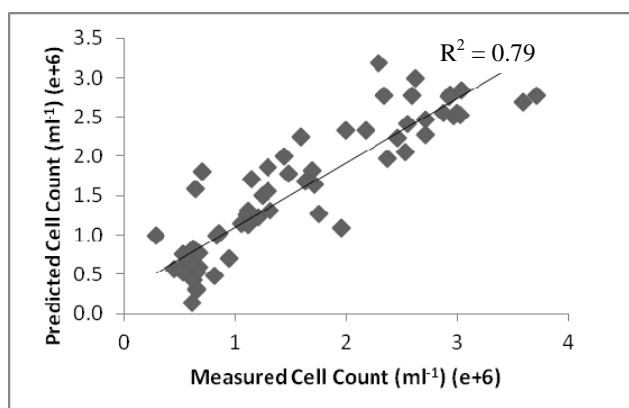
Figure 1. Linear regression plot of predicted versus actual cell counts (ml^{-1}) for the *Nannochloropsis oculata* reflectance data set.

The best transmittance model, treated with standard normal variant (SNV) and 1st derivative (13 smoothing points using the Savitsky-Golay method), gave an R^2 value of 0.79 and an RER value of 7.88. Therefore the best overall model for predicting cell counts from those calculated may appear to be the untreated (raw data) reflectance NIR model. However, the transmittance model, 2nd derivative (37 smoothing points), could be a more appropriate choice, being more robust, having good R^2 and RER values and accounting for a substantial amount of the variance (Table 1). While these results are adequate they are still below the top values reported in other studies (Lieve *et al*., 2011). While it has been shown in other studies

(Cordoba-Matson *et al*., 2010) that colour measurements can be correlated to cell density, those measurements which have been looked at in this study have shown to be independent of cell density.

Table 1. Summary of partial least squares regression (PLS) prediction results for cell counts, from 60 samples.

Treatment[a]	RMSECV	R^2	L[b]	Variance[c]		RER
				X	Y	
Raw Data (R)	433805	0.79	9	100	99	7.89
2der37 (T)	454243	0.77	4	98	88	7.53
Standard normal variant (SNV) 1der13 (T)	434409	0.79	4	98	90	7.88

[a] Key for parameters: R = Reflectance; T = Transmittance; 2der37 = 2nd derivative treated, 37 smoothing points using Savitsky-Golay method; 1der13 = 1st derivative treated, 13 smoothing points using Savitsky-Golay method.
[b] Number of loadings.
[c] % Explained variance using L for X (spectra) and Y (reference data).

Conclusions

The NIR measurements show "poor to fair" prediction models for cell counts. The models calculated in this study are suited to screening applications but are not sufficient for more accurate predictions. This study shows some basis for using NIR spectroscopy for quantitative estimations of microalgal biomass. This was a small scale study; however it does show the potential of using NIR spectroscopy as a rapid on-line system for cell density prediction. A more comprehensive sampling effort over a longer period of time and with more replicates is needed. Further studies should include increasing sample and treatment sizes, as well as using different strains of algae.

References

Bellon-Maurel, V., McBratney, A. (2011) Near-infrared (NIR) and mid-infrared (MIR) spectroscopic techniques for assessing the amount of carbon stock in soils - Critical review and research perspectives, *Soil Biology & Biochemistry* 43, 1398-1410.

Bernard, O. (2011) Hurdles and challenges for modelling and control of microalgae for CO2 mitigation and biofuel production, *Journal of Process Control* 21(10), 1378-1389.

Córdoba-Matson, M.V., Gutiérrez, J., Porta-Gándara, M.A. (2010) Evaluation of *Isochrysis galbana* (clone T-ISO) cell numbers by digital image analysis of colour intensity, *J Appl Phycol* 427–434.

Fagan, C.C., Everard, C., O'Donnell, C.P., Downey, G., Sheehan, E.M., Delahunty, C.M., O'Callaghan, D.J. (2007) Evaluating mid-infrared spectroscopy as a new technique for predicting sensory texture attributes of processed cheese. *Journal of Dairy Science* 90, 1122–1132.

Gulllard, R., Ryther, J. (1963) Studies on marine planktonic diatoms. I. *Cyclotella nana* Husted and *Detonula confervacea* Cleve. *Can J Microbiol* 8,229-239.

Lieve, M., Laurens, L., Wolfrum, J. (2011) Feasibility of Spectroscopic Characterization of Algal Lipids: Chemometric Correlation of NIR and FTIR Spectra with Exogenous Lipids in Algal Biomass, *Bioenerg. Res* 4, 22-35

Strober, W. (2001) Monitoring Cell Growth. In: Coligan J.E., Bierer, B.E., Margulies, D.H., Sherach, E.M., Strober, W. *Current Protocols in Immunology* vol. 5. USA: John Wiley & Sons.

Williams, P. C. (2003) Near-Infrared Technology – Getting the best out of light. A short course in the practical implementation of near infrared spectroscopy. 1.1 ed. Nanaimo, Canada.

THE VISUAL ASSESSMENT OF SOIL STRUCTURE UNDER DIFFERENT FIELD MANAGEMENT PRACTICES IN IRELAND

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Abstract

Finding simple, reliable and quick tools for assessing differences in soil quality resulting from different management practices is a concern for both scientists and land managers. Conventional methods for evaluating soil quality requires specific knowledge. Although the visual soil structure assessment method provides an easily understood and quick test for assessing soil structural quality, it has not been evaluated under a wide range of different management system, regardless of soil type, as a practical tool for assessing effect of management practices on soil quality. In this study, visual assessment of soil structure quality (VESS) was tested under different management systems for tillage and grass fields in order to indicate the validity of VESS for differentiating the effects of soil management practices on soil structure quality. Tillage sites were characterized based on type of tillage and crop cultivation, and pasture sites were classified according to intensity of management practices. The VESS method resulted in significant differences due to management system for both arable and pasture fields. Therefore, it could be a quick means of assessing the quality of soil structure as result of different management systems.

Introduction

Soil and crop management practices can enhance or reduce soil quality as a result of increase or decrease in soil productivity (Pankhurst et al., 2003; Ogle et al., 2012). Conventional methods for measuring soil properties and evaluating soil quality as result of different management practices requires specific knowledge and considerable time and money (Guimaras et al., 2011). Therefore finding simple, reliable and quick means to demonstrate the effect of management on soil quality is a concern for both scientists and land managers. In the past decades, visual methods for evaluating soil quality based on field assessment and measurements have been developed (Ball et al., 2007; Roger-Estrade et al., 2004). These methods provide an easily understood and quick test, which helps land managers make decision as part of their soil management system. Furthermore, they do not require particular knowledge and specific equipment to do visual methods, which provide a rapid, meaningful result. (Giarola et al., 2010). Peerlkamp (1959) introduced a visual soil structure assessment (VSSA) method that has been developed by Ball et al (2007). This method uses a chart of structural quality for a block of soil, which is extracted and manipulated, in order to distinguish key factors for classifying soil in five categories and to give it a score from 1 (good soil) to 5 (poor soil). Visual keys such as size, shape and appearance of aggregates, porosity, clustering, thickness and deflection of roots and difficulty in extracting the soil block are considered in VSSA method. The final grade is calculated by averaging the scores multiplied by the thickness of each layer in the soil (Ball et al., 2007). Visual soil structure assessment correlates well with measured soil physical properties and it may provide a quick and semi-quantitative evaluation of soil qualities and productivity (Mueller et al., 2009). Visual assessment of soil structure quality (VESS) has the potential for practical evaluation of soil physical quality of Oxisols in different tillage systems and it provides an appropriate technique to select a proper mechanical and biological management system in order to achieve sustainable soil productivity. (Giarola et al., 2010). Soil bulk density, porosity, water infiltration rate, and soil penetration resistance are usually exploited for evaluating soil structure (Giarola et al., 2010). Therefore, they can be utilized for assessing the VESS's

results in different management system. **The objective of this paper was to evaluate the performance of VESS method for assessing soil structural quality in arable and grass fields under different soil management systems.**

Materials and Methods

Site characterization
The study was conducted on 36 sites from grassland and cropland in combination with different land management practices in Ireland. The management practices under arable and pasture management were:
Arable:
  A) Minimum tillage system with single crops (MS)
  B) Minimum tillage system with crop rotation (MR)
  C) Conventional Tillage system with single crops (CS)
  D) Conventional Tillage system with crop rotation (CR)
Pasture:
  E) High intensive managed pasture (HIP)
  F) Medium intensive managed pasture (MIP)
  G) Low intensive managed pasture (LIP)

Field study and visual assessment of soil structure:

At each site a 30 m^2 plot was layed out with random orientation in a representative part of the field. Five sub-plots 2 m^2 were then selected across the central diagonal of the main plot for replicate sampling. The sites were selected in areas of uniform soil and land cover. At each sub-plot the VESS method was performed. The soil block was manually broken up along fracture lines, and gently crumbled to expose aggregate units (Guimaraes et al., 2011 and Ball et al., 2007). The horizontal layers were carefully identified and depth of each layer was measured then soil quality score (SQR) was defined by comparison with the visual key for each layer also considering difficulty of soil block extraction, size and shape of aggregates, mottling and root clustering and deflection (Ball et al., 2007). Soil and crop management practices were recorded through individual semi-structured interviews with the farmer. A questionnaire was developed about the necessary information regarding management regime at each site.

Statistical Analysis
Nonparametric tests were performed for soil structure scores, which are ordinal-scaled data in different management using SPSS software. Differences of means for metrically scaled data were evaluated with Fisher's Least Significant Difference (LSD) test or the t-test. In addition K mean clustering was used for classifying intensity of pasture management.

Result and Discussion

Tillage sites were characterized based on type of tillage (conventional and minimum tillage) and type of rotation (single crop or rotation). Mean soil quality difference under tillage are summarized in Table 1, Pasture sites were differentiated according to type of farms (only dairy farm, only beef farm, beef and dairy farm, mix of sheep and other cattle), frequency of reseeding (less than 10 years, 10 to 20 years, more than 20 years and no reseeding), stocking rate, grazing and silage management system. Mean soil quality differences under pasture are presented in Table 2.

Table 1. Mean comparison results on tillage

management practices	N	SQS mean	SQS range	mean difference	P- value	comparison's method
M	35	1.945	1_ 3	0.346***	0.002	Mann-Whitney
C	50	2.293	1 - 3.87			
R	55	2.121	1 - 3.86	0.086	0.749	Mann-Whitney
S	30	2.206	1.23 - 3.87			
MR	25	2.065	1_ 3	0.4098*	0.066	the Wilcoxon test
MS	10	1.6542	1.23 - 2			
CR	30	2.167	1 - 3.86	0.31467	0.234	the Wilcoxon test
CS	20	2.482	2 - 3.87			

N, minimum tillage; C, conventional tillage; MR, minimum tillage with Crop rotation; MS, minimum tillage with single crop; CR, conventional tillage with crop rotation; CS, conventional tillage with single crop; N, Number of samples; SQR, soil quality scores;; ***. Difference is significant at the 0.001 confidence level (2-tailed). **. Difference is significant at the 0.05 confidence level (2-tailed). * Difference is significant at the 0.1 confidence level (2-tailed).

Visual soil structural qualities were significantly different between the conventional tillage and minimum tillage system at $p<0.01$. VESS could differentiate the effects of ploughing on soil structural quality. Soil quality rating (SQR) tended to increase as a result of conventional management. Although single and rotation cultivation treatments were not discriminated with VESS, they were different in combination with tillage type and revealed a significant impact of tillage practices on soil structure (Lothar Mueller II, 2009). In addition, VESS significantly differentiated high intensity pasture from the low and medium intensity sites. Visual soil quality scores were larger in high intensity sites compared to low and medium intensity sites, which mean VESS can be used to distinguishing the effect of intensity on soil quality under pasture.

Table 2. Mean comparison results on pastures

management practices		Means Difference	Std. Error	P-value	95% Confidence Interval		comparison's method
					Lower Bound	Upper Bound	
M	B	0.03489	0.21352	0.871	-0.3892	0.459	LSD
	B+D	0.68320**	0.22852	0.004	-1.1371	-0.2293	
	D	1.26267**	0.24934	0	-1.7579	-0.7674	
B	B+D	0.71809**	0.15235	0	-1.0207	-0.4155	
	D	1.29756**	0.18209	0	-1.6593	-0.9359	
B+D	D	0.57947**	0.19947	0.005	-0.9757	-0.1832	
HIP	MIP	1.05257**	0.12483	0	0.8046	1.3005	LSD
	LIP	1.3430**	0.15118	0	1.0428	1.6433	
MIP	LIP	0.2905	0.1477	0.052	-0.0028	0.5838	

M, mix sheep and cattle farm; B, beef farm; D + B, dairy and beef farm; D, dairy farm; HIP, high intensive managed pasture; MIP, medium intensive managed pasture; LIP, low intensive managed pasture; LSD, Least Significant Difference; **. Difference is significant at the 0.01 confidence level (2-tailed). *. Difference is significant at the 0.05 confidence level (2-tailed).

Conclusions

The influence of different management practices on soil structural quality were distinguishable by using of visual soil structure assessment. Type of tillage and crop rotation effects on soil structure could be distinguished and confirmed the result of Mueller et al (2009). Furthermore, the method had the ability to demonstrate negative effects of intensity under pasture in Ireland. This study shown that field assessment of soil structural quality presented by Ball et al (2007) could be a reliable and quick mean for assessing the quality of soil structure as result of different management practices under pasture and to some extend under tillage in Ireland.

References

Ball BC, Batey T, Munkholm LJ. Field assessment of soil structural quality – a development of the Peerlkamp test. Soil Use and Management. 2007;23(4):329-37.

Giarola NFB, Da Silva AP, Tormena CA, Ball B, Rosa JA. Visual soil structure quality assessment on Oxisols underno-tillage system. 2010;67(4) :479-482

Guimarães RML, Ball BC, Tormena CA. Improvements in the visual evaluation of soil structure. Soil Use and Management. 2011;27(3):395-403.

Mueller L, Kay BD, Hu C, Li Y, Schindler U, Behrendt A, et al. Visual assessment of soil structure: Evaluation of methodologies on sites in Canada, China and Germany: Part I: Comparing visual methods and linking them with soil physical data and grain yield of cereals. Soil and Tillage Research. 2009;103(1):178-87.

Mueller L, Kay BD, Deen B, Hu C, Zhang Y, Wolff M, et al. Visual assessment of soil structure: Part II. Implications of tillage, rotation and traffic on sites in Canada, China and Germany. Soil and Tillage Research. 2009;103(1):188-96.

Ogle SM, Swan A, Paustian K. No-till management impacts on crop productivity, carbon input and soil carbon sequestration. Agriculture, Ecosystems & Environment. 2012;149(0):37-49.

Pankhurst CE, Magarey RC, Stirling GR, Blair BL, Bell MJ, Garside AL. Management practices to improve soil health and reduce the effects of detrimental soil biota associated with yield decline of sugarcane in Queensland, Australia. Soil and Tillage Research. 2003;72(2):125-37.

Roger-Estrade J, Richard G, Caneill J, Boizard H, Coquet Y, Defossez P, et al. Morphological characterisation of soil structure in tilled fields: from a diagnosis method to the modelling of structural changes over time. Soil and Tillage Research. 2004;79(1):33-49.

THE EFFECTIVENESS OF MOLE DRAINAGE TREATMENTS

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Abstract

Effective artificial drainage can be used to increase the productivity and length of grazing season on heavy, wet soils. High rainfall on soils with impeded drainage results in surface pugging and poaching damage and structural degradation by grazing livestock. This leads to lower grass yields and a curtailed grazing season with a resulting loss of income for the farmer. The effect of a number of mole drainage techniques was investigated on a clay loam soil at Solohead Research farm in order to establish their influence on soil physical properties, surface damage, plot scale water balance and grass production.

Introduction

Soils with a hydraulic conductivity less than 0.1 m/day are considered impermeable; the required drain spacing in such a soil, for adequate drainage, is of the order of 1.5 to 2.5 m. As such, conventional piped systems are uneconomical for normal agricultural enterprises on this soil type. It is therefore necessary to utilise drainage methods that incorporate a soil disruption technique (Galvin, 1982). Soils with clay content >30% are suitable to mole ploughing due to the requirement for a high soil cohesive force to maintain channel stability. The soil at the study site is classified as a clay loam (35% sand, 35% silt, 30% clay).

Mole drains are formed with a mole plough comprised of a torpedo-like cylindrical foot attached to a narrow leg, followed by a slightly larger diameter cylindrical expander. The foot and trailing expander form the mole channel while the leg creates a narrow slot that extends from the soil surface down to the mole channel depth (Cavelaars, Vlotman et al., 1994). The success of mole drainage depends on the formation of cracks in the soil that radiate from the tip of the mole plough at shallow depths as the soil is displaced forwards, sideways and upwards at an angle of approximately 45° to the horizontal (Smedema & Rycroft, 1983). Below a critical depth, dependent on soil mechanical strength and mole plough geometry, the soil flows forwards and sideways, inducing compaction at the foot of the plough. Thus the action of the mole plough creates both a zone of increased hydraulic conductivity adjacent to the mole leg (shallower depths) and a channel for water conveyance and outflow at moling depth, when the soil is sufficiently plastic.

The ideal time to carry out the mole ploughing is when the upper soil layers are dry enough to cause maximum cracking and provide adequate traction and the soil at mole depth is sufficiently plastic, i.e. close to the plastic limit. Therefore under Irish climactic conditions ideal moling is carried out in mid summer. If mole drainage is carried out when the upper soil layers are too wet, it is possible to form a good mole channel however crack formation in the vicinity is severely reduced (Galvin, 1982). In this scenario mole drains do not provide a satisfactory drainage system. Gravel filled moles employ the same principles as ordinary mole drains but are required where an ordinary mole will not be maintained open for a sufficiently long period to render its application economical. This is the case in unstable soils having low clay content.

The overall objective of the study is to examine the effectiveness of a number of mole drainage techniques in relieving soil wetness and increasing herbage production on a low permeability soil.

Materials and Methods

Site Description.
Experiments were conducted at the Teagasc Solohead Research Dairy Farm (latitude 52° 30' N; 08° 12' W; altitude 95 m a.s.l.). The area of the farm is 63 ha. The topography of the farm is relatively flat sloping gently from the north-west of the site. The soil has clay-loam soil texture; 35% sand and 30% clay in the upper 100 cm of the soil and a shallow water table (1.5±0.3 m bgl (summer) to 0.6±0.2 m bgl (winter). Drainage is impeded and contributes to waterlogged conditions under high rainfall. Pastures are predominantly composed of perennial ryegrass. The average length of the grazing season was 255 days between 2003 and 2006 when average annual rainfall was 963 mm (Humphreys et al., 2009) compared with 232 days between 2007 and 2009 when average annual rainfall was 1173 mm (Humphreys et al., 2010). The shorter grazing season in the wet years was due to the need to keep cows indoors to avoid pugging damage due to reduced soil bearing capacity and by lower pasture production

Experimental setup
In August 2010 the site was profiled and an open collection drain installed. The area to be drained was divided into four blocks, each roughly 60 m wide and 120 m long. Each block was sub-divided into four plots each 14 m wide and 120 m long. Four treatments were imposed: (i) no intervention, (ii) mole ploughing carried out in January 2011 (poor conditions) (iii) mole ploughing carried out in July 2011 (ideal conditions) and (iv) gravel mole ploughing carried out in July 2011. Mole drains were formed at 0.60 m depth, with a 1.2 m spacing while gravel mole drains were installed at 0.45 m depth also at 1.2 m spacing.

A range of soil conditions were established by the treatments imposed and by depth of groundwater along the gradient in each experimental plot. Drainage plots were surrounded by an isolation ditch, which will hydrologically isolate the plots from the surrounds. Collection gullies were established at the edges of all plots which feed into an overland flow collection channel and subsequently the overland flow collection point at the end of each plot. Soil and water measurements were undertaken at the four locations in each of the drainage plots (based on position up-gradient from the collector drain) along a gradient of groundwater depth and soil moisture content. Measurements of soil physical properties, soil water characteristics, surface damage and herbage response were taken at these locations throughout the duration of the study.

The drainage plots were grazed as blocks, with one plot from each treatment being grazed at any one time. Before each grazing, herbage cuts were taken to estimate yield from each treatment. Soil surface damage owing to grazing stock was measured after each grazing.

Each artificial drainage system was monitored continuously for runoff (field surface) and drainage flow volumes (at 0.45-0.60 m depth) by means of a system of flow collection and measurement tanks. Flow was from each of the sixteen treatments plots directed to either an overland or drainage flow collection tank which was fitted with an area/velocity sensor connected to a Sigma 920 flowmeter (HACH Company, Maryland, USA) to monitor and log the height of the water crest above the overflowing v-notch weir and flow velocity to establish flow rate from the system at any given time.

Results and Discussion

Only preliminary results are available as experimental work is on-going. The flow measurements taken over the winter period indicated that the drains were effective in removing excess water. Rainfall data and hydrographs for undrained control plots, summer moled plots and gravel moled plots for a relatively wet two-week period in late November/early December 2011 (Figure 1) indicate substantial surface run-off and mole

flow. The drainage treatments did not significantly affect surface run-off from the plots. In mole drained plots mole discharge and surface run-off were similar rates while the in gravel moled plots the rate of surface run-off was lower than the rate of gravel mole discharge at peak flows. The very high level of rainfall on November 29th shows the efficiency of the gravel moles in dealing with extreme events. High flow volumes were recorded immediately after the event, with comparatively low discharges in subsequent days. The mole drained plots showed a lower peak discharge followed by similar discharge levels in subsequent days. In general hydrographs showed great variety with outflows depending on soil moisture status as well as precipitation events.
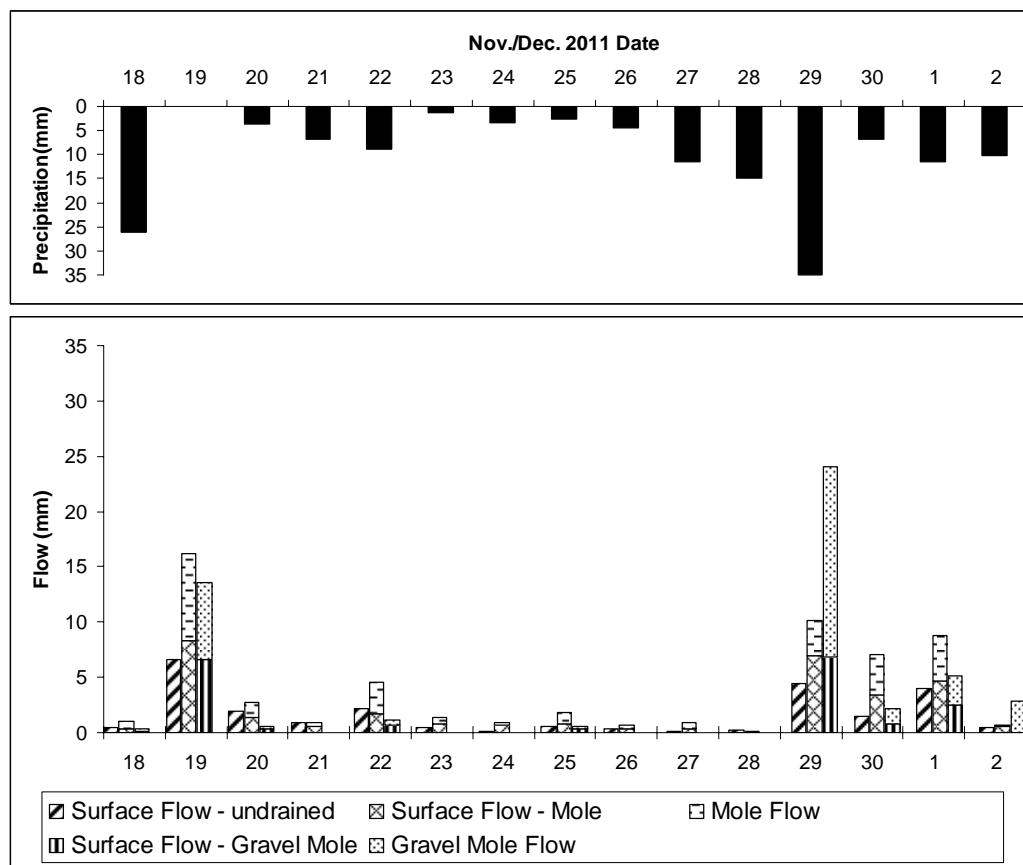
Figure 1. A typical precipitation and subsequent drainage plot discharge sequence

Ongoing data collection in the 2012 grazing season will allow comparisons to be made between the herbage yield, soil surface damage, soil moisture content and water table level. A relationship should be apparent between water table level and both herbage yield and surface deformation and damage. Mulqueen (1985) showed increases in pasture yield of up to 31% where the water table level was lowered from the ground surface compared with saturated plots.

Conclusions

Many areas of Irish farmland are under-exploited. Effective drainage in these cases would allow a longer grazing season, increased pasture production as well as greater trafficability and workability. In Ireland, rainfall ranges from 800 to 1600 mm yr^{-1} excluding mountainous areas. Evapotranspiration is approximately 450 mm yr^{-1} and as such effective drainage is high in areas of high rainfall. The efficiency of varying drainage techniques needs to be investigated. Drainage treatments in heavy, wet soils, principally soil disruption techniques (mole drains, gravel moles and sub-soiling), have in the past been implemented with varying

degrees of success. While drain design and performance have been evaluated, the current objective of correlating soil wetness and physical properties and grass growth response has not been widely investigated.

Acknowledgements

References

Burke, W., Mulqueen, J. and Butler, P. 1974. Aspects of the hydrology of a gley on a drumlin. Irish Journal of Agricultural Research 13:215-229.

Cavelaars, J. C., W. F. Vlotman, et al. (1994). Subsurface Drainage Systems. Drainage Principles and Applications. H. P. Ritzema. Wageningen, International Institute for Land Reclamation & Improvement. pp. 827-929.

Galvin, L. F. (1982). The Drainage of Impermeable soils. Land Drainage: Proc. C.E.C seminar. M. J. Gardiner. Rotterdam, A.A. Balkema: 85-103.

Galvin, L.F. 1983. The drainage of impermeable soils in high rainfall areas. Irish Journal of Agricultural Research 22: 161-187.

Gardiner M, Radford J (1980) Soil Associations of Ireland and their Land Use Potential. Soil Survey Bulletin No. 36, An Foras Taluntais, Dublin, Ireland.

Humphreys J. Casey I.A. and Laidlaw A.S. (2009) Comparison of milk production from clover-based and fertilizer N-based grassland on a clay loam soil under moist temperate climatic conditions. Irish Journal of Agricultural and Food Research, 71-89.

Humphreys, J., Keogh, B. Phelan, P., and Casey, I.A. (2010) Post grazing height and productivity of white clover-based systems of dairy production. Grassland Science in Euorpe, Proceedings of the 23rd General Meeting of the European Grassland Federation. Kiel, Germany. 15, p. 958.

Mulqueen, J. (1985). Effects of saturation on pasture production on a clay loam pseudogley soil. In: "Agricultural Water Management" (Editors: A.L.M. Van Wijk and J. Wesseling) EEC, pages 85-93.

Mulqueen, J. (1998). Depth, Spacing and Length of Mole Drains with Applications to Afforestatiion. Irish Journal of Agricultural Research 37: 39-49.

Robinson, M., Mulqueen J. and Burke, W. 1987. On flows from a clay soil - seasonal changes and the effect of mole drainage. Journal of Hydrology 91: 339-350.

Smedema, L. K. and D. W. Rycroft (1983). Land Drainage: Planning and design of agricultural drainage systems. Ithaca, New York, Cornell University Press: 376.

PHENOXYALKANOIC ACID HERBICIDE SORPTION PROCESESS IN A HAPLIC CAMBISOL UNDER CONTRASTING MANAGEMENT

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Abstract

The adsorption and desorption behaviour of two phenoxyalkanoic acid herbicides (MCPA and MCPP-p) in a Haplic Cambisol under contrasting management was examined using the batch equilibrium method. The experimental data of MCPA and MCPP-p fit the Freundlich and the linear model very well ($R^2 > 0.99$). The exponents of the adsorption Freundlich isotherm were close to unity ($1/n = 0.91\text{-}0.98$), suggesting linear adsorption. Generally, MCPP-p showed lower adsorption potential compared to MCPA. There was no significant difference by management ($p > 0.05$). Desorption revealed hysteresis as the K_f parameters for desorption were greater than corresponding K_f parameters for adsorption. This study also confirmed that both MCPA and MCPP-p are highly mobile and therefore may pose a high risk of surface and groundwater pollution in Ireland.

Introduction

Ionisable pesticides such as phenoxyalkanoic acid herbicides are often found in groundwaters and/or surface waters, in some cases at concentrations in excess of the EU drinking water limit 0.1 µg L^{-1}, because they are tend to be mobile in soils and aquifers (Harrison et al., 1998).Since MCPA and MCPP-p are weak acidic herbicides, pH is an important factor affecting their chemical status. As pH becomes greater than dissociation constant (pK_a), dissociated (deprotonated, anionic) groups will dominate while at pH less than pKa, molecular (neutral) species will dominate. Protonation of the organic matter functional groups is also affected by pH (Khan, 1978), and therefore influence its sorptivity potential. At pH values where both organic acids and acidic functional groups are fully deprotonated, hydrophobic sorption should be minimal. Cultivation practices on arable soils leads to reduction in concentration of soil organic carbon (SOC) and nutrient reserve in contrast to grass managed soils (Wang et al., 2008). Although, arable soils have usually improved pH due to better targeting of lime use and deeper cultivation on i.e. calcareous soils and luck of agricultural practices such as liming causes a decrease in pH with increasing age of grassland, but no-till practices significantly increase cation exchange capacity (CEC). Because both, physico-chemical properties of herbicides and soil are responsible for the sorption processes, soils of different management may affect the final distribution of the same pesticides in the environment, therefore the objective of this study was **to quantify the adsorption and desorption processes of two phenoxyalkanoic acid herbicides in a Haplic Cambisol under contrasting management.**

Materials and Methods

Soil
A representative site of tillage (N 52° 51´, W 006° 55´) and grassland (N 53° 51´, W 007° 54´) was sampled. Tillage site was mainly devoted to wheat production whereas pasture site was permanent grassland under grazing. Five sub-samples per site were removed from random locations from the surface layer (0-15 cm depth) with a Dutch auger. Each sub-sample was air dried, sieved to 2-mm and then bulked to create a composite sample for each site. The soils were analysed for properties (Table 1) thought to be related to adsorptive capacity.

Chemicals
Analytical grades of MCPA (99.5% purity) and Mecoprop – p (98.0% purity) were obtained from Dr. Ehrenstorfer (Germany). MCPA has relatively high water solubility (0.825 g L^{-1} at 20°C) with pK$_a$ value of 3.07 which means that MCPA is mostly neutral at pH < 3.07 and becomes negatively charged at pH > 3.07. Water solubility of Mecoprop-p is also high (0.860 g L^{-1} at 20°C) and its dissociation constant (pK$_a$) has a value of 3.86 and at pH > 3.86 Mecoprop-p becomes negatively charged.

Adsorption - desorption batch equilibrium study
The experiment was conducted by the standard batch equilibrium method (OECD, 2000) using 25 mL glass centrifuge tubes with Teflon-lined screw caps. In the kinetic the samples were analysed at 2, 4, 6, 8, 12 and 24 hours, centrifuged, and the supernatants were recovered and extracted. The kinetic study was performed at single herbicide concentration. The adsorption isotherm study was performed at five MCPA or Mecoprop – p concentrations, and analysed at previously established equilibrium. Control and blank samples were handled identically to the experimental samples. Desorption isotherms were determined immediately from all equilibrium points of the adsorption isotherm for individual compounds in duplicates as a single step desorption process. The time needed to reach desorption equilibrium was determined beforehand in desorption kinetic. At adsorption equilibrium, the supernatants were removed and replaced by the same amount of herbicide free aqueous 0.01 M CaCl$_2$. The tubes were agitated to disperse the sediment pellets, shaken until an approximate desorption equilibrium time and centrifuged. All supernatants were extracted immediately and analysed.

Chromatography and extraction of samples
The chemical analyses were undertaken in the Department of Agriculture, Food and Forestry Pesticide Control Laboratory (Celbridge, Co. Kildare, Ireland; ISO/IEC 17025). MCPA, Mecoprop – p and the mix of both were extracted from supernatants manually using a vacuum manifold and reversed phase Strata X cartridges (Phenomenex, UK). The elutions were injected to HPLC – DAD (Agilent Technologies). The herbicides were analysed at a wavelength of their maximum adsorption (230 nm). The lowest limit of detection achieved was 100 µg L^{-1}.

Data analysis
Adsorption isotherms were obtained by plotting the amount of MCPA and Mecoprop – p adsorbed per unit weight of the soil (oven dry basis) (Cs, mg kg^{-1}) against the amount of herbicides in the remaining solution at equilibrium (Ce, mg L^{-1}). This can be described by the linear isotherm model: $Cs = K_d Ce$.

Adsorption-desorption data were also fit to the linearized form of the Freundlich model:
$\log Cs = \log K_f + \frac{1}{n} \log Ce$, where K$_f$ and n are the empirical Freundlich constants

representing intercept and slope of the isotherm respectively. K$_f$ describes the degree of sorption and 1/n takes into account the nonlinearity in the sorption isotherms.

Table 1. Selected properties of Haplic Cambisol used in the study

Soil	pH (0.01 M CaCl$_2$)	% OC	CEC (cmol kg^{-1})	% sand	% silt	% clay	Texture
T	5.7	3.6	15.6	68	27	5	Sandy loam
G	5.1	3.9	17.0	68	19	13	Sandy loam

Results and Discussion

Adsorption – desorption study

The adsorption of these herbicides tended to be linear ($1/n$ = 0.91-0.98). The linear isotherm (C-shape) suggests a constant partitioning of herbicide between adsorption sites and solution and that the sorption is not affected by the herbicide concentration (Giles, 1960). It can be seen from Table 2 that the adsorption experimental data fit both the Freundlich and the linear model ($R^2 > 0.99$) and since the exponents ($1/n$) of the Freundlich isotherm are close to unity, either the Freundlich (K_f) and the distribution (K_d) coefficient can be used for the modelling purposes. The values of the two adsorption coefficients are comparable with no significant statistical differences between them ($p > 0.05$). Generally, the adsorption of MCPP-p was lower than of MCPA and this was significant in the tillage soil for K_d parameter ($p = 0.046$), while the differences between K_f values were almost significant ($p = 0.058$). There were no significant differences between herbicide adsorption in the grassland soil (K_f, $p = 0.251$ and K_d, $p = 0.305$).

Organic carbon adsorption constant (K_{oc}) calculated from the linear model, were used to predict the mobility of MCPA and MCPP-p in both soil with respect to leaching (Table 2). Both herbicides showed very high (5) mobility potential as per McCall et al. (1980). Because the K_{oc} values were not statistically different between the soils, a high risk of groundwater contamination may come from both soils. However, MCPP-p appeared to be even more mobile than MCPA, and this was significant in the tillage soil ($p = 0.018$), but not significant in the grassland soil ($p = 0.293$). Relatively low adsorption of both acidic herbicides and consequently high mobility may be related to their dissociation, as pH of the two soils was greater than pK_a of the chemicals, and therefore both MCPA and MCPP-p occur in the forms of anions, which are repelled by negatively charged functional surfaces of soil particles and for that reason less adsorption takes place. It can be seen that less adsorption was found in the till managed soil but the differences were not statistically significant ($p > 0.05$).

Table 2. MCPA and Mecoprop-p adsorption isotherm parameter for the linear and the Freundlich model. Number in brackets for K_d represent standard deviation ($n = 20$). Number in brackets for K_{oc} gives the mobility class as per McCall et al. (1980)

Compound		Linear isotherm			Freundlich isotherm		
	Soil	K_d (L kg^{-1})	K_{oc} (L Kg^{-1})	R^2	K_f (mg$^{1-1/n}$ kg^{-1}) (L)$^{1/n}$	$1/n$	R^2
MCPA	T	1.50 (0.33)	41.90 (5)	0.999	1.80	0.91	0.998
	G	1.96 (0.42)	49.94 (5)	1.000	2.29	0.91	0.999
MCPP-p	T	1.09 (0.14)	30.45 (5)	0.992	1.12	0.98	0.998
	G	1.71 (0.20)	43.57 (5)	1.000	1.87	0.96	0.999

As shown in Table 3, desorption data fit very well the Freundlich and the linear model ($R^2 > 0.99$). In case of MCPA, the slope of desorption isotherm was closer to unity than for adsorption while desorption slopes of MCPP-p isotherm showed values greater than 1. Obtained K_f desorption values were generally higher (Table 3) than the corresponding K_f for adsorption and this hysteresis is often observed phenomenon meaning that adsorption is not always reversible. The difference between K_f parameters for adsorption-desorption was significant in the grassland soil, $p = 0.004$ (MCPA) and $p = 0.031$ (MCPP-p) respectively. There were no statistical differences in the tillage soil. Higher K_f values for desorption in the grassland soil may be related to the organic carbon and clay content. The desorption rates from the single desorption step of both herbicides ranged from 28.0 to 34.0 %.

Table 3. MCPA and Mecoprop-p Freundlich desorption parameters

Compound	Soil	Kf (mg $^{1-1/n}$ kg $^{-1}$) (L)$^{1/n}$	1/n	R^2	Kd (L kg^{-1})	S.D. (n = 10)	R^2
MCPA	T	4.04	0.98	0.996	4.09	0.77	0.998
	G	4.35	0.93	1.000	4.28	0.83	1.000
MCPP-p	T	3.48	1.01	0.999	3.58	0.65	0.999
	G	4.87	1.03	1.000	4.98	0.67	0.999

Conclusions

Phenoxyalkanoic acids are highly mobile herbicides posing risk to surface or groundwater contamination. Relatively low adsorption by soil and consequently high mobility may be particularly of interest in vulnerable aquifers such as sands and gravels. However, pH of many soils in Ireland is greater than the dissociation constant (pK$_a$) of both acidic herbicides and therefore, they will occur as anionic molecules that will be repelled by negatively charged functional surfaces of soil particles, thus increasing their mobility. Greater adsorption and consequently lower desorption was observed in the grass managed soil, although more data are needed to verify whether the grassland soils offer better protection of surface and ground water to leaching of phenoxyalkanoic acids herbicides in Ireland. Moreover, more effort is needed to obtain site specific K$_d$ values at herbicide concentration that represents field conditions since K$_{oc}$ parameter may not always be a good predictor for sorption and transport modelling of phenoxyalkanoic herbicides as suggested by Buss et al. (2006).

Acknowledgements

References

Buss S.R., Thrasher J., Morgan P. and J.W.N. Smith. 2006. A review of mecoprop attenuation in the subsurface. *Quarterly Journal of Engineering Geology and Hydrogeology*, 39 (3), pp. 283-292.

Giles C. H., MacEwan T. H., Nakhwa S. N., & Smith D. (1960). Studies in sorption. Part XI. A system of classification of solution adsorption isotherms and its use in diagnosis of adsorption mechanisms and in measurement of specific areas of solids. *Journal of Chemical Society*, 111, 3973-3993.

McCall P.J., Swann R.L., Laskowski D.A., Unger S.M., Vrona S.A. and Dishburger H.J. 1980. Estimation of chemical mobility in soil from liquid chromatographic retention times. *Bulletin of Environmental Contamination and Toxicology*, **24(1)**, pp. 190-195.

Khan S.U. 1978. The interaction of Organic Matter with Pesticides. In Schnitzer M. & S.U. Khan (Eds.) *Soil Organic Matter*, (pp. 137-172). Elsevier Science Publishers B.V., Amsterdam, The Netherlands

OECD. 2000. OECD guidelines for testing of chemicals. Test guideline 106: adsorption-desorption in soils. Organisation for Economic Co-operation and Development, Paris.

Wang Z.P., Han X.G. and L.H. Li. 2008. Effects of grassland conversion to croplands on soil organic carbon in the temperate Inner Mongolia. *Journal of Environmental Management*, 86 (3), pp. 529-534.

Appendix 1
(Research projects in progress which have not been included in the Research Review)

Alobaidly M and F Butler. Risk profile: salmonella in poultry for the United Arab Emirates (**PhD**). Funding provided by Crown Prince of Abu Dhabi Bureau.

Collins P. and Butler F. Risk assessment of Norovirus (**MSc**). Food Institutional Research Measure (FIRM).

Doyle P and F Butler. Utility of HACCP to minimise risk of pathogenic bacteria in farm milk (**PhD**).

Galbally P, C Fagan, J Finnan, D Ryan, K McDonnell. Impact of biosolid amendments to src willow plantations on groundwater concentration-trends **(PhD).** Teagasc Waslsh Fellowship**.**

Hunt K, K. Jordan1 and F Butler. Coagulase-positive Enterotoxins of Staphylococcus aureus isolates from Milk used in Raw Milk Farmhouse Cheese (**PhD**). Food Institutional Research Measure (FIRM).

Luijckx NL and F. Butler. Vulnerabilities in the food chain: Risk ranking of contaminants in relation to vulnerability (**PhD**). European Commission (EC) ΣChain (FP6) research project.

Mussida A and F Butler. Implementation of sampling plan and application of microbiological criteria for *Cronobacter Sakazakii* in Ireland (**PhD**). Food Institutional Research Measure (FIRM) administered by the Irish Department of Agriculture, Fisheries and Food.

Pavlis M. and Cummins E. Assessing the vulnerability of groundwater to pollution (**PhD**). Department of Agriculture Fisheries and Food, as administered under the Research Stimulus Fund.

Velusami B, H Grogan, T P Curran and B McGuinness. Hydrogen sulphide gas emissions from spent mushroom compost during disturbance and removal **(PhD).** Teagasc/Walsh Fellowship.

Walsh J and Ward S. Carbon trading and management (**PhD**). Science Foundation Ireland under Grant Number 6C/CP/E001.

Appendix 2

(Profiles of Postdoctoral Research Scholars only includes: Drs Gonzales Barron, Boots, Coffey, Corkery, Drummond, ElMasry, Esquerre, Gowan, García Martín, McCarthy, Morsy, Ni Chualain, Tansey, Wu, Qin-An Zhang, Zhihang Zhang).

Ursula Andrea Gonzales-Barron, BSc, Eng, PhD

Project Title: Microbial Risk Assessment Network of Ireland

Project Leader: Prof. Francis Butler

Abstract

The overall objective of the Network is the application of microbial quantitative risk assessment to underpin national risk management actions. Currently, the researchers of the Network are generating novel modeling tools in this emerging area of risk analysis and are addressing how microbial quantitative risk assessment can be used as a risk management tool to develop appropriate food safety objectives, related industry performance objectives and performance criteria for microbial pathogens of major public health concern.

Background, Skills & Qualifications

Dr. Gonzales-Barron, an honours graduate from the Faculty of Food Industries at the National Agricultural University La Molina in Peru (1999), obtained her PhD degree at the Biosystems Engineering Department of University College Dublin, Ireland (2006). She has considerable expertise in the use of a series of classical and Bayesian predictive statistical tools for food safety applications including modelling and simulation for the conduction of risk assessments, particularly those of food pathogens. She is experienced also in predictive microbiology modelling, statistical process control and acceptance sampling, meta-analysis, zero-modified count data models for microbial load. Her current goal is to integrate all this knowledge into the development of food safety objectives and performance objectives. Dr. Gonzales-Barron has also worked on other quality aspects of food, food traceability and biometrics.

Recent publications

- **Gonzales-Barron, U., Redmond, G., & Butler, F.** (2010). *A risk characterisation model of Salmonella Typhimurium in Irish fresh pork sausages*. Food Research International, Special Issue 'Salmonella in Foods'**.** Under review.
- **Gonzales-Barron, U., & Butler, F.** (2010). *The use of meta-analytical tools in risk assessment for food safety*. Food Microbiology, Special Issue 'Predictive Modelling in Foods'. In press.
- **Gonzales-Barron, U., Kerr, M., Sheridan, J., & Butler, F.** (2010). *Count data distributions and their zero-modified equivalents as a framework for modeling microbial data with a relatively high occurrence of zero counts***.** International Journal of Food Microbiology, 136: 268–277.
- **Gonzales-Barron, U., Soumpasis, I., & Butler, F.** (2009). *An appraisal of the use of meat juice serology monitoring data for estimating prevalence of caecal Salmonella carriage of pigs at slaughter by means of herd-level and animal-level simulation*. Journal of Food Protection, 72(2): 286-294.
- **Gonzales-Barron, U., Soumpasis, I., Butler, F., Duggan S., Prendergast, D., & Duffy, G.** (2009). *Estimation of prevalence of Salmonella spp. on pig carcasses and pork joints using a quantitative risk assessment model aided by meta-analysis*. Journal of Food Protection, 72(2): 274-285.
- **Ktenioudaki, A., Butler, F., Gonzales Barron, U., Mc Carthy, U., & Gallagher, E.** (2009). *Monitoring the dynamic density of wheat dough during fermentation*. Journal of Food Engineering, 95(2): 332-338.
- **Gonzales-Barron, U., Butler, F., McDonnell, K., & Ward, S.** (2009). *The end of the identity crisis? Advances in biometrics markers for animal identification*. Irish Veterinary Journal, 63(3): 204-208.

Bas Boots M.Sc. Ph.D.

Project title: µAQUA, Universal Microarrays for the Evaluation of Fresh-Water Quality Based on the Detection of Pathogens and their Toxins

Project Leader: Professor Nick Holden

Abstract

The threat of waterborne diseases is predicted to increase in the the future. To avoid outbreaks, water quality needs to be monitored and a universal method for rapid and cost-efficient detection of waterborne pathogenic microbes has been sought after for many decades. Traditional methods are laborious, require high levels of expertise and typically focus on only one or a few organisms at once. µAQUA aims to develop a universal microarray chip equipped with species specific oligonucleotide probes targeting protozoa, bacteria, viruses and cyanobacteria. Bioindicators for water quality will also be incorporated. My contribution to the project is the designing and testing of probes that target pathogenic members of the protozoa *Cryptosporidium*, *Giardia*, *Naegleria* and *Entamoeba* in environmental water samples. The project also involves monitoring of three Irish rivers, draining agricultural intense and urbanised catchment areas. Furthermore, the microarray data will have to be linked to samples with known concentrations of pathogens for validation and supplemented by tests in the field.

Background, Skills & Qualifications

I graduated with a M.Sc. in Environmental Sciences (Soil, Water & Atmosphere) from Wageningen University, the Netherlands in 2006. I have done research on soil carbon sequestration under elevated levels of atmospheric CO_2 at the ETH Eschikon, Switzerland and the University of California, Davis, USA. I also explored how invasive earthworms interact with native animals and can alter carbon cycling within a forest at the University of Georgia, Athens, USA. During that time I became intrigued with the world of microbes and pursued a Ph.D. in microbial ecology at the University College Dublin, from which I graduated in 2010. During this period I carried out field experiments and used molecular techniques to study, amongst other topics, symbiotic relationships between ants and microbes. I have developed a great interest in the application of statistical methods, which has lead to a short post-doc to analyse large datasets obtained from experiments involving ruminants and mitigating microbial methane production. I also volunteered to work on methanogenic processes and microbial ecology in marine sediments which are being invaded by exotic oysters. Currently, I have joined the UCD School of Biosystems Engineering as a post-doctoral researcher to work with professor Nick Holden on the EU FP7 funded project µAQUA.

Recent Publications

- Boots et al., 2012. Pedobiologia, 55, 33-40.

- Lillis L., Boots B. et al., 2011. Applied Microbial Ecology, 111, 1426-1435.

- Keith A.M., Boots, B. et al., 2011. European Journal of Soil Biology, 49, 55-62.

- Snyder B.A., Boots B., Hendrix P.F., 2009. Soil Biology and Biochemistry, 41, 1442-1449.

- Boots B., and Brussaard L., 2006. Brochure. Wageningen University, 28p.

- Van Kessel C., Boots B., et al., 2006. Global Change Biology, 12, 2187-2199.

Rory Coffey, BAgrSc, MSc(Eng), PhD.

Project Title: Development of integrated modelling techniques to assess impacts of climate change on pathogens and wateshed management.

Project Leader: Dr. Enda Cummins

Abstract
Contamination of water sources with pathogenic organisms (e.g. *E. coli, Cryptosporidium*) represents a high risk to public health and the environment. Given that fecal pathogen contamination accounts for a majority of the water-quality impairments worldwide, an increased focus on the impact of forthcoming climate variation is required. Contemporary prediction of such issues requires intensive field trials, monitoring and steps that inhibit integration to a streamlined assessment system. Such time, labour and cost intensive methods limit the development of future catchment evaluation techniques. Catchment modelling techniques represent new environmental applications that are becoming increasingly used internationally to address issues on the management of water resources. However, there has only been limited work on integrated modelling of pathogens and climate change scenarios in catchment systems (due to high technological and methodological complexity). The objective of this work is to integrate the effects of climate change on waterborne pathogenic organisms and transport of such substances to water sources.

Background, Skills & Qualifications
I completed my undergraduate studies in 2003 with an honors degree in Agricultural Science (Engineering Technology) from UCD. Subsequentley, I received a funded Research Masters scholarship from UCD Biosystems Engineering focussing on risk assessment in the food chain. Work involved the development of a Feed Chain Risk Assessment (FCRA) for bovine animals in Ireland and identification of measures to reduce human exposure to mycotoxins resulting from the consumption of food products of bovine origin. My PhD (at UCD Biosystems Enegineering), funded by the Enviornmental Protection Agency, was awarded in 2010. The objective of this work was to assess, develop and apply a microbial model capable of predicting concentrations of pathogenic organisms in Irish drinking water catchments. Following my PhD I took up a postdoctoral position within UCD Biosystems Engineering as a teaching/research fellow and progessed research initiatives in the area catchment modelling. Currently I am funded as an EU FP7 Marie Curie International Outgoing Fellow and based at the Centre for Watershed Studies, Department of Biological Systems Engineering, Virginia Tech, USA as a visiting scholar.

Peer-reviewed Publications
Coffey R., Cummins E., Dorai-Raj S, O' Flaherty V. and Cormican M. (2012). *Modelling of pathogen indicator organisms in a Small-Scale Agricultural Catchment Using SWAT*. Human and Ecological Risk Assessment. In Press.
Coffey R., Cummins E., O' Flaherty V. and Cormican M. (2010). *Analysis of the Soil and Water Assessment tool (SWAT) to model Cryptosporidium in surface water sources*. Biosystems Engineering, 106 (3): 303-314.
Coffey R., Bergin D. and Cummins E. (2010). *Use of meta-analysis to assess the effect of conventional water treatment methods on the prevalence of Cryptosporidium spp. in drinking water*. Human & Ecological Risk Assessment, 16 (6): 1360-1378.
Coffey R., Cummins E., Bhreathnach N., Cormican M. and O' Flaherty V. (2010). *Development of a pathogen transport model for Irish catchments using SWAT*. Journal of Agricultural Water Management, 97 (10): 101-111.
Coffey R., Cummins E. and Ward S. (2009). *Exposure Assessment of mycotoxins in dairy milk*. Food Control, 20 (3): 239-249.
Coffey R., Cummins E., Cormican M., O' Flaherty V. and Kelly S. (2007). *Microbial exposure assessment of waterborne pathogens*. Human and Ecological Risk Assessment, 13 (6): 1313-1351.

Gerard Corkery NDipEng, BAgrSc, PhD

Project title: An investigation of heating systems (technology and fuel type) for poultry houses; and the feasibility of integrating "smart systems" technology in relation to poultry house heating / climate control systems, house lighting and bird performance (growth rate).

Project Leader: Professor Shane Ward

Abstract

The project will evaluates a range of poultry housing and associated heating systems in use in Ireland, the energy conversion technologies (heating systems) available commercially and their suitability for use in poultry houses. Emphasis will be placed on minimising energy use, including the use of waste materials, such as poultry litter. Heat and RH distribution within the house will be a key consideration for bird live weight gain. A review of the potential benefits arising from using "smart systems" to link the environment in the poultry house with the performance of the heating system, leading to enhanced bird performance (growth and health) will also being investigated.

Background, skills & Qualifications

I obtained a Diploma in Agricultural Engineering from IT Tralee in 2002 and subsequently went on to obtain my primary degree in BAgrSc Engineering Technology from University College Dublin in 2005. I was awarded a PhD degree in Engineering from Biosystems Engineering, UCD in 2010. My PhD focused on the use of biometrics as a method for identification and traceability of animals and poultry. During this time I worked on 2 DAFF FIRM funded projects. After receiving my PhD, I was employed under the Charles Parsons Energy Research Programme within Biosystems Engineering and the SAFSVM, School Innovation Programme as a research manager. Presently, I am working as a Postdoctoral Researcher in collaboration with Biosystems Engineering & Carton Bros (poultry producers).

Recent publications

- McInerney, B., **Corkery, G**., Ayalew, G., Ward, S., and McDonnell, K. 2011. *A preliminary in vivo study on the potential application of a novel method of e-tracking in the poultry food chain and its potential impact on animal welfare.* Computers and Electronics in Agriculture, *Volume.79, Issue 1, Oct 2011, Pages 51-62.*

- McInerney, B., **Corkery, G**., Ayalew, G., Ward, S., and McDonnell, K. 2011. *Preliminary in vivo study on the potential application of a novel method of e-tracking to facilitate traceability in the poultry food chain.* Computers and Electronics in Agriculture, *Volume 77, Issue 1, June 2011, Pages 1-6.*

- McInerney, B., **Corkery, G**., Ayalew, G., Ward, S., and McDonnell, K. 2010. *A preliminary in vivo study on the potential application of e-tracking in poultry using 2D barcodes.* Computers and Electronics in Agriculture, *Volume 73, Issue 2*, *August 2010*, *Pages 112-117*.

- **Corkery, G**., Gonzales Barron, U., Ayalew, G., Ward, S., and McDonnell, K. 2009. *A preliminary investigation of avian comb as a potential biometric marker for identification of poultry.* Transactions of the ASABE, 52(3): 991- 998.

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Liana Drummond, BSc. Eng., MSc., PhD.

Project Title: COOL-MEAT: A novel method for improving the vacuum cooling of cooked meats

Project Leader: Prof. Da-Wen Sun

Abstract
Strict EU guidelines demand that cooked meat joints including ham, turkey, chicken, pork and beef be cooled within rigid time limits after cooking. Conventional cooling methods depend on heat conduction to cool the inside of the joints, but the relatively low thermal conductivity of meat, coupled with restrictions on the minimum temperature of the cooling medium (to avoid surface freezing) makes it difficult to increase the rate of cooling significantly. Vacuum cooling is a rapid evaporative cooling technique for moist and porous products that offers many advantages over conventional cooling methods. However it leads to substantial weight loss and as a consequence, vacuum cooked meats are slightly less tender, drier and darker. A novel combined cook–cool technique known as immersion vacuum cooling (IVC), whereby the vacuum cooling of cooked meat is performed together with some of its cooking solution, was explored for its potential use for rapid cooling of water-cooked meat joints. Reduced yield losses and improved quality for cooked pork ham and large cooked beef joints have been reported. This project will build on this past research in order to apply and validate the technique in industry and to plan for the post-project commercial scale up of the IVC system and its subsequent market entry, whereby its uptake will improve the competitiveness of European Small and Medium Enterprises (SMEs) from the cooked meats sector.

Background, Skills & Qualifications
Graduated in 1991 at the University of Rio de Janeiro, Brazil with a BSc. in Chemical Engineering and in 1997 from the South Bank University, London, UK, with a MSc. in Food Safety and Control. Worked as a Research Assistant in Delft University of Technology: TU Delft, in The Netherlands, as part of a research team responsible for developing and testing new applications for a novel separation process (eutectic freeze crystallization). Awarded a PhD from the Biosystems Engineering Department in UCD, in 2008. The research work conducted was on an innovative combined cooking/cooling technology for cooked meat products – Immersion Vacuum Cooling. The research advanced the understanding and application of vacuum cooling allowing its application to large cooked beef products, providing rapid cooling within established quality and safety parameters. Recently appointed for a postdoctoral position in Biosystems Engineering, working on the development of IVC for the cooked meat industry, particularly aimed at European SMEs, with the objective of a potential scale-up and commercial application of this technology.

Peer-reviewed Publications

Feng, C., **Drummond**, L., Zhang, Z. and Da-Wen Sun, D.-W. (2011). *Vacuum Cooling of Meat Products: Current State-of-the-Art Research Advances*. Critical Reviews in Food Science and Nutrition, (in press).
Drummond, L., Sun, D.-W., Vila, C.T. and Scannell, A.G.M. (2009). *Application of immersion vacuum cooling to water-cooked beef joints – quality and safety assessment*. LWT - Food Science and Technology 42(1), 332-337.
Drummond, L. and Sun, D.-W. (2008). *Temperature evolution and mass losses during immersion vacuum cooling of cooked beef joints – a finite difference model*. Meat Science 80(3), 885-891.
Drummond, L. and Sun, D.-W. (2008). *Immersion vacuum cooling of cooked beef – safety and process considerations regarding beef joint size*. Meat Science 80(3), 738-743.
Drummond, L.S. and Sun, D.-W. (2006). *Feasibility of Water Immersion Cooking of Beef Joints: Effect on Product Quality and Yield*. Journal of Food Engineering 77(2), 289-294.

Gamal ElMasry, BSc, MSc, MEng., PhD

Project title: Rapid, Objective and Quantitative Determination of Meat Quality by Non-Destructive and Non-Contact Hyperspectral Imaging System"

Supervisor: Professor Da-Wen Sun

Abstract
Hyperspectral imaging or imaging spectroscopy is a new technique that combines both imaging and spectroscopy techniques to acquire spatial and spectral information from an object. The three-dimensional image obtained from hyperspectral imaging is called "hypercube". While the two spatial dimensions (x and y) describe the spatial features of the objects, the third dimension (λ) provides the spectral information for each pixel on the hyperspectral image cube. Because of this combined feature of imaging and spectroscopy, hyperspectral imaging can enhance the capability of detecting some chemical constituents in an object as well as their spatial distributions. Therefore, this project aims to develop a novel hyperspectral imaging system for quantitative and objective determination of meat quality. In order to do this, meat muscle of different attributes will be investigated in visible and near infrared (VIS/NIR) ranges of spectrum and the most critical image attributes relevant to meat quality (palatability) such as protein, water and fat content will be investigated. Measurements based on traditional instruments and sensory analysis will be also carried out to test, train and validate the hyperspectral imaging system, leading to the establishment of reliable meat quality predictors.

Background and skills
I have completed BSc and MSc degrees in Suez Canal University, Agricultural Engineering Department, Egypt. I have also a Master of Engineering (MEng) degree in Environmental Science and Technology, IHE Institute, The Netherlands (2003). My PhD was a joint research project between Suez Canal University (Egypt) and McGill University (Canada) on non-destructive quality evaluation of food products using hyperspectral imaging. I worked as a postdoctoral researcher in several laboratories in Norway, Japan and Ireland for quality evaluation and safety of agricultural produces. Currently, I am working in Biosystems Engineering Department, UCD, as a postdoctoral researcher under the guidance of Prof. Da-Wen Sun.

Selected Peer reviewed journal articles
ElMasry, G., Sun, D.-W., Allen, P. (2012). Near-Infrared Hyperspectral Imaging for Predicting Colour, pH and Tenderness of Fresh Beef. Journal of Food Engineering, 110 (1): 127-140.

Jackman, P., Sun, D.-W. & **ElMasry, G.** (2012). Robust colour calibration of an imaging system using a colourspace transform and advanced regression modelling. Meat Science, 91 (4): 402-407.

Kamruzzaman, M., **ElMasry, G.**, Sun, D-W, Allen, P. (2012). Prediction of some quality attributes of lamb meat using NIR hyperspectral imaging and multivariate analysis. Analytica Chimica Acta, 714 (10): 57-67.

ElMasry, G., Sun, D.-W., Allen, P. (2011). Non-destructive determination of water-holding capacity in fresh beef by using NIR hyperspectral imaging. Food Research International, 44 (9): 2624-2633.

Carlos Alberto Esquerre Fernandez, BSc, MSc, PhD

Project title: Study of mushroom (*Agaricus bisporus*) production and distribution chain conditions

Project Leader: Professor Colm O'Donnell

Abstract

This project evaluates the influence of distribution conditions on the quality of mushrooms, the most important horticultural export in Ireland, in close partnership with industry. Abuse of temperature during production, distribution and retail is a major quality and safety concern for food producers as well as retailers. This project also focuses on the development of sensing technologies for the mushroom industry based on Thermal Imaging and HyperSpectral Imaging (HSI). These sensing technologies are applied to facilitate the real-time monitoring of mushroom quality (using HSI) during processing and packaging and the acquisition of information on the spatial distribution of storage temperature conditions (using TI). This project will facilitate the adoption of a Process Analytical Technology (PAT) philosophy in the mushroom industry.

Background, Qualifications and Skills

My main research interests are application of sensor technology and chemometric analysis. I obtained a PhD in Biosystems Engineering from University College Dublin in 2011. During my PhD research I investigated the use of chemometric analysis of near infrared spectroscopy and spectral imaging data for quality assessment, and was awarded travel by the CNIR (2010) and ICNIRS (2011).

Prior to this I lectured La Molina National Agrarian University (Peru) when I obtained my MSc in Food Technology at Santiago de Chile University (Chile), and my BSc in Food Engineering at La Molina National Agrarian University.

Recent publications

C. Esquerre, A.A. Gowen, J. Burger, G. Downey, C.P. O'Donnell, Suppressing sample morphology effects in near infrared spectral imaging using chemometric data pre-treatments, Chemometrics and Intelligent Laboratory Systems, (2012).

C. Esquerre, A.A. Gowen, G. Downey, C.P. O'Donnell, Selection of variables based on most stable normalised partial least squares regression coefficients in an ensemble Monte Carlo procedure, J. Near Infrared Spectrosc., 19 (2011) 443-450.

A.A. Gowen, G. Downey, **C. Esquerre**, C.P. O'Donnell, Preventing over-fitting in PLS calibration models of near-infrared (NIR) spectroscopy data using regression coefficients, J. Chemom., 25 (2011) 375-381.

A.A. Gowen, F. Marini, **C. Esquerre**, C. O'Donnell, G. Downey, J. Burger, Time series hyperspectral chemical imaging data: Challenges, solutions and applications, Anal. Chim. Acta, 705 (2011) 272-282.

A.A. Gowen, C.P. O'Donnell, **C. Esquerre**, G. Downey, Influence of polymer packaging films on hyperspectral imaging data in the visible-near-infrared (450-950 nm) wavelength range, Appl. Spectrosc., 64 (2010) 304-312.

A.A. Gowen, G. Downey, **C. Esquerre**, C.P. O'Donnell, Use of spectral pre-processing methods to compensate for the presence of packaging film in visible–near infrared hyperspectral images of food products, J. Spect. Imag., 1 (2010) 1-10.

Aoife Gowen, BA M.Sc., PhD

Project Title: Aquasense (FP7 Marie Curie International Outgoing Fellowship)
Project Leader: Dr. Colm O'Donnell

Abstract

The overall objective of Aquasense is to investigate the potential use of Aquaphotomics combined with near infrared spectroscopy (NIRS) and hyperspectral imaging (HSI) for detection of contamination in water with the following specific aims:

1. Develop new knowledge in the theory of Aquaphotomics through application of perturbation spectroscopy to water systems
2. Identification of water absorbance patterns for water systems subjected to a range of physical and chemical perturbations
3. Develop algorithms for the detection of contaminants in water using NIRS and HSI
4. Evaluate performance of NIRS and HSI compared with standard methods for water contaminant detection

Background, Qualifications and Skills

Dr. Gowen's research area is multidisciplinary in nature, comprising broadly of applications of sensor technology and multivariate data analysis (chemometrics). She joined UCD School of Biosystems Engineering in 2007 as a postdoctoral fellow, working on the development of sensors for non-destructive assessment of food quality. She was responsible for setting up the very first facility for hyperspectral imaging (HSI) for food quality analysis in Ireland by procuring equipment and creating collaborations with some of the leading researchers in the World. This opportunity enabled her to transfer her extensive knowledge of food engineering, mathematical modelling as well as imaging science to the emerging areas of HSI, spectroscopy and chemometrics. She has since gained international recognition in these research domains, as evidenced by invited talks at major international conferences, journal editorial boards, book chapters, research papers and funding awards. She has published 40 papers, presented research at 29 international research conferences, edited 1 book and written 8 book chapters. Her h-index, reported on March 29th 2012 is 8.

Recent Publications

[1] Burger, J., **Gowen, A.** (2011). Data handling in Hyperspectral Image Analysis. Chemometrics and Intelligent Laboratory Systems, 108:13-22

[2] **Gowen, A**., Marini, F., Esquerre, C., O'Donnell, C., Downey, G., Burger, J. (2011). Time series hyperspectral chemical imaging data: challenges, solutions and applications. Analytica Chimica Acta, 705, 272-82.

[3] **Gowen, A**., Tsenkova, R., Bruen, M., O'Donnell, C. (2011). Vibrational spectroscopy for water quality analysis: a review. Critical Reviews in Environmental Science and Technology, DOI:10.1080/10643389.2011.592758

[4] **Gowen, A**., Tsuchisaka, Y., O'Donnell, C., Tsenkova, R. (2011). Investigation of the potential of Near Infrared Spectroscopy for the detection and quantification of pesticides in aqueous solution. American Journal of Analytical Chemistry, 8: 53-62

[5] **Gowen, A**, O'Sullivan, C, O'Donnell, C. (2012). Terahertz time domain spectroscopy and imaging: emerging techniques for food process monitoring and quality control. Trends in Food Science and Technology. In Press, http://dx.doi.org/10.1016/j.tifs.2011.12.006.

[6] Esteve, L., **Gowen, A**., Hurburgh, C., O'Donell, C. (2012). Feasibility of conventional and Roundup Ready® soybeans discrimination by different near infrared reflectance technologies, Food Chemistry, 134, 1165-1172.

[7] Esquerre, C., **Gowen, A**., O'Donnell, C.P. and Downey, G. (2012). Suppressing sample morphology in near infrared spectral imaging of agriculture products by chemometric pre-treatments Chemometrics and Intelligent Laboratory Systems. Invited paper, In Press, http://dx.doi.org/10.1016/j.chemolab.2012.02.006.

Juan Francisco García Martín, BSc, MSc, PhD

Project Tittle: Novel method for assisting and accelerating the aging process of wine (ULTRAFINEWINE).

Project Leader: Professor Da-Wen Sun

Abstract

Wine producers are constantly striving to achieve a stable product with an extended period of peak taste and bouquet. Naturally aged wine tends to be milder tasting and smoother to drink than non-aged wine. Research to date has revealed that the aging process can be enhanced with by the application of high pressures and temperatures over time. This project will build on past research that has demonstrated promising results for the application of temperature and pressure by ultrasonic radiation which can alter the interaction of wine ingredients to obtain chemical changes in the wine resembling many years of natural ageing. A prototype ultrasound device will be designed, built and integrated into existing wine fermentation vats in order to validate its usefulness at industrial scale for the production of homogenous wines with an extended shelf-life in very short periods of time compared to natural ageing.

Background, Skills & Qualifications

Juan Francisco García Martín earned a BSc in chemistry in 2001 at the University of Jaén (Spain) and then he moved to Lyon (France), where he was PhD student at the Université Claude Bernard Lyon I during 6 months. He returned to the University of Jaén (Spain) where he obtained a MSc in Biotechnology and Agri-Food Engineering in 2003 and a PhD summa cum laude in 2007. His Thesis, which was focused on the production of bioethanol and xylitol from biomass, was awarded two Spanish National Research Environment Prizes. During this period he cooperated with the Université Paul Sabatier Toulouse III (France), including several short-term research visits. From 2008 to 2010, he was postdoctoral researcher at the University of Granada (Spain) in the field of ecological detergents formulation. He is currently working in the School of Biosystems Engineering of the University College Dublin (Ireland) in the ULTRAFINEWINE Project (grant agreement n° 262614), which is funded by the European Community's Seventh Framework Programme (FP7/2007-2013).

Recent publications

Jurado E., Vicaria J.M., **García Martín J.F**., García Román M. (2012) 'Wettability of Aqueous Solutions of Eco-Friendly Surfactants (Ethoxylated Alcohols and Polyoxyethylene Glycerin Esters)'. *Journal of Surfactants and Detergents*, 15(3):251–258.

García Martín J.F., Sánchez, S and García J. (2012) 'Ethanol from Biomass: Application to the Olive-Pruning Debris' In: Carasillo, D.A (eds). *Liquid Fuels: Types, Properties and Production*, Nova Science Publishers, New York, pp: 239-254.

García Martín, J.F., Sánchez, S., Metz, R. (2012) 'Kinetics Model of the Thermal Oxidation of Indium Powder'. *Oxidation of Metals*, 77(1-2):1-7.

Jurado E., Vicaria J.M., **García Martín J.F.** (2011) 'Composiciones de tensioactivos altamente humectantes'. ES 2352934 B2 Spanish Patent Application.

Ultan Mc Carthy, BSc, M.Sc, MBA, PhD

Project Title: Development of a Remote Environmental Monitoring and Diagnostics in the Perishables Supply chain

Project Leader: Prof Ismail Uysal (USF) / Prof Francis Butler (UCD)

Abstract
RFID technology is gaining widespread acceptance in supply chain management applications. In its simplest format RFID technology can provide unique identification and store product specific information directly on the product via an attached tag. This tag and information can be wirelessly synchronised (via radio waves) to a centralised database via a reader providing vital real time product specific information to all trading partners. As a technology RFID is constantly evolving via added functionality, revolutionizing global supply networks and asset management applications. The most common of these value adding capabilities include the sensor tags. Sensor tags have the ability to remotely record a variety of environmental conditions (temperature, humidity, location co-ordinates etc). All this information is automatically synchronised with a centralised database.
The aim of this work is the development of an automated fully autonomous remote environmental monitoring system for global scale food supply chain management applications. This system will function via wireless GSM or satellite connectivity linking trading partners directly to the product resulting in leaner more responsive global food supply chains. A secondary deliverable is the economic assessment of the integration of such smart sensing system in the global supply chain via KPI benchmark indicators.

Background, Qualifications and Skills
I currently hold a visiting researcher position at Biosystems Engineering from the University of South Florida. Prior to this I completed my Ph.D in the Department of Biosystems Engineering UCD focusing on the operational parameters of RFID technology in the Irish food supply chain. Following this my MBA degree focused on the ability of RFID and related automatic identification technologies to add value to the organisation at local, national and international scale in the attainment of a sustainable compeditive advantage. I also hold a BSc in Food technology from UCC (2003) and an MSc in Engineering technology from UCD (2005).

Recent Publications
- Mc Carthy, U., Ayalew, G., Butler, F., McDonnell, K. & Ward, S. (2011). The case for RFID application in the meat supply chain in the Irish context. Agricultural Engineering International: the CIGR Ejournal 13(3).
- Mc Carthy, U., Ayalew, G., Butler, F., McDonnell, K. & Ward, S. (2011). Ultra High Frequency (UHF) Radio Frequency Identification in Food Supply Chain Management Applications. Supply-Chain Management: Theories, Activities/Functions and Problems. ISBN: 978-1-61668-284-2. www.novapublishers.com
- Mc Carthy, U., Ayalew, G., Corkery, G., Laniel, M., Uysal, I., Butler, F., McDonnell, K. & Ward, S., Emond, JP. (2012). RFID and the EPCglobal Network as a Pivotal Tool in the Development of a Sustainable Organisational Competitive Advantage. "Advances in Business and Management. Volume 5". ISBN: 978-1-62100-510-0. www.novapublishers.com
- Mc Carthy, U., Laniel, M., Uysal, I., Corkery, G., Butler, F., McDonnell, K. & Ward, S. (2013). Sustainable Global Food Supply Networks. "Sustainable Food Processing". UNDER REVIEW. ISBN: 9780470672761. Blackwell Publishing. http://eu.wiley.com/WileyCDA/
- Laniel, M., Mc Carthy, U., Uysal, I. (2013). Wave propagation: An RFID Perspective. Wave Propagation, ISBN 980-953-307-376-2. UNDER REVIEW Academy Publish. http://www.academypublish.org/

Noha ElSayed Morsy, BSc, MSc, PhD

Project title: Spectroscopic Technique for Food Authentication by Detecting Adulteration and Microbial Spoilage**"**

Supervisor: Professor Da-Wen Sun

Abstract
The determination of food authenticity and the detection of adulteration are major issues in the food industry, and are attracting an increasing amount of attention. Proper product description is of crucial importance in ensuring fair trading practices and enabling consumers to make liable choices. Food authenticity issues in the form of adulteration and improper description have been around for a long time and probably for as long as food has been offered for sale. Adulteration of food can be in the form of complete or partial omission or abstraction of valuable constituents; whole or partial substitution of food component with an undeclared alternative (usually cheaper); concealment of damage or inferior foodstuffs and/or adulteration by adding undeclared substances or material to increase product bulk or weight or make the product appear better value than it is. With food products major authenticity issues concern the substitution of high value raw materials with cheaper materials. On the other hand, with increased expectations for agricultural products of high quality and safety standards, the need for accurate, fast and objective quality determination of food characteristics continues to grow. Although there are some traditional methods for discovering and detecting wide range and low levels of food adulteration, spectroscopic methods are attractive options due to the speed of analysis and minimal sample preparation. Therefore, this project aims to investigate the feasibility of NIR spectroscopy for quality monitoring and authentication in minced meat to discover adulteration by offal, liver, kidney, tongue and pork as well as predicting the microbial load in minced meat due to abuse storage.

Background and skills
I have completed BSc and MSc degrees in Department of Food Science and Technology, Faculty of Agriculture, Suez Canal University, Egypt. My PhD study was focused on using some postharvest treatments and minimal processing techniques for enhancing the shelf life of some agricultural products. Currently, I am a visiting researcher in School of Biosystems Engineering, UCD under the guidance of Prof. Da-Wen Sun.

Selected Peer reviewed articles

Morsy, N., Alixos, N., Prats-Montalbán, J., Blasco, J., ElMasry, G., Sun, D-W. & Allen, P. (2011). Classification of Chicken Ham Qualities by Computer Vision and Imaging Spectroscopy. CIGR Section VI International Symposium on Towards a Sustainable Food Chain Food Process, Bioprocessing and Food Quality Management, Nantes, France - April 18-20, 2011.

Talensa, P., Mora, L., **Morsy, N.**, Barbin, D., ElMasry, G. &Sun, D.-W. (2012). Prediction of water and protein contents and quality classification of Spanish cooked ham using NIR hyperspectral imaging. Meat Science (Accepted).

Morsy, N. & Sun, D.-W. (2012). Robust Linear and Non-linear Models for Detection and Quantification of Adulterants in Fresh and Frozen-Thawed Minced Beef. Journal of Food Chemistry (Submitted).

Ciara Ní Chualáin, BSc. PhD.

Project Title: Universal microarrays for the evaluation of fresh-water quality based on detection of pathogens and their toxins

Project Leader: Professor Nick Holden

Abstract
Monitoring the quality of drinking water is of paramount importance for public health. "Water is not a commercial product but a heritage that must be protected, defended and treated as such", (Water Framework Directive 2000/60/EC). The threat of waterborne diseases in Europe will predictably increase in the future as the human population increases and as a result of globalization and migration from non-EU countries and of climate change. Development of efficient, sensitive, robust, rapid and inexpensive tests to monitor various aspects of water quality represents an essential milestone within the strategy for control and prevention of diseases caused by waterborne pathogens and by algal toxins. Traditional methods for the detection of waterborne pathogens, based on cultivation, biochemical characterisation and microscopic detection are laborious and time-consuming; molecular biological tools have now greatly enhanced our ability to investigate biodiversity by identifying species and to estimate gene flow and distribution of species in time and space. µAQUA aims to design and develop a universal microarray chip for the high-throughput detection in water of known and emerging pathogens (bacteria, viruses, protozoa and cyanobacteria) and to assess the water quality monitoring the presence of select bioindicators (i.e. diatoms).

Background, Skills & Qualifications
I graduated in 2005 from National University of Ireland, Galway with a BSc. in Marine Science. I specialised in marine zoology with particular emphasis on parasitology. My degree project involved important fisheries science skills, such age and sex determination of teleosts, and identification of the metazoan parasite species infecting conger eels. In 2010, I was awarded a PhD from the Galway-Mayo Institute of Technology. My thesis provided the first epizootiological data on pink crab disease in Ireland, caused by the parasitic dinoflagellate *Hematodinium* sp.. I assessed the most suitable diagnostic methods for continued monitoring of *Hematodinium* sp. in Irish crustacean fisheries through the comparison of haemolymph smears, histology and a genus-specific PCR assay. I examined biotic and abiotic factors, and spatial and temporal differences in relation to *Hematodinium* sp. infection prevalence and infection intensity. I also conducted a series of laboratory experiments to examine potential infection routes of the parasite and to monitor disease progression in naturally infected *C. pagurus.* After my PhD I worked in the Marine Institute, the national reference laboratory for monitoring bacteriological & viral contamination in bivalve shellfish. My main task was the detection of norovirus in shellfish and wastewater using quantitative real-time reverse transcription PCR procedures and also the detection of *E. coli* & FRNA bacteriophages. I recently joined the µAqua team in Biosystems Engineering which aims to develop a universal microarray chip for the detection of drinking water pathogens.

Peer-reviewed Publications
Ní Chualáin, C & Robinson, M (2011) Comparison of assessment methods used to diagnose *Hematodinium* sp. infections in *Cancer pagurus* L. ICES Journal of Marine Science 68:454-462

Ní Chualáin C, Hayes M, Allen B, Robinson M (2009) *Hematodinium* sp. in Irish *Cancer pagurus* fisheries: infection intensity as a potential fisheries management tool. Diseases of Aquatic Organisms 83: 59-66

In progress: Ní Chualáin, C & Robinson, M Investigation into *Hematodinium* sp. prevalence and infection intensity in *Cancer pagurus* from Malin Head, in relation to habitat and host factors.

Fergal Tansey B.Sc., Ph.D.

Project Title: Development of a National Food Microbial Database and its implications for food chain integrity

Project Leader: Prof. Francis Butler

Abstract

The main objective of the Food for Health Research Initiative (FHRI) part-funded Safe and Healthy Foods project is to develop and maintain a state-of-the-art National Food Microbial Database (www.microbialdatabase.ie). The project partners are the Food Safety Authority of Ireland (FSAI), the Department of Agriculture, Food and the Marine (DAFM), the Marine Institute (MI), Teagasc Food Research Centre (TFRC), Ashtown, TFRC, Moorepark, University of Ulster, Jordanstown (UUJ) and University College Dublin (UCD). UCD is working with Open Sky Ltd. (database provider), in conjunction with the other project partners (data providers), to develop the web-based database. The database will be populated with up to 4 years validated foodborne pathogenic data, including molecular data, from data providers by the end of 2012. Database development is in the final phase and is on target to be fully operational by the end of April 2012. Project partners and other key stakeholders will have full access to the database. The database will be initially populated with state approved data on four bacteria (Campylobacter spp., Escherichia coli O157, Listeria spp., and Salmonella spp.) and noroviruses in shellfish, covering 22 food and 5 environmental categories. It is envisaged that the database will set a benchmark standard at international level for web-based microbial databases, foster international links, strengthen links between existing national surveillance systems, improve data quality and identify data gaps.

Background, Qualifications and Skills

Fergal Tansey is a post-doctoral researcher based at the UCD School of Biosystems Engineering (www.ucd.ie/biosystems). He is a project manager on the FHRI part-funded project, Safe and Healthy Foods, developing a National Food Microbial Database for both foodborne bacteria and viruses, in conjunction with the other project partners (www.microbialdatabase.ie). He has previously worked at UCD on a EU FP6 funded project, Sigmachain (www.sigmachain.eu). He has also worked in the food industry and in food research in technical and managerial roles within Unilever Plc., Glanbia Plc. and TFRC, Ashtown. He has his own food safety consultancy company, Biotec (www.biotec.ie).

Recent Publications

Tansey, F., Gormley, R. and Butler, F. (2010). The effect of freezing compared with chilling on selected physico-chemical properties and sensory properties of *sous vide* cooked carrots. *Innovative Food Science and Emerging Technologies*, 11, 137- 145.

Di Wu, BSc, Eng, MSc, PhD

Project title: Prediction of eating qualities of salmon fillet from colour, marbling and surface texture features using hyperspectral imaging technique

Project Leader: Professor Da-Wen Sun

Abstract

The development of rapid and accurate quality and safety inspection systems with the function of visualizing attribute distribution are important for the Irish salmon industry to ensure the safe production of salmon products during processing operations and the labeling of products correctly related to the quality, safety, authenticity and compliance. With the integration of the main advantages of spectroscopy and imaging, hyperspectral imaging technique can simultaneously acquire spectral and spatial information in one system, leading to its capability of measuring both external physical and morphological characteristics and internal quality attributes from a salmon fillet. In order to do this, a reliable hyperspectral imaging system with quantitative models will be trained, established, and validated for rapid and non-invasive measurement of quality and safety attributes of salmon fillets based on the most critical image features extracted from visible and invisible (near infrared) hyperspectral images of salmon fillets and their reference attribute values, which will be measured by using traditional instruments and sensory analysis.

Background, skills & Qualifications

I have completed BSc (2006) and PhD (2011) in Zhejiang University, Biosystems Engineering Department, China. During my PhD, I used microscopy imaging, spectroscopy, hyperspectral imaging, and nuclear magnetic resonance (NMR) combined with image process algorithms and chemometrics for rapid and non-invasive determination of quality attributes of microalgae such as microscopic morphological features, growth information, qualities of algal oils and algal powders. Currently, I work in School of Biosystems Engineering, UCD, as a postdoctoral researcher under the guidance of Prof. Da-Wen Sun.

Recent publications

Wu D, Wang S, Liu K, Yu X, he Y & Wang Z (2012) Rapid measurement of morphological features of Spirulina microalgae filaments using microscopy and image processing algorithms. Biosystems Engineering, 112(1), 35-41.

Wu D, Nie PC, Cuello J, He Y, Wang ZP & Wu HX (2011) Application of visible and near infrared spectroscopy for rapid and non-invasive quantification of common adulterants in *Spirulina* powder. Journal of Food Engineering, 102(3), 278-286.

Wu D, Nie PC, He Y & Bao YD (2012) Determination of calcium content in powdered milk using near and mid-infrared spectroscopy with variable selection and chemometrics. Food and Bioprocess Technology, 5, 1402-1410.

Wu D, He Y, Shi JH & Feng SJ (2009) Exploring near and midinfrared spectroscopy to predict trace iron and zinc contents in powdered milk. Journal of Agricultural and Food Chemistry, 57(5), 1697-1704.

Wu D, He Y & Feng S (2008) Short-wave near-infrared spectroscopy analysis of major compounds in milk powder and wavelength assignment. Analytica Chimica Acta, 610(2), 232-242.

Qing-An Zhang, B. Eng., M. Eng., PhD

Project title: Novel method for assisting and accelerating the aging process of wine

Project Leader: Professor Da-Wen Sun

Abstract

The ageing process is an important step for producing high quality wine products. Naturally aged wine tends to be milder tasting, smoother to drink and have a higher metabolism than non-aged wine. The traditional ageing technology is based on the storage of wine in oak barrels or bottles, while there are some disadvantages about it including time-consuming, cost and space of storing barrels or bottles of wine, and possible contaminations. This project is built on past research that has demonstrated promising results for the application of temperature and pressure by ultrasonic radiation which can alter the interaction of wine ingredients to obtain chemical changes in the wine resembling many years of natural ageing. A prototype ultrasound device will be designed, built and integrated into existing wine fermentation vats in order to validate its usefulness at industrial scale for the production of homogenous wines with an extended shelf-life in very short periods of time compared to natural ageing.

Background, skills & Qualifications

I joined UCD in 2011 as a postdoctoral researcher under the guidance of Prof. Da-Wen Sun, working on the project of Novel method for assisting and accelerating the aging process of wine. My current research interest is the detection and control for food ingredients changing during processing with novel technology including ultrasound, mircowave, etc. Prior to joining UCD, I worked as an associate professor in ShaanXi Normal University, China. The courses I taught include food analysis and inpection, food safety and control, and food nutriology. I obtained my PhD in applied chemistry from ShaanXi Normal University of China in 2010. During my PhD, My work is oriented to rapidly screen antioxidants from natural products using new technology of extraction, separation, purification, and characterization. I have successfully constructed the on-line HPLC-DPPH-UV/VIS-MS screening system for antioxidants in our Lab. I was awarded an M.Eng. in Food Sience from ShaanXi Normal University (2002) and a B. Eng. in Food Science and Engineering from HeNan Institute of Science and Technology (1999) in China, respectively.

Recent publications

Li T., Qu X.-Y., **Zhang Q.-A.**, *Wang Z.-Z. (2012). Ultrasound-assisted extraction and profile characteristics of seed oil from Isatis indigotica Fort*. Industrial Crops and Products, 35(1): 98-104.

Mou Z.-L., Zhao L.-J., **Zhang Q.-A.,** Zhang J., Zhang Z.-Q. (2011). *Preparation of porous PLGA/HA/collagen scaffolds with supercritical CO2 and application in osteoblast cell culture*. The Journal of Supercritical Fluids, 58(3): 398-406.

Jia X.-Y., **Zhang Q.-A.,** Zhang Z.-Q., Wang Y., Yuan J.-F., Wang H.-Y., Zhao D. (2011). *Hepatoprotective effects of almond oil against carbon tetrachloride induced liver injury in rats.* Food Chemistry, (125): 673-678.

Zhang Q.-A., Zhang Z.-Q., Yue X.-F., Fan X.-H., Li T., Chen S.-F. (2009). *Response surface optimization of ultrasound-assisted oil extraction from autoclaved Almond powder*. Food Chemistry, (116): 513-518.

Zhang Q.-A., Fan X.-H., Zhang Z.-Q., Zhang B.-S., Zhang Z.-Q., Jia X.-Y. (2009). *Optimization of SC-CO_2 extraction of oil from almond pretreated with autoclaving*. LWT-Food Science and Technology, (42):1530-1537.

Zhihang Zhang, BEng., PhD.

Project Title: A novel method for improving the vacuum cooling of cooked meats

Project Leaders: Prof. Da-Wen Sun

Abstract
In order to minimise the growth of pathogens in the cooked meat industry, strict EU guidelines demand that cooked meat joints must be cooled within tight time limits after cooking. Compared to conventional cooling methods, vacuum cooling is a rapid evaporative cooling technique for moist and porous products that offers many advantages over conventional cooling methods, such as short processing time, extension of product shelf life and improvement of product safety and nutritional content. However it leads to considerable weight loss and, due to high moisture loss, vacuum cooked meats are slightly less tender, drier and darker. A novel technique known as immersion vacuum cooling (IVC) has recently been researched, whereby the vacuum cooling of cooked meat together with some of its cooking solution was explored for its potential use for rapid cooling of water-cooked meat joints. Reduced yield losses and improved quality for cooked pork ham have been reported. This project will build on this past research in order to apply and validate the technique in industry and to plan for the post-project commercial scale up of the IVC system and its subsequent market entry, whereby its uptake will improve the competitiveness of European SMEs from the cooked meats industry.

Background, Skills & Qualifications
I got my Bachelor degree in Food Engineering in Shanghai fisheries University. My thesis was about ice cream manufacture. After graduation, I did research in School of Light Chemistry and Food Science in South China University of Technology, as a PhD student, for about 4 years. During the period, I was involved in many projects, like date exploitation, sugar manufacture, crystallization of an antibiotic, beer brewing, vinegar soft drink exploitation, and solution of sedimentation in soy sauce. Thereafter, I pursue a doctoral study in UCD. During the study, I carried out an EU project, about vacuum cooling of cooked ready-meal components, like meat (beef, pork and lamb), carbohydrate (rice, pasta and potato), vegetables (broccoli, carrot) and sauces. Between 2005 and 2008, I presented food safety training to food companies in Ireland, on behalf of FSAI. In 2008, I completed the PhD degree in Biosystems Engineering Department, UCD, with the thesis "Experimental and numerical study of vacuum cooling of cooked diced beef and rice". Between 2008 and 2010, I worked as a postdoctoral researcher in UCD, on a project named MINICRYSTAL, which used power ultrasound to reduce freezing time of meat and improve quality of frozen meat. I am currently working for the above mentioned project.

Peer-reviewed Publications
Z. Zhang and D.-W. Sun. (2006). Effects of cooling methods on the cooling efficiency and quality of cooked rice. *Journal of Food Engineering*, 77 (2), 269-274.
Z. Zhang and D.-W. Sun. (2006). Effect of cooling methods on the cooling efficiencies and qualities of cooked broccoli and carrot slices. *Journal of Food Engineering*, 77 (2), 320-326.
Z. Zhang and D-W. Sun. (2009). *Comparison of cooling of cooked vegetables between vacuum cooling and traditional cooling methods.* Ireland Chinese Association of Environment, Resources & Energy (ICAERE). UCD, Dublin, Ireland.
H. Kiani, **Z. Zhang**, A. Delgado and D.-W. Sun. Ultrasound Assisted Nucleation of Some Liquid and Solid Model Foods during Freezing. *Food Research International*, (in press).
H. Kiani, **Z. Zhang** and D.-W. Sun. Investigation of the effect of power ultrasound on the nucleation of water during freezing of agar gel samples in tubing vials. *Ultrasonics Sonochemistry*, (in press).
H. Kiani, **Z. Zhang** and D.-W. Sun. The effect of ultrasound irradiation on the convective heat transfer rate during immersion cooling of a stationary sphere. *Ultrasonics Sonochemistry*, (in press).

Appendix 3

UCD School of Biosystems Engineering : Postgraduates
2011/12 as photographed by Sean Kennedy

Alobaidly Mohamed J

Askari Mohammad
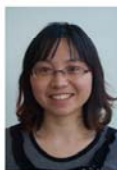
Brennan Liam

Butler Eoin

Chadwick Dara

Cogan David

Collins Patrick

Cui Junfang

Cushen Maeve

Donnelly-Swift Ross

Douglas Barbin

Doyle Pat

Everard Colm

Eyonganyoh Remi

Farrelly Damien

Fay Robert

Feng Chaolui

Feng Yaoze

Galbally Paul

Gillespie Gary

Harris Suvi

He Hongiu

Hunt Karen

Kadam Shekhar

Kamruzzaman Mohammed

Kenny Colum

Kerebel Anthony

Kiani Hossein

Labite Herve

Lewis Gillian

Lu Jia

Luijckx Niels

Mac Suibhne Seosamh

Martin Juan Garcia

Meehan Peter

Mousavi Zeinabossadat ...

Murphy Fionnuala

Mussida Arianna

O' Reilly Aodhagan

O'Connell Jerome

O'Flynn Michael

Pavlis Michael

Piwowareczyk Agnieszka

Tao Yang

Touhy Patrick

Udayakumar Neetha

Vega Lucia Berlanga

Velusami Bala

Vero Sara

Walsh John

Wang Yuling

Xu Yue

Yan Mingjia

Zhang Xiaolei

Zhao Ming

Appendix 4

UCD School of Biosystems Engineering : Staff and Post Docs
2011/12 as photographed by Sean Kennedy

Butler Francis

Byrne Brian

Coffey Rory

Corkery Gerard

Cummins Enda

Curran Tom

Devlin Ger

Drummond Liana

Elmasry Gamal

Esquerre Carlos

Everard Colm

Fitzpatrick Anthony

Francisco Juan

Gonzales Barron Ursula

Gowen Aoife

Grace Pat

Grace Patrick

Holden Nicholas

Kennedy Sean

LI Dejun

Martin Juan Garcia

Mc'Donnell Kevin

Morsy Elsayed Noha

Northridge James

O'Donnell Colm

Owende Philip

Poschl Martina

Redmond Grainne

Shanahan Conor

Sheridan James

Solan Paddy

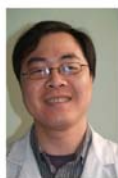Sun Da Wen

Taleus Oliag Pau

Tansey Fergal

Tiwari Uma

Walsh Eilin

Ward Shane

Zhang Zhihang

Znang Qing An