FOREWORD

The Fifteenth Annual Research Review describes the ongoing research programme in Biosystems Engineering at University College Dublin from over 100 researchers (10 academic staff, 2 technicians, 28 postdoctoral researchers and 62 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 five awards for presentational excellence at the Fourteenth Annual Biosystems Engineering Research Seminar held in University College Dublin on Friday 12th March 2010.

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    5 May 2010

*MEngSc1, MSc1, MAgrSc1 = Research Masters (Mode 1)
MEngSc2, MSc2 = Taught Masters (Mode 2)
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Abstract
A near-infrared (NIR) hyperspectral imaging system in the range 900-1700 nm was developed for quality grading of pork meat. Pork samples were pre-classified in three quality grades, as reddish-pink, firm and non-exudative (RFN), pale, soft and exudative (PSE), and dark, firm and dry (DFD) based on measurements of colour, texture and exudation. Spectral data extracted from tested pork classes have shown that there are differences among pork meat qualities allowing the classification of samples based on their spectral features. Some significant wavelengths that are linked to the drip loss, pH and colour attributes were identified from the first derivative plots of the mean spectra. Principal component analysis (PCA) has shown that the spectral information can easily differentiate pork meat according to quality characteristics. Results indicated a potential application of hyperspectral technique as a fast and non-destructive assessment method of pork quality evaluation.

Introduction
Conventional meat grading routines and quality evaluation methods of meat and meat products are laborious, destructive and associated with inconsistency and variability due to human inspection. The meat industry needs efficient technologies for assessment of food quality in order to save time and reduce cost. Hyperspectral imaging has emerged to integrate imaging and spectroscopic techniques in one system. In recent years there has been growing interest in this technology from researchers around the world regarding its application for food products. Studies on hyperspectral imaging for direct pork meat quality determination such as drip loss, pH, marbling and colour has recently been investigated (Qiao et al., 2007a, b, c) using a pushbroom hyperspectral imaging system in the visible and very near infrared range (400-1000nm). The results nominated hyperspectral imaging technique as a non-destructive method for fast detection of pork quality. However, to our knowledge no research attempts have been conducted using hyperspectral imaging in the near-infrared range for pork samples. On the contrary, there are some research endeavours in studying the applicability of hyperspectral imaging for quality evaluation of beef, chicken and fish (Peng and Wu, 2008; Yang et al., 2009; ElMasry and Wold, 2008). Indeed, there is a need for studying the unique features of this technology to aid in designing the future real-time quality evaluation systems. The objective of this study is to investigate the potential of hyperspectral imaging in near-infrared region (900-1700 nm) for pork quality assessment.

Materials and Methods
Sample preparation and measurement of meat quality attributes
Teagasc Food Research Centre Ashtown (Dublin, Ireland) provided a set of 75 fresh pork chops (1 inch) from the Longissimus dorsi muscle (loin). Samples were vacuum packed and sent to the Computerized Food Technology Laboratory at UCD, Belfield, Dublin, Ireland. After measuring colour, pH and drip loss for each sample, a hyperspectral image was acquired for each pork sample. Meat quality attributes were measured at 2 days post-mortem and the samples were
allowed to bloom for one hour before measurements. Drip loss was determined as a percentage of weight loss after 1 day of storage at 4°C (Honikel, 1998). Four pH measurements were taken using a pH meter (Orion 3 Star, Thermo Fisher Scientific Inc., USA) and then averaged to give only one pH value for each loin eye. Colour (expressed as $L^* a^* b^*$) was measured using Minolta colour meter (CR-400, Konica Minolta Corp., Japan) in six different locations in each sample, and then averaged for each loin eye. The samples were classified into three different quality grades based on colour lightness value ($L^*$), ultimate pH and drip loss, according to Warner et al. (1997), as RFN (40 samples), PSE (20 samples), and DFD (15 samples).

**Hyperspectral image acquisition and imaging processing**

Hyperspectral images were collected in reflectance mode using a pushbroom hyperspectral imaging system (Figure 1), consisting of a spectrograph (ImSpector, N17E, Spectral Imaging Ltd, Finland), a camera (Xeva 992, Xenics Infrared Solutions, Belgium), illumination source (tungsten-halogen V-light, Lowell Light Inc, USA), a conveyer (MSA15R-N, AMT-Linearways, SuperSlides & Bushes Corp., India) and a computer supported by data acquisition software (SpectralCube, Spectral Imaging Ltd., Finland). One hyperspectral image in a raw format was taken for each sample.

![Hyperspectral imaging system](image)

Figure 1. Hyperspectral imaging system used for image acquisition

A visual inspection of the acquired images revealed that the spectral images from the first four and the last fifteen wavelengths had a high level of noise, thus not being useful for data extraction. The images were then resized to 237 bands in the spectral domain, ranging from 910 nm to 1700 nm.

To correct the images from the dark current of the camera, dark and white hyperspectral images were taken. Both images were used to calibration of the sample images. A relative reflectance image was calculated with Equation (1): \[ I = \frac{I - B}{W - B} \]

where $I$ is the relative-reflectance image; $I_0$ is the original raw image; $B$ is the dark image (0 % reflectance) acquired with the cap covering the lens and lights turned off, and $W$ is the white image (~100 % reflectance) acquired from a white reference tile.

A region of interest (ROI) was manually selected comprising the whole loin eye area. For each image, a mean reflectance spectrum (910 to 1700 nm) of the ROI was calculated by averaging the spectral responses of each pixel in the ROI. In total, 75 mean reflectance spectra were obtained, one for each sample. ROI selection and reflectance spectra extraction from the hyperspectral images was performed using the software ENVI 4.6.1 (ITT Visual Information Solutions, Boulder, CO, USA).

In this study, principal component analysis was performed on the spectral data of pork samples and the resulting loadings were then used to extract the useful information attributed to difference in pork meat qualities according to the values of colour, pH and drip loss. First derivative of the mean spectra was also used to identify the effective wavelengths in the studied spectral range. The data analysis and image processing procedures were executed using Matlab 7.7.0 (The MathWorks Inc, MA, USA).

**Results and Discussion**

The typical average reflectance spectra obtained for the 40 RFN, 20 PSE and 15
DFD samples in the range from 910-1700 nm are shown in Figure 2.

Figure 2 Average spectra of three different pork quality classes: Pale, soft and exudative (PSE), Reddish-pink, firm, non-exudative (RFN) and dark, firm and dry (DFD) pork.

Each spectrum represents the average for the loin eye area of the samples. The spectra showed similar patterns, but differ on the reflectance absolute values mainly in the range from 910 to 1400 nm. DFD samples showed the lowest reflectance values along the spectra, while PSE samples had the highest values. It was also observed a slight difference in the range above 1650 nm.

These wavelengths can be used for further tests to identify and classify pork meat with reduced data processing.

The first three principal components were responsible for 99.4% of variability of the data. The first, second and third principal components variability are 82.3%, 14.3% and 2.8%, respectively.

Figure 5. Principal component analysis of the spectral data at the selected wavelengths (947, 1134, 1201, 1318 and 1378 nm).

As shown in figure 5, almost all PSE samples are located in the positive area of both PC1 and PC2, while the DFD samples are almost entirely located in the negative area indicating inverse relationship among these two quality classes. The principal components method is able to differentiate pork samples based on the reflectance values obtained.

Conclusions
The study demonstrated the potential of NIR hyperspectral imaging coupled with principal components analysis for evaluating quality attributes of pork meat. Optimal wavelengths were identified using first derivative of the main spectra. Further work will be performed to develop algorithms of image processing and classification based on the selected optimal wavelengths for achieving better accuracies for pork quality assessment.
Acknowledgements

The authors would like to gratefully acknowledge the financial support from the Food Institutional Research Measure (FIRM) strategic research initiative of the Irish Department of Agriculture, Fisheries & Food.

References


CLASSIFICATION OF PRE-SLICED TURKEY HAM USING NIR HYPER SPECTRAL IMAGING

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Abstract

This study was carried out to develop a hyperspectral imaging system in the near infrared (NIR) region (900-1700 nm) to assess the quality of cooked turkey hams. Different qualities of turkey hams were studied based on their chemical ingredients and processing parameters used during processing. Hyperspectral images were acquired for ham slices originated from each quality grade and then their spectral data were extracted. Spectral data was analyzed using Principal component analysis (PCA) to reduce the high dimensionality of the data and for selecting some important wavelengths. Out of 241 wavelengths, only five selected wavelengths (980, 1061, 1141, 1215 and 1326 nm) were considered to be the optimum wavelengths for the classification and characterization of turkey hams. The data analysis showed that it is possible to separate different quality turkey hams with few numbers of wavelengths on the basis of their chemical composition.

Introduction

The ham processing industry needs non-invasive, efficient and effective technologies for quality assessment of ham products. Producers and processors incur economic losses when meat quality is not accurately judged. In practice, the quality of turkey ham is normally assessed subjectively by an experienced grader and the outcome of subjective grading may vary with different inspectors. Therefore, a rapid, objective and non-destructive technique is needed for fast classification and characterization of turkey ham quality, and is desired by the meat industry.

Hyperspectral imaging techniques provides spatial information, as regular imaging systems, along with spectral information for each pixel in an image.

Due to the advantages of non-destructive, free of chemical preparation and fast inspection speed, hyperspectral imaging has been studied extensively for determining properties of fruits (Lu, 2003; Mehl et al., 2004), vegetables (Ariana et al., 2006; Cheng et al., 2004) and meat (Barlocco et al., 2006; Chan et al., 2002; Savenije et al., 2006; Park et al., 2004). The current hyperspectral imaging systems cannot directly be implemented in an online system for sorting and classification of agricultural product because of the extensive time required for image acquisition and subsequent analysis (ElMasry et al., 2008). However, hyperspectral imaging can be a very useful research tool for determining important spectral bands, which later can be implemented in a multispectral imaging system. There are various contributions on the usefulness of spectroscopy (NIRS) to predict quality attributes of meat and hams (Garci’a-Rey et al., 2005; Sheridan et al., 2006; Ortiz et al., 2006). However, to our knowledge, no research endeavours have been reported with respect to characterizing turkey hams into different quality groups using Hyperspectral imaging systems. The objective of this research is to investigate the potential of hyperspectral imaging in the spectral region between 900 and 1700 nm for the classification and characterization of turkey hams.

Materials and Methods

Preparation of turkey ham samples

Turkey hams with four quality classes based on different moisture content and different processing parameters were manufactured in Ashtown Food Research
Centre (AFRC), Dublin, Ireland. All hams were made by using whole butterfly turkey breast with the injection of different percentages of brine solutions (wet curing by injection) in addition to other ingredients and processing parameters. The four types of hams were identified as: B1, B2, B3 and B4, respectively. All samples were formed after tumbling, netting, vacuum shrink packaging, pot moulded, steam cooked at 80°C to a core temperature of 72°C. All cooked turkey blocks were then chilled in pot moulds to 4°C. All evaluated ham slices (four qualities, on the basis of moisture content) possess a discoloured or pale appearance with a large degree of colour uniformity making difficult for visual characterization or description. The actual average values of moisture content in the injected brine were 83.7%, 89.2%, 91.08% and 92.24%, for B1, B2, B3 and B4 respectively. Images were acquired immediately after slicing the hams to 10-mm-thick slices.

**Hyperspectral imaging system**

A laboratory NIR hyperspectral imaging system (900-1700 nm) as shown in Figure 1 was developed to acquire hyperspectral images for the turkey ham slices. The hyperspectral imaging system consists of a spectrograph (ImSpector N17E, Specim, spectral imaging Ltd, Oulu, Finland), a high performance camera (Xeva 992, XC 130 Xenics, Belgium), an illuminator (V320, 500W, Lowel V-lightTM, NY, USA), a conveyor translation stage (GPL-DZTSA-1000-X, Zolix Instrument Co. Ltd, China) and a computer supported with image acquisition software (SpectralCube, Spectral Imaging Ltd., Finland). The subsequent calibration, analysis and extracting spectral data from the image were performed with software ENVI 4.6.1 (ITT visual information solutions, Boulder, CO, USA). The actual optical sensitivity of this system ranges from 900 to 1800 nm but the best working sensitivity was nearly from 910 to 1700 nm to avoid low signal-to-noise ratio.

**Image acquisition and pre-processing**

During image acquisition, ham slices were conveyed one at a time to the field of view (FOV) of the camera with an optimized velocity of 2.7 cm/s. Upon entering the FOV, a hyperspectral image of the sample was taken and the image was sent to the PC through a USB port for storage. The images were calibrated due to dark current effect of camera, and to obtain relative reflectance using equation 1.

\[
I = \frac{I_0 - D}{W - D}
\]

where \(I\) is the relative-reflectance corrected image; \(I_0\) is the original raw image; \(D\) is the dark image (with 0% reflectance) obtained by covering the lens with an opaque cap and \(W\) is the white reference image (white tile with 99% reflectance).

**Segmentation of images**

The images were segmented to isolate the ham portions in a clear background with the aid of ENVI software (ITT visual information solutions, Boulder, CO, USA). Image at wavelength 941 nm was subtracted from the image at wavelength 1416 nm and then the resulting image is segmented with a minimum threshold of 0.17 and a maximum threshold of 1.0 to get the whole object (turkey hams with fat) in black background. Similarly, subtracting band at 1215 nm from band at 1269 nm was conducted followed by simple thresholding to isolate the fat part from the ham part. After masking the whole spectral image with this final segmented image, the target object (only turkey ham without fat) was obtained in black background. After segmentation,
each image (images containing only turkey and images containing only fat) was used for the extraction of spectral information.

**Data analysis**

The spectral data were extracted from each slice of different ham qualities and analysed using principal component analysis (PCA) and linear discriminant analysis (LDA) to reduce the dimensionality and to classify the samples.

**Results and discussion**

**Spectral Reflectance**

The mean spectra in the range of 910-1700 nm of the four tested blocks of turkey ham qualities are shown in Figure 2.

The overall features of the average spectra of hams showed that there are noteworthy differences among ham blocks in terms of their spectral attributes indicating differences in their chemical compositions. The absorption bands observed at 980 and at 1460 nm ascribed to OH stretch second overtones are mainly related to water content of the samples. Water is the main component of turkey slices ranging for 83.7% to 92.24%. Around 1200 nm, absorption bands are related to CH stretch second overtone (Cozzolino and Murray, 2004).

As seen in Figure 2, the Block-1 (the lowest moisture content of 83.7%) differs to a large extent from the other three ham quality blocks in its reflectance pattern. This indicates that a two-stage separation procedure may be considered indicating the facility of discriminating this black from the other quality blocks of high moisture contents. As illustrated in Figure 2, the blocks containing higher moisture contents (B2, B3 and B4) possessed lower reflectance value throughout the whole spectrum compared with the first block. At 1650 nm, the reflectance values of the high moisture blocks are higher than those of the first block but this difference is not considered to be noticeable. The difference among blocks of high moisture content could not be noticed by visual inspection of the spectral curve, but it could be inferred by multivariate analysis of their spectral data.

**Selection of Effective Wavelengths**

Principal component analysis (PCA) was carried out first using the all spectral data extracted from all turkey ham quality blocks, and the loadings of PCA results were plotted against the wavelengths (Figure 3) to select the most versus wavelengths plots.

The mean spectra in the range of 910-1700 nm of the four tested blocks of turkey ham qualities are shown in Figure 2.

![Figure 2](image1.png)

Figure 2. Spectral features of turkey hams. (Moisture content: B1-83.7%; B2- 89.2%; B3- 91.08% and B4: 92.24%).

The overall features of the average spectra of hams showed that there are noteworthy differences among ham blocks in terms of their spectral attributes indicating differences in their chemical compositions. The absorption bands observed at 980 and at 1460 nm ascribed to O H stretch second overtones are mainly related to water content of the samples. Water is the main component of turkey slices ranging for 83.7% to 92.24%. Around 1200 nm, absorption bands are related to C H stretch second overtone (Cozzolino and Murray, 2004).

As seen in Figure 2, the Block-1 (the lowest moisture content of 83.7%) differs to a large extent from the other three ham quality blocks in its reflectance pattern. This indicates that a two-stage separation procedure may be considered indicating the facility of discriminating this black from the other quality blocks of high moisture contents. As illustrated in Figure 2, the blocks containing higher moisture contents (B2, B3 and B4) possessed lower reflectance value throughout the whole spectrum compared with the first block. At 1650 nm, the reflectance values of the high moisture blocks are higher than those of the first block but this difference is not considered to be noticeable. The difference among blocks of high moisture content could not be noticed by visual inspection of the spectral curve, but it could be inferred by multivariate analysis of their spectral data.

**Selection of Effective Wavelengths**

Principal component analysis (PCA) was carried out first using the all spectral data extracted from all turkey ham quality blocks, and the loadings of PCA results were plotted against the wavelengths (Figure 3) to select the most versus wavelengths plots.

![Figure 3](image2.png)

Figure 3 Identification of effective wavelengths from loading-wavelength plot.

Five wavelengths (980, 1061, 1141, 1215 and 1326 nm) were selected as the most effective wavelengths which can be used to discriminate between different blocks of turkey ham qualities.
Once the important wavelengths were selected, the PCA was carried out again but this time by using spectral values at those selected wavelengths only. As shown in Figure 4a, it is easy to classify the four blocks of turkey into two groups (low and high moisture groups) using their reflectance values at the selected five wavelengths (Figure 4a) considering the first block as the low moisture group and the other three blocks as the high moisture group. Also, it is evident from Figure 4a that both low and high moisture ham classes could be differentiated easily from fat spectra because they have distinct spectral signatures. However, these selected five wavelengths were not able to separate ham blocks to more than two moisture classes as shown in Figure 4b. By using only two wavelengths (980 and 1140 nm), B1 and B2 were able to be differentiated and separated as distinct groups as low and intermediate moisture groups respectively (Figure 4c). However, B3 and B4 are overlapped with each other treating as a third group of a high moisture class (Figure 4c). This result implies that turkey hams can be classified on the basis of their moisture into three distinct classes (low, intermediate and high).

**Conclusion**
The study justifies the potentiality of the NIR hyperspectral imaging for the classification of different quality cooked turkey ham slices. It is possible to obtain the optimum wavelengths from Principal component analysis (PCA) that could be used later in a multispectral imaging system for real-time applications.

**Acknowledgements**
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CLASSIFICATION OF LAMB MUSCLES BY NIR
HYPERSPECTRAL IMAGING

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Abstract
The potential of NIR hyperspectral imaging (900-1800 nm) to classify four types of lamb muscles were investigated. Muscles from semitendinosus (ST), semimembranosus (SM), Longissimus dorsi (LD) and Psoas Major (PM) of Charollais breed at 2-day post-mortem were tested in this study. Principal component analysis (PCA) was used for dimensionality reduction and to aid in visualizing the hyperspectral data. Four most effective wavelengths (980, 1141, 1208 and 1441 nm) were then selected by PCA loading for the classification purposes. The results showed that hyperspectral imaging has a great capability for the classification of lamb muscles.

Introduction
NIR hyperspectral imaging is an emerging, non-contact analytical technology that combines both imaging and NIR spectroscopy to acquire both spatial and spectral information from an object. A NIR hyperspectral imaging system collects image data by arranging it to a three-dimensional “hypercube” which can be analyzed to determine physical and chemical features of an object. They are created when hundreds of single gray scale images are stacked on top of each other. Each of these gray scale images represents a single band of spectral wavelength. Each pixel in an NIR hyperspectral image represents a spectrum of that specific point (Williams et al., 2009). Consequently, the image contains chemical information in every pixel.

Because of the combined features of imaging and spectroscopy, hyperspectral imaging can be used to detect physical and geometrical features as well as chemical and molecular characteristics of an object (Qiao et al., 2007). Recently, NIR hyperspectral imaging has been evaluated for quality and safety inspection of many agricultural products such as meat (Naganathan et al. 2008b), fruits (Lu, 2003) and vegetables (Ariana et al., 2006).

There is great potential to work on hyperspectral imaging systems to extract the spectral information for the evaluation of meat quality. However, hyperspectral technology cannot be directly implemented as it is in an online system for quality evaluation because of the extensive time needed for image acquisition and subsequent analysis (Mehl et al., 2002). However, hyperspectral imaging can be a very useful research tool for determining key wavelengths, which later can be implemented in a multispectral imaging system. These key wavelengths can be obtained through a variety of strategies (ElMasry et al., 2007). Many studies have been carried out regarding lamb meat characteristics. But, up to date, no research has been conducted for the quality evaluation of lamb meat by hyperspectral imaging. As a first attempt, in this study, the potential of NIR hyperspectral imaging techniques were evaluated for the discrimination of lamb muscles. Therefore, the specific objective of the current study is to evaluate NIR hyperspectral imaging as a tool for the classification of lamb muscles and to indentify key wavelengths that can be used for multispectral imaging for lamb muscles classification in a real time.

Materials and methods
Sample preparation
Lamb samples for this study were collected from Ashtown Food Research Centre (AFRC), Teagasc, Dublin 15, Ireland. Ten animals of Charollais breed
were slaughtered and dressed according to Current EU regulations. After slaughter, carcasses were chilled at 4°C for 24 h. Muscles from **semitendinosus (ST)**, **semimembranosus (SM)**, **Longissimus dorsi (LD)** and **Psoas Major (PM)** were selected for the experiment. Samples (slices) with 1 inch thick were dissected from each muscle using a scalpel and cutting machine. Each sample was individually vacuum packed and shipped to the laboratory of Biosystems Engineering, University College Dublin in an ice box and kept at 4°C for 2 days post-mortem before image acquisition.

**NIR Hyperspectral imaging system**

The schematic representation of NIR hyperspectral imaging components is shown in Fig 1. The NIR hyperspectral imaging system consists of a spectrograph (ImSpector N17E, Specim, Finland), a camera (XEVA 992, XC 130 XenICs, Belgium), an illuminator (Lowel V-light™, NY, USA), a conveyer, a motor and a PC with image acquisition software.

![Fig 1. NIR hyperspectral imaging system](image)

**Hyperspectral image pre-processing**

Hyperspectral images were saved in raw format and then the Environment for Visualizing Images (ENVI) software (Research Systems Inc., Boulder, CO, USA) was used for further image processing, analyzing and extracting reflectance spectra. First, hyperspectral image was calibrated to reflectance values and then calibrated images were used for segmentation for the separation of object (muscle without adjoin fat and background).

**Reflectance calibration**

The recorded hyperspectral image of the sample was corrected for absolute reflectance and calculated using the following equation (ElMasry et al., 2009):

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

Where \( R_0 \) is the raw hyperspectral image of the lamb sample, \( D \) is the dark current image (approximately with 0% reflection) and \( W \) is the white reference image taken from a standard white reference board (approximately 99% reflectance). The spectral data for processing was limited to 910–1700 nm with 237 spectral bands due to the high noise level beyond this range.

**Segmentation of images**

All images are processed and analyzed individually and the following procedure was used for the segmentation of each image. First, the background was removed from the lamb muscle image by applying masking. To do this, subtraction was applied between images and then segmented with threshold value between 0.09 and 1. This segmented image was then masked by calibrated image and obtained an image with fat and lean only. Again, segmentation was performed for the detection of fat to this image between threshold value of 0.055 and 1. Finally, the lamb lean portion was isolated by subtracting the last segmented image (containing only fat portion) from the first segmented image (containing both lean and fat portions) to produce a lean part in a black background. The isolated lean portion was then treated as ROI to be used for extracting spectral data from each muscle.

**Results and discussion**

**Average reflectance spectra**

The average reflectance spectra for each lamb muscle in the spectral range of 910-1700 nm are shown in Fig 2. Although the spectral curves of the muscles show a similar trend, the spectral profiles are substantially distinguished from each other. PM and ST muscles showed higher
reflectance values than those of LD and SM. The higher reflectance value of muscles was due to the higher brightness of muscles.

**Fig 2. Features of reflectance spectra**

**Principal Components Analysis (PCA)**
PCA was applied on the spectra to reduce the dimensionality and to examine qualitative differences in the spectra between the muscles. Figure 3 shows the score plot of PC1 and PC3, which reveals the feasibility of discrimination between the muscles. However, this plot only demonstrates the qualitative difference without referring to quantitative classification.

**Linear discriminant analysis (LDA)**
The first five PCs account for 99.68% of the total variation of the reflectance data and these five PCs were used as inputs for LDA classification. Table 1 shows the classification results in the form of a confusion matrix. Correctly classified muscles are shown on the diagonal. It is clear that LDA can classify PM, ST, LD and SM with accuracy of 89%, 100%, 90% and 90%, respectively. Therefore, four lamb muscles were classified with 92% accuracy. Qiao et al. (2007) reported that, it is possible to separate different quality classes of pork meat with accuracy about 87.5% by hyperspectral imaging. Using only the spectra, Juarez et al. (2008) discriminated six types of Southern Spain lamb types with accuracy around 83% by visible spectroscopy. Therefore, the results suggest that the NIR hyperspectral imaging has the potential to classify lamb muscles without any physicochemical information combined in the spectral data.

**Table 1: Classification matrix of different muscles by LDA**

<table>
<thead>
<tr>
<th>Muscle name</th>
<th>classified into</th>
<th>Accuracy (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PM</td>
<td>8</td>
<td>89</td>
</tr>
<tr>
<td>ST</td>
<td>0 10</td>
<td>100</td>
</tr>
<tr>
<td>LD</td>
<td>0 9</td>
<td>90</td>
</tr>
<tr>
<td>SM</td>
<td>0 1 9</td>
<td>90</td>
</tr>
</tbody>
</table>

**Determination of key wavelengths**
The loading spectra of PCA were used for selecting key wavelengths. The loading of the first three principle components in the entire spectral range are presented in Fig 4. The wavelengths corresponding to the highest absolute peaks and valleys were selected as key wavelengths. Four most important wavelengths (980, 1141, 1208 and 1441 nm) were selected by using loading of PCA for the classification purposes. These important wavelengths can be used for lamb muscle classification using multispectral imaging instead of the whole spectral range.
Fig 4. Loading plot of the first three PCs

Conclusions
A NIR hyperspectral imaging system was developed to classify lamb muscles with the extracted reflectance data as input. The results suggested that NIR hyperspectral imaging can be used as a non-destructive tool for the classification of lamb muscles. Using NIR hyperspectral imaging, it is possible to classify lamb muscles with overall accuracy about 92%. More research is needed incorporating more samples as well as different muscles (from beef and pork) to improve accuracy and robustness of classification.

Acknowledgement
The authors would like to acknowledge the funding of the Irish Government Department of Agriculture, Fisheries and Food under the Food Institutional Research Measure (FIRM) programme.

Reference
Abstract

Due to the large variety of fruit used, smoothies contain varying amounts of different health promoting phytochemicals. A model was developed in this study to evaluate the impact of different fruit combinations on the phytochemicals presence in smoothies. The model provides an average distribution of specific phytochemical subgroups within a smoothie based on the frequency of consumption. A Monte Carlo simulation will be used to evaluate the uncertainty and variability within the model and aid in the development of a distribution curve. A scenario analysis will also be developed to look at the impact of different model assumptions and input parameters.

Introduction

Phytochemicals refer to every naturally-occurring chemical in plants including fruits, vegetables and grains. Fruits contain high levels of phytochemicals and associated with many health promoting properties (Lui et al., 2004). Many epidemiological studies have shown consistent association between the consumption of diets rich in fruits and vegetables and a lower risk of chronic diseases including cancer, cardiovascular disease, hypertension and diabetes (Apostolidis et al., 2006; Amic et al, 2007). Phytochemicals can be classified as carotenoids, phenolics, alkaloids, nitrogen-containing compounds, and organosulfur compounds (Lui et al., 2004). Phenols are the major group of phytochemical which are further classified into anthocyanins, anthochlors, benzofurans, chromones, coumarins, minor flavonoids, flavonones and flavonols, isoflavonoids, lignans, phenols and phenolic acids, phenolic ketones, phenylpropanoids, quinonoids, stilbenoids, tannins and xanthones (Dillard and German, 2000). For example, apples contain 53-109 mg/100g of flavonoids, strawberries contain 46 – 62 mg/100g of phenolic acids whereas grapes contain 396 to 424 mg/100g of phenolic acid (Boyer & Liu, 2004; Yang et al., 2009; Ordidge et al., 2010). In a recent study, Jenkin et al. (2008) reported that strawberry supplementation reduced cholesterol levels which lower coronary heart disease risk.

Smoothies are an increasingly popular way of consuming fruits which has increased with market growth of 214% in 4 years. Smoothies are blended drinks consisting of a number of ingredients including fruit (or less commonly vegetables), fruit juice, ice, yoghurt and milk. There are three main types of smoothies: fruit only, fruit and dairy, and functional. Functional smoothies, such as those that contain probiotics, have appeared only very recently on the market. Smoothies are commonly sold as a drink, snack or meal alternative and are available either ready-made or made-to-order (SafeFood, 2009).

The objective of this study is to quantify the variability and uncertainty in the level of various phytochemical subgroups in different fruit smoothie recipes and, through a consumption survey, assess the level of phytochemical intake by different demographics.

Materials and Methods

Model development:
Data on different fruit smoothie combinations was gathered. The fruits most commonly used in smoothies were selected. These were strawberries, raspberries, apples, grapes and cranberries. The various phytochemicals associated
with these fruits were gathered and it was decided to focus on the presence of all phenolics, all flavonoids and all anthocyanins within each. Three smoothie combinations were formulated (Table 1). Total phenol content for combination 1 and 2 and total anthocyanin levels were looked in combination 3.

Table 1. List of Smoothie combinations used in preliminary modelling

<table>
<thead>
<tr>
<th>Combination 1</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Apple - fresh</td>
<td>45</td>
</tr>
<tr>
<td>Grapes - fresh</td>
<td>20</td>
</tr>
<tr>
<td>Strawberry - fresh</td>
<td>20</td>
</tr>
<tr>
<td>Cranberry juice/concentrates</td>
<td>15</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Combination 2</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grapes - fresh</td>
<td>40</td>
</tr>
<tr>
<td>Raspberry - fresh</td>
<td>20</td>
</tr>
<tr>
<td>Strawberry - fresh</td>
<td>20</td>
</tr>
<tr>
<td>Cranberry juice/concentrates</td>
<td>20</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Combinations 3</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cranberry - fresh</td>
<td>30</td>
</tr>
<tr>
<td>Strawberry - fresh</td>
<td>20</td>
</tr>
<tr>
<td>Raspberry - fresh</td>
<td>30</td>
</tr>
<tr>
<td>Grape juice</td>
<td>20</td>
</tr>
</tbody>
</table>

The effects of processing on the final phytochemical concentration within the smoothie will also be determined using existing scientific and technical literature. The processing steps involved in the production of smoothies are illustrated in Figure 1.

Various processing steps may reduce the amount of photochemical. As the effects of these steps are yet to be determined, it was assumed a 2 – 5% decrease in phytochemical concentration was associated with production. By using a mathematical calculation the amount of total phenol content and anthocyanin was calculated as shown in Table 2.

A smoothie consumption study (Safefood, 2009) of citizens of the Republic of Ireland and Northern Ireland was examined to determine the volume of smoothies being consumed thus allowing for the calculation of daily or weekly phytochemical exposure due to smoothies. The effect of uncertainty and variability of the data will be evaluated by running a Monte Carlo simulation with 10,000 iterations.

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. Together, these scenarios 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.

Figure 1. Flow diagram of smoothie production.

Results and Discussion

A survey of the island of Ireland (Safefood, 2009) found that of the people
who drink smoothies, roughly a third will have between 2 and 5 smoothies a week. The survey also indicated that the most frequent quantity of smoothie consumed per drinking occasion was either a 200ml glass, a 250ml bottle/container or a 400 ml or above dome container. Taking an example of each combination listed above and assuming a 2 – 5% loss due to processing, an average value for the total number of phenolics and anthocyanins consumed per week per person was calculated. As can be seen in table 2, if a person was to consume a 200 ml glass of smoothie combination 1, two to five times a week their total phenolics consumption would be between 0.85 g and 2.19 g. If the same person was to consume the same amount of smoothie combination 2 their total phenolic intake per week would be between 0.55 g and 1.43 g. Similarly, combination 3 would provide between 0.63 g and 1.63 g of anthocyanins per week. Apostolidis et al (2006) shows that consumption of 3.89 g of total phenolics per week can have a radical inhibitory effect (roughly 50%) on diabetes and hypertension development. As smoothie consumption provides a lower amount of total phenolics, up to 2.19 g in combination 1, the inhibitory effect would in turn be lower, the exact extent of which is yet to be determined.

Conclusions
This study represents a preliminary effort to model various fruit combinations and their effects on the phytochemical content of the smoothie produced. The model also takes into account variability caused by processing and gives an average distribution based on the frequency of consumption. Further work will be required for the addition of extra smoothie combinations, the expansion of phytochemical subgroups studied, the development of a better understanding of the loss of phytochemicals due to processing and the addition of a Monte Carlo simulation to measure the uncertainty and variability of the results.

### Table 2. Total Phenolic and Anthocyanin concentrations within each smoothie combination

<table>
<thead>
<tr>
<th>Smoothie</th>
<th>Total Phenolic g/100ml</th>
<th>Total Anthocyanin g/100ml</th>
</tr>
</thead>
<tbody>
<tr>
<td>Combination 1</td>
<td>0.224</td>
<td>0.106</td>
</tr>
<tr>
<td>Combination 2</td>
<td>0.145</td>
<td>0.158</td>
</tr>
<tr>
<td>Combination 3</td>
<td>0.162</td>
<td>0.158</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>% loss (2 to 5% assumption)</th>
<th>2% loss</th>
<th>5% loss</th>
<th>2% loss</th>
<th>5% loss</th>
</tr>
</thead>
<tbody>
<tr>
<td>Combination 1</td>
<td>0.219</td>
<td>0.212</td>
<td>0.219</td>
<td>0.212</td>
</tr>
<tr>
<td>Combination 2</td>
<td>0.143</td>
<td>0.139</td>
<td>0.143</td>
<td>0.139</td>
</tr>
<tr>
<td>Combination 3</td>
<td>0.162</td>
<td>0.158</td>
<td>0.162</td>
<td>0.158</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Total Consumed in 1 Week</th>
<th>2 times</th>
<th>5 times</th>
<th>2 times</th>
<th>5 times</th>
</tr>
</thead>
<tbody>
<tr>
<td>Combination 1</td>
<td>Regular glass</td>
<td>0.850 – 0.877</td>
<td>2.124 – 2.192</td>
<td>0.850 – 0.877</td>
</tr>
<tr>
<td></td>
<td>Small bottle</td>
<td>1.062 – 1.096</td>
<td>2.656 – 2.739</td>
<td>1.062 – 1.096</td>
</tr>
<tr>
<td>Combination 2</td>
<td>Regular glass</td>
<td>0.553 – 0.571</td>
<td>1.303 – 1.427</td>
<td>0.553 – 0.571</td>
</tr>
<tr>
<td></td>
<td>Small bottle</td>
<td>0.692 – 0.713</td>
<td>1.709 – 1.873</td>
<td>0.692 – 0.713</td>
</tr>
<tr>
<td></td>
<td>Dome container</td>
<td>1.196 – 1.141</td>
<td>2.766 – 2.853</td>
<td>1.196 – 1.141</td>
</tr>
<tr>
<td>Combination 3</td>
<td>Regular glass</td>
<td>0.63 – 0.649</td>
<td>1.575 – 1.626</td>
<td>0.63 – 0.649</td>
</tr>
<tr>
<td></td>
<td>Small bottle</td>
<td>0.788 – 0.892</td>
<td>1.963 – 2.031</td>
<td>0.788 – 0.892</td>
</tr>
<tr>
<td></td>
<td>Dome container</td>
<td>1.26 – 1.3</td>
<td>3.18 – 3.25</td>
<td>1.26 – 1.3</td>
</tr>
</tbody>
</table>

### References


Safefood (2009) Smoothies: Consumer knowledge, attitudes and beliefs around the nutritional content of smoothies, Ireland, safefood.

EXPOSURE ASSESSMENT MODELLING OF \(\beta\)-GLUCAN IN FUNCTIONAL FOODS ON THE IRISH MARKET.

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Abstract
The principles of Monte Carlo simulation modelling are used to assess human dietary exposure to \(\beta\)-glucan in Ireland. This study looks at the development of a consumer-level baseline model (including scenario analysis) to assess human exposure to \(\beta\)-glucan through a variety of products. Daily individual exposure amounts are determined using available scientific data:

1. A survey of breads, cereals and yogurts on shop shelves in Ireland was carried out to evaluate \(\beta\)-glucan levels in these products. The survey totalled 310 products, with only 41 displaying \(\beta\)-glucan containing ingredients.

2. The results of the North/South Ireland Food Consumption Survey were used to evaluate serving sizes and frequency of consumption.

3. Data collated in 1 and 2 are combined in an exposure model and a sensitivity analyses will be used to evaluate significant sources of \(\beta\)-glucan in the human diet.

Introduction
Functional foods are defined as "foods and food components that provide a health benefit beyond basic nutrition", including: conventional, fortified, enriched and enhanced foods. Fibre is seen as a health promoting substance, and \(\beta\)-glucan is an important functional ingredient of fibre (FDA, 2010). Key components of soluble fibre are \(\beta\)-glucan (1-4), \(\beta\)-glucan (1-6), which are non-starch polysaccharides (strings of glucose molecules) that occur naturally in the endosperm cell walls of oats and throughout the endosperm of barley (Figure 1). \(\beta\)-glucans have known health benefits, namely cholesterol-lowering effect (McIntosh et al, 991; Newman et al 1989), regulating blood glucose and insulin response in diabetics (Cavallero et al 2002) and even reducing cancer risk (Jacobs et al 1998). The FDA recommended intake of \(\beta\)-glucan is 3g per day. In order to realise an intake of 0.75g of \(\beta\)-glucan, 3g of NSP (non-starch polysaccharides) needs to be consumed. In 1997 the FDA approved (using results of clinical trials) that a health claim could be made for foods that contain 0.75 gram of \(\beta\)-glucan per serving.

The objective of this study is to model the exposure of the Irish population to \(\beta\)-glucans in commercially available foodstuffs.

In Ireland \(\beta\)-glucan containing ingredients of shelf foodstuffs are not necessarily advertised and so are ascertained indirectly. Currently no legislation exists for suppliers to detail ingredient quantities, unless the ingredient occurs in the product name, or is an allergen. (Food Safety Association of Ireland). This study uses previously published findings of \(\beta\)-glucan content in commercial foodstuffs as its source, and includes factoring in the modelling process.

Figure 1: Components of cereal grain
The North/South Ireland Food Consumption Survey (North/South Survey) was conducted between 1997 and 1999 by the Irish Universities Nutrition Alliance (IUNA). The North/South Survey placed food products into

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Monte Carlo simulation methods are used in studying systems with a large number of coupled degrees of freedom, and are useful for modelling phenomena with significant uncertainty in inputs. In this case the varying degrees include effects of processing on β-glucan content and likelihood of person eating β-glucan enriched food in each category. The method allows for testing the sensitivity of each input.

In defining the domain of inputs, we include likely β-glucan content of; raw oats and barley (for yogurts), cooked oats and barley (for cereals and breads). The likelihood of an individual ingesting such a foodstuff is also included.

Materials and Methods

The shop survey results are displayed in Tables 1a and 1b. The table also shows the IUNA measure of consumption for each category. The table confirms the low prevalence of display of ingredient quantities.

Table 1a: Nutritional Alliance survey food categories

<table>
<thead>
<tr>
<th>North/South Survey Category Number</th>
<th>North/South Survey Category Name</th>
<th>North/South Survey - Mean Intake (grams/day)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>Wholemeal and Brown Breeds &amp; Rolls</td>
<td>45</td>
</tr>
<tr>
<td>6</td>
<td>&quot;Ready-to-eat&quot; Breakfast Cereals</td>
<td>19</td>
</tr>
<tr>
<td>7</td>
<td>Other breakfast cereals (e.g. porridge)</td>
<td>15</td>
</tr>
<tr>
<td>15</td>
<td>Yogurts</td>
<td>16</td>
</tr>
</tbody>
</table>

Table 1b: Products from shop survey

<table>
<thead>
<tr>
<th>SHOP SURVEY</th>
<th>Shop Survey - Number of products in North/South survey category</th>
<th>Number of products advertising quantities</th>
<th>Number of products advertising Grain/Fibre (no quantities)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>61</td>
<td>3 - Grain 1 - Fibre</td>
<td>6 - Grain 5 - Fibre</td>
</tr>
<tr>
<td>6</td>
<td>21</td>
<td>30 - Grain 35 - Fibre</td>
<td>16 - Grain 32 - Fibre</td>
</tr>
<tr>
<td>7</td>
<td>13</td>
<td>12 - Grain 11 - Fibre</td>
<td>1 - Grain 2 - Fibre</td>
</tr>
<tr>
<td>15</td>
<td>74</td>
<td>2 - Grain</td>
<td>1 - Grain</td>
</tr>
</tbody>
</table>

Several authors have quantified β-glucan content of grains (Grausgruber et al. 2004, Welch et al. 2000, Ajitumar et al. 2005). For example Luhaloo (1997) reports content found in commercial oat brans. He notes the wide variation (4.7-8.3%) in mixed-linkage β-glucan found. Modelling will be factored to allow for this spread. Additionally many authors have noted the deleterious effect of processing on β-glucan content. Rakha (2009) surveyed rye products and found that the processes of bread manufacture could degrade β-glucan content significantly.

The modelling is to include influencing factors: eg; likely β-glucan content of oats or barley constituent (distribution type, average and spread), likely manufacture process and resultant β-glucan content. A schematic of the modelling process is given in Figure 2.

Sensitivity analyses will need to be run to find the notable influencing factors.

The North/South survey measured the mean intake as 45 g/d for wholemeal brown breads and rolls, 19 and 16 for RTE and other cereals respectively, and 16 for yogurts. The shop survey of 87 breads found 61 in this category.
Figure 2: Schematic representation of influencing factors on β-glucan ingestion

Model development
Factors influencing the level of β-glucan ingested from each relevant category, using scientific literature sources, include type and number of manufacturing processes each grain type undergoes, spread of available foods and their details for each category.

In addition to the baseline model, hypothetical scenarios can be developed taking the variability in the input data into account and looking at the impact of model uncertainties and input parameters.

Sensitivity analysis of the model evaluates the inputs. The analysis identifies model parameters that significantly influence the level of β-glucan ingested and thus allow us to gain insight into the behaviour of the model. A sensitivity analysis can be used to simplify the model complexity by highlighting the critical inputs and thus may help in communicating the model structure and results. The model can predict average β-glucan intake as a percentage of total intake for the relevant food category.

Results and Discussion
A framework model has been developed and will be used to develop a quantitative model to evaluate human exposure to β-glucan. Data has been collated for products potentially containing β-glucan from a shop survey and consumption data was obtained from the North/South survey. This will be used in the development of probability distributions within the model. Several factors will be included for modelling, including the effect of manufacturing on β-glucan content, type of processing on harvested grain, declared (advertised) grain content of product.

Conclusions
Simulation modelling is an effective technique in predicting outcomes for complex scenarios with fluctuating inputs. Using such modelling to determine β-glucan exposure results in usable data. The method also displays the importance of each input and how as each input term changes the output is affected. In this study the Monte Carlo simulation is one of the reliable ways to calculate the population’s exposure to available functional foods.

Acknowledgements
The author wishes to acknowledge the support and guidance of Dr Enda Cummins and Uma Tiwari in developing this paper.

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brans. Journal of the Science of Food and Agriculture, 76 (1), 142-148
RISK RANKING OF CHEMICAL CONTAMINANTS IN PORK.

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Abstract
Introduction of chemical residues into food and the food chain in recent times is on the increase; this has led to cases of severe illness. Some of these illnesses have been linked to pork and pork products from resulting contamination. Contamination, sometimes from veterinary drugs, occurring anywhere along the production of pork products can have adverse effects on the safety of products.

This study will look at the development of a chemical risk ranking methodology to provide useful information on the relative risks associated with the presence of chemical contaminants in pork. For a good development of quantitative risk ranking methodology for potentially toxic or deleterious chemical contaminants in pork, it is very important to note that this risk-ranking exercise is not intended for the estimation of risks associated with any one particular contaminant; instead, it is intended to be a tool for ranking of the relative risks of contaminants to aid in setting priorities for allocating resources in a risk-based manner. Risk ranking is a useful and valuable methodology that can be used for identifying the most significant risks in food products. Pork and pork products are susceptible to contaminants be it physical, biological, or chemical contaminants. A number of studies have been carried out on chemical contaminants in pork and some have identified chemical residues as a serious food hazard, which has brought the need to quantitatively risk chemical contaminants in pork and pork products chain to validate its safety.

Risk assessment in this study involves these four basic steps: (a) what can go wrong? (Hazard Identification); (b) what is the likelihood it would happen? (Risk Estimation); (c) Development of ranking list; and (d) Comparing risk and placing them in order.

A risk ranking model can be utilised in the first step of HACCP programme (FAO, 1997), which is hazard identification of chemical risk assessment involving gathering and assessing potential contaminants identified in pork and pork products, a ranking methodology can then be employed to rank contaminants to assess potential hazards by implementation of appropriate critical control points. Quantitative risk ranking using risk estimation considers two parameters; exposure (dose) and allowable daily intake (ADI). ADI value is an estimate of the amount of a substance, expressed on a body weight basis that can be ingested daily over a lifetime without appreciable risk to the consumer. Any risk ranking criteria for hazards should ideally have some objective measure of ‘risk’. In the context of food, the concept of risk generally incorporates a measure of the severity of the hazard and exposure to the hazard (as measured by consumption of contaminated food), i.e. Risk = severity × Exposure.

The objective of this study is to develop a systematic method of identifying, comparing and risk ranking of chemical contaminants in pork.
Methodology

Chemical Hazard Identification
The occurrence and consumption data was sourced. This was performed by reviewing (a) scientific literature taken from recent and relevant publications, (b) Residue database such as National food residue database (NFRD) and Veterinary residue committee (VRC).

Chemical Characterisation
Where such residues are found, they were assessed using a process of ‘Risk Assessment’. This is often done by comparing the amount a consumer might have eaten with the Acceptable Daily Intake, or ADI. Using the relevant data to measure (a) Severity of exposure (b) Properties of contaminants (c) Adverse effect related to ingestion. A preliminary assessment will be collected for acceptable level of exposure.

Exposure Assessment
This involves assessing the amount of contaminant in pork and the probability of hazards occurring and the ensuing implications. Investigating the degree of animal exposure and, consequently, human exposure and highlighting the possible pathways that the contaminant can reach the host.

Risk Ranking System / Characterisation
This is a method for arranging information on contaminants, food production processing and consumption to contrast and evaluate different chemicals and rank them by a score.

Results and Discussion
The parameter used to rank potential contaminants was developed. Chemical contaminants were categorised into low risk, medium risk and high risk based on their level of toxicity. Risk were compared and placed in order of authorised, unauthorised and banned substances based on WHO/FAO regulations. Table 1 shows some contaminants that were sourced from NFRD and VRC. Figures 1 and 2 show the level of Copper and Ochratoxin A found in pork respectively. The Risk Assessment Process was very important in this study as it helped in Hazard Identification, Hazard Characterisation, Exposure Assessment and Risk Characterisation.

<table>
<thead>
<tr>
<th>Substances / Chemicals</th>
<th>NFRD No. of Samples analysed</th>
<th>VRC No. of samples analysed</th>
<th>Summary Non-compliant or detected samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Selenium</td>
<td>100</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>Dioxins</td>
<td>14</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>Copper</td>
<td>100</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>Tetracycline</td>
<td>108</td>
<td>80</td>
<td></td>
</tr>
<tr>
<td>Chlortetracycline</td>
<td>772</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>Coplanar PCBs</td>
<td>3</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>Ochratoxin A</td>
<td>147</td>
<td>72</td>
<td></td>
</tr>
<tr>
<td>PAHs</td>
<td>31</td>
<td>14</td>
<td></td>
</tr>
<tr>
<td>oxytetracycline</td>
<td>772</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Sulphadiazine</td>
<td>773</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>Tin</td>
<td>100</td>
<td>9</td>
<td></td>
</tr>
<tr>
<td>Zinc</td>
<td>100</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>Salinomycin</td>
<td>100</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>Nitrite *</td>
<td>8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tetracycline</td>
<td>80</td>
<td>42</td>
<td></td>
</tr>
<tr>
<td>Nitrofuran</td>
<td>20</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>Marbofloxacin*</td>
<td>7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chlorotetracycline</td>
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<td>4</td>
<td></td>
</tr>
<tr>
<td>Sulphonamide</td>
<td>989</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>Tetracycline</td>
<td>989</td>
<td>8</td>
<td></td>
</tr>
<tr>
<td>Carbadox (QCA)</td>
<td>94</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Salinomycin</td>
<td>9</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Cadmium</td>
<td>47</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Ivermectin</td>
<td>550</td>
<td>1</td>
<td></td>
</tr>
</tbody>
</table>

Conclusion
Chemical contaminants constitute serious health hazards in food. Quantitative risk ranking methodology can be used to rank chemical contaminants in pork and other food products. It can also be used to assess the risk, toxicity and quantity of chemical contaminant consumed in food. This work has provided useful information on risks associated with some chemical contaminants in pork based on residue data from NFRD and VRC.
COPPER LEVEL IN PORCINE MUSCLE

![Copper level in porcine muscle](image)

**Figure 1:** Copper level in porcine muscle

0chratoxin A in kidney and muscle of porcine

![Ochratoxin A in kidney and muscle of porcine](image)

**Figure 2:** Ochratoxin A in kidney and muscle of porcine

**Abbreviations**
- NFRD: National Food Residue Database.
- VRC: Veterinary Residues Committee
- HACCP: Hazard Analysis and Critical Control Points
- WHO: World Health Organisation
- FAO: Food and Agriculture Organisation of United Nations

**References**

National Food Residue Database. (1996-2000). Welcome to the National Food Residue Database (NFRD), developed by Ashtown Food Research Centre, TEAGASC. Retrieved March 2010, from nfrd.teagasc.ie


RISK RANKING OF CHEMICAL CONTAMINANTS IN BEEF

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Abstract
Prevention of the contamination of foods is a key food safety issue. The identification and characterisation of contaminants is the first step in their reduction or elimination.

The purpose of this study is to estimate the potential risk of chemical contaminants in beef and to rank them according to their severity. This study will identify the possible contaminants, characterise them and give them a score from highest to lowest.

Introduction
The introduction of chemical residues into the food production process is still a risk for food safety. These chemical contaminants include pesticides, veterinary drugs and hormone residues, contamination of heavy metals, trace elements and toxins. Harmful effects to humans, including carcinogenic, teragenic and mutagenic effects; allergic reactions and increased resistance of bacteria to antibiotic treatments may be caused by these chemicals (Wang et al., 2009).

Most veterinary and chemical drugs are banned in the European Union and can only be administered in certain circumstances under strict control. These veterinary and chemical drugs frequently have anabolic effects and are used for therapeutic and prophylactic purposes as well as for improving breeding efficiency. These substances can remain in all animal treated derived foods. Usually, chemical contaminants are added as illegal growth promoters, improving feed conversion efficiency and improving the lean to fat ratio. Contaminants that were released into the environment decades ago, may still cause problems, whilst new products and substances are now being developed, used and discarded as well (Toldra and Reig, 2006). Chemical residues in food are subject to research, surveillance and testing activities. In Ireland, these activities are undertaken by statutory authorities, academic institutions and research institutes and private and public testing laboratories. The analysis of data on residues in food is compared to residue limits predetermined by regulatory bodies (NFRD, 2006).

Human and animal health is being increasingly quantitatively assessed using risk ranking models. Hazard ranking is useful to identify those substances that may pose a high risk, but it may mistakenly incorporate substances which cause little or no risk because of small quantities released and it may eliminate high volume chemicals which are comparatively harmless (Arnot et al., 2006). The objective of this study is to provide a systematic method of identifying; recording and comparing chemical contaminants in beef and to semi quantitatively assess and rank chemicals according to severity.

Methodology
Chemical hazard identification
Evidence of contamination in published data will be the criterion used to identify the chemical residues. This will be performed by reviewing data sources such as (i) scientific literature taken from relevant and recent publications (ii) databases such as the National Food Residue Database (NFRD) and the Veterinary Residue Committee (VRC) (iii) recent publications and surveys (iv) EU databases and incident reports.
Chemical characterisation
Characterisation of the chemicals will be carried out using relevant data as above to measure (i) potency and severity (ii) contaminant physical and chemical properties (iii) animal and human host factors (iv) sensitivities of populations (v) strain virulence (vi) factors related to conditions of ingestion and the likelihood of problems from ingestion of a given amount of contaminant will be examined. For chemical hazards, various data will be collected for acceptable exposure levels.

Exposure assessment
This involves assessing the amount of contaminant in beef and the probability of hazards occurring and also the ensuing implications. Exposure assessment will also involve investigating the degree of animal exposure and, consequently, human exposure and highlighting the possible pathways that the contaminant can reach the host.

Risk Ranking System
This is a method for arranging information on contaminants, food production processing and consumption to contrast and evaluate different chemicals and rank them by a score.

Results
Table 1 above summarises all the different contaminants which will be considered for this study and are mainly sourced from Irish sources (National Food Residue Database) and UK sources (Veterinary Residue Commission). Of the 157 chemical contaminants which were analysed in these databases, 39 chemicals were found to either be non compliant or were detected in beef samples.

<table>
<thead>
<tr>
<th>Chemical</th>
<th>NFRD No. of samples analysed</th>
<th>VRC No. of samples analysed</th>
<th>No. of samples Non-compliant or with detected residue</th>
</tr>
</thead>
<tbody>
<tr>
<td>Avermectins</td>
<td>652</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Cadmium</td>
<td>310</td>
<td>38</td>
<td></td>
</tr>
<tr>
<td>Chlortetracycline</td>
<td>199</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>Coccidiostats</td>
<td>41</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>Coplanar PCBs</td>
<td>5</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>Copper</td>
<td>125</td>
<td>125</td>
<td></td>
</tr>
<tr>
<td>Dieldrin</td>
<td>1083</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>Dihydrostreptomycin</td>
<td>1426</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>Doramectin</td>
<td>275</td>
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<td></td>
</tr>
<tr>
<td>Florfenicol</td>
<td>138</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>Furazolidone</td>
<td>642</td>
<td>13</td>
<td></td>
</tr>
<tr>
<td>Hexachlorohexane</td>
<td>1031</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>Ibuprofen</td>
<td>545</td>
<td>1</td>
<td></td>
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<tr>
<td>Ivermectins</td>
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<td>183</td>
<td>3</td>
</tr>
<tr>
<td>Lead</td>
<td>451</td>
<td>180</td>
<td>65</td>
</tr>
<tr>
<td>Neomycin</td>
<td>1290</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Nitrofurans</td>
<td>637</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>Nortesterone</td>
<td>2743</td>
<td>4776</td>
<td>3</td>
</tr>
<tr>
<td>Oestradiol</td>
<td>1856</td>
<td>5</td>
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</tr>
<tr>
<td>Organochlorines</td>
<td>85</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Oxfendazole</td>
<td>550</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>Oxytetracycline</td>
<td>407</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>PCBs</td>
<td>402</td>
<td>49</td>
<td></td>
</tr>
<tr>
<td>Permethrin</td>
<td>1022</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Phenylbutazone</td>
<td>259</td>
<td>929</td>
<td>1</td>
</tr>
<tr>
<td>Progesterone</td>
<td>1221</td>
<td>3385</td>
<td>0</td>
</tr>
<tr>
<td>Pyrethroids</td>
<td>420</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Salbutamol</td>
<td>627</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Selenium</td>
<td>125</td>
<td>125</td>
<td></td>
</tr>
<tr>
<td>Sulphonamides</td>
<td>835</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>Sum of marker PCBs</td>
<td>11</td>
<td>11</td>
<td></td>
</tr>
<tr>
<td>Sum of non-ortho PCBs</td>
<td>11</td>
<td>11</td>
<td></td>
</tr>
<tr>
<td>Sum of ortho PCBs</td>
<td>11</td>
<td>11</td>
<td></td>
</tr>
<tr>
<td>Sum of PCDDs and PCDFs</td>
<td>16</td>
<td>16</td>
<td></td>
</tr>
<tr>
<td>Testosterone</td>
<td>1743</td>
<td>1984</td>
<td>1</td>
</tr>
<tr>
<td>Tyllosin</td>
<td>1290</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Tyreostats</td>
<td>2133</td>
<td>8</td>
<td></td>
</tr>
<tr>
<td>Zeranol</td>
<td>3767</td>
<td>2773</td>
<td>0</td>
</tr>
<tr>
<td>β-Agonists</td>
<td>107</td>
<td>1</td>
<td></td>
</tr>
</tbody>
</table>

27
The data collected was analysed and graphed as can be seen in two examples in Figures 1 and 2. This was done to determine the probability of the chemical hazard occurring in beef and the concentrations at which they have been detected. Data was also accumulated from scientific journals such as Science Direct and Web of Knowledge, as well as food databases, to characterise the chemical in terms of acceptable exposure levels and potency and severity. This information highlights the impact of the given contaminant. From this accumulated data of the probability of occurrence, exposure and severity of the contaminant, it is possible to rank the risks from highest to lowest.

From Figure 1, it can be seen that nortestosterone occurs mainly from 0-5µg/Kg. Nortestosterone is a growth promoting hormone and it is illegal to administer to food producing animals in the EU. Whereas copper concentration occurs mainly from 3-3.99 mg/Kg for lyophilised tissue and from 0-0.99 mg/Kg for fresh tissue of beef. Copper has been strongly implicated in neurodegenerative diseases such as familial amyotrophic lateral sclerosis (FALS), Alzheimer's disease, and prion diseases of neuronal spongiform encephalopathy (Puig and Thiele, 2002).

Fig 1. Concentration (mg/kg) of Nortestosterone found in beef samples from the Veterinary residue committee

Fig 2. Concentration (mg/Kg) of Copper in beef samples from the NFRD database
**Conclusion**
Risk ranking is focused on identifying risks and establishing risk reduction methods for high risk hazards. Initial results suggest that there are many chemicals which are non-compliant with EU regulations. It is strongly recommended that these chemicals be brought in line with EU specifications. In order to determine the risks associated with these chemicals, it is proposed to develop a risk ranking model, based on the characteristics of the chemicals. The implementation of this model will determine which chemical residues are most hazardous to enable intervention strategies to be applied at critical stages for the added protection of both animal and human health.

**References**


NANOPARTICLE MIGRATION AND EXPOSURE ASSESSMENT
FROM FOOD PACKAGING

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Abstract
Nanoparticles are novel entities generally between 1-100 nm. The reactive behaviour of some elements at the nanoscale can be different compared to larger particles of the same compound due to changes in volume to surface area ratio, thus new applications have emerged for these particles that are likely to change the way food is perceived, stored, monitored and processed. The perception of an emerging technology as “risky” could render it unmarketable, especially in a sensitive area such as food. The novel behaviours exhibited by nanoparticles may create novel risks. For this study a framework model is proposed to assess the risk of nanoparticle migration from nanoparticle food packaging to food and the resulting likelihood of human exposure.

Introduction
Nanotechnology is potentially one of the most significant technologies of the 21st century with far ranging applications throughout the global economy (Taylor, 2008). For the food industry, an industry where competition is intense and innovation is vital, nanotechnology has emerged as a potential technology to aid advances in producing improved quality food with functionalised properties. The integration of nanotechnology with food and its interrelated sectors is in its infancy but there have been many developments in the field. It can be applied in the food sector from primary production to stock monitoring at a retail level. One promising application of nanotechnology emerging in the food sector is food packaging. Antimicrobial effects, oxygen scavenging, and improved light and gas barrier properties are some novel features that nanoparticles can bring to food packaging materials.

However, concerns have arisen with regard to potential human exposure to nanoparticles. This could result in nanoparticles gaining access to tissues in the human body or even crossing the blood brain barrier. This may result in accumulation of toxic contamination and therefore adversely affect human health (Chau et al., 2007) and/or having environmental implications (see figure 1.). As with other new technologies, the rush to market may outpace the investigation into possible health and environmental implications (Morgan, 2005).

The objective of this study is to evaluate the potential for nanoparticle migration from food packaging to food surfaces and to estimate likely human exposure to nanoparticles following the consumption of meat subjected to such packaging conditions. This study presents an initial framework for this evaluation.

Materials and Methods
Migration
The key factors affecting this form of exposure are analysed (see figure 2) including nanoparticle characteristics, chemical composition, dimensions and bioavailability. Many packaging characteristics must be considered such as nanoparticle application/integration method, pore size and nanoparticle density. Rate of migration is also affected by the duration of time that the food is in contact with the material, temperature and...
Figure 1. Potential Nanomaterial Exposure Routes
food packaging contact surface area. Migration tests will be designed and carried out for various food packaging matrices which are associated with nanoparticles of different metals (supplied by project partners). These tests will be carried out under controlled temperatures and for specific periods of time. Analysis of samples will be performed by Environmental Scanning Microscopy, Energy Dispersive Spectroscopy and Wavelength Dispersive Spectroscopy.

Framework Model
Meat samples will be wrapped in packaging materials. The packaging materials will have nanoparticles of differing elemental composition either incorporated into the matrix or spin coated onto the packaging surface. The meat samples, wrapped in the nano packaging will in turn be wrapped in aluminium foil to allow for close contact between the food and the packaging material. These samples will be stored at two temperature treatment levels, 5°C and 15°C, and for three periods of time; 2 days, 4 days and 6 days.

Analysis
After this protocol has been carried out, images of the meat samples will be taken using an Environmental Scanning Electron Microscope. These images allow for the use of Energy Dispersive Spectroscopy (EDX) analysis which results in an elemental graph for pinpointed areas on the image. Following this, the samples will be further analysed using Wavelength Dispersive Spectroscopy (WDS). Using the graphical readout from the EDX, an element can be chosen to be quantified in the sample. In this case, the quantification of the element that the nanoparticles are composed of is of interest. Quantification will be done using WDS which quantifies concentration results in ppm.

This proposed framework model represents the experimental protocol and design that will be carried out in an initial attempt to quantify human exposure to nanoparticles from nanoparticle food packaging.

Exposure Assessment
Inhalation, ingestion and skin contact and subsequent penetration of dermal layers are ways in which nanoparticles can gain access to the body (Wijnhoven et al., 2009). Human exposure via ingestion is the focus of this project and specifically the likely route of loose nanoparticles from the polymer matrix or those that are free to move from the polymer matrix migrating to the food matrix.

Results and Discussion
It is expected that there may be some migration of the various nanoparticles from the range of polymer matrices into which they have been incorporated. It is anticipated that the migration may vary with temperature and storage duration.

Conclusions
A lesson that the scientific community must learn from the introduction of new technologies in the past is that the area of food is particularly sensitive to consumer perception. The risky perception of a technology can lead to consumer rejection (e.g. G.M. foods). As the exploitation of nanotechnology becomes more commonplace, many new products are emerging on the market, particularly in the US and Japan. This increase in available nanotechnology related products will inevitably increase both human and environmental exposure to nanomaterials. Thorough risk assessment in the area of nanotechnology in the food sector should clarify potential risks.
Acknowledgements

The authors acknowledge funding for this project by FIRM as administered by the department of Agriculture, Fisheries and Food.

References


PREDICTIVE MODELLING TO ASSESS THE LEVEL OF β-GLUCAN AND ITS MOLECULAR WEIGHT DURING BARLEY BREAD MAKING

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Abstract
Incorporation of barley β-glucan as a functional ingredient has many health promoting effects for humans. Composite flour was formulated by substituting the wheat flour (WF) with barley whole meal flour (BF) and other ingredients. The high molecular weight (HMw) of β-glucan in composite flour gradually degrades to medium molecular weight (MMw) and to lower molecular weight (LMw) during the bread baking process. The model observed a 25 % and 7 % reduction in HMw and MMw, respectively and a subsequent increase in LMw by up to 30 % for baked breads. A sensitivity analysis highlighted the significant impact the addition of barley flour (BF) had on the level of β-glucan and Mw distribution within the baked bread with positive correlation coefficients of 0.70 and a negative correlation coefficient of 0.70 was observed for β-glucan and 0.50 Mw for the amount of WF in the composite flour. The analysis also showed the importance of mixing time (Mt), fermentation time (Ft), molecular weight of WF and baking loss on the level and Mw of β-glucan in baked breads. The model serves as a tool to facilitate both product and process development for functional foods.

Materials and Methods
Model inputs:
The simulated mean level of β-glucan from sixty popular hull-less barley cultivars collated from the scientific literature was 5.68 g /100g (Tiwari and Cummins, 2008). Wheat flour with a minimum of 0.30 and maximum of 1.0 g/100g of β-glucan content (Cavallero et al, 2002) was used as a basic ingredient to make various composite flour combinations of wheat and barley flour. Figure 1 details the milling and baking process involved.

Model development:
Processing of hull-less barley:
Barley processing involves several steps including cleaning, grading and tempering the model assumed fixed factor of 1. Pearling (P) level up to 30 to 40 % increased the level of β-glucan, therefore a polynomial equation was fitted from a dataset of Izydorczyk et al. (2003). The molecular weight for wheat and barley flour was collated from scientific literature
sources (Cui et al., 2000; Andersson et al., 2004) (Table 1).

Figure 1 Flow diagram for milling and bread making process

Bread making process:
Composite flour was formulated using a uniform distribution with a minimum of 0 and maximum of 100 g substitution of wheat flour for barley flour. Other ingredients such as sugar (4 g), salt (2 g), yeast (3 g), fat (3 g) and water (assuming 65 % weight of the flour) were included as the standard method. Mixing and fermentation time plays a vital role in bread making process. To capture the uncertainty a uniform distribution was fitted to the mixing time (Mt) with a minimum of 3 and maximum of 10 min. To simulate fermentation time (Ft) a minimum of 0 and maximum of 60 min was used to model BG the model Mw degradation, factors were calculated from a dataset of Andersson et al. (2004). Studies show that there is no significant effect of baking time (Btime) and temperature (Btemp). Hence, this model assumed a fixed factor of 1 (no effect) for the influence of Btime (15 to 25 min) and Btemp (215 to 240 °C) on the Mw of β-glucan for the conditions specified. The weight loss during baking was assumed to vary with a minimum of 10 % to a maximum of 15 % (FAO, 2007) depending on baking time and temperature. The simulation was performed using the parameters and calculations presented and the model run for 10,000 iterations with @Risk add-on package (Palisade Software, Newfield, NY, USA).

Results and Discussion
BG and Mw of the β-glucan level in formulated breads:
The predicted mean β-glucan level for baked WF bread was 0.26 g/100g, whereas for BWMF with WF the mean β-glucan content was 2.79 g/100g. The level of β-glucan in composite flour and resulting bread was significantly increased with a decrease in the amount of WF used in the composite flour, whereas the greater the ratio of barley flour to WF the greater the impact on the level of β-glucan (Figure 2a). The simulated model shows the shift in molecular weight from HMw towards LMw for all composite flour breads, whereas a shift in MMw to LMw was observed in WF bread. The mean Mw for WF bread was reduced from 0.13 × 10^6 (flour) to 0.08 × 10^6 g/mol (baked bread) and a significant reduction was observed in mean Mw which reduced from 1 × 10^6 to 0.53 × 10^6 g/mol for WF substituted with BF (Figure 2b). A decrease ~36 % in HMw β-glucan was observed with corresponding increase in MMw and LMw β-glucan. The simulated Mw distribution of β-glucan showed a 20 % reduction in HMw β-glucan during the fermentation process for all composite flour breads when compared to the initial recipe.

Sensitivity analysis for the level of BG and its Mw in baked bread:
The sensitivity analysis of β-glucan showed a negative influence from the addition of WF with a correlation coefficient of -0.73, while a positive correlation coefficient of 0.73 was noted for the addition of barley flour. This shows that the major influence on β-glucan levels in baked bread is quantity of BF added. The analysis also showed the importance
of the level of barley β-glucan content and also noted a reduction in β-glucan during the baking process (BGloss) with a negative correlation coefficient of 0.19 in baked bread. Therefore a short fermentation time may limit the degradation of high molecular weight β-glucan. The greater the proportion of barley flour added to the wheat flour the greater the level of the β-glucan and its molecular weight, although this addition may be at the expense of organoleptic quality of the baked bread.

**Conclusions**

The substitution of wheat flour with barley flour significantly improves the nutritional quality of white bread (100 % WF) by increasing the level and molecular weight of β-glucan. The higher molecular weight of β-glucan in composite flour significantly reduced during the bread baking process. The authors wish to acknowledge the Irish Department of Agriculture and Food for their funding of this project under the Food Institutional Research Measure.

**Acknowledgements**

References


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THE EFFECT OF POWER ULTRASOUND ON THE FREEZING RATE AND DRIP LOSS OF IMMERSION FROZEN CHICKEN BREAST MEAT

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Abstract

The efficient freezing and thawing of chicken meat is vitally important to the poultry sector. New technological advances have seen the potential use of power ultrasound to the immersion freezing of food products, which has many advantages. Applying ultrasound to freezing processes reduces the freezing time through the zone of ice crystal formation, resulting in better quality frozen products. The application of ultrasound promotes the growth of small uniform sized ice crystals within a product which in turn results in decreased drip loss and decreased freezing damage. Different variables affect the ultrasound assisted immersion freezing process differently, such as the type of holder that the sample is held in, the ultrasonic power level intensity, and the time that the product is exposed to ultrasound.

Introduction

Freezing is a popular, widespread and efficient preservation method that is used to preserve the structural and nutritional values of food products (Li and Sun, 2002). However, if a product is not frozen in the correct manner freezing can cause severe damage to tissues, resulting in softening and drip loss, which diminishes the product quality. These phenomena are to be avoided and so new efficient freezing methods are being developed. One such freezing method sees the use of power ultrasound as a processing freezing aid. Power ultrasound is a form of low frequency high power ultrasonic waves that is particularly beneficial to freezing processes. The objective of this study is to test the impact of the ultrasonic power level intensity, and the time that the product is exposed to ultrasound on the freezing rate and drip loss of chicken meat samples.

The freezing of a product covers 3 distinct phases (Fig. 1); the pre-cooling phase where the product temperature is cooled to the initial freezing point of the product \( t_f \); the phase change period, where the free water within the product changes into ice crystals; and the tempering phase where the product reaches a constant subzero storage temperature (generally -18°C):

![Fig 1: Three distinctive phases of the freezing process.](image)

The time that the product spends in the phase change or water-ice transition period is critical to the quality of the frozen product and directly determines the size and number of ice crystals...
within the food product (Fellows, 2000). Thus, the phase change period should be quickly passed through, so as to ensure a fine crystal structure that prevents freezing damage of foods. Under the influence of ultrasound, food materials can be frozen with a reduced freezing time through the zone of ice crystal formation, i.e. the phase change period, (Leadley and Williams, 2006) as it is shown in Fig. 1.

Many of the beneficial affects of ultrasound to different processes are associated to cavitation, and more specifically transient cavitation. Cavitation is the formation, growth and violent collapse of small bubbles or voids in liquids under alternating pressure cycles (Simal et al., 1998). The formation and collapse of cavitation bubbles acts as nuclei for ice crystal growth. Furthermore cavitation induces the creation of micro currents within the freezing medium, which create turbulence that increases the heat transfer rate from the product to the freezing medium. This turbulent agitation caused by cavitation increases the removal rate of the latent heat of freezing of water thus allowing for free water in the product to freeze more quickly. Consequently, water changes phase into ice crystals at a much faster rate greatly reducing the time the product spends in the phase change period, which greatly reduces the freezing time. One way to represent the freezing rate, and which will be used in this work, is to use a characteristic freezing time, defined as the period for the centre temperature of the product to change from the initial freezing point ($t_f$) to the temperature in which for example, 80% of the free water is converted to ice. As mentioned before, the application of ultrasound is extremely useful in terms of product quality since it reduces the time through the water-ice transition period. As it is well known, the freezing rate greatly affects the size and distribution of the ice crystals within a product. Slow freezing rates leads to the formation of a small number of large ice crystals, which can impinge intra and inter cellular stress to the cellular structure, resulting in disruption and breakdown of the tissue structure (Li and Sun, 2003). Consequently, when the product is thawed cellular water containing nutrients is lost from the product as drip loss. Therefore, faster freezing rates are then preferred.

Power ultrasound has been proved useful to control the crystallization process by influencing both nucleation and ice crystal growth. The more ice crystal nuclei created by cavitation the greater the number of ice crystals formed in a product. Furthermore the alternating ultrasound waves cause ice crystals already formed to fracture into smaller ice crystals (Zheng and Sun, 2006). In this respect ultrasound allows for a large average small ice crystal size distribution to be formed in a product during freezing, which implies minimal cellular disruption, then minimum drip loss, and finally frozen products of improved quality.

**Materials and Methods**

**Sample Preparation**

Fresh breast chicken meat will be cut into two uniform samples of the exact same shape and weight. If possible the samples will be cut from the same chicken breast in order to prevent experimental uncertainty. One sample will be used to record the temperature–time profiles by using a T-type thermocouple placed in its centre. The other sample, which is not structurally altered by the insertion of the thermocouple, will be used for determining the drip loss. The initial water content of the meat will be
determined using a 5 g sample of remaining chicken meat. All samples will be kept refrigerated at 4±1°C allowing the samples to achieve an initial sample uniform temperature.

**Ultrasound Equipment**

Two ultrasonic immersion bath systems will be used in this work, a 25KHz immersion ultrasonic bath system (CQBF-1025 726, Research Institute China, China Shipping Company, China) with an actual dissipated power output range from 5 W to 170 W, and a 40KHz immersion ultrasound bath system (Elma MC 30015 Elma Gmbh &Co., KG Germany) with actual dissipated powers of up to 201 W. Both tanks are covered with insulation material for preventing heat losses to the surrounding. In both ultrasonic systems, ultrasound is transmitted into the freezing medium by means of six transducers attached to the base of the steel tank. The freezing medium for both baths consists of a 50%:50% ethylene glycol and water mixture, which is kept at the desired temperature by circulating the refrigerant fluid from a refrigerated circulator.

**Experimental Procedure**

Experimental runs will be carried out to compare samples frozen by immersion freezing (control), and samples frozen by immersion freezing assisted by the application of ultrasound (treatment). Fig. 2 shows a schematic representation of the sample layout. Chicken samples will be removed from the refrigerator, and a T-type thermocouple will be inserted into the centre of Sample 1; while Sample 2 will be placed beside Sample 1 before dipping them in the freezing solutions. It is important to ensure that the sample holder is placed directly over the transducers of the ultrasonic bath so that the chicken meat samples are fully exposed to the ultrasound waves. Care will be taken also to ensure that the samples are always held in the same position for every experimental run since the ultrasonic field varies within the ultrasonic bath. A data logger (Squirrel 2040, Grant Instruments Ltd., Cambridge, UK) will be used to record the temperature. Freezing is considered complete when the centre temperature reaches -18°C.

![Fig 2: Schematic representation of sample layout](image)

Power ultrasound will be applied to the treatment sample intermittently, since ultrasound application produces heat that is adverse to the freezing process. The total sum of time exposure to ultrasound will be referred to as the treatment time. Ultrasound will only be applied to the phase change period. After freezing, Sample 2 will be blotted in paper, then immediately placed in a closed container and weighed (weight after freezing). Sample 2 is then thawed at 20°C for approximately two and a half hours, which is approximately the time for the centre temperature to reach 0°C. The thawed sample is reweighed after being blotted (weight after thawing). The difference in the weights of the samples after freezing and thawing is used to determine the drip loss. The effect of different ultrasonic power levels, sample holder types and exposure times on the freezing rate (expressed as the characteristic freezing
time) and drip loss of chicken meat will all be examined. A statistical test (ANOVA) will then be performed on the data collected from at least three replications.

**Expected Results**

*Freezing Rate*

It is expected that the application of ultrasound will increase the freezing rate or reduce the characteristic freezing time of the chicken samples. Results will show that the freezing curve of the treatment sample will exhibit a much faster and reduced characteristic freezing time when compared to the samples frozen without ultrasound application (control). These expected results are assumed to be due to cavitation whereby cavitation bubbles produced by ultrasound coupled with microstreaming, creates micro currents in the freezing medium, which in turn increases the rate of heat removal from the sample, thus reducing the characteristic freezing time. Cavitation bubbles also act as nuclei for ice crystal growth and promotes the fast formation of ice crystals further reducing the freezing time. However, the total exposure time to ultrasound will have an impact on the freezing rate. If the exposure time to ultrasound is too high, and because ultrasound generates heat, the temperature of the freezing medium will rise thus impeding the freezing process. This is known as the thermal effect of ultrasound. On the other hand, if the exposure time is too low, the freezing medium will not experience sufficient turbulence and consequent sufficient agitation for increasing the rate of heat transfer from the product to the freezing medium. In this respect, an ideal exposure time to ultrasound is needed to produce optimum freezing rates.

*Drip loss*

The application of ultrasound will have an expected positive result on drip loss since applying ultrasound to freezing processes promotes rapid formation of ice crystal nuclei and the growth of small ice crystals throughout the product. This ensures that the average ice crystal size distribution in the product is regulated at a guaranteed reduced size. These small ice crystals impinge less stress to the cellular structure of the chicken meat. Consequently the microstructure of the sample remains intact and there are no cellular ruptures. This causes intracellular fluids to remain intact and the muscular tissue of the chicken meat to remain firm and tense reducing the drip loss, and importantly improving the texture and quality of the final product.

**References**


MEASUREMENT OF MOISTURE DIFFUSIVITY OF FLOUR

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Abstract
In this project moisture diffusivity of flour is measured. This is completed by usage of a simultaneous thermal analyser. The moisture diffusivity of flour occurs in one-dimensional and there is constant diffusivity. The results reported are predicted results and experimental results will be compared to known literature results.

Introduction
For many industrial processes heat and moisture transfer is important for advancement of existing technology used. Flour is a fine powder that originates from grain and is utilised in baking. Most flour has a vast amount of gluten and this with its strong elastic properties forms a network that traps gases. With these gases the dough rises and results in soft bread.

In the flour-making process after the wheat has been purified it goes through conditioning or tempering. This is where moisture content is controlled so to allow the outer layer of the bran to be removed during grinding. Wheat is graded and with different moistures is blended to achieve different products.

Transportation of moisture has been known to vary from food to food because of physical properties (Gely and Santalla, 2007). This transportation can be described as diffusivity. Diffusion is a process by which matter is transported from one part of a system to another as a result of random molecular motions (Crank, 1975). In other studies the drying curves have been useful for information to illustrate the mechanism, of moisture transport and the determination of the effective moisture diffusivity (Saravacos and Maroulis, 2001).

Moisture diffusivity data on foods is very limited due to diverse experimental methods, different methods of analysis used, composition and structure variation of foods.

In this project diffusion occurs in one-dimensional i.e. it is bounded by two parallel planes and that there is constant diffusivity. Saravacos and Charm, (1962) were the first to report moisture diffusivities of food materials that was recovered from drying data assumed the constant diffusivity. For this dimensional form Fick diffusion equation is applied:

\[
\frac{\partial m}{\partial t} = D \frac{\partial^2 m}{\partial x^2}
\]  

(1)

Where \( m \) = moisture content at position \( x \) at time \( t \), \( D \) = moisture diffusivity (m\(^2\)/s). In flour, diffusion is assumed to travel vertical upwards and that initial concentration is constant. Under these conditions there should be a constant diffusivity yielding the solution.

\[
\frac{M - M_e}{M_e - M} = \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp \left( \frac{-(2n+1)^2 \pi^2 D t}{4L^2} \right)
\]  

(2)

Where \( M \) and \( M_e \) = amounts of diffusant sorbed after time \( t \) (s) and infinity (equilibrium), \( D \) = diffusivity (m\(^2\)/s) and \( L \) = thickness (m) (Saravacos and Maroulis, 2001). The mass ratio \( (M/ M_e) \) is equal to the ratio of moisture contents, \( Y = (X-X_e)/(X_e-X_e) \), which is a high temperature drying reduces to \( (X_e/X_e) \), since \( X_e \to 0 \) (Crank, 1975).

The objective of this project is to determine moisture diffusivity of flour by means of A Simultaneous Thermal Analyser.
Materials and Methods

Flour Samples
The flour that is used in this project was a commercial brand, SuperValu Self-Raising Flour. The sample was made up by adding water and mixing the flour and water until sampling condition was achieved i.e. well saturated sample. The samples were then stored at 4°C in a sealed container until use. The sample was then mixed thoroughly before testing.

Simultaneous Thermal Analyser (STA) – Experimental Setup
A Rheometric Scientific STA 625 was used for the experimental tests. The Simultaneous Thermal Analyser (STA) includes a Differential Scanning Calorimeter (DSC) and a Thermal Gravimetric Analyser (TGA). The DSC measures energy changes and the TGA measures mass changes. The STA employs simultaneous measurement of energy, heat and mass changes in a sample.

Results and Discussion

Determination of Moisture Diffusivity
It is assumed that moisture diffusion is in one-dimensional meaning that it is bounded by two parallel planes (e.g. the planes at \(x = 0, x=1\)) (Crank, 1975). The sample is in a non-steady state.

It is also assumed that there is uniform diffusivity and this is constant and so moisture constant \(M\), and initial boundary conditions give:

\[
MR = \frac{M - Me}{Mo - Me}
\]  

From equation (3) Efermov et al., (2008) stated that to calculate the moisture ratio (MR) with accuracy \(\delta = 4\%\). The accuracy was defined as \(100 \times \frac{(M_e - M_o)}{M_e} \%\), where \(M_e\) and \(M_o\) are the exact and reduced solutions (Efermov et al., 2008). There have been discrepancies in kinetics data that occur between experiments and analytical solutions (Efermov et al., 2008).

Predictive Results

Fig 1: Predictive values of moisture diffusivity of model foods at 25°C

Fig 2: Predictive values of moisture diffusivity of model foods at 60°C
As literature is limited for flour Table 1 displays predictive results and Fig 1 and Fig 2 present moisture diffusivities from the literature and model-calculated values for selected food materials as a function of moisture content and temperature.

Moisture diffusivity tends to increase with the moisture content and the temperature (Saravacos and Maroulis, 2001). In Fig 1 there was a slight increase of diffusivity at 25°C but at 60°C there was a constant diffusivity confirming constant diffusivity.

**Effect of Measurement, Temperature and Pressure**

Saravacos and Maroulis (2001) reported that the method of measurement may have an intense effect on the value of moisture diffusivity of a semisolid, i.e. well saturated flour. The change is associated with the physical change with the food.

Drying causes a major physical and structural change in food product. The STA produces high temperature and so physical changes will occur. Saravacos and Maroulis (2001) also stated that, theoretically, diffusivity is meant to be independent of the sample’s shape but various results have been discovered with a food of different dimensions.

Pressure has shown to have a significant effect on the moisture diffusivity of a porous substance (Saravacos and Maroulis, 2001). With this knowledge samples will be replicated to ensure accurate results.

**Conclusions**

From a variation of Fick’s diffusion equation the moisture diffusion of flour can possible be found and compared to known and limited literature. An outcome of this project is that there potential to further the knowledge of moisture transfer in bone-dry substances. These outcome could possible be economical and environmental benefits to the food industry.

**Acknowledgements**

The author would like to thank Dr. Pat Grace and Tony Fitzgerald, Senior Technician officer for all their advice and help.

**References**


THERMAL INACTIVATION OF SALMONELLA IN DOMESTIC COOKED SAUSAGES

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Abstract
Time-temperature profiles were created to determine the inactivation of *Salmonella* in domestic cooked pork sausages through the use of thermocouples. Thermocouples were inserted into the sausages longitudinally prior to cooking and the data was recorded in a data logger. Preliminary results presented in this study show that the core temperatures of the sausages reached the recommended temperature of 70°C within 12-15 minutes according to packaging instructions. The achieved temperatures were enough to kill any pathogenic bacteria present.

Introduction
Hand-washing and safe food preparations are key ways of preventing and controlling the spread of the infection. Whilst such standards are enforced in commercial kitchens, the level of knowledge of these techniques in domestic kitchens is unknown, and evidence from studies worldwide suggests that food borne illnesses most commonly occur in the household setting (Worsfold and Griffith, 1997). Correct food handling, storage and preparation in domestic kitchens would prevent a large number of food poisoning cases/outbreaks. (Safefood, 2002)

More pork meat per capita is consumed in Ireland than any other meats. Greater than 50% of pork meats consumed is in a processed variety such as sausages. (Safefood, 2008)

*Salmonella* is the second most reported cause of food-borne diseases in humans in Europe. Infections can range from a mild to severe gastroenteritis and in some vulnerable groups, such as children and the elderly, can be fatal. Risks for consumers are typically from under-cooking of pig meat or cross contamination to other foods. Thorough cooking and strict kitchen hygiene will prevent or reduce the risk posed by *Salmonella* contaminated pig meat. (EFSA, 2008). *Salmonella* is not particularly heat-resistant and therefore to inactivate bacterial pathogens such as salmonellae, food should be cooked to a core temperature of 75°C or an equivalent time temperature combination (e.g. 70°C for 2 minutes) (NSAI, 2007).

The objective of this study is to create time temperature profiles for the domestic cooking of sausages through frying, grilling and deep fat frying.

Materials and Methods
Materials
Fresh pork sausages were purchased from a local supermarket and were stored at refrigeration temperature between 1-5°C. Vegetable oil was used for frying the sausages.

Methods
The sausages were cooked in a frying pan with a small amount of vegetable oil, for 12-15 minutes according to the manufacturers’ instructions. A
A thermocouple was inserted longitudinally (Fig 1) into the sausage prior to cooking so as to measure the temperatures during cooking. A data logger was then used to log the temperature changes in both the sausages and the cooking oil at 30 second intervals. The results of these were then downloaded onto excel from the data logger and time-temperature profiles were created.

**Results and Discussion**

Currently the experiment is only at a preliminary basis; therefore the data published below is from preliminary trials carried out in February 2010. Three jumbo sausages (11cm, 2.5cmφ) have been tested in the preliminary trials and the results for each of them are as follows:

In Trial 1 the sausage was cooked on a hot frying pan at a medium high temperature with hot cooking oil. After 12 minutes the internal temp of the sausage had reached 100.8°C and the sausage was a golden brown colour on the outside. The oil temperature was recorded at 166.85°C after 7 minutes. The temperature changes can be seen in Fig 3. Channel 1 represents the internal temperature change of the sausage and Channel 2 represents the temperature change in the vegetable oil.

In the second trial the frying pan was pre-heated for five minutes at a medium temperature and the sausage was cooked for 15 minutes. After 12 minutes the temperature of the sausage was 78.7°C and after 15 minutes the temperature was 82.2°C. However, although the internal temperature of 75°C was exceeded the outside of the sausage was still pale and little or no browning occurred.

The temperature change for trial 2 can be seen in Fig 3 below.

In trial 3, the sausage was cooked at medium-high temperature with a cold frying pan and cold cooking oil for 15 minutes. The sausage had reached an
internal temperature of 75°C after 10 minutes and after 15 minutes the temperature was 92.2°C and the temperature of the cooking oil was 206.59°C. Similar to Trial 2, the internal temperature of 75°C was exceeded but the sausage was still pale and uncooked on the outside. These results can be seen below in Fig 4.

![Fig 4 Temperature Changes in Trial 3](image)

As the results above show all of the sausages reached well above the recommended temperature of 70°C, which indicates that any *Salmonella* that may be present should be destroyed, however the sausages did not look cooked on the outside as 2 out of the 3 trials were still a pale colour after cooking for a period of time. The recommended cooking time for the sausages according to the manufacturers’ instructions was 12-15 minutes. Each of the sausages were cooked within this time range and the correct temperature was achieved for inactivating *Salmonella* so therefore if the sausages are cooked for 12-15 minutes it can be assumed that the pathogen *Salmonella* is completely destroyed.

**Conclusion**
The results so far from the time temperature profiles created for the inactivation of *Salmonella* in sausages show that the recommended temperature for the inactivation has been achieved when cooking the sausages to the manufacturers’ instruction (12-15 minutes).

**Further Work to Be Carried Out**
To investigate the inactivation of *Salmonella* further, other methods of domestic cooking will be carried out such as grilling and deep fat frying.

To help give a visual concept of the time temperature profiles, thermal imaging will be used. This process may be difficult to carry out as it needs to be done rapidly, therefore the results may be slightly inaccurate. A thermal imaging camera will be used to carry out this visual analysis; this will give a better spatial imaging of the cooking temperatures.

The data between the thermal imaging and thermocoupling will be linked to give a representation of the rate of pathogen inactivation that occurs in the domestic cooking of pork sausages.

**References**


Safefood (2002) A Study of Consumer Food Safety Knowledge, Microbiology and Refrigeration Temperatures in Domestic Kitchens on the island of Ireland


Introduction of robust population descriptors (i.e. median and median absolute difference) and elimination of random variables in the ensemble Monte Carlo uninformative variable elimination (EMCUVE) method are proposed to reduce process time and improve the performance of PLS models. Robust EMCUVE (REMCUVE) successfully retained most of the original variables and eliminated all uninformative variables, even when noise was added on simulated datasets. This method required 52 to 62 % less process time than the conventional EMCUVE method in treating near infrared (NIR) datasets.

Introduction

Multivariate calibration models of spectral data are affected by the presence of atypical objects (clusters or outliers) and uninformative variables. Calculation of predictions $\hat{y}$ ($n \times 1$) by a linear least squares model from NIR spectral data could be expressed by the following equation:

$$\hat{y} = X\beta' + b_0$$

(1)

where $X$ ($n \times p$) is the matrix of predictors of $n$ objects and $p$ variables (wavelength or wave numbers), $\beta'$ is the regression coefficient vector transposed ($p \times 1$) and $b_0$ is the offset of the model. Different approaches have been proposed to select the most informative variables or to eliminate uninformative variables in partial least square (PLS) regression models. The most generally used are genetic algorithms (GA)(Roger and Bellon-Maurel 2000), variable importance on projection (VIP)(Wold, Johansson et al. 1993) and successive projection algorithm (SPA)(Araújo, Saldanha et al. 2001). An ensemble Monte Carlo (MC) procedure to improve the predictive ability of PLS based models by eliminating uninformative variables from the X matrix has been recently proposed (Han, Wu et al. 2008). The EMCUVE method is based on the analysis of $\beta$ when the original matrix of predictors is augmented by an equal number of random variables. $M$ objects (where $M<n$) from the calibration set are selected to build PLS models estimating the regression coefficients; this procedure is repeated $N$ times to calculate the normalised coefficient $c_j$ for each variable which is define by:

$$c_j = \frac{\bar{\beta}_j}{s(\beta_j)} \quad j = 1, 2, 3, ..., p$$

(2)

$$s(\beta_j) = \left( \frac{\sum_{i=1}^{N} (\beta_{ij} - \bar{\beta}_j)^2}{N - 1} \right)^{0.5}$$

(3)

where $\bar{\beta}_j$ and $s(\beta)$ are the mean and standard deviation of regression coefficient of $j$th variable, and $\beta_{ij}$ is the regression coefficient for the $j$th variable in the $i$th PLS model. A threshold, $c_{crit}$, for elimination of uninformative variables is defined as the maximum $c_j$ for the random variables; only original variables with $c_j$ values greater than $c_{crit}$ are retained. This MC procedure is repeated $K$ times. Those variables which are selected equal or more than $\eta x K$ times are used to build the final PLS model, where $\eta$ is a fraction ($0 < \eta \leq 1$).

The aim of this study was to reduce the process time and improve the robustness of the ensemble Monte Carlo uninformative variable elimination method.
Proposed method

The regression coefficient for a given variable presents a long-tailed distribution when the MC procedure is applied; therefore, the use of median and median absolute deviation (MAD) is proposed to estimate the normalised coefficient $c_j$ instead of the mean and standard deviation as implemented in the EMCUVE. Normalised coefficients calculated in this way should be more robust since they are less affected by extreme values. Additionally, from the population of normalised coefficients generated in the ensemble Monte Carlo procedure, the median corresponding to each original variable is compared to a selection criterion ($c_{crit}$); in this way, the proposed method, Robust EMCUVE (REMCUVE), does not require the addition of random variables.

Procedure

Ensemble Monte Carlo uninformative variable elimination

The EMCUVE method was applied according to the procedure described by Han et al. (2008) using half of the samples to build PLS models ($M = 0.5n$); $\eta$ values of 0.2, 0.4, 0.6, 0.8, 1.0 were investigated.

Robust EMCUVE

The robust ensemble Monte Carlo uninformative variable elimination method consists of the following steps:

Step 1: M calibration samples are selected randomly to build a PLS model. Repeat N times.

Step 2: Estimate $c_j$.

Step 3: Repeat steps (1) to (2) K times.

Step 4: Examine different threshold values (for example 1, 2, 3, 4 and 5) eliminating those variables with a value of $|\text{median}(c_j)|$ lower than the proposed value; build PLS models with selected variables for each scenario, and select as $c_{crit}$ value that which produces the minimum RMSE by leave-one-out cross-validation in all calibration samples.

In order to avoid the comparison of under-fitted or over-fitted models, the number of components was determined before and after the variable selection procedure. This was necessary because noisy, uninformative variables and outliers affect PLS model performance.

Simulated data

Three sets of simulated data were built; an original noise-free data set (SIM), a noise-free set with uninformative variables (SIMUI) and a data set with some noise (SIMUIN) as suggested by Centner and collaborators (Centner, Massart et al. 1996) but with 100 samples in each set.

NIR data

The Carra data set contains NIR measurements (1100–2500 nm) collected from carrageen powders. Concentration of kappa carrageen was the response variable modelled (Dyrby, Petersen et al. 2004). The Water data set contained Vis-NIR measurements (350–2500 nm) made at the surface of a wood plug. The water content was measured on each plug, creating the response vector (Persson, Sjostrom et al. 2002). A Gas oil data set contains NIR measurements (4900–9000 cm$^{-1}$) of gas oil samples; the property of interest is the hydrogen content determined by NMR (Fernández Pierna, Jin et al. 2003). The data sets were divided into a calibration and a validation set.

Results and Discussion

Simulated data

Table 1 shows the root mean square error of cross-validation (RMSECV) by leave-one-out cross-validation and the number of components included in the model for SIM, SIMUI and SIMUIN data sets and the number of original variables and uninformative variables (UI) kept by each selection method studied as well the best threshold for EMCUVE and IEMCUVE methods.

As expected, the predictive ability of PLS models, assessed by RMSEP, was notably affected by the presence of uninformative variables in data sets SIMUI and SIMUIN, but noise added in SIMUIN did not affect significantly the performance of PLSR when all variables were included in the model. EMCUVE kept all of the original variables in SIM dataset, most of them in
both SIMUI and SIMUIN datasets, and excluded all UI variables. REMCUVE performed in similarly than EMCUVE but required 20 to 30% less processing time. The variables selected by VIP were the same in SIMUI and SIMUIN dataset, including some UI variables. SPA selection ability was drastically affected by the presence of noise in the SIMUIN dataset; since most of UI variables were selected. The models developed with the variables selected by GA had good predictive ability, although some UI variables were not excluded in SIMUIN dataset.

Table 1. Number of variables retained and used to build PLS models, number of components employed and root mean square of error of cross-validation (RMSECV) for simulated data sets SIM, SIMUI, and SIMUIN

<table>
<thead>
<tr>
<th></th>
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<th>Number of variables</th>
<th>Number of components</th>
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<tr>
<td>SIM</td>
<td>PLS</td>
<td>100</td>
<td>5</td>
<td>1.11 x 10^-15</td>
</tr>
<tr>
<td>SIM</td>
<td>EMCUVE η = 0.20</td>
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<td>1.11 x 10^-15</td>
</tr>
<tr>
<td>SIM</td>
<td>VIP</td>
<td>29</td>
<td>5</td>
<td>1.11 x 10^-15</td>
</tr>
<tr>
<td>SIM</td>
<td>SPA</td>
<td>5</td>
<td>5</td>
<td>1.14 x 10^-15</td>
</tr>
<tr>
<td>SIM</td>
<td>GA</td>
<td>15</td>
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<tr>
<td>SIMUI</td>
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<tr>
<td>SIMUI</td>
<td>EMCUVE η = 0.80</td>
<td>92</td>
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<tr>
<td>SIMUI</td>
<td>REMCUVE C crit = 3</td>
<td>89</td>
<td>5</td>
<td>1.38 x 10^-15</td>
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<tr>
<td>SIMUI</td>
<td>VIP</td>
<td>46</td>
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<td>0.061</td>
</tr>
<tr>
<td>SIMUI</td>
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<td>1</td>
<td>1.144</td>
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<tr>
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<tr>
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<td>3</td>
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<td>VIP</td>
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Table 2. Number of variables retained and used to build PLS models, number of components employed, root mean square error of cross-validation on calibration set (RMSECV) and root mean square of error on prediction on validation set (RMSEP) for NIR data sets Carra, Gas oil and Water.

<table>
<thead>
<tr>
<th></th>
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<th>RMSEP</th>
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<th>Number of variables</th>
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<td>0.045</td>
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<td>0.046</td>
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<tr>
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<tr>
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<td>5.95</td>
<td>4</td>
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</table>
**NIR data**
The performance of EMCUVE and REMCUVE in Carra, Gasoil and Water sets were similar, eliminating 1770 and 1726 variables respectively without affecting the prediction error of the models in the Gas oil dataset (Table 2). The REMCUVE procedure required between 52 to 62 % less processing time than EMCUVE, the reduction in process time increasing with the size of the data set.

**Conclusions**
Both EMCUVE and REMCUVE methods were more robust to the presence of random variables and noise since they produced RMSECV values lower than those obtained by PLS, GA, VIP, and SPA in simulated data sets SIMUI and SIMUIN. On simulated and NIR data sets studied, the performance of REMCUVE was better or similar to EMCUVE but with significant less computational process time required.

**Acknowledgements**
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**References**


Estimation of partial least squares regression prediction uncertainty when the reference values carry a sizeable measurement error. *Chemometrics and Intelligent Laboratory Systems* 65(2): 281-291.


CRYSTALLIZATION PHENOMENA DURING FREEZING OF FOODS

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Abstract
Water crystallization involving nucleation and crystal growth have been of interest for many years. In this article, the crystallization process, water crystallization and the methods of monitoring freezing process are analyzed. A wide range of methods have been used to evaluate the water crystallization process including light microscopy, electron microscopy, MRI and NMR methods. One of the most researched subjects in freezing processes had been the crystal size distribution and its impact on the structure and quality of the product. It is therefore worthy to study the ice crystallization phenomena in relation to ice crystal size distribution. This requires the knowledge of crystallization kinetics and the methods of controlling it in terms of final crystal size and the location of the crystals. Along with rapid freezing techniques, novel methods have also emerged dealing with ways to control crystal size distribution in foods. The positive effect of ultrasound on crystallization during freezing has proved useful recently and its application to food freezing is promising.

Introduction
Freezing is among the most popular and efficient methods of food preservation. Extensive research have been carried out on freezing rate and its relation to crystal size distribution inside foods, location of the crystals and their impact on the structure and quality of the product. It is well known that formation of ice crystals would affect and damage the cellular structure of food and agricultural materials and efforts have been made to diminish this effect. Minimizing the size of the ice crystals via accelerating the heat removal process have been the main strategy. However, in some processes such as freeze drying and freeze concentration, large ice crystals are preferred. Since crystallization occurs during food freezing, it is important to acquire in-depth knowledge of the ice crystallization phenomena that include nucleation and crystal growth, and utilize such information in quality assessment of the final product. Modelling of the process is useful as well. The aim of this article is to study the crystallization process, water crystallization, the approaches to model the crystallization process, and to provide an overview of new developments in these fields.

Methods for examining crystallization during freezing
Different methods have been used to visualize the freezing process, ice crystals and the microstructure of frozen (-thawed) foods. Direct observation of freezing front (simultaneous freezing and microscopy), indirect observation (observations of the spaces left by the ice in the tissue) and MRI analysis have been among the main methods used. Direct observation is mainly suitable for transparent solutions and has been used to evaluate the freezing process by continuous imaging techniques (Petzold & Aguilera, 2009). The structure of frozen foods and model foods has been also evaluated by cryo-SEM, SEM, and light microscopy after preparation of the specimen (indirect observation). Cryo-fixation, freeze fixation, freeze substitution, freeze drying and chemical fixation after thawing have been among the preparation techniques (Sun & Li, 2003; Haiying et al., 2007; Van Buggenhout et al., 2007; Delgado & Rubiolo, 2005; Bomben & King, 1982; Miyawaki et al., 1992; Woinet et al., 1998). MRI and NMR have also proved to be good methods for monitoring the freezing process. However, these instruments are not always flexible for specific requirements and also are sometimes expensive (Hills & Remigereau, 1997; Mahdjoub et al., 2006).
Environmental scanning electron microscopy (ESEM) can also be used with the advantage of not requiring any preparation step (Kirk et al., 2009). Figure 1 displays an example of fresh and frozen then thawed carrot observed by ESEM. Cells are affected by freezing, some broken apart cell walls are observed in the frozen-thawed sample.

Discussion
Crystallization process
Crystallization process consists of two distinct stages namely nucleation and crystal growth. Nucleation is defined as the formation of a new crystal and happens either in a crystal-free solution (primary nucleation) or at the presence of formerly created crystals (secondary nucleation). Primary nucleation can be either homogeneous (if a solution contains neither solid foreign particles nor crystals) or heterogeneous (if foreign particles are present). The other step of crystallization process is crystal growth. The interaction between the growth and nucleation processes defines the crystal size distribution which depends on supersaturation or supercooling degree. (Mersmann, 2001; Price, 1997).

Two significant developments in crystallization process over the last years have been the application of modelling tools such as CFD, and also new crystallization methods such as supercritical crystallization, sonocrystallization, laser-induced crystallization and capillary crystallization (Banga et al., 2004; Price, 1997).

Crystallization kinetics and modelling
Nucleation can be explained on the basis of changes in Gibbs energy as follows:

\[ \Delta G = \Delta G_s + \Delta G_v \]

where \( \Delta G \) is the overall excess free energy, \( \Delta G_s \) is the surface excess free energy, and \( \Delta G_v \) the volume excess free energy (Mulin, 1961). This equation has a maximum amount \( \Delta G_c \) for a distinct critical radius, \( r_c \). If the radius of the created cluster is lower than \( r_c \), an attaching molecule requires energy to reach to the \( \Delta G_c \). On the other hand, the \( \Delta G \) for a molecule to be absorbed on a crystal with a radius higher than \( r_c \) will be lower than \( \Delta G_c \). Therefore this crystal will be stable and will grow. The number of stable nuclei \( n_c \) could be estimated as (Messmann, 2001; Mulin, 1961):

\[ n_c = n_0 \exp \left( -\frac{\Delta G_c}{kT} \right) \]

and the nucleation rate (Messmann, 2001):

\[ B = KZn_c \]

where \( n_0 \) is the concentration of monomers in the supersaturated solution, \( k \) is the Boltzmann constant (Eq. 2) and \( T \) is the temperature. \( K \) (Eq. 3) is the rate at which clusters cross the barrier and \( Z \) is the imbalance factor. A foreign substance present in a supersaturated solution reduces the energy required for nucleation. The decrease in free energy depends on the contact angle of the solid phase, \( \Theta \) (Myerson & Ginde, 2002) (Figure 2).
Lower contact angles provide a more active surface for nucleation. Equation 3 could also be used for describing heterogeneous nucleation. The main theories used to explain crystal growth include surface energy, adsorption layer and diffusion theories (Mullin 1961). The following simple empirical equation can be used for describing crystal growth rate G, (Price 1997, Myerson & Ginde, 2002):

\[ G = K_g \Delta C^g \exp(-E_g/RT) \]  \hspace{1cm} (4)

where \( K_g \) is the growth rate constant, \( \Delta C \) the supersaturation, \( g \) the growth exponent on supersaturation, \( E_g \) the activation energy for growth, \( R \) the universal gas constant, and \( T \) the absolute temperature.

Figure 2. Nucleation on a foreign particle for different wetting angles.

Crystallization of water

The only ice crystal form of importance in most foods at atmospheric pressure is the hexagonal crystallization unit or dendrite (Petzold & Aguilera, 2009). Along with rapid freezing techniques, some new methodologies have been employed to control the crystallization of water and enhance the freezing process via reduction of ice crystal size or restricting water crystallization. These new developments include high pressure shift freezing, ultrasound assisted freezing, bacterial crystallization of water, ice nucleation proteins, dehydrofreezing and antifreeze agents (Li & Sun, 2002b). The critical zone of water crystallization, from about -1°C to -8°C, should quickly be passed so as to ensure a fine ice crystal structure that prevents the food from tissue damage. One way of representing the freezing rate and then freezing efficiency, is to use a characteristic freezing time, \( t_c \), to the diameter of ice crystals, \( D \), and proposed the following model:

\[ D = a + b \ln t_c \]  \hspace{1cm} (5)

where \( a \) and \( b \) are regression constants.

Some efforts have been also carried out to quantify the ice crystallization in gels or foods (Miyawaki 2001).

Ultrasound assisted crystallization of water

Ultrasound waves have known to improve crystallization processes (Acton & Morris 1992). With the application of power ultrasound during the freezing process, the number of nuclei can be increased, the freezing efficiency can be improved and the microstructural properties of frozen foods are better preserved. Other advantages include, increase in heat and mass transfer rates, and initiation of ice nucleation since the initial nucleation temperature can be dictated (Zheng & Sun, 2005; Li & Sun 2002; Sun & Li 2003). Ice crystals also fracture under the alternating acoustic stress leading to crystal size reduction (Acton & Morris, 1992).

Conclusions

Freezing of foods is a complex process involving water crystallization. An overview of the crystallization process, crystallization modelling and water crystallization were provided, and the methods to monitor the crystallization phenomenon were also presented. Analyzing the water crystallization in foods quantitatively and relating the processing parameters to the crystal size distribution and crystal location is helpful for controlling the water crystallization phenomenon and for achieving the required results during the freezing process. In particular, novel methods such as ultrasound assisted freezing have shown to positively affect the crystallization process and could then be useful in controlling the crystallization phenomenon. Therefore, the study of the crystallization process is useful to perceive
the efficiency of the freezing process and the final product quality.

Acknowledgements

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References


QUALITY, ANTIOXIDANT AND STORAGE PROPERTIES OF FRUIT SMOOTHIES

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Abstract
High hydrostatic pressure (HHP) processing, uses pressure to inactivate foodborne microbes rather than heat and could result in products with fresh-like characteristics. Fruit smoothies are perceived as healthy by consumers and could increase fruit consumption, which is scientifically linked to a decreased incidence in many diseases. Smoothies were prepared with apple (29.5), apple juice (29.5), strawberry (21), banana (12) and orange (8% w/w per 250 ml sample). HHP samples were processed using isostatic pressure (450 MPa), held for 1, 3 and 5 mins at ambient (20 °C) temperature. Thermally processed samples were heated to a core temperature of 70 °C until a time-temperature (P 70>10 min) equivalent to 6 log reduction of vegetative cells. Samples were stored at 2-4 °C and tested for quality (pH, titratable acidity, soluble solids, moisture content, colour, sensory acceptability and complex rheology), antioxidant content [anti-radical power (ARP) and total phenols (TP)] and storage (TVC) properties on days 1, 10, 20 and 30. No significant differences (P>0.05) between fresh and processed smoothies for pH, titratable acidity and sensory acceptability were detected. HHP samples had lower (P<0.001) Hunter “L” and “a” values than fresh or thermally processed smoothies. Moisture values ranged (P<0.001) from 86.5 (fresh) to 86.0% (HHP: 5 mins). Soluble solid content was higher (P<0.001) in HHP samples than fresh. Fresh and thermally processed samples had a higher (P<0.001) ARP values than HHP samples. However, HHP (5 mins) samples had a higher (P<0.001) TP content than fresh or thermally processed smoothies. Sample degradation occurred throughout the course of the study with samples generally performing better between days 0 to 10 with a reduction (P<0.001) in quality across all parameters by day 30. However, all samples maintained microbiologically stability throughout storage.

Introduction
Fruit and vegetable consumption is declining in Europe. Fruits are a major source of dietary fibre and antioxidants. Epidemiological evidence has linked fruit consumption to a decreased incidence of many diseases. Therefore, there is a need for products that can enhance/augment daily fruit intake e.g. fruit smoothies (good consumer recognition and perceived as healthy). High hydrostatic pressure (HHP) processing yields products with fresh-like characteristics as it uses pressure to inactivate foodborne microbes rather than heat, which offers similar benefits but can lead to flavour impairment and textural changes1.

The aim of this study was to study the effects of high pressure thermal processing on the antioxidant, rheological and quality parameters of fruit smoothies.

Materials and methods

Preparation of samples
Product composition was based on a commercially available smoothie (GLSA, Portugal) for maximum industrial relevance. Strawberries (cv. Sabrosa; Spain) apples (cv. Braeburn; France), apple juice from concentrate (Tesco value, Ireland), bananas (cv. Nino; Cameroon) and oranges (cv. Navel-late; Spain) were obtained from a local retailer. Fruit was visually assessed for ripeness and any fruit found to be under/over ripened was discarded. Smoothie composition by weight was whole apple (29.5), apple juice from concentrate (29.5), strawberry (21), banana (12) and orange (8%). Fruit was
blended in a homogeniser (Robot Coupé Blixer 4® mono, Bourgogne, France) for 3 minutes. All smoothie samples were transferred and sealed into HHP grade polyethylene terephthalate (PET) bottles (250 ml) supplied by a local manufacturer (The Packaging Centre, product code 18PBC250J, Dublin, Ireland). Fresh control smoothies were chilled (2-4 °C) immediately, while other samples were subjected to subsequent processing (section 2.3).

**High pressure and thermal processing treatments**

Smoothie samples (250 ml) were placed in a high pressure vessel (100mm internal dia × 254mm internal height, Pressure Engineered System, Belgium) filled with a mixture of water and rust inhibitor (Dowcal N, 60% v/v in distilled water) and subjected to pressure of 450 MPa for 1, 3, or 5 mins at ambient temperature (~20°C). Time taken to reach the target pressure was approximately (60-100 sec) and depressurisation took 10 s.

Thermal processing was carried out by loading samples into a pilot scale retort (Barriquand Steriflow, Roanne, France). Core temperature profiles and P0 values were recorded during the process, using an Ellab E-Val TM TM9608 data module (Ellab [UK] Ltd., Norfolk, England) connected to a laptop. A standard Ellab SSA-12080-G700-TS temperature probe was inserted through an Ellab GKM-13009-C020 packing gland (20 mm) into one of the samples to record cook cycle. Temperature was monitored every 10 s. The samples were heated to achieve a process equivalent to 70 °C for 10 mins at the end of the cook-cool cycle and samples were stored for 0, 10, 20 & 30 days at 4 °C. Prior to any thermal treatment, all Ellab unit probes were calibrated against a JOFRA (ATC-155B) calibration unit at temperatures of 70, 80 and 90 °C and all results associated with the calibration did not exceed ±0.1 °C. After processing, samples were removed and tested for instrumental colour before being freeze-dried and extracted in methanol for antioxidant indices.

**Antioxidant assays**

Methanolic extracts were prepared as described by Patras Brunton, Pieve, and Butler (2009)1.

Total antioxidant activity was measured using the DPPH (2,2-Diphenyl-1-Picrylhydrazyl assay) assay as described by Goupy, Hughes, Boivin and Amiol (1999)2. The antioxidant activity was expressed in mg Trolox equivalent (TE) per 100 g dry weight sample (mg TE 100/gDW).

**Total phenolic content (TP)**

Total phenols (TP) were determined using the Folin-Ciocalteu (FC) procedure according to the method of Singleton, Orthofer and Lamuela-Raventos (1999)3. Total phenolic activity was expressed in mg Gallic acid equivalent (GAE) per 100 g dry weight sample (mg GAE 100/gDW).

**Rheological measurements**

Oscillatory rheological measurements were performed on a low torque rheometer (Physica MCR 301, Anton Paar GmbH, Graz, Austria) fitted with parallel plate (50 mm; smooth) geometry. Samples were placed onto the base plate (test gap of 1 mm) and when the plates reached the trimming distance (1.025 mm), the excess was removed and the testing geometry was covered by the temperature hood. Samples were rested (5 min) to achieve a constant test temperature (25 °C), and for relaxation of residual stresses. A preliminary amplitude sweep was performed to identify the linear viscoelastic (LVE) region of the samples and the strain (0.1%) that should be used for the resultant frequency sweep. A frequency sweep from 0.1 to 10 Hz was performed and the results for storage modulus (G'), loss modulus (G''), and complex modulus (G*) were recorded.

**Total titratable acidity (TTA) measurement**

TTA was measured as described by AOAC method (1995)4.
Soluble solids (SS)
Percentage soluble solids (%SS) was measured using a refractometer (Atago U.S.A., Inc., USA). Approximately 5g of homogenous apple puree was pressed through muslin. The residue was transferred onto a prism and SS were measured. The refractometer was calibrated with distilled water.

Sensory analysis
Panellists (15 per panel) were asked to mark a 6 cm line with endpoints of 0 (unacceptable) and 6 (very acceptable). The samples were presented in small plastic thimbles. Each taster was given 3 coded test samples and five panels were carried out and the results were averaged.

Microbiological assessment
Samples (25g) were microbiologically assessed for on site at the AFRC commercial laboratory, for Total Viable Counts (TVC) using accredited methodologies.

Statistical analysis
Data were analysed statistically by Fischer analysis of variance (ANOVA). Statistical design was 5 processes x 4 test days x 3 replicates.

Results and Discussion
In general, sample degradation occurred throughout the course of the study with samples generally performing better between days 0 to 10 with a reduction in quality across all parameters by day 30. For example, significant differences were observed between days 1 and 30 for TTA (P<0.001), SSC (P<0.001) and sensory acceptability (P<0.01) (Table 1). Day 1 samples had higher (P<0.001) L* and a* values than day 30 samples as expected. Fresh and thermally processed samples had a higher (P<0.001) ARP values than HHP samples. (data not shown). However, HHP (5 mins) samples had a higher (P<0.001) total phenol content than fresh or thermally processed smoothies (Figure 1). Complex viscosity decreased (P<0.001) over the duration of the storage period (Figure 2).However, all samples maintained microbiologically stability throughout storage.

Conclusion
Processors seeking a higher quality product with more fresh-like characteristics could consider HHP processing as an alternative to fresh or traditional thermal processing provided the HHP process is optimised to maximised product quality. Results indicated that some high pressure holding times performed equally or better than their thermal counterparts for certain quality parameters. All samples maintained microbiological stability throughout the storage period. By day 30, some product separation had occurred and may explain the observed decrease in viscosity.

Acknowledgements
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References
Table 1: Effect of storage on quality parameters of fruit smoothies

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<td>P&lt;0.001</td>
</tr>
<tr>
<td>LSD</td>
<td>0.40</td>
<td>0.61</td>
<td>0.53</td>
<td>0.42</td>
<td>0.21</td>
</tr>
</tbody>
</table>

SA - Sensory acceptability was assessed along a 6cm line with 0 unacceptable and 6 very acceptable; TTA- Total titratable acidity (meq/100g); SSC - Soluble solids (°Brix)

Figure 1: Effect of processing and storage on total phenol content

Figure 2. Effect of storage on the complex viscosity of fruit smoothie
DEVELOPMENT OF FRESH-CUT APPLE SLICES WITH ADDED PROBIOTIC BACTERIA

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Abstract
Probiotic dairy foods, e.g. yoghurts, are well recognised by most consumers and command a significant market share. However, many people are allergic or intolerant to dairy products and an alternative option is desirable. The aim of this study was, therefore, to apply a probiotic micro-organism (Lactobacillus rhamnosus GG) to fresh-cut apple wedges and measure entrapment and stability of the microorganism. Instrumental eating quality parameters (Colour Lab, texture, soluble solids, titratable acidity and pH) and sensory acceptability were also monitored to investigate if application of the probiotic significantly influenced eating quality. All samples sets contained ca. 10⁸ cfu/g over the test period of 10 days, which is sufficient for a probiotic effect and is comparable to counts of probiotic bacteria in commercially available dairy products. Physicochemical properties of the apple wedges remained stable over the 10 day period. Cryo-scanning electron and confocal scanning laser microscopy demonstrated good adherence of L. rham. GG to the surface of apple wedges.

Introduction
In the early years bacteria have been generally apparent as an undesirable cause for many diseases, although scientific research has done much to reduce their negative image. A dietary trend is now emerging for the search of friendly or healthy bacteria to take advantage of their beneficial health effect. Development of health promoting foods is one of the key factors for the food industry due to an increasing demand of foods enriched with physiologically active components such as probiotics. The most commonly used definition for probiotics is defined by Fuller (1989): Probiotics are live microbial feed supplements which beneficially affect the host animal by improving its intestinal microbial balance. Several scientific studies have shown that these microbial cells have a beneficial effect on the health and well-being on the human host (Salminen et al., 1998) if directed in the right amounts. Regular consumption of viable probiotics can improve health benefits such as reduction of cholesterol, control of gastrointestinal infections, improvement of lactose tolerance, anti-microbial activity, anti-cariogenic properties, anti-diabetic effect, anti-diarrhoeal effects, anti-mutagenic properties and immune system stimulation.

The objective of this study was to apply a probiotic microorganism (Lactobacillus rhamnosus GG) (L. rham. GG) to fresh-cut apple wedges thereby producing a doubly functional food product, i.e. the inherent functionality of the apple wedges plus the added functionality of L. rham. GG.

Materials and methods
Preparation of probiotic solution
Lyophilized cultures were grown in MRS broth overnight at 37°C. The cells were then washed with citric acid-sodium: citrate buffer (pH 3.8) by centrifugation at 7000 rpm for 15 min. Washed cells were then re-suspended in citric acid: sodium citrate buffer (pH 3.8).

Sample preparation
Apples (cultivar Braeburn) were purchased in a local supermarket, washed in water, cored and cut with a stainless-steel knife into wedges (each ca. 10g). Five skin-on wedges from each of five apples were used for infusion. The wedges were then dipped for 10 min in probiotic
solution containing approx. 10^10 cfu/ml of LGG. The wedges were then drained for 2 min and dipped for 2 min in a 6% (w/v) solution of browning inhibitor Natureseal® AS1 (AgriCoat Ltd., UK). The wedges were again drained for 2 min packed in clear trays (15 cm x 10.5 cm x 3 cm; heat sealed with a breathing film and stored at 2–4 °C for 10 days. Breaburn apple wedges were dipped in Natureseal® AS1 browning inhibitor as described above and were used as a control treatment. All samples were prepared in 3 replicates and tests were carried out on the samples on day 0, 2, 4, 6, 8 and 10.

**Enumeration of LGG in apple wedges**

On each test day one wedge containing LGG was removed from each tray (n=3) and macerated in 2% tri-sodium citrate solution [1:10 (w/v)], serially diluted in MRD and plated on Rogosa Agar. All plates were incubated aerobically at 37 °C followed by enumeration.

**Colour measurement**

The colour of the apple wedges was measured using a HunterLab D25A DP-9000 colour meter (HunterLab, Reston, VA, USA). The colour for 5 wedges per replicate was measured and expressed as a three dimensional Lab colour solid expressed as browning index (BI).

**Measurement of firmness**

The firmness of apple wedges was measured on 5 wedges for each treatment using a Texture Analyzer TA-XT2i (Stable Micro Systems, Godalming, UK) fitted with a 25 kg load cell and equipped with a Warner–Bratzler Blade. The wedge was fractured by a downward motion (10 mm/min) of a steel blade with a thickness of 3 mm. The maximum force (highest value in N) applied to break the wedge was used to quantify the firmness.

**Measurement of TTA and pH**

For total titratable acidity (TTA) approx. 5g of apple pulp were diluted in 100ml of distilled water and 3-4 drops of indicator phenolphthalein was added. The solution was then titrated with a 0.1N NaOH solution beyond pH 8.1. The TTA calculated as a percentage of malic acid. pH was measured on homogenous apple pulp with an Orion pH meter.

**Sensory evaluation**

A blind study was used to evaluate the overall acceptability of apple wedges containing LGG and control wedges by an untrained 25 member taste panel. Each panellist was given a plate containing 2 wedges (1 probiotic, 1 control). Panellists were asked to quantify the using a scale from 0 (unacceptable) to 6 (very acceptable). The evaluation was performed only on day 0.

**Cryo scanning electron microscopy (Cryo-SEM)**

Apple wedges (control and probiotic-treated, day 0) were examined using Cryo-SEM. For fracture surfaces, thin sections approximately 5 x 5 x 2mm were cut with a razor blade and mounted into a slotted aluminium sample holder using OCT embedding compound. The sample was then plunge-frozen into liquid nitrogen slush (-196 °C) and transferred under vacuum to the cold stage using the Alto 2500 cryo-transfer device (Gatan Ltd., Oxford, UK). After sublimation at -95 °C for 2 min, the sample was cooled to -125 °C, sputter coated with platinum and transferred to the cold stage for imaging at -125 °C.

**Confocal scanning laser microscopy (CSLM)**

CSLM in conjunction with in situ viability staining was used, based on a method by Auty et al. (2001), to visualise the distribution and viability of probiotic organisms on the surface of the wedges at day 0 and day 10.

**Statistical analysis**

The statistical design was 2 dips (control, probiotic) x 6 test days (0, 2, 4, 6, 8, 10) x 3 replicates with 35 degrees of freedom (df) followed by ANOVA.

**Results and Discussion**

**Survival of L. rham. GG**

LGG was tested for its ability to survive on apple wedges at 2-4 °C. On each test day three apple wedges were taken and enumerated. All apple wedges had a
concentration of $10^8$ cfu/g over the 10 days storage period, and was adsorbed in some manner on the apple wedges (Fig. 1). LGG was chosen for this trial as it is a commercial available bacteria and it has also been reported to be resistant to gastrointestinal conditions (Succi et al. 2005).

![Figure 1. Enumeration of L. rham. GG after incubation on Rogosa agar for 72-96 h in log_{10} cfu/g over 10 days storage at 2–4 °C.](image)

**Physicochemical evaluation**

No significant difference in instrumental colour values (HunterLab) between control apple wedges and infused apple wedges was noted ($P > 0.05$). BI for control apple wedges ranged from 23.2 to 25.9 while probiotic apple wedges showed similar patterns ranging from 23.4 on day 0 to 25.6 on day 10. Natureseal® products have been studied extensively and have shown to be effective in prevention of colour deterioration (Rößle et al., 2009).

Shear values for control apple wedges and probiotic apple wedges showed no significant difference ($P > 0.05$, Table 1). However, shear values changed significantly ($P < 0.001$) over the 10 day period. Between day 0 and 2 shear values increased which could be due to the AS1 browning inhibitor. As Natureseal® AS1 has calcium content of 90 mg 100 g⁻¹ (Rößle et al., 2009) the firming effect could be due to cross-linking of both cell wall and middle lamella pectin by calcium ions.

Values for total titratable acidity (TTA) for control apple wedges and infused apple wedges showed no difference as shown in Table 1 ($P > 0.05$). TA ranged from 0.53 to 0.59% malic acid with the highest value for control apples. The stability of TTA of probiotic apple wedges was expected as the pH (3.8) of the citric acid sodium citrate buffer was adjusted according to the inherent pH of the apple batch.

**Table 1. Physicochemical properties of apple wedges containing L. rham. GG (probiotic) and control apple wedges stored for 10 days at 2 – 4 °C storage period.**

<table>
<thead>
<tr>
<th>Day</th>
<th>BI (%)</th>
<th>TTA (%</th>
<th>pH</th>
<th>Shear (N)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>0</td>
<td>23.2</td>
<td>0.58</td>
<td>3.77</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>23.6</td>
<td>0.59</td>
<td>3.74</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>24.7</td>
<td>0.53</td>
<td>3.79</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>25.1</td>
<td>0.56</td>
<td>3.75</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>25.8</td>
<td>0.56</td>
<td>3.76</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>25.9</td>
<td>0.55</td>
<td>3.76</td>
</tr>
<tr>
<td>Probiotic</td>
<td>0</td>
<td>23.4</td>
<td>0.56</td>
<td>3.76</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>23.1</td>
<td>0.55</td>
<td>3.78</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>24.7</td>
<td>0.55</td>
<td>3.76</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>24.9</td>
<td>0.58</td>
<td>3.75</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>25.1</td>
<td>0.55</td>
<td>3.76</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>25.6</td>
<td>0.58</td>
<td>3.75</td>
</tr>
</tbody>
</table>

**Sensory evaluation**

Sensory evaluation was conducted on day 0 to indicate the differences between sample sets of control and probiotic apple wedges (Table 1). Panellists did not express a preference for apple wedges containing LGG over control apples. 13 tasters preferred control wedges while 12 preferred probiotic apple wedges. Similarly, overall acceptability of the samples was the same with a mean value of 4.25 for control and 4.20 for probiotic apple wedges showing that probiotic apple wedges were accepted well by the panellist ($P > 0.05$, Table 1).

**Cryo-SEM observation**

Cryo-SEM revealed the presence of numerous rod-shaped bacteria on the cut, treated surface of the apple wedges (Fig 2). No bacteria were seen within the apple tissue either within cells or at intercellular junctions (Fig 3).
Confocal scanning laser microscopy
CSLM of apple wedge surfaces revealed large numbers of unevenly distributed viable bacteria on day 0 (Fig 4). High numbers of viable bacteria were still present at day 10 but there appeared to be a relative decrease in the number of non-viable bacteria (Fig 5). This reflects the results shown in Fig 1.
COMPARISON OF RGB AND HYPSERSPECTRAL IMAGING FOR DETECTION OF CASING SOIL ON MUSHROOM SURFACES

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Abstract
The potential of red-green-blue (RGB) and hyperspectral imaging (HSI) in the visible-near infrared (445 - 945 nm) wavelength range to detect casing soil and discriminate between it and enzymatic browning or undamaged tissue on mushroom (Agaricus bisporus) surfaces was investigated. A calibration set of 108 damage free mushrooms, grown under controlled conditions in a research station, were first tested as undamaged class (U) and then were divided into 2 groups of 54 samples. The first group was smeared with casing soil and designated as casing soil class (C) and the second group was subjected to vibrational damage resulting in enzymatic browning and designated as damaged class (D). Partial least squares discriminant analysis (PLS-DA) models were developed to classify mushroom tissue as one of the three classes investigated (U, C and D) using pixel spectra from each class. Prediction maps were obtained by applying the developed models to the hyperspectral images of candidate mushrooms. Percentages of pixels classified into each class were also calculated for the mushrooms studied in the calibration set. Results obtained showed that the developed models performed satisfactorily to discriminate between the 3 classes studied. Comparison of red-green-blue (RGB) and hyperspectral image analysis showed that HSI was better able to identify the regions containing casing soil.

Introduction
In the commercial production of Agaricus bisporus mushrooms, a nutritional composted substrate colonised with mycelium is covered with a casing soil layer to initiate the development of sporophore (fruit body) production (Flegg and Wood, 1985).

Agaricus bisporus mushrooms are valued for their white appearance; however, harvested mushrooms commonly contain casing soil particles which adhere to the surface, giving the produce an unpleasant appearance.

The European Union provides guidelines for classification of cultivated mushrooms according to their appearance. Mushrooms classified as “Extra class” have superior quality; only very slight superficial defects are permitted and they should be practically free of casing material. Mushrooms in “Class I” have good quality and slight defects in shape and/or colouring, slight superficial bruising and only slight traces of casing materials are permitted. Mushrooms classified as “Class II” may have defects in shape or colouring, slight bruising or damage to the stalk, hollow stalks, slight internal moisture of stalks, and traces of casing material (Freshfel Europe, 2004).

RGB image analysis has been used for food quality characterization and defect detection for different agri-food products such as grains (Venora et al. 2009). More recently, HSI has emerged as a powerful technique in quality and safety evaluation of a variety of agricultural food products such as fruits, vegetables, meat, poultry and grains (Gowen et al. 2007). HSI offers many advantages such as simple and easy to use instrumentation, non-contact and non-destructive sample evaluation, estimation of both concentration and distribution of sample constituents and simultaneous identification of several components on a sample (Gowen et al. 2008; Qin et al. 2009).

The objective of this study is to compare RGB and hyperspectral imaging for detection of casing soil particles on mushroom surfaces.
Materials and Methods

Sample preparation
A total of 108 damage free mushrooms, each with a diameter of 3 – 5 cm, were harvested in October 2009. The damage free samples were first tested as undamaged class (U). They were divided into 2 equal groups; 54 mushrooms were distributed in 6 different plastic trays and were smeared with casing soil to make the casing soil contamination (C). This was done by manual application of casing soil to the mushroom surface using a spatula. The second group of mushrooms were subjected to damage by physical vibration using a mechanical shaker (Promax 2020, Heidolph Instruments, Schwabach, Germany) for 60 s at 400 rpm to induce enzymatic browning (D). The damaged samples were then distributed into 6 trays for scanning.

Hyperspectral imaging system
A hyperspectral imaging systems (DV optics) in the Vis-NIR range (445-945 nm) has been developed to investigate the spectral characteristics of white mushrooms (Agaricus bisporus). The main components of this system are: objective lens, spectrograph, camera, acquisition system, moving table, and illumination via fiber optic line lights (Gowen et al. 2008). Hyperspectral images were obtained in the aforementioned wavelength ranges with spectroscopic resolution of 5 nm. The effective resolution of the CCD detector was 580 x 580 pixels by 12 bits. Hyperspectral images of mushroom trays were obtained and 1000 reflectance (R) spectra of each individual mushroom were selected randomly to construct the PLS model.

RGB images
RGB false colour images of calibration set were obtained by calculating L* , a* and b* values from each image spectra using Spectral Scanner software (DV Optics, Padua, Italy) and the RGB coordinates were extracted (Slawomir, 2007). The same modelling strategy as that described in Fig. 2 was also applied to the RGB images of the calibration set in order to compare the potential of HSI and RGB techniques in discriminating between the 3 classes studied.

Modelling
Fig. 2 shows a flowchart of the data processing and analysis strategy employed in the study. After acquisition, hyperspectral images of individual mushrooms were pre-processed by masking in order to separate the mushroom from the image background. The mask was created by thresholding the mushroom image at 840 nm (images at this wavelength provided good contrast between mushroom and background) and setting all background regions to zero. Non-zero elements of the image were then extracted and the mean spectrum was calculated for each mushroom. Multiplicative scatter correction (MSC) was used as a spectral pre-treatment to reduce the influence of scatter effects and other sources of variations (e.g. differences in mushroom sample height and shape). The mean spectrum of each mushroom was used as the target spectrum for applying MSC.

![Fig. 1. Flowchart of data processing and analysis strategy employed in this study.](image)
class. In the first model, the response variable (Y) for undamaged samples was set to one and that for the other 2 classes was set to zero in order to differentiate between undamaged issues and the other 2 classes. The same strategy was used for the other 2 models to differentiate between casing soil particles and the rest (second model) and discriminate between enzymatic damaged regions and the rest (third model). This procedure was repeated 100 times and the resultant 100 regression vectors for each of the models were averaged.

Results and discussion
The average MSC pre-treated reflectance spectra of the 3 classes (U, C and D) of samples (average of 1,000 spectra randomly selected from the calibration set of spectra described in 2.3.2.) are shown in Fig. 2. It can be seen that the average reflectance values for the U class is higher than that of the C and D classes. Moreover, the spectra for U and C classes have similar profiles, while the mean spectra of D class samples exhibit a different profile. The difference in reflectance values between different classes is relatively high across the visible wavelength range between 445 to 645 nm; this is related to the colour differences between the different groups, also evident in Fig. 1. In the longer wavelength region, from 645 to 945 nm, the curves become similar and the spectra of C and D class samples are overlapping. Standard deviation curves are similar across the whole wavelength range studied.

Fig. 2. MSC pre-treated average reflectance spectra of the 3 classes investigated, where U = undamaged mushroom tissue, C = casing soil, D = enzymatic damage (thick lines) and their corresponding standard deviations (thin lines).

Fig. 3 demonstrates prediction maps obtained by applying the PLS-DA models to all RGB and HSI data with their corresponding RGB images in order to discriminate between mushrooms in U, C and D classes. In this figure, red, green and blue are representing regions that have been classified as U, C and D respectively.

![Fig. 3](image)

Although, the results obtained by analysis of RGB images were promising in predicting enzymatic damage (D) on the mushrooms’ surface, some of the other 2 classes (U and C) were misclassified as D which showed the lower potential of RGB images analysis in comparison with HSI analysis to discriminate between the 3 classes studied. Moreover, RGB image analysis had a lower ability to identify casing soil particles on mushroom surface in comparison with HSI analysis.

In order to quantify the performance of the RGB and HSI based models, the percentages of pixel values classified as each of the 3 different classes were calculated (Table 1). It can be seen that for the U class samples, 81.08 % and 81.79 % of pixels have been classified correctly in HSI and RGB images, respectively which suggests similar performance of the first model when applying on both types of images. For D class samples, RGB imaging showed better performance by classifying 98.15 % of enzymatic damaged regions as D though HSI method classified 89.83 % of enzymatic damaged areas as D which was also reasonable. In terms of C class
samples, it should be mentioned the whole surface of mushrooms were not covered by casing soil and the obtained value of 41.49 % by HSI method was satisfactorily reasonable, while using RGB method 74.57 % of C class were misclassified as U class which suggested poor performance of the model in this case.

Table 1: Average percentages of pixel values classified for each class using the 3 PLS-DA models obtained by both RGB and HSI data

<table>
<thead>
<tr>
<th>Actual Class</th>
<th>HSI analysis</th>
<th>RGB image analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>First model:</td>
<td>Second model:</td>
<td>Third model:</td>
</tr>
<tr>
<td>U and the rest (%)</td>
<td>81.08</td>
<td>45.18</td>
</tr>
<tr>
<td>C and the rest (%)</td>
<td>13.97</td>
<td>41.49</td>
</tr>
<tr>
<td>D and the rest (%)</td>
<td>4.95</td>
<td>13.33</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Actual Class</th>
<th>HSI analysis</th>
<th>RGB image analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>First model:</td>
<td>Second model:</td>
<td>Third model:</td>
</tr>
<tr>
<td>U and the rest (%)</td>
<td>81.79</td>
<td>74.57</td>
</tr>
<tr>
<td>C and the rest (%)</td>
<td>8.88</td>
<td>9.21</td>
</tr>
<tr>
<td>D and the rest (%)</td>
<td>9.33</td>
<td>16.22</td>
</tr>
</tbody>
</table>

Conclusions
Three PLS-DA models were developed to discriminate between 3 classes studied (U, C and D). HSI data correlated well with mushroom surface characteristics and the constructed models performed well for discriminating purposes. Comparison of HSI analysis with conventional RGB image analysis demonstrated the enhanced capability of HSI in identifying different classes studied, especially in identifying samples contaminated with casing soil. Currently, grading of mushrooms by visual inspection is both labor intensive and somewhat subjective. The introduction of optically based methods such as HSI would facilitate more objective quality monitoring. However, the drawbacks of using HSI in this context include high equipment cost and relatively long computational time required for analysis of HSI data; this limits its utilization in real time quality monitoring. Therefore, in order to facilitate online imaging based mushroom grading on an industrial scale, a multi-spectral approach which is cost effective and fast may be preferable. Further work is required to identify the optimal wavelength regions in the development of such a system.

Acknowledgment
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References
THE INFLUENCE OF SIMULATED HARVEST TRAFFIC ON
SOIL COMPAC TION, CROP RESPONSE AND BIOMASS YIELD
IN THE TRAFFICKED ZONES OF A MATURE MISCANTHUS
CROP

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Abstract
During harvest operations in Miscanthus, vehicles traffic the rhizome network in the soil and the effects of such trafficking are sometimes evident in the form of poor crop regrowth consistent with the location of wheel traffic. An experiment was conducted that simulated two harvest traffic systems (Baler System and Forager System) in order to determine the effects of each system on soil compaction, crop response and biomass yield.
Soil penetration resistance (SPR) was measured to assess the level of soil compaction. Crop response was assessed throughout the growing season by monitoring stem numbers and stem height while the crop was harvested to assess the biomass yield. There was very little difference in SPR values across all treatments. Stem numbers were significantly lower and stem height was noticeable lower in trafficked zones when compared to untrafficked control zones while biomass yield was substantially lower in the trafficked zones.

Introduction
Miscanthus x giganteus is a woody rhizomatous C₄ 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. For utilization of Miscanthus as special building materials and geotextiles, whole stems are required and machines for mowing and bundling of whole stems are a necessity (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).
Soane and van Ouwerkerk (1994) stated that soil water content is the most important factor influencing soil compaction processes while Defossez et al. (2003) concurred stating that severe soil compaction problems are most likely in those parts of the world where highly mechanised agriculture is carried out on land subject to high rainfall. In Ireland, the predominantly wet climatic conditions and the relatively fine textured soils combine to make most soil very liable to compaction (Fortune and Burke, 1985).
Soil compaction is a stress factor that negatively affects plant growth, but its effects vary between species and with the soil compaction range (Alameda and Villar, 2009). 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 soil compaction was slightly higher where land had been trafficked by tractor and machinery wheels, however, there was no significant effect on crop re-growth, based on the number of shoots per square metre.

The objective of this research was to investigate the influence of simulated harvest traffic on soil compaction, crop response and biomass yield in the trafficked zones of a mature Miscanthus 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 growing in soil that was described as a well-drained, friable, gravelly/sandy loam. The crop in the trial area was harvested and cleared manually to avoid wheel traffic on the soil in advance of applying treatments. The experimental plots were arranged in a complete block design with four replications. Each plot measured 3.00 metres wide and 25.00 metres long. The selection of equipment to simulate Miscanthus harvest traffic in this experiment was based on two common harvest systems employed in Ireland – the Baler System and the Forager System. The experiment consisted of three treatments:

1. Control – No traffic
2. Simulated Baler Traffic
3. Simulated Forager Traffic

Simulated Baler Traffic applied combined axle loading of 35.045 tonnes on the surface of the soil and consisted of trafficking the following components and individual axle loads on the appropriate plots:

(a) Tractor and Mower/Conditioner
   (Axle loads - 3080 kgs, 3370 kgs, 1190 kgs)
(b) Tractor and Baler
   (Axle loads - 3115 kgs, 3500 kgs, 2130 kgs)
(c) Tractor and Front-End-Loader with bale
   (Axle loads - 2505 kgs, 1430 kgs)
(d) Tractor and Loaded Bale Trailer
   (Axle loads - 2715 kgs, 4810 kgs, 7200 kgs)

Simulated Forager Traffic applied combined axle loading of 23.255 tonnes on the surface of the soil and consisted of trafficking the following components and individual axle loads on the appropriate plots:

(a) Small Forage Harvester
   (Axle loads - 670 kgs, 7860 kgs)
(b) Tractor and Loaded Forage Trailer
   (Axle loads - 2715 kgs, 4810 kgs, 7200 kgs)

Electronic weighpads were used to measure the static axle loads of all the equipment employed in the experiment. Tyre inflation pressures were adjusted based on the tyre manufacturers’ recommendations for the individual axle load.

The experiment was conducted on the 17th April 2009 in wet weather conditions and at high gravimetric soil moisture content. Essentially, a ‘worst case scenario’ with regard to axle load and soil moisture content was examined. Soil moisture content (MC), assessed using the thermo-gravimetric method was measured in all plots immediately after applying treatments. Each plot was also assessed for soil penetration resistance after treatments were applied to assess soil compaction. All SPR measurements were carried out when the soil moisture content was at or near ‘field capacity’.

The crop received no inputs during the growing season with regard to fertiliser and plant protection products. In the trafficked zone of each plot, sub-plots of one square metre were outlined and this area was monitored on a weekly basis to assess regrowth by counting stem numbers per square metre and by measuring stem height. These sub-plots were harvested on October 27th 2009 and total biomass yield (grams per square metre) was calculated on a dry matter basis.

All data was subjected to a one-way analysis of variance (ANOVA) at the 5% level of significance using MINITAB 15 (Minitab® Statistical Software).

Results and Discussion
Soil compaction results (Fig. 1) show average SPR values in megapascals (MPa), measured at 1 cm increments, to a depth of 50 cm. Each data series on the graph was compiled using data obtained from forty
penetrations of individual treatments - ten penetrations per plot and four replicate plots.

SPR values were significantly higher in the control plots (no traffic) when compared to the trafficked zones of Simulated Baler Traffic plots at a depth of 10 cm and 20 cm. Very little variation in SPR values was recorded between the control plots and the trafficked zones of Simulated Forager Traffic plots. The control zone SPR values averaged 1.8 MPa at a depth of 10 cm and 2.5 MPa at 20 cm deep. This represents a very compact soil condition that would not support growth of a cereal crop (Taylor, 1971).

Crop regrowth results (Figs. 2 and 3) show average Stem Numbers per square metre and average Stem Height respectively.

Stem numbers were significantly higher in the control plots when compared to the trafficked zones of both the Simulated Baler Traffic and Simulated Forager Traffic plots throughout the growing season. When stem numbers stabilised in late August, the control plots averaged approximately 50 stems per square metre while the trafficked zones of the other two treatments averaged approximately 40 stems per square metre.

Stem height was noticeably higher in the control plots when compared to the trafficked zones of both the Simulated Baler Traffic and Simulated Forager Traffic plots for most of the growing season. When growth ceased in mid-October, stem height in the control plots averaged 240cm approximately while stem height in the trafficked zones of the other two treatments averaged 220cm approximately.

Biomass yield results (Fig. 4) show biomass yield in grams of dry matter per square metre. Stem biomass was substantially higher, though not statistically significant, in the control plots when compared to the trafficked zones of both the Simulated Baler Traffic and Simulated Forager Traffic plots. An average yield of 1690 grams per square
metre (16.9 tonnes per hectare) was recorded in the control plots while the trafficked zones of the other two treatments yielded 834 and 827 grams per square metre respectively (8.34 and 8.27 tonnes per hectare). In the UK, long-term average harvestable yields from a mature crop (i.e. excluding the first 3 years), have exceeded 16 oven dry tonnes per hectare per year (odt/ha/yr) at the most productive experimental sites (DEFRA, 2007).

**Conclusions**
The very high SPR values recorded in this experiment and especially those recorded in the control plots suggest that the soil was in a compact state in advance of treatments being applied. This was possibly as a result of the soil being subjected to annual harvest traffic for several years. However, the yield recorded in the control plots (16.9 tonnes per hectare dry matter) suggests that Miscanthus can tolerate a compact soil condition.
The crop regrowth results showed that stem numbers and stem height were depressed in field zones that were trafficked by heavy axle loads in moist soil conditions and consequently biomass yield was also depressed.
The authors acknowledge that a 'worst case scenario' was tested in this experiment with regard to axle loading, intensity of trafficking and soil moisture conditions. It is also notable that the trafficked zones represent approximately 33% of total field surface area. Taking these factors into account, it must be reasonable to expect that when the biomass yield results are available for whole plots and not just the trafficked zones of plots, there will be less difference between the biomass yield of control plots when compared to the biomass yield of Simulated Harvest Traffic plots.

**Acknowledgements**
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VEGETATION INDICES FOR THE DETECTION OF VEGETATION DISTURBANCE ON IRISH PEATLANDS

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Abstract
Vegetation indices can offer an accurate and reliable method of detecting vegetation change in a habitat/ecosystem. In this study four different vegetation indices; NDVI, NDMI, MSAVI and EVI2, were tested on various habitats in the Wicklow Mountains National Park. NDVI showed high saturation throughout all habitat types, while NDMI index values were erratic and difficult to analyse. MSAVI and EVI2 produced good results, with EVI2 being the preferred index due to its high correlation to LAI.

Introduction
Satellite based vegetation indices are now widely used in a variety of terrestrial science applications, with the primary aim been the detection and monitoring of vegetation biomass (Jiang et al., 2007). A Vegetation Index (VI) can be described as a number that is generated by some combination of remote sensing bands (Rondeaux et al. 1996). In electromagnetic spectrum, the response of green vegetation can be described by high red absorption and conversely high NIR reflectance (Huete et al., 1997). It is this contrast (ratio) in absorption and reflectance that constitutes much of the vegetation indices used today. VI’s can be highly correlated to vegetation health, abundance and vigour, as well as more physical measurements such as Leaf Area Index (LAI), Gross Primary Productivity (GPP) and Photosynthetically Active Radiation (PAR) (Huete et al., 1997 and Jiang et al., 2007).

The objective of this study was to test several different VI’s in the Wicklow Mountains and evaluate their effectiveness at detecting different habitats, as well as vegetation change, on an upland blanket bog. This study was part of an overall project on detecting vegetation disturbance on Irish peatlands.

Methods
Study Site
The study site was located in Wicklow Mountains National Park (53° 09’ N, 6° 18’ W) on the east coast of Ireland (Figure 1). Annual rainfall is between 1300 and 2400 mm with low evapotranspiration levels for most of the year due to high altitudes and low temperatures (Connolly et al., In Press). Much of the Wicklow Mountains is protected by EU habitat directives such as SAC (Special Area of Conservation) and SPA (Special Protection Areas), however anthropogenic disturbance is prominent throughout the area. Peat harvesting, drainage and land reclamation, afforestation, burning and over grazing all present a threat to the ecology of this environment, and may have implications for the soil carbon stock now and into the future (Connolly et al., In Press).

Figure 1. Location map for the study site
Data

The VI images were based on five ETM+ multispectral images (Table 1) acquired from the US Geological Survey’s archive of Landsat imagery (USGS 2009). A vegetation map, derived from 5 m resolution Quickbird data as well as 1 m aerial photography from 2006, was acquired from the National Parks and Wildlife service (NPWS). These data aided in the interpretation of the VI images by assessing each index’s ability to distinguish the various habitats within the study site.

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Table 1. Metadata for the five Landsat ETM+ images

Preprocessing

The imagery was geo-registered to a predefined master image using Erdas Imagine’s AutoSync module. A projective transform model was used in conjunction with the 20 m DEM (Digital Elevation Model), as it provided greater sub-pixel level accuracy when compared to some of the more traditional linear models (e.g. affine and polynomial). The Root Mean Squared (RMS) threshold was set to 0.3, ensuring a high level of sub pixel registration, which is necessary to achieve errors of ≤ 10% in change detection studies (Coppin et al., 2004). All rectified imagery was resampled using the cubic convolution resampling method.

The combination of low sun angle and rugged terrain can lead to irregularities in sun illumination between north and south facing slopes. Similar vegetation types may, as a result, show varying radiance values, depending on such radiometric attributes. This phenomenon can be especially problematic when dealing with image classification or change detection studies (Civeo 1989, Riaño et al., 2003, Gao et al., 2009). Analysis in this study on the effect of sun elevation on the \( \cos(\theta) \) term of Chavez’s (1996) atmospheric correction equation revealed a threshold sun elevation of 42°. Any imagery acquired below this elevation (Table 1) would require some form of topographical normalisation to limit the effect of shadowing. Nichol et al.’s (2006) two stage topographical correction procedure was applied to band 4 (NIR) data for all images. After normalisation the variance between north and south facing was considerably reduced, resulting in a more even image in terms of illumination and radiometric characteristics.

Vegetation Indices

In this study four different indices were tested:

- Normalised Difference Vegetation Index: \( \text{NDVI} = \frac{\text{NIR} - \text{R}}{\text{NIR} + \text{R}} \) (Sellers., 1985)
- Normalised Difference Moisture Index: \( \text{NDWI} = \frac{\text{NIR} - \text{SWIR}}{\text{NIR} + \text{SWIR}} \) (Wilson et al., 2002)
- Soil Adjusted Vegetation Index: \( \text{SAVI} = \frac{1 + L (\text{NIR} - \text{R})}{\text{NIR} + \text{R} + L} \) (Huete., 1988)
- Enhanced Vegetation Index: \( \text{EVI2} = 2.5 \frac{\text{NIR} - \text{R}}{\text{NIR} + 2.5 \text{R} + 1} \) (Jiang et al., 2007)

Random samples from each VI image were taken within the boundaries of Wicklow National Park (Figure 1) to evaluate each index’s effectiveness at depicting peatland habitats. Samples points were stratified based on the NPWS 2006 habitat map, thereby ensuring that there was at least 40 sample points or more per habitat.

Results and Discussion

A scatter plot of EVI2 versus NDVI for the various habitats in the Wicklow Mountains using Landsat ETM+ data is depicted in Figure 2. In general, the two indices have a curvilinear relationship, with NDVI producing higher index values throughout. As the graph approaches 1.0 in both axes, the trajectory of the NDVI data tends to flatten out. NDVI is prone to “saturation” in highly vegetated habitats (Rondeaux et al., 1996) due to the formula structure. Figure 2 illustrates this phenomenon with the asymptotic trajectory of the NDVI data from 0.8 to 0.9. The sensitivity of NDVI to red band data is shown by the relatively high values
for Upland Blanket bog when compared to EVI2. In summer this habitat tends to have a low NIR to Red ratio, giving a high NDVI value. The issue of soil contamination of NDVI (Huete et al., 1997) is clearly shown by the deviation in burnt pixels between NDVI and EVI in Figure 2. Soil background contamination occurs when the spectral profile of soil is correlated to moisture content, i.e. variation in NDVI occurs not because of vegetation change, but due to soil moisture change. Soil contamination can be especially problematic in peatlands when dealing with change detection, as exposed soil can register similar values to vegetation, thereby masking actual change that may have occurred on the ground. EVI2 overcomes the issue of soil contamination by having additional weighting on red band data. EVI2’s emphases on NIR data is illustrated by the low index values for conifer plantation when compared to NDVI. NIR data in Landsat is primarily associated with leaf structure, therefore the low LAI of conifer needles, when compared to broadleaf’s, gives such habitats a low EVI2 value. The average reflectance/ index values for the various habitats in Wicklow Mountains National Park is plotted in Figure 3. The dependence of EVI2 and SAVI on NIR data is clearly illustrated by their high correlation with band 4 data in Figure 3. NDMI, while showing good divergence between habitats, seemed overall erratic.

![Figure 2. Scatter plot of EVI2 vs NDVI for Wicklow Mountains in 28/08/2001](image1)

![Figure 3. Average Index values for VI’s and band 3/4 of Landsat ETM+](image2)
Conclusion
It was expected that moisture content would be the dominant factor in NDMI’s behaviour. However, it was difficult to establish a pattern to the data, and therefore NDMI was deemed unsuitable for this study. NDVI produces the highest index values throughout, however the saturation of the index in summer months, as well as the effects of soil and atmospheric contamination, deem this index unsuitable for this study. The structure of EVI2 and SAVI made these indices favourable in a habitat such as upland blanket bog. The chlorophyll content of much of the vegetation in these habitats is relatively low for much of the year; therefore indices that rely on absorption in the red part of the electromagnetic spectrum (i.e. NDVI) will, as a result, have a low dynamic range of index values. NIR reflectance on the other hand is generally high in peatlands, mainly due to the variability in leaf structure within the various vegetation types. EVI2 has shown high correlation to LAI (Rocha et al. 2009), which can be an important parameter in vegetation disturbance studies. It is for this reason that EVI2 was chosen over SAVI for the purpose of habitat detection and vegetation change in this study.

Acknowledgements
The authors wish to thank the Environmental Protection Agency (EPA) for their financial support under the STRIVE fellowship.

References


REMOTE SENSING AS A TOOL TO MONITOR SLURRY SPREADING IN LINE WITH THE NITRATES DIRECTIVE

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Abstract
Remote sensing offers a solution to monitoring slurry spreading on grasslands. Monitoring farmlands can be difficult and not always feasible. To overcome this it may possible to detect differences in the spectral signature of grasslands that have recently been sprayed with slurry.

Introduction
Grasslands cover about 50% of Ireland (Bossard et al., 2000). The majority of which is for agriculture (CSO 2003). Grasslands play an important role in the storage and sequestration of greenhouse gases (Levy et al., 2007). The management of Ireland’s grasslands is governed by national and international legislation. One such piece of legislation is the Nitrates Directive (91/676/EEC). This EU legislation concerns the protection of waters against pollution caused by nitrates from agriculture (Jordan et al., 2005). In Ireland nitrogen can be applied in the form of artificial and natural fertilizer, such as slurry (Hutchings et al., 2007). Slurry is a semi-liquid natural fertilizer made primarily from livestock faeces. Slurry Nitrogen is made up of ammonium (NH3) and nitrous oxide (N2O) (Fangueiro et al., 2008).

The Nitrates Directive came into effect in 1991 and since 2006 the Nitrates Action Programme has strengthened statutory support for the protection of waters against pollution from agricultural sources (Environ, 2010). The directive provides a framework for action to reduce and prevent Nitrogen levels in catchments of rivers and groundwater affected by Nitrogen pollution and to reduce eutrophication of freshwater bodies, estuaries and coastal waters.

Lack of storage for slurry is the main cause of spreading slurry when conditions are unsuitable (Holden et al., 2004). The mandatory legislative measures affecting farmers are:
1. Restrictions on the amount of chemical and organic fertilizer applied.
2. Prohibition on spreading fertilizers near watercourses, boreholes or protected areas.
3. Environmental considerations no spreading on steeply sloping, frozen, snow covered or waterlogged fields.
4. Closed periods for the application of chemical and organic fertilizer.
5. Minimum requirements for organic manure storage capacity.
6. Slurry must be spread close to the ground.
7. Records must be kept with details of livestock coping regimes and fertilizer applications (European Communities, 2005).

It is not always possible or feasible to monitor every farm to make sure that slurry spreading does not occur during periods of prohibition. For this reason it is important to find a solution that allows relatively quick and cost effective means of monitoring farms. Remote sensing may provide us with this tool.

The objective of this project is to develop a low cost remote sensing tool for reliable, rapid, spatially extensive quantification of the presence of slurry applied to fields.
Materials and Methods

Sites

Initially the field sites will be from Teagasc research centres located in Moorepark, Fermoy Co. Cork. Grange Beef Research Centre, Dunsany, Co. Meath and Johnstown Research Centre in Johnstown Castle, Co. Wexford. See Fig 1. Mean average rainfall for Ireland is between 750 and 1000mm (Met Éireann, 2010). The wettest months in all areas are December and January. Slurry is spread from the end of January to the start of November with certain flexibility around the starting and finishing dates depending on the location of the farm. Rainfall is a major restriction for when slurry can be spread, it cannot exceed 2.5mm on the day of spreading (Holden et al., 2004).

All three sites have state of the art laboratory facilities and keep detailed records of all activities carried out. It is important to have detailed records of when slurry has been spread to enable correct imagery to be used. Moorepark facility is used for dairy cow research. Grange Beef Research Centre has 250ha of grassland used for the production of beef. Johnstown Research centre is Ireland’s leading research centre for soils and has over 250 ha of farmland (Teagasc, 2010).

Data

In order to monitor slurry spreading this project will use satellite imagery. Remotely sensed data will be obtained from satellite operators such as NASA (Landsat), ESA (SPOT), IRS (IRS) and also from EUFAR programme. Previous studies carried out within the Bioresources Research Centre have shown that Landsat data is freely and easily obtained. The Landsat program includes Landsat 5 TM and Landsat 7 ETM+. Landsat satellites have taken images of the continents for over three decades (Landsat, 2010). Landsat 5 has had problems over its lifespan and images from this satellite are not always available (Landsat, 2010).

It is necessary to obtain satellite data for sites on which slurry was spread during periods when such spreading is prohibited, for all the spectral signature of slurry on grass to be determined. If records cannot be obtained for the Republic of Ireland then data from Northern Ireland and the United Kingdom will be analysed.

This issue of cloud cover is a major obstacle to obtaining clear images from satellites. This will be taken into account when doing the project as other research is currently been carried out in the Bioresources Research Centre to overcome this.

Satellite and ground assessment

Erdas Imagine 9.3 Software will be used to analyse the images obtained. This software is a remote sensing application which will allow for the processing of the geospatial raster data. The data will then be analysed to obtain spectral signatures for grasslands that have been:

1. Grasslands free from slurry
2. Grasslands recently sprayed with slurry
3. Grasslands sprayed with slurry after a period of time.

Site evaluation will be carried out to determine the ratio of grass to soil. Depending on the time of year the grass may be cut due to the production of silage. This will mean that the grass will be shorter and may expose more soil. Slurry that is now spread over this grass may also be spread over exposed soil. The spectral reflectance from
plants is caused by scattering from discontinuities in the refractive index within the leaves (Zwiggelaar 1998). The spectral reflectance of soil will be different from grass.

A review of farm records to see when spreading has occurred and the conditions in which it was spread will be analysed.

Factors such as adverse weather conditions will be monitored and reviewed to see if this will attribute to lower detection rates.

Conclusions
Under the Nitrates Directive, a reliable way of monitoring the spreading of slurry over grasslands is required. This may be achieved by using remote sensing. Remote sensing offers a quick and accessible method of monitoring large areas of grasslands over more conventional methods.

Acknowledgements
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European Communities (Good Agricultural Practice for Protection of Waters) Regulations (2005) Statutory Instruments, S.I. No. 788 of 2005


RISK RANKING OF PHARMACEUTICALS IN WATER – A CASE STUDY ON ANTIBIOTICS / EDCS

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Abstract
Antibiotics and hormonally active agents are used as contraceptives and to treat bacterial infections. They persist in the environment in wastewater, surface water and groundwater. These organic contaminants, such as sulfamethoxazole which is used as treatment for malaria, have subsequently been discovered in drinking water. This poses a potential risk to human health.

This study is based on qualifying and quantifying risk by using a probabilistic assessment and modelling approach. Risk ranking will then be carried out on a variety of substances including antibiotics and EDCs.

Introduction
Scientific progress has lead to the rapid acceleration in the development of modern medicines and increased availability. This coupled with a rapidly growing population has lead to a huge uptake in the use of pharmaceutical products. Antibiotics and Endocrine Disrupting Compounds (EDCs) have emerged in the last decade as being two substances of particular concern.

Due to incomplete metabolism in humans, a percentage of these compounds are emitted into the sewage system, passing to waste water treatment plants. The processes in use for waste water treatment are ineffective in removing these compounds and will allow a certain proportion to discharge to natural aquatic environments. This pollutes the ecosystem with potential to propagate throughout the food chain e.g. EDCs in aquatic water have been observed causing sexual developmental and reproductive problems in mussels and fish.

Large quantities of antibiotics are dispensed to treat diseases and infection caused by bacteria in humans and animals every year. In a study, Huang et al. (2001) reported that up to 90 percent of the administered antibiotics can be excreted without undergoing metabolism. Endocrine disrupting compounds, also referred to as hormonally active agents, can be naturally occurring or of anthropogenic origin. At certain concentrations and time points during development and reproduction they trigger responses from the endocrine system which are detrimental to many wildlife species and also humans. Hormones, pesticides and thousands of everyday products are sources of EDCs. Typically ECDs from steroid hormones used in concentrated animal feeding operations and female contraceptives will enter the sewage system.

The objective of this study is to develop a preliminary (baseline) computer model with risk ranking and using a probabilistic modelling approach to model a specific antibiotic such as sulfamethoxazole or EDC such as the synthetic estrogen 17\(\alpha\)-ethinylestradiol. This model will be based on pharmaceutical contaminants in water and a selected antibiotic or EDC.

Materials and Methods
Figure 1 shows the schematic representation of how pharmaceuticals enter the water environment. This will form the basis of the proposed model.

Entry of Pharmaceuticals into the Water Environment
Pharmaceuticals made for human use or veterinary purposes end up in the aquatic environment mainly by human excretion to sewage systems (Kolpin et al., 2002).
Flushing of unused medications, animal feedlot and farm discharges are other sources. Once excreted, pharmaceuticals e.g. antibiotics, undergo various processes such as sorption, abiotic and biotic transformation (Huang et al., 2001).

Pharmaceuticals such as the female contraceptive contain estrogens which are a source of EDCs. They are absorbed into the bloodstream where a certain amount is metabolised by the liver and the remainder is excreted and enters the wastewater treatment system. The contaminants then enter the wastewater treatment plant at the sewage inlet. Pre-treatment screens the sewage and removes grit. Primary treatment or sedimentation is then used to remove grease and oils and homogenise the liquid. Secondary treatment involves a number of stages which degrade the biological content of the sewage including aeration. Occasionally the liquid undergoes tertiary treatment e.g. disinfection, before it is discharged into a receiving water body.

Pharmaceutical contaminants released into waterbodies can also bio-accumulate in aquatic species. This is another concern as there are very few studies on the health effects of chronic low-level exposure to pharmaceuticals. The data will be collected from scientific literature and used as an input for the risk ranking and for exposure assessment using probabilistic modelling approach. In some cases that same water is abstracted for drinking water and undergoes various unit processes - such as screening, coagulation, sedimentation, filtration and disinfection - to remove particles, dissolved chemicals and pathogens. This treated water is then used for human consumption. In a recent study, Benotti et al. (2009) assessed the actual concentrations in drinking water to which people were exposed to pharmaceutical compounds, such as antibiotics and EDCs. In their study sulfamethoxazole was found in highest concentrations of 110 ng/L in the source water. After water treatment and distribution to taps, levels were reduced to 0.39 ng/L.

Risk Ranking and Exposure Assessment using Probabilistic Modelling
A qualitative exposure assessment will be conducted initially and subsequently developed into a quantitative risk assessment. Risk assessment is defined by Hathaway et al. (1988) as “the qualitative...
or quantitative estimation of the likelihood of adverse effects from exposure to specified health hazards or from the absence of beneficial influences”.

Data for the risk ranking will be collated from scientific literature – e.g. estrogen biodegradation kinetics and formulae (Gaulke et al., 2009). Figure 2 gives a schematic showing the risk assessment framework that will be used.

Severity of adverse effect ranked 1 - 5 where 1 is a minor fluctuation in population of a particular plant or animal, 5 is complete irradiation from the habitat.

Likelihood, ranked 1 – 5, where 1 is a low probability of a contamination in sufficient concentration to cause harm and the susceptibility is low, and 5 is a high probability of contamination in large enough concentration to cause harm and where susceptibility is at the highest elevated level.

Available research (i.e. known variables), will be ranked 1 – 5, where 1 is a risk that is known and its effects understood, and 5, where no knowledge of the risk exists. In this model, the higher the number, the greater the risk ranking. Research will be validated on comparable studies so that the out coming ranking is consistent with available data. The ranking will then be compared with standards for drinking water quality. Further, the risk will be accounted for by representing data as probability distributions (discrete or continuous, e.g. normal or triangular), which allows data with uncertainty to be modelled.

Computer Model Design & Development
A model is a representation of a real system and aims to simulate what occurs or what may occur. The data are collated from the scientific literature and mathematical calculation will be used to evaluate the model and ranked as previously outlined using available risk ranking modelling programmes. Additionally, to capture the uncertainty and variability in the model, probability distributions will be determined using the Monte-Carlo simulation technique or any other available packages. The model will then be verified and validated by a sensitivity analysis.

Exposure Assessment
The human exposure level will be modelled based on the average human consumption of water per day and the exposure level of sulfamethoxazole.

Results and Discussion
Risk assessment and risk ranking has developed out of the need of guidance for policy makers to determine whether a risk is acceptable or not and computer simulation modelling allows these complex scenarios to be assessed.

Pharmaceuticals in the Environment
A specific antibiotic such as sulfamethoxazole or an EDC such as the synthetic estrogen 17α-ethinylestradiol will be used to develop the model. Sulfamethoxazole is used to treat malaria, conjunctivitis and urinary tract infections while 17α-ethinylestradiol is used in combined oral contraceptive pills.
**Risk Ranking & Risk Assessment**

The collated data will be assessed for risk ranking as previously mentioned in the methodology. Once the severity is identified, the model will be validated with a probabilistic approach.

**Probabilistic Modelling**

Once the database is developed and ranked on basis of severity, the model will be applied to probabilistic modelling using Monte Carlo simulation technique. Sensitivity analysis will be conducted to identify the important risk parameter of the drinking water.

**Human Exposure Assessment**

The human exposure level to sulfamethoxazole through drinking water will be assessed from the model output. This will be further compared to standards of water quality.

**Conclusions**

Pharmaceuticals consumed by humans are not completely metabolised and are excreted into sewage. Existing wastewater treatment methods do not completely remove these from the water and subsequently carried over to drinking water.

Risk ranking describes the probability of occurrence and severity of antibiotic sulfamethoxazole exposure in drinking water. The uncertainty of levels humans are exposed to will be captured by the probabilistic approach.

**References**


PROBABILITY RISK RANKING OF PESTICIDES USED IN IRISH AGRICULTURE

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Abstract

In agriculture, a wide range of pesticides are used in the management and control of weeds, pathogens and pests. It is widely recognised that exposure to pesticides can have potentially negative effects on human health and the ecosystem. Given the environmental and human health concerns, it is necessary to assess the risk posed by pesticides in the environment. In this study, a chemical ranking system, based on Monte-Carlo simulation techniques, was developed to rank the main pesticides used in agriculture in Ireland according to the risk of groundwater contamination. A preliminary risk ranking is provided with MCPA obtaining the highest rank, followed by mecoprop, isoproturon, chlormequat, metamitron, mecoprop-P, chlorothalonil, fenpropimorph glyphosate and mancozeb, respectively. A sensitivity analysis on MCPA revealed that the soil sorption coefficient, recharge coefficient and half life were the most important parameters which affected model predictions (with the correlation coefficient values of -0.46, 0.45 and 0.31, respectively). The model represents an initial attempt to identify the pesticides which pose the greatest risk of groundwater contamination and provide greater insight into the risk of groundwater resource contamination in Ireland.

Introduction

The use of pesticides is a key strategy of pest control in agriculture, forestry and in urban amenity areas. It has been estimated that 1.2 – 2.5 millions tons of pesticides have been used annually in the world (Green Communities Canada, 2008).

In the Irish agricultural sector for example, an extensive family of pesticides which include herbicides, fungicides and, insecticides are used to prevent crop attacks. The pesticide surveys organised by the Department of Agriculture and Food showed that herbicides were the most widely used pesticide type (DAFF, 2003, 2004). More specifically, MCPA, glyphosate, mecoprop-P and isoproturon were the most extensively used herbicides.

Despite their utility, pesticides can pose a serious threat to human and ecosystem health. It is necessary to assess the potential risk among chemicals used in the same field in respect to their relative risk to the environment. The work presented in this paper is part of the national project Assessment of the vulnerability of groundwater to pesticide inputs from Irish Agriculture.

The objective of this study is to rank the contamination risk of various pesticides used in Irish agriculture and to identify those posing the greatest environmental risk to the groundwater, and potentially requiring greater management in their use.

Materials and Methods

A recent study highlights a great diversity of pesticides risk ranking tools (Labite et al., 2010). Among these tools, the Leached quantity can be used in Irish conditions to assess the potential contamination risk as it combines a wide range of factors which include soil conditions, pesticide properties and application factors (Trevisan et al., 2009; Padovani et al., 2004) (Fig 1).

In this study, uncertainties and variability were taken into account by using probabilistic density distributions for the various input parameters based on current available scientific data and according to
the environmental settings. The input parameters were combined onto a spreadsheet (Microsoft Excel, 2007) running the @Risk add-on package (Palisade Software, Newfield, NY, USA) and the simulation was performed using Latin Hypercube sampling. The applied probabilistic distributions to the main inputs are detailed in Table 1.

A sensitivity analysis based on the Rank correlation coefficient was carried out to assess the influence of the model inputs on the model predictions.

A sensitivity analysis on MCPA revealed that the soil sorption coefficient (Koc), recharge coefficient, and half life were the most important parameters which affected model predictions (with the correlation coefficient value of -0.46, 0.45 and 0.31 respectively (Fig 3).

**Table 1: Model inputs and distributions**

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<td>Bulk density in g/cm³</td>
<td>Discrete (L1,L2,L3,L4:P1,P2,P3,P4)</td>
</tr>
<tr>
<td>P1 proportion of clay soil with bulk density range L1</td>
<td>Uniform (1.25,1.28)</td>
</tr>
<tr>
<td>P2 proportion of loam soil with bulk density range L2</td>
<td>Uniform (1.14,1.49)</td>
</tr>
<tr>
<td>P3 proportion of clay loam soil with bulk density range L3</td>
<td>Uniform (1.28,1.35)</td>
</tr>
<tr>
<td>P4 proportion of sandy loam soil with bulk density range L4</td>
<td>Uniform (1.28,1.64)</td>
</tr>
<tr>
<td>Soil field capacity in cm³/cm³</td>
<td>0.3486×Sand+0.0039×Clay0.039216×OC-0.0738×BD</td>
</tr>
<tr>
<td>Soil particle density</td>
<td>2650 (fixed value)</td>
</tr>
<tr>
<td>Porosity</td>
<td>1×BD/1000/PD</td>
</tr>
<tr>
<td>soil air content</td>
<td>FC-P</td>
</tr>
<tr>
<td>Potential evapotranspiration</td>
<td>Uniform (0,0.001705)</td>
</tr>
<tr>
<td>Evapotranspiration coefficient</td>
<td>Uniform (0.9,0.95)</td>
</tr>
<tr>
<td>Actual evapotranspiration</td>
<td>PE×EC</td>
</tr>
<tr>
<td>Rainfall</td>
<td>Uniform (0.6751,3.343)</td>
</tr>
<tr>
<td>Effective rainfall</td>
<td>RF×AE</td>
</tr>
<tr>
<td>Recharge coefficient</td>
<td>Uniform (0.05,0.9)</td>
</tr>
<tr>
<td>Groundwater recharge</td>
<td>RC×ER</td>
</tr>
<tr>
<td>Groundwater level</td>
<td>Uniform (0.5,2.5)</td>
</tr>
<tr>
<td>Interception fraction</td>
<td>Uniform (0,0.89)</td>
</tr>
<tr>
<td>Application rate</td>
<td>See table 2</td>
</tr>
<tr>
<td>Soil organic carbon content</td>
<td>See table 2</td>
</tr>
<tr>
<td>Henry’s constant</td>
<td>See table 2</td>
</tr>
</tbody>
</table>

Data used in this model were obtained from Irish studies where available. Data from other countries and the literature were used when Irish specific data were not available.

**Results and Discussion**

The model was run in Excel for 10,000 iterations and the simulated outputs can be used to assess the potential of pesticides leaching to groundwater (Table 3).

Based on the leached quantity value, the highest rank was obtained by MCPA followed by mecoprop (Fig 2). The leached quantity of some pesticides exceeded the 0.1 μg/l drinking water threshold (CEC, 1994).
Table 2: Pesticides input data

<table>
<thead>
<tr>
<th>Parameters</th>
<th>$R$ (in g/m²)</th>
<th>$Kh$</th>
<th>$Koc$ in cm³/g</th>
<th>$DT50$ in days</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pesticides</td>
<td>Fixed value</td>
<td>Fixed value</td>
<td>Distribution</td>
<td>Distribution</td>
</tr>
<tr>
<td>MCPA</td>
<td>0.160352</td>
<td>1.10E-08</td>
<td>Triang</td>
<td>BetaGeneral</td>
</tr>
<tr>
<td></td>
<td>($\alpha_1$=3.7873, $\alpha_2$=3.9003, min=49.225, min =88.024)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>glyphosate</td>
<td>0.102776</td>
<td>6.60E-19</td>
<td>BetaGeneral</td>
<td>BetaGeneral</td>
</tr>
<tr>
<td></td>
<td>($\alpha_1$=8084.4, most likely=15340, max=22734)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>chlorothalonil</td>
<td>0.05321</td>
<td>1.36E-05</td>
<td>BetaGeneral</td>
<td>BetaGeneral</td>
</tr>
<tr>
<td></td>
<td>($\alpha_1$=2.2688, $\alpha_2$=12.288, min=1374.2, max=5212.4)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mecocrop-P</td>
<td>0.051962</td>
<td>4.14E-11</td>
<td>Uniform (min=52.9995, max=60.6672)</td>
<td>BetaGeneral</td>
</tr>
<tr>
<td></td>
<td>($\alpha_1$=1.2606, $\alpha_2$=1.264, min=8.7893, max=13.0474)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>chlormequat</td>
<td>0.100281</td>
<td>6.50E-13</td>
<td>188.5</td>
<td>BetaGeneral</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Uniform (min=16.999, max=31.3)</td>
<td></td>
</tr>
<tr>
<td>mancozeb</td>
<td>0.188929</td>
<td>1.76E-10</td>
<td>Uniform (min=1942.96, max=2337.22)</td>
<td>BetaGeneral</td>
</tr>
<tr>
<td></td>
<td>($\alpha_1$=1.3344, $\alpha_2$=1.3322, min=5.0477, max=23.739)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>isoproturon</td>
<td>0.131481</td>
<td>3.80E-09</td>
<td>Uniform (min=81.996, max=150.338)</td>
<td>BetaGeneral</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Triang (min=7.1144, most likely=14.303, max=21.423)</td>
<td></td>
</tr>
<tr>
<td>fenpropimorph</td>
<td>0.029482</td>
<td>5.50E-05</td>
<td>BetaGeneral</td>
<td>BetaGeneral</td>
</tr>
<tr>
<td></td>
<td>($\alpha_1$=0.99957, $\alpha_2$=0.99919, min=9363.02, max=10155.68)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>metamitron</td>
<td>0.074303</td>
<td>4.60E-11</td>
<td>Uniform</td>
<td>BetaGeneral</td>
</tr>
<tr>
<td></td>
<td>($\alpha_1$=1.9768, $\alpha_2$=1.968, min=8.9547, max=28.101)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>meccocrop</td>
<td>0.127442</td>
<td>1.40E-09</td>
<td>BetaGeneral</td>
<td>BetaGeneral</td>
</tr>
<tr>
<td></td>
<td>($\alpha_1$=3.4262, $\alpha_2$=3.5707, min=36.879, max=49.852)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 3: Model calculation of the Leached quantity

<table>
<thead>
<tr>
<th>Description</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Step 3 Retardation factor RF:</td>
<td>$1+(BD\times OC\times Koc/FC)+(AC\times Kh/FC)$</td>
</tr>
<tr>
<td>Step 3 Residence time RT (in years)</td>
<td>$L\times FC\times RF/GR$</td>
</tr>
<tr>
<td>Step 3 Attenuation factor AF</td>
<td>$(-\text{expo}(RT/DT50))$</td>
</tr>
<tr>
<td>Main output</td>
<td>Leached quantity $LQ$ in (µg/l)</td>
</tr>
</tbody>
</table>
The sensitivity analysis highlighted that pesticide properties (e.g. Koc) was more important than site conditions on influencing the leaching potential in Irish soils, this highlighted the importance of pesticide selection.

**Future work**
Ongoing work includes the refinement of the model based on currently available data in order to improve the accuracy of model predictions. Additionally, toxicity will be combined to the leach quantity evaluation to provide a human health based risk ranking tool.

**Conclusions**
The leached quantity approach can be used to compare the potential negative effects of pesticides on the environment and human health. Based on the preliminary exposure assessment, the highest rank was obtained by MCPA. The risk ranking procedure identified pesticides requiring further quantitative investigation. Toxicity will be included in future studies.

**Acknowledgements**
This work was funded by the Irish Department of Agriculture, Fisheries and Food (DAFF) under the Research Stimulus Fund

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**References**


A GIS MODEL FOR THE ASSESSMENT OF GROUNDWATER VULNERABILITY TO POLLUTION

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Abstract

A GIS model to estimate the intrinsic vulnerability of groundwater to pollution has been developed specifically for the Irish conditions. It builds upon existing methods of groundwater vulnerability assessment that have been developed in Ireland, but it also incorporates additional parameters to consider important factors that influence groundwater vulnerability such as precipitation quantity and topsoil permeability. In addition, it offers the possibility to produce dynamic maps, thus allowing the identification of high risk areas, while also facilitating easy and efficient updates of these maps on a real time basis according to changing weather conditions or to alternative scenarios. In the future the model will be further developed to assess the risk posed by the use of pesticides for agricultural purposes.

Introduction

Vulnerability assessment can be defined as the attempt to estimate the probability of the contaminants reaching the groundwater after introduction at some location above the aquifer system (NRC 1993). The assessment of groundwater vulnerability can have several applications, from defining suitable ways for controlling vulnerability and updating the knowledge of a region's hydrologic resources, to determine the appropriate changes in land-use activities, and prioritise areas for resources allocation. Although it is a relatively new field in hydrology, it has undergone great advances mainly due to the advent of Geographic Information Systems (GIS). Usually vulnerability assessment is applied in two phases. First, the available hydrogeological, geological and hydrological factors are combined to assess the vulnerability likelihood across the area of study, and then the outcome is evaluated for its consistency against available data of groundwater quality or expert knowledge of the groundwater regime. Consequently, in areas where discrepancies have been observed, more data are collected so that the properties of a particular contaminant or group of contaminants, in addition to the intrinsic vulnerability of the area, can be taken into account. The first step of vulnerability assessment is termed intrinsic vulnerability while the latter is termed specific vulnerability (Daly et al., 2002). It should also be noted that intrinsic vulnerability assessment provides a worst-case scenario of the groundwater vulnerability likelihood (Voigt et al., 2004). The model developed in this study currently focuses on the intrinsic vulnerability of groundwater. The model incorporates three parameters which attempt to estimate: a) the protectiveness of the overlying layers, b) the reduction of protection due to concentration of water flow and c) the influence of precipitation, respectively (fig.1).

Fig.1. The model’s parameters

The objective of this work is to develop a GIS model that will incorporate all the factors which are important to describe the intrinsic vulnerability of groundwater to pollution.
Materials and Methods

Process
To construct the model in a GIS environment, a series of geoprocessing tools were linked together in the ModelBuilder graphic modelling interface, which is part of the ArcGIS 9.3 software. The following process was adopted in order to develop the three parameters.

For the first parameter it is assumed that direct (diffuse) recharge occurs through the soil and that the amount of water that recharges depends on the permeability and thickness of the topsoil and subsoil. Three different datasets were used: a) the soil associations map of Ireland by Gardiner and Radford (1980), which gave an estimation of the topsoil’s permeability and thickness, b) the groundwater vulnerability map produced by the GSI was used to derive permeability and thickness values for the subsoil, c) the subsoil map produced by Teagasc at the scale of 1:50000, provided the locations of outcropping rock and peat soil (fig.2). The rationale behind the analysis is that the less permeable and thicker the topsoil and subsoil are, the less vulnerable a location is in terms of groundwater pollution. Additionally, peat soils are important in the analysis because even a thin layer of peat can significantly decrease groundwater recharge and, hence, groundwater vulnerability (Misstear et al. 2009). Finally, the areas where the rock is at ground surface were considered to offer very little protection from pollution to the groundwater and, thus, were characterised as of extreme vulnerability.

However, water flow can bypass the soil strata through surface karst features which act as conduits by reducing the time needed by the surface water to reach groundwater. This phenomenon is known as concentrated water flow and can be observed as direct recharge occurring through karstified rocks such as the Burren in Co Clare, indirect recharge that occurs through allogenic or autogenic sinking streams and point recharge via swallow holes and other surface depressions (Drew, 2008). For the aforementioned parameter two scenarios were considered: a) the catchment area of swallow holes and losing streams and b) locations of outcropping rock (fig.3). In both scenarios the effect that topography and vegetation have on surface water flow was additionally considered. More specifically, for the former scenario the steeper the slope and the less the vegetation, the more recharge can occur. For the latter scenario the more flat the area and the less the vegetation the more recharge can occur.

To estimate the vulnerability increase due to the allogenic recharge of sinking streams, a watershed of the size of 5km was delineated around the point that the stream submerges under the surface and, additionally, a buffer of 100 metres was drawn around the stream itself. For the autogenic recharge, streams and other water bodies such as turloughs were

![Fig.2. The data inputs of the overlying layers parameter](image)

![Fig.3. Stages in the modelling of concentration flow](image)
The last parameter was developed using historic data of rainfall for the last 24 years from 232 stations around the country. Of major importance in the analysis was to identify the extreme events of rainfall that significantly increase the amount of recharge, and subsequently, of pollution. In the analysis the term wet year was used to define a year that the precipitation is 0.15 times higher than the average precipitation at that station. This value served as a threshold, above which to select the dates to be included in the investigation. The analysis used two metrics to quantify the reduction of an aquifer protection due to rainfall. The first metric calculated the average rainfall for all the wet years, while the second metric was the ratio of the average rainfall over the number of rainy days. The former metric gave an estimation of rainfall quantity and the latter an estimation of the temporal distribution.

**Results and Discussion**

The resulting model (fig.5) is a unique representation of groundwater vulnerability due to the number of parameters incorporated, but also owing to the physical-based approach which has been adopted to describe the way that the water flow (surface and underground) influences the transport of pollutants. Accurate analysis of the model results will be acquired after addressing the error and uncertainty related to the model’s parameters and data inputs. Error analysis can be performed by using a simulation technique (e.g. Monte Carlo) to run the model with different combinations of data inputs and parameters and derive probabilities of a phenomenon occurring at each location. During the sensitivity analysis it is possible to systematically change a parameter in order to define the influence the parameter change has on the model. The final step in the analysis will be to define the error associated with the model predictions, a process which is known as model validation. In order to validate this model, data of dissolved oxygen concentration in groundwater will be employed to develop a statistical model using the “weights of evidence” (WofE) method. The WofE statistical method attempts to correlate prior knowledge with the hypothesis, which for the needs of vulnerability assessment can indicate the probability of contaminants occurrence. WofE is based on the Bayes’ theorem that is expressed by the equation: \( p(\theta|y) = \frac{p(y|\theta)p(\theta)}{p(y)} \). Where \( p(\theta) \) the density of training points indicating prior knowledge, \( p(y|\theta) \) the likelihood and \( p(\theta|y) \) the updated knowledge contained in the posterior density (Congdon, 2006). The advantages of WofE are that it provides an effective way of self-learning from existing data and that it has increased accuracy because it uses ancillary information.

**Conclusions**

The model of groundwater vulnerability to pollution has been successfully completed for the entire country at the River Basin District level. The next step of the analysis will be to estimate the error associated with the model’s input data and parameters and to determine the accuracy of the final results. A combination of statistical methods and standard GIS techniques will be used for that purpose.

**Acknowledgements**

The authors wish to acknowledge funding for this project by the Department of Agriculture, Fisheries and Food under the STIMULUS Research Programme.

**References**

[Fig.4. Stages to calculate the quantity and temporal distribution of precipitation]


Fig. 5. The flow diagram and the resulted map of groundwater vulnerability based on the GIS model

Flow diagram legend

Groundwater Vulnerability Index
- X
- E
- H
- M
- L
- H/L
- Water
- No data
THE EFFECTS OF CONVENTIONAL TREATMENT ON ANTIMICROBIAL RESISTANT BACTERIA- A META-ANALYSIS

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Biosystems Engineering, UCD School of Agriculture, Food Science and Veterinary Medicine, University College Dublin, Belfield, Dublin 4, Ireland.

Abstract
Antimicrobial drug residues and their metabolites reach the aquatic and terrestrial environment primarily through wastewater treatment plants. In addition to the potential direct negative health effects, there is potential for the development of antibiotic resistant bacteria, particularly where residue levels are below the minimum inhibitory concentration (MIC). This has resulted in global concern about antibiotic resistance and consequently antibiotic redundancy and therapeutic failure. A meta-analysis study was carried out to analyse the effect of wastewater treatment plant (WWTP) processing on the prevalence of fluoroquinolone resistant E. coli within bacterial populations. An increase of multiple antibiotic resistant (MAR) bacteria and single antibiotic resistant (SAR) E. coli was documented (3%, p <0.05, 2%, P<0.05, respectively). Further investigation is required to analyse uncertainties and to discover the risk of antibiotic resistance to human health and the environment.

Introduction
Human and animal bacteria are continuously being released into the environment, commonly via wastewater (e.g. human excretion and egestion into the sewer system, cattle defecation directly into streams). Many of these organisms can possess antibiotic resistance genes. These genes, through the use of vectors such as plasmids, have the ability to spread among foreign and indigenous water and soil bacteria communities. Simultaneously, antibiotics from industrial and agricultural origins are entering the water environments. Their presence can potentially alter microbial ecosystems. Even more disturbingly, their presence can allow for the further development of resistant genes within the bacterial populations which can again consecutively be spread through bacterial populations (Baquero et al., 2008).

The spread of antibiotic resistance has resulted in a crisis in the treatment of infectious diseases in humans (Schlüter et al., 2007). Kunin (1997) believes that the current condition is ‘antibiotic Armageddon’.

Antibiotic resistance is thought to come about through bacteria coming in contact with a compound and evolving to form resistance. As many bacteria can replicate within 20-30 minutes, they have the ability to adapt rapidly to their surrounding environment. Unfavourable conditions, such as antibiotic presence can result in the adaptation of bacteria to enhance survival, and thus resistant genes are formed (Kümmerer, 2008). Worryingly WWTPs seem to be the optimal habitat for antimicrobial resistance formation. Bacteria are permanently exposed to sub MIC (i.e. a concentration too low to negatively affect the bacteria (Kümmerer, 2008)) of a multitude of antibiotics. This highlights the need for further investigation of the effects of treatment processing on resistant bacteria to determine whether specialised treatment is necessary to limit the formation of antibiotic resistance.

The objective of this study was to carry out a Meta-analysis of the effect of WWTP processing on antimicrobial resistant bacteria.

Materials and Methods
Meta Analysis
Meta-analysis is a method of integrated statistical analysis of a number of
independent studies (Mullen, 1989). It is possible to achieve a more precise estimation of a process with increased statistical power through the use of Meta-analysis (Barron et al., 2008). Combing results from many studies generates a comprehensive opinion of an effect such as WWTP processing on the rate of antibiotic resistance.

Data acquisition

4 studies consisting of 17 data samples were analysed (Hassani 1992; Reinthaler, 2003; Garcia et al., 2007; Lefkowitz and Duran, 2009) for the effect of WWTP on the population proportion of single antibiotic resistant *E. coli*. 5 studies consisting of 89 data samples were analysed (Silva, 2006; Gallert, 2005; Garcia et al., 2007; Lefkowitz and Duran, 2009; Zhang et al., 2009) for the effect of WWTP processing on the proportion of MAR bacteria. Data was analysed using Mix 1.7 software to give a graphical and numerical output of effect probability.

Results and Discussion

The effect of WWTP processing on the prevalence of SAR *E. coli* is displayed in Fig. 1. The output of a 2.1% increase is statistically significant (*p* = 0.0004) with a confidence interval between 0.9-3.2%. The prevalence of SAR *E. coli* increased as a result of WWTP processing. Similarly, the effect of WWTP processing on MAR bacteria (Fig. 2) was statistically significant (*p* < 0.001). The population prevalence was seen to increase (after treatment) by 3% with a confidence interval of between 2 - 4%.

These results are similar to the findings of Bell et al., (1983). They documented an increase in the percentage of MAR faecal coliforms after WWTP processing, and showed the ability for the resistant bacteria to transfer resistant genes.

**Figure 1:** The effect of WWTP processing on the prevalence of single antibiotic resistant *E. coli*

**Figure 2:** The effect of WWTP processing on the prevalence of multiple antibiotic resistant bacteria (Where MD: mean difference or change in % resistance)
Based on Darwin’s theory of natural selection (“preservation of favourable variation and the rejection of injurious variation” (Darwin, 1859)), as the proportion of MAR bacteria and SAR E. coli were higher within the final effluent than influent, it can be postulated that there is a selective pressure or an advantage to becoming resistant (such as survival through the WWTP). Therefore it is possible to hypothesise that WWTPs encourage the selection of MAR bacteria.

Conclusions

The results presented here questions our understanding of the effect of WWTP on antibiotic resistance and highlight the need for further investigation into the risk of antibiotic residues in the environment. Antibiotic redundancy is the main consequence of concern. If resistance within environmental populations continues to increase as documented here it may not be possible to create new antibiotics at the rate at which they become redundant. However, it is uncertain whether the presence of antimicrobials is accredited to the increases in population resistance. The majority of resistance transfer may be originating from already present resistant bacteria. These uncertainties highlight the need for further investigation of resistance in the environment. Thus, the appropriate measures can be taken to reduce the anthropogenic problem.

Acknowledgements

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References


DEALING WITH UNCERTAINTY IN ASSESSING ENVIRONMENTAL RISK OF NANOMATERIALS

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Abstract
Risk assessments require accurate and relevant data relating to the material or action in question in order to make informed decisions. In the case of predictive risk assessment of emerging pollutants there are often large gaps in the available data and so bridging data or educated extrapolations from available data are required. In this study a method to deal with uncertainty over the potential aquatic transport characteristics of nanomaterials is presented. Limited available data is adjusted (using trend factors developed from literature) according to its relevance to commercial and environmental scenarios in order to assess potential transport of these materials upon aquatic release. This method takes into account the inherent variability and uncertainty in applying the available data and is applicable to more relevant data once this becomes available.

Introduction
The unique and enhanced characteristics of materials at the nano-scale, and new techniques to manipulate materials at this scale, have resulted in their application in many products and processes. This includes the environmental sector, where nano-scale characteristics and surface functionalisation improve chemical reactivity, antibacterial action and dispersion. These characteristics have also caused concern regarding their potential for unintended environmental release and subsequent environmental and human exposure (O’Brien and Cummins, 2008).

Understanding the behaviour of nanomaterials is essential in predicting their environmental transport and persistence potential. Due to the large variation in the physical and chemical characteristics of nanomaterials, there is uncertainty as to their exact behaviour and mechanisms upon release to different environmental media.

In aquatic environments there are many processes that will affect the fate of nanomaterials, such as degradation, adsorption to organic matter, aggregation and sedimentation. Each of these processes will be governed by material and environmental factors such as size, surface area, surface charge, surface functionalisation, pH, dissolved organic carbon content, etc (O’Brien and Cummins, 2009). Specific materials and environments will result in specific behaviour, with some materials predicted to behave in a similar fashion to well studied substances such as natural colloids and metals.

A responsible way of dealing with large uncertainties regarding nanomaterial behaviour is needed when performing predictive risk assessments. In the absence of definitive studies, all available data must be utilised in the most appropriate way, where all uncertainties and assumptions are transparent and measurable, with the potential to apply more appropriate data when available (O’Brien and Cummins, In Press).

The objective of this study is to develop a method to capture current knowledge on the transport and persistence of nanomaterials in aquatic environments for use in predictive risk assessment.

Materials and Methods
Available data relating to nanomaterial transport and persistence in aquatic environments was assessed, where the quantitative effect or qualitative trend in aquatic behaviour was correlated to environmental or material characteristics. In addition to this, data relating to the bulk form of the material and other substances that may be relevant to the behaviour or
mechanisms of the nanomaterial under assessment was assessed. For the purposes of this study the focus shall be on the aggregation of nanomaterials in aquatic environments and its effect on transport potential.

Table 1: Aggregation distribution adjustment factors (Assessed Vs Study)

<table>
<thead>
<tr>
<th>Material</th>
<th>Mean</th>
<th>S.D.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Primary aggr./particle size (nm)</td>
<td>10^{10} = 1 x Pert (50,75,100) or Sqrt(Mean)</td>
<td>n/a = ×2</td>
</tr>
<tr>
<td>Aquatic pH - pH_{zpc}</td>
<td>5.2 Uniform (1.5,2.8)</td>
<td>n/a = ×2</td>
</tr>
<tr>
<td>Surface coating b</td>
<td>Yes = × Uniform (10^{-2},10^{-3})</td>
<td>n/a = ×2</td>
</tr>
<tr>
<td>DOC (material solubility) c</td>
<td>10^{-2} = 1 x Pert (1,250,250) or Sqrt(Mean)</td>
<td>n/a = ×2</td>
</tr>
<tr>
<td>Ca^{2+} (ionic strength) d</td>
<td>10^{-2} = 1 x Pert (500,750,1000) or Sqrt(Mean)</td>
<td>n/a = ×2</td>
</tr>
</tbody>
</table>

n/a Not available

b. Trend from Phenrat et al. (2007)
c. Trend from Limbach et al. (2008) & Velzeboer et al. (2008)
d. Trend from Fang et al. (2009)

In order to assess disparate data relating to aquatic transport or persistence, a suitable distribution was fitted to each data set. These distributions were then adjusted according to the material under investigation. Differences in the characteristics of the material assessed to those employed in the study (from which the base data set was developed) result in an adjustment of the mean and/or standard deviation of the original distribution. These adjustment factors may also take into account variability in material and environmental characteristics.

Many of these adjustment factors are represented by a distribution as the effect of differences between environmental/assessed material and study characteristics are not quantifiable. The adjustment factors employed represent a general trend determined from literature and so the distributions represent the potential boundaries of the effect of the specified trend. These additional adjustment factors may be seen in Table 1.

Where more base distributions are considered and adjusted, these adjusted distributions may be combined to give a single aggregate size distribution, though this is not considered in this study. These adjusted distributions represent current knowledge in nanomaterial transport or persistence in aquatic environments for use in risk assessment.

Case Studies
The aquatic aggregation and subsequent transport potential of two nanomaterials is assessed here. The characteristics of these materials are presented in Table 2.

The characteristics of the aquatic environment under investigation are presented in Table 3.

Aquatic Transport
The transport and fate of nanomaterials in an aquatic environment is represented in this study by their initial aggregation in natural aquatic environments, subsequent transport characteristics and their adsorption to natural organic matter (NOM).

Table 2: Material characteristics

<table>
<thead>
<tr>
<th></th>
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<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Material</td>
<td>TiO_{2}</td>
<td>Ag</td>
<td>TiO_{2}</td>
</tr>
<tr>
<td>Particle size (nm)</td>
<td>25</td>
<td>10</td>
<td>330</td>
</tr>
<tr>
<td>SA (mg/g)</td>
<td>50</td>
<td>10</td>
<td>n/a</td>
</tr>
<tr>
<td>pH_{zpc}</td>
<td>5.2</td>
<td>Uniform (1.5,2.8)</td>
<td>5.2</td>
</tr>
<tr>
<td>Density (g/cm^3)</td>
<td>3.9</td>
<td>10.5</td>
<td>3.9</td>
</tr>
<tr>
<td>Surface coatings</td>
<td>N</td>
<td>N</td>
<td>N</td>
</tr>
<tr>
<td>Solubility</td>
<td>Insoluble</td>
<td>Slightly soluble</td>
<td>Insoluble Slightly soluble</td>
</tr>
</tbody>
</table>
Table 3: Aquatic characteristics

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Type</td>
<td>Freshwater</td>
<td>Milli-Q water</td>
<td>Freshwater</td>
</tr>
<tr>
<td>pH</td>
<td>Gamma (31.1, 0.2)</td>
<td>7</td>
<td>Normal (8.1, 1)</td>
</tr>
<tr>
<td>DOC (mg/L)</td>
<td>Weibull (6.5, 7.4)</td>
<td>0</td>
<td>Uniform (8.5, 8.9)</td>
</tr>
<tr>
<td>Ca²⁺ (mg/L)</td>
<td>Fitted data</td>
<td>0</td>
<td>Lognormal (56.6,0.8)</td>
</tr>
<tr>
<td>Depth (Average) (m)</td>
<td>1.5</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>River speed (m/s)</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Two studies were chosen, from which the base distribution data was generated, Adams et al. (2006) (TiO₂ size distribution in minimal Davis medium and Milli-Q water) and Griffitt et al. (2008) (Ag size distribution in moderately hard freshwater). The material and solution characteristics used in these studies may be seen in Tables 2 and 3 respectively. The resulting base aggregate size distributions may be seen in Figures 1 and 2.

\[
D_r = \left( \frac{2}{9} \left( \frac{\rho_p - \rho_f}{\mu_f} \times g \times r^2 \right) \times s_r \times \frac{d_a}{2} \right)
\]

Where:
- \(D_r\) = Aquatic transport dist. (m)
- \(\rho_p\) = Particle density (kg/m³)
- \(\rho_f\) = Fluid density (kg/m³)
- \(g\) = Gravitational accel. (m/s²)
- \(r\) = Particle radius (m)
- \(s_r\) = River speed (m/s)
- \(d_a\) = Average depth of river (m)

Figure 1: Base aquatic aggregate size distribution (Milli-Q water): TiO₂

Figure 2: Base aquatic aggregate size distribution (moderately hard freshwater): Ag

These base distributions were adjusted according to the assessed material and environmental characteristics in Tables 2 and 3. Provisional transport properties were calculated from the resulting adjusted aggregate distributions using the material (Table 2) and environmental (Table 3) characteristics in the following simple Stokes equation:

Probability of aggregate adsorption to organic matter in freshwaters, and subsequent sedimentation was adjusted from existing studies (Blaser et al. 2008; Fang et al. 2009) according to environmental and material characteristics (not shown). The predicted fraction of nanoparticles “free” in aquatic environments and the associated adjustment factors may be seen in Table 4.

Table 4: Aquatic “free” nanoparticles distribution and adjustment factors

<table>
<thead>
<tr>
<th>Study</th>
<th>Aquatic fraction - “Free”</th>
<th>Mean (adj.)</th>
<th>S.D. (adj.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blaser et al. (2008)</td>
<td>Pert (1.95,2.22,2.27)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fang et al. (2009)</td>
<td>Uniform (0.05,1.15)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- Aquatic pH - \(pH_{\text{pHc}}\)^a
- Ca²⁺ (ionic strength)^b
- DOC (& material solubility)^c

\(a.\) Trend from Dunphy et al. (2006)
\(b.\) Trend from Fang et al. (2009)

Results and discussion

These material and environmental inputs, combined with current knowledge into aquatic behaviour, results in the following adjusted aggregate transport distributions
(mean adjustment factors applied) and partitioning to different aquatic states (“free” nanoparticle fraction shown) for the two investigated materials (Table 5).

Table 5: Aquatic (river) nanomaterial transport and fate distributions

<table>
<thead>
<tr>
<th>Nanomaterial</th>
<th>TiO₂</th>
<th>Ag</th>
</tr>
</thead>
<tbody>
<tr>
<td>Predicted aquatic transport category (% likelihood)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1. (&lt; 0.1 km)</td>
<td>56</td>
<td>39</td>
</tr>
<tr>
<td>2. (0.1-1 km)</td>
<td>42</td>
<td>41</td>
</tr>
<tr>
<td>3. (1-10 km)</td>
<td>2</td>
<td>18</td>
</tr>
<tr>
<td>4. (&gt; 10 km)</td>
<td>0</td>
<td>2</td>
</tr>
<tr>
<td>Aquatic partitioning: “free” nanoparticles (% of total released)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1. (&lt; 0.1 %)</td>
<td>80</td>
<td>4</td>
</tr>
<tr>
<td>2. (0.1-1 %)</td>
<td>20</td>
<td>42</td>
</tr>
<tr>
<td>3. (1-10 %)</td>
<td>0</td>
<td>52</td>
</tr>
<tr>
<td>4. (&gt; 10 %)</td>
<td>0</td>
<td>2</td>
</tr>
</tbody>
</table>

Conclusions
The distributions generated as part of this study represent current knowledge into the transport characteristics of these nanomaterials, incorporating uncertainty and variability factors. As more relevant data comes to light a more representative distribution may be generated.

The method employed to generate these distributions may also be applied to other nanomaterials and uncertainty/variability factors may be refined according to current knowledge.

Acknowledgements
The authors wish to acknowledge the funding from the Environmental Protection Agency under the Environmental RTDI Programme 2000 – 2006. Project ref no: 2006-RCA-20

References
O’Brien, N., Cummins, E., Nano-Scale pollutants: Fate in Irish surface and drinking water regulatory systems, Human and Ecological Risk Assessment, In press
LIFE CYCLE COMPARISONS OF GREENHOUSE GAS EMISSIONS FROM PASTURE-BASED DAIRY PRODUCTION OF IRELAND

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2 Moorepark Dairy Production Research Centre, Teagasc, Fermoy, Co Cork

Abstract
The objective of this paper was to estimate the change in greenhouse gas (GHG) emissions from Irish dairy production when mineral fertilizer N is replaced by biologically (white clover) fixed N. Nearly 80% of the nitrous oxide (N2O) emissions due to agriculture are related to the use of fertilizers. Based on the comparative experiment at Teagasc Solohead Research Farm for the years 2003-2006, the GHG (CO2, CH4 and N2O) emissions from clover-based (WC) and mineral-N-fertiliser-based (FG) dairy production were compared using life cycle assessment (LCA) tools. Compared with the FG system, emission of fertilizer use in the WC system was reduced by 67.4% and the overall emission from producing 1 kg ECM from WC was thus reduced by 13.3%.

Introduction
There is a growing concern about the effect of GHG emissions on the global climate change. In Ireland, agriculture is the single largest contributor to overall emissions at 26.8% (Environment Protection Agency 2008), and beef and dairy production currently account for 58% of agricultural output at producer prices (Department of agriculture fisheries and food of Ireland, 2008), thus the dairy GHG emissions of dairy farms are of considerable importance.

Life Cycle Assessment (LCA) can be used to address agricultural system impacts (ISO 2006; van der Werf, Tzilivakis et al. 2007). Simapro is a powerful LCA software developed by PRé Consultants (PRé 2007).

The main GHG from agricultural production are CO2, CH4, and N2O. Nearly 80% of the N2O 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, Verhagen et al. 2005) found that white clover had a marked effect on the GHG emissions. Compared to grass/fertiliser-N system, the indirect emissions on the grass/clover farm were 32% lower per ha and 22% lower per kg milk. Meanwhile, James suggested that the recycling of N from grazed herbage to the soil via the grazing cows was the main cause of lower N-use efficiency (Humphreys, O'Connell et al. 2008), which implies that white clover may not effect significantly on the N loss on farm.

The objective of this paper was to develop a LCA model of two contrasting dairy systems in Ireland (with and without white clover), to assess the potential of white clover for reducing GHG emissions.

Materials and Methods
The four parts of LCA methodology were implemented as follows:

Goal and scope
The goal of this study was to assess the potential of white clover for reducing GHG emissions. This paper is based on the comparative experiment at Teagasc Solohead Research Farm for the years 2003-2006 (Humphreys et al., 2009), in which two dairy systems, one based on
permanent grassland and the other on grass/clover pastures, were defined. The two systems were summarised in Table 1.

The system boundary was defined at the dairy unit on farm (Fig. 1). For resources coming from outside of the farm, e.g. concentrate feed, fertilizers, only their production and transportation were included in the inventory. Infrastructure was not included as it was assumed to be the same in the two systems. Based on average market price during 2000 and 2006, economic allocation between milk and meat (average 91% and 9%) was used to divert some burden to the co-product meat.

The functional unit (FU) was defined as 1 kg energy corrected milk (ECM) (Sjaunja et al., 1990).

\[
\text{kg ECM} = \text{kg milk} \times (0.25 + 0.122 \times \text{Fat\%} + 0.077 \times \text{Protein\%})
\]

Life Cycle inventory

Only GHG emissions associated with milk production at farm were assessed. Some of the data during the period of experiment (2003-2006) were not available and best guess was applied. Some of the emission factors were summarized in Table 2.

Life cycle Impact assessment

The mid-point method, “IPCC 2007GWP 100a” in Simapro method library was used to assess the environmental impact per FU, which defined that the Global Warming Potential (GWP) of CO2 (with a time span of 100 years) as 1, of CH4 as 25, and of N2O as 298 (PRé, 2007). The total emissions of GHG were determined as follows:

\[
\text{GHG effect} = \sum \text{GWP}_i \times m_i
\]

Where \(m_i\) is the mass (in kg) of the emitted gas (Heijungs, Guinee Å et al. 1992). The total impact was expressed as kg CO2 eq (equivalents) per FU.

Interpretation

Comparison between the two systems was made by the emissions per FU.

Results and Discussion

The emissions per FU and the contributions of the three GHGs are shown in Fig. 2. The WC system has 13.3% overall lower GHG emissions per FU than the FG system. In agreement with
literatures (Cederberg and Mattsson 2000), methane was the main contributor to the GHG emissions per FU, and clover in WC has little impact on that. However, the most significant reduction in GHG/FU was resulted from the reduced nitrous oxide in the WC system (32.5% lower).

The contribution of the main processes were shown in Figure 3. Enteric fermentation dominated the life cycle of milk production up to the farm gate, which contributed (44.7% and 51.6% in FG and WC systems). The second largest contributor was the manure management, which has no significant change between the two systems. Fertilizer process (including the production, transportation and spreading of fertilizer on farm) was the largest contributor to the difference of the two systems, which is 67.4% lower in WC system. That reflects the major differences between the two systems: the amount of fertilizers used in FG was 208.8kg/ha, while in WC was 76.2 kg/ha.

Direct comparison (GHG per FU) with literatures is difficult with different characterization factors and impact categories are used. For example, Casey and Holden (2005a) adopted that GWP of CO₂ (with a time span of 100 years) is 1, of CH₄ is 21, and of N₂O is 310, and so does Ciderberg and Matteson (Cederberg and Mattsson 2000). However, in the IPCC 2007 GPW 100a method, not only are the characterization indicator defined differently (1, 25, and 298), but also other emissions are included, such as ‘carbon dioxide, fossil’, ‘methane, biogenic’. A critical analysis of approach is required.

In this paper the two systems have 13.3% difference in total emissions per kg ECM, which is considerably lower than the 22% indicated by Schils et al (2005). This is probably a result of small difference between the management of the two systems. However, it is also because Schils et al (2005) took into carbon sequestration into account, which brought negative emissions of 0.47 and 0.41 kg CO₂ eq per FU in grass/fertilizer and grass/clover system, respectively.

One of the concerns with white clover is that the emissions associated with it may not be necessarily lower, since the recycling of N from grazed herbage to the soil via the grazing cows was the main cause of lower N-use efficiency (Humphreys, O’Connell et al. 2008), and there is potential risk that when the fixed N becomes available to grass, it is also exposed to leaching to the ground water, which may result in eutrophication. Meanwhile, if the clover content in the grassland is considerably higher, there is a risk of N₂O and NH₃ volatilization (Schils, Verhagen et al. 2005). However, early stage of experiment in Solohead implied that there were no significant difference in N₂O or NH₃ emissions between grass/fertilizer and grass/clover pasture, and leached N was also low (McNamara 2008).

In this paper IPCC Tier 1 was used for calculating the GHG emissions from manure management and crop residue, which may not be an appropriate procedure. More site-specific EFs and full testing of assumptions are needed for further evaluation of the WC and FG comparisons.
Conclusions
The result shows that compared with the FG system, emission of fertilizer use in the WC system was reduced by 67.4% and the overall emission from producing 1 kg ECM from WC was thus reduced by 13.3%.

Acknowledgements
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References


AN EVALUATION OF ANAEROBIC DIGESTION AS A WASTEWATER TREATMENT METHOD

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Bioresource Research Centre, Biosystems Engineering, UCD School of Agriculture, Food Science and Veterinary Medicine, University College Dublin, Belfield, Dublin 4

Abstract

Under the EU Directive on urban wastewater treatment, wastewater quantities above 2,000 PE (population equivalent) must be treated. Wastewater must reach a discharge standard of 125mg O₂ l⁻¹. Anaerobic Digestion (AD) is seen as a cost effective wastewater treatment method due to the production of biogas fuel. However, the quality improvement of wastewater after the AD process is questionable. This project will evaluate effluent quality before and after the anaerobic digestion process.

Introduction

It was reported by the Environmental Protection Agency (EPA) in July 2009 that wastewater from more than half of the country’s sewage treatment plants failed to reach EU quality standards in 2006 and 2007. New wastewater discharge licensing was introduced in 2007. Under this licence local authorities that do not comply with the required standards could receive fines between 5,000 and 500,000 euro. Furthermore, under the EU Directive on urban wastewater treatment, wastewater above 2,000 PE (population equivalent) must be treated. As a result wastewater must reach a discharge standard of 125mg O₂ l⁻¹. The urban wastewater treatment directive deals with wastewater from industrial and urban areas.

There are a number of wastewater treatment methods. These methods include aerobic treatment such as lagoons and Anaerobic Digestion (AD). AD has the advantage of producing biogas in the form of methane which can be used as a fuel. As a result AD is seen as a cost saving method. The other advantages to the AD method in comparison to aerobic treatment include less land required, reduced sludge volume and the avoidance of odours (Olthof and Oleskiewicz 1982; Deepak and Polprasert 1998).

Even though anaerobic digestion has distinct advantages in wastewater treatment, there are still concerns over the effluent quality. AD can achieve up to 98% Chemical Oxygen Demand (COD) removal. However, the remaining COD maybe still too high to discharge into water bodies (Barker, 1999).

The main objective of this project is to evaluate the anaerobic digestion technique on the quality improvement of wastewater.

Materials and Methods

To evaluate the water quality from AD treatment, samples will be analysed before and after the AD process.

Testing parameters

Table 1 shows the parameters that will be used to evaluate the wastewater. The methods used are taken from the Association of Official Analytical Chemists (AOAC), American Water Work Association (AWWA) and the Water Environment Federation (WEF). The HACH methods used are based on the standard methods from these organisations.
Table 1: Testing parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Biological Oxygen Demand (BOD)</td>
<td>Traditional 5 day</td>
</tr>
<tr>
<td>Chemical Oxygen Demand (COD)</td>
<td>HACH</td>
</tr>
<tr>
<td>Total Organic Carbon (TOC)</td>
<td>Carbon Analyser</td>
</tr>
<tr>
<td>Total Organic Matter (TOM)</td>
<td>Carbon Analyser</td>
</tr>
<tr>
<td>pH</td>
<td>pH probe recorder</td>
</tr>
<tr>
<td>Volatile Fatty Acids (VFA)</td>
<td>HACH</td>
</tr>
<tr>
<td>Calcium</td>
<td>HACH</td>
</tr>
<tr>
<td>Phosphate</td>
<td>HACH</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>HACH</td>
</tr>
<tr>
<td>Heat flow</td>
<td>Differential Scanning Calorimetry</td>
</tr>
</tbody>
</table>

**AD location**
The samples for this project will be collected from two anaerobic digesters. The first AD is located at Carbery Milk Products in Ballineen, Co. Cork. This AD consists of two Internal Circulation (IC) reactors. Spent wash, post whey with protein and lactose removed is anaerobically digested at Carbery. The second AD is located at Osberstown wastewater treatment plant, Naas. The Osberstown AD is mesophilic and it consists of two tanks with a capacity of 1,317m³ each.

**Collection of samples**
The samples will be collected using a composite sampler over a 24 hour period. A composite sample is more representative of the entire effluent compared to grab samples. The samples will be tested once a week for an eight week period. The collection of the effluent samples from the anaerobic digester will be delayed by the retention time of the influent. This will result in influent and effluent samples being collected from the same batch of wastewater. As the samples will be tested in UCD, they need to be transported in a cool environment. A cooler box will be used to keep the samples below 4°C.

**Analysis**
The Organic Loading Rate (OLR), Hydraulic Retention Time (HRT), anaerobic digester performance and biogas produced will be taken into consideration for this study. These parameters have a major influence on the effluent quality. Biogas production can be calculated using the following formula.

\[
\text{Biomass} = \text{Inflow} \times \left( \frac{\text{COD in feed}}{1000} \right) \times \text{Reactor efficiency} \times 0.42
\]

Mean and standard deviation will be calculated to compare the results. A comparison will then be made between the results of the two anaerobic digesters.

**Results and Discussion**
As the experiments have not yet been carried out, no definitive results have been obtained. The following studies are representatives of expected results when reviewing current literature:
Olthof and Oleskiewicz (1982) carried out an evaluation of the anaerobic digestion for treating sunflower flour wastewater.

The anaerobic digester was a Mesophilic (35°C) fluidized-bed reactor. The composition of the wastewater was 4.7 for pH, 10.6g/l for total COD and 10.2g/l for soluble chemical oxygen demand. This experiment showed AD can achieve a COD removal in the range of 80 - 98.3% efficiency. The best residual COD achieved was 390mg/l COD total and 200mg/l COD soluble. These results were achieved with a Hydraulic Retention Time (HRT) of 20 days and an Organic Loading Rate (OLR) of 0.64 g COD/l day.

In an experiment carried out by Deepak and Polprasert (1998), a number of wastewaters from AD were tested for COD removal. Table 2 summarises these results. As can be seen, COD removal ranged from 52% to 90% depending on OLR, HRT and wastewater material.

As part of the research carried out by Deng et al. (2005), COD removal of swine wastewater was investigated using an Internal Circulation (IC) anaerobic reactor. The IC reactor could remove about 80% of COD with Organic loading rate of 6-7kg COD/ (m³/day).

Yue Lin et al. (1998) studied the pollution removal of septage and landfill leachate using anaerobic digestion. COD was removed by 86%, ammonia nitrogen by 69%, total phosphorus by 86%, Volatile solids by 28%, carbohydrate by 82% and protein by 80%. The AD used for this experiment was mesophilic with organic loading at 0.315kg COD/m³/day, solids retention time (SRT) at 20 days.

Past research indicates that COD removal can be expected to be in the range of 50 – 98%. This parameter is dependent on OLR, HRT and the performance of the anaerobic digester. The outcome is unclear for the other parameters. There seems to be a lack of study carried out on spent wash and urban wastewater in the other parameters being tested in this project.

In the case of Thailand, there are twelve distilleries that have their own full-scale anaerobic treatment plant (volume = 3000m³). In each distillery an estimated amount of about 15,000kg COD/d has been eliminated by anaerobic treatment. An estimated amount of over 1.2 million m³ of methane gas is produced per year in Thailand. This gas can replace around 0.75 million litres of fuel oil in the factory operation per year (Deepak and Polprasert 1998).

<table>
<thead>
<tr>
<th>Wastewater</th>
<th>COD Range (g/L)</th>
<th>OLR (kgCOD/m³.d)</th>
<th>HRT (days)</th>
<th>COD removal (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slaughter-house</td>
<td>0.2-0.8</td>
<td>1.0</td>
<td>0.40</td>
<td>52</td>
</tr>
<tr>
<td>Pineapple canning</td>
<td>3.0-8.0</td>
<td>9.0</td>
<td>0.9</td>
<td>90</td>
</tr>
<tr>
<td>Polyester</td>
<td>15-30</td>
<td>4.5</td>
<td>6.0</td>
<td>88</td>
</tr>
<tr>
<td>Distillery</td>
<td>55-70</td>
<td>7.0</td>
<td>8.0</td>
<td>52</td>
</tr>
</tbody>
</table>

Table 2: COD removal using AD for industrial waste (Deepak and Polprasert 1998)
Conclusions

Apart from Chemical Oxygen Demand (COD) there seems to be a lack of past research into the parameters being tested in this project. Perhaps this is due to AD effluent generally being post-treated aerobically in order to return the water to nature (Moletta 2005). The EPA is more concerned about the final effects on the environment.

Anaerobic digestion can play a major role in wastewater treatment as well as in the renewable energy sector. Thailand’s implementation of anaerobic digestion shows that high levels of COD removal can be achieved while reducing a dependency on fossil fuels.

This project will evaluate the anaerobic digesters performance in treating wastewater effluent within the context of the EU urban wastewater treatment directive. This will be achieved by using Carbery group as an example for an agri-food company and Osberstown wastewater treatment plant as an urban wastewater supply,

Acknowledgements

The authors would like to gratefully acknowledge Carbery Group and Osberstown wastewater treatment plant for allowing me to take samples from their anaerobic digesters.

References


EU Directive 91/271 (Urban wastewater treatment)


Utilising Scooter-type Motorcycles as a Mobile Mechanical Power Source in South-East Asia: Feasibility Analysis

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Abstract
An experimental heat transfer model for small-scale spark-ignition engines was applied to a Honda Wave NF100 to predict heat flux from the flowing combustion gases to the internal cylinder walls at steady-state conditions. This model represents the first step in the process of determining required volume of coolant required to safely and efficiently operate this engine in a stationary position, where ambient air flow is negligible. The model presented in this paper provides a reasonable approximation of coolant requirements over the engines operational range and will form the basis for further heat transfer calculations required for the specification and design of the cooling system.

Introduction
This study aims to investigate the potential utilisation of scooter-type motorcycles in improving the availability of agricultural mechanisation technology to rural populations in South East Asia. The first stage of this theoretical analysis is to quantify the coolant load requirements of an air-cooled motorcycle during stationary steady-state operation. This is a critical stage in the design process as the heat rejection from the internal combustion reaction to the adjacent heat transfer surfaces must be known to adequately size the cooling system. The cooling system needs to be designed to ensure critical surface areas are kept well below design limits to ensure safe and efficient operation. This report aims to determine the feasibility of the stationary operation of these motorcycles to generate useful mechanical work through an innovative power transmission system. This system will later be assessed in a small-scale irrigation context by utilising the mechanical power output to drive a small centrifugal pump.

Materials and Methods
The motorcycle chosen for study in this report is the Honda Wave NF100. The Honda Wave is an affordable, entry-level four-stroke scooter-type motorcycle common to South-East Asia, the chosen study area. Table 1 details the specifications of the motorcycle chosen for study in this report.

Table 1: Honda Wave NF100 Specifications
(Motor, 2010)

<table>
<thead>
<tr>
<th>Honda Wave NF100</th>
</tr>
</thead>
<tbody>
<tr>
<td>Engine type</td>
</tr>
<tr>
<td>Displacement [cm³]</td>
</tr>
<tr>
<td>Bore, B [cm]</td>
</tr>
<tr>
<td>Stroke, S [cm]</td>
</tr>
<tr>
<td>Compression ratio, r.cp</td>
</tr>
<tr>
<td>Head geometry</td>
</tr>
</tbody>
</table>

This data was supplemented with dynamometer test results on the same motorcycle, conducted at standard atmospheric conditions (300 K, 100 kPa) in Phnom Penh, Cambodia in October 2009 by a third party contributor. The results of this test are displayed below in Table 2.

Table 2: Wave NF100 dynamometer test results

<table>
<thead>
<tr>
<th>Speed [rpm]</th>
<th>3100</th>
<th>3900</th>
<th>4300</th>
<th>4900</th>
<th>5800</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fuel inflow [g/min]</td>
<td>4.8</td>
<td>8.1</td>
<td>15.7</td>
<td>16.2</td>
<td>18.6</td>
</tr>
<tr>
<td>Brake power [kW]</td>
<td>0.8</td>
<td>1.8</td>
<td>3.6</td>
<td>3.6</td>
<td>4.2</td>
</tr>
<tr>
<td>Brake torque [Nm]</td>
<td>9.0</td>
<td>19.2</td>
<td>31.8</td>
<td>25.9</td>
<td>23.8</td>
</tr>
</tbody>
</table>

In order to estimate the coolant load that of an air-cooled spark-ignition engine, a heat transfer model is required to predict the heat flux from the combustion reaction to the internal cylinder walls. Most previous investigations into the heat transfer of spark-ignition engines have been conducted on large displacement, multi-cylinder models which can exhibit heat transfer characteristics vastly different to smaller displacement models. Recently (Wu et al., 2006) developed a model of heat transfer by convection from the flowing gases within the piston cylinder of a small-scale engine. This model was based on a single 125 cc spark-ignition engine (Suzuki AN125) and was later
found to be inaccurate for others (Wu et al., 2009). A later study by the same author developed a second model for predicting the heat transfer rate for different engines using a modified Stanton number on the basis of experimental investigations with two engines. This later model was then used to predict heat flux, global heat transfer, heat release rate and cylinder pressure. When comparing the predicted results of this new model with collected experimental data it was found that the proposed model fits the real engine operational characteristics with a greater degree of accuracy over most operational conditions (Wu et al., 2009). It is suggested by the authors that this model can be applied widely to investigations involving small-scale engines and was hence chosen as the basis for the heat transfer analysis of the engine of the Honda Wave NF100.

Modelling Methodology

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**Air-Standard Otto Cycle Calculations**

The operational limits of the chosen engine were modelled as an air-standard Otto cycle. To simplify calculations a number of assumptions were made to make computations more manageable. The gas mixture was treated as air, with ideal gas properties, for the entire operational cycle. For the first half of the operational cycle this is a reasonable assumption as the cylinder gas is predominately air, with only 7% fuel vapour (Heywood, 1988). During the second half of the cycle, following combustion, using the approximated air values were found to produce only minimal error (Heywood, 1988). A closed operating cycle was assumed in which exhaust gases are returned to the intake system. The combustion process is simplified as an instantaneous heat addition stage at constant volume.

1: Intake The intake stroke introduces air at atmospheric pressure into the piston cylinder. This is a reasonable approximation as the inlet process of a real engine is found to be slightly less than atmospheric pressure due to pressure losses in the intake manifold (Heywood, 1988). The temperature of the gas mixture during the intake stroke increases it flows though a hot intake manifold, the temperature in hence assumed to be 333 K. The ideal gas constant for air used in calculations is 0.287 [kJ/kg.K]. The cylinder dimensions and gas mixture mass were calculated from the following expressions:

\[
\begin{align*}
T_2 &= \frac{M \cdot Q \cdot T_1}{M \cdot C_p} \\
Q &= \frac{C_p}{C_m} \left( \frac{T_2}{T_1} \right)^{\gamma - 1}
\end{align*}
\]

2: Isentropic Compression With the exception of the limits of this stroke this is generally accepted as a good approximation of real engine compression (Heywood, 1988). In a real engine the limits of this stroke are affected by the intake valve timing at the beginning of the stroke and the firing of the spark plug at the conclusion of the stroke. The specific heat ratio, k is assumed constant throughout the engine cycle and is approximated at 1.4. The temperature and pressure following isentropic compression were calculated to be:

\[
T_3 = T_2 \left( \frac{V_2}{V_1} \right)^{\gamma - 1} \\
P_3 = P_2 \left( \frac{V_2}{V_1} \right)^{\gamma}
\]

3: Constant Volume Combustion The compression stroke is followed by an instantaneous constant-volume heat addition step that approximates the engine combustion process. The timing of the combustion process is influenced by the design of the engine and the engine speed but is assumed in this analysis it is assumed to occur precisely at TDC to simplify analysis. The exhaust residual remaining in the cylinder from the previous cycle is assumed to be four percent and the air-fuel ratio of the gas mixture is set at 15. Combustion results in complete combustion of iso-octane fuel.

\[
T_4 = T_2 + \frac{M \cdot Q \cdot T_1}{M \cdot C_p} \\
T_5 = T_2 + \frac{M \cdot Q \cdot T_1}{M \cdot C_p}
\]

4: Isentropic Expansion The high pressure and enthalpy values of combustion products drive the expansion power stroke of the engine. High pressure forces the piston back towards BDC. This
stroke is approximated as an isentropic expansion process and appears to be a reasonable approximation of a real engines operation. In this Otto analysis the exhaust valve is assumed to open at precisely at BDC with the cylinder pressure instantaneously reaching atmospheric pressure conditions, neglecting the blowdown process. This assumption has little influence on later calculations as the intake and exhaust strokes are assumed to cancel each other thermodynamically in the heat transfer model. Internal temperature and pressure conditions prior to the exhaust valve opening were calculated in the same manner as the compression stroke.

The variation of the cylinder volume, \( V_{cyl}(\theta) \) and pressure, \( P_{cyl}(\theta) \) can then be calculated for the entire cycle with respect to the engine crank angle with the following expressions. The instantaneous pressure increase due to combustion was approximated by substituting previously calculated value at the point of combustion. The constant \( R \) in this case can be approximated as half the stroke length.

\[
V_{cyl}(\theta) = V_{ci} + \frac{V_{ci}}{2} \left[ 1 + R \cos \theta - (R^2 - \sin^2 \theta)^{1/2} \right]
\]

\[
P_{cyl}(\theta) = P_{cyl}(0) \left( \frac{V(\theta) - V(0)}{V(\theta)} \right)^{k}
\]

**Heat Flux Calculations**

An approximate relationship between the engine operational cycle and resultant heat flux (\( q_{cyl} \)) of the flowing cylinder gas to the combustion chamber walls is dominated by forced convection governed by the following equation:

\[
\frac{\partial T_{sp}}{\partial t} = h (T_{sp} - T_{wall})
\]

\( h \) refers to the heat transfer surface and \( h \) is defined as the empirical heat transfer coefficient which is assumed constant for the entire heat transfer surface. The spark plug temperature, \( T_{sp} \) was derived experimentally and expressed by the following empirical expression.

\[
T_{sp} = a_{sp1} \omega_{e} + a_{sp2} \omega_{e}^2 + a_{sp3} P_{man}^2 + a_{sp4} \omega_{e} P_{man}
\]

\( \omega_{e} \) is the mean piston speed and the density of the flowing gases, \( \rho \), is assumed constant and the intake manifold pressure is assumed to be 1 bar. The empirical \( a \)-values are as follows: \( a_{sp1} = -0.4375; \quad a_{sp2} = -0.0128; \quad a_{sp3} = 23.987; \quad a_{sp4} = -0.0266; \quad a_{sp5} = 0.1408; \) and \( a_{sp6} = 111.754 \) (Wu et al., 2009). The temperature of the flowing cylinder gases, \( T_{sp} \) can be calculated with the ideal gas state equation.

\[
T_{sp} = \frac{R_{g} V_{cyl}(\theta) V_{cyl}(\theta)}{M_{m} \rho}
\]

The mass of the gas mixture within the cylinder, \( M_{m} \) is assumed constant throughout cylinder compression, combustion and expansion, and to vary with respect to volume during intake and exhaust strokes.

The expression for the Stanton number is an improvement on the previous model as it describes the variation of the Stanton number with respect to the engine speed and geometry as a function of the crank angle. This new empirical relationship was proven to be 30.3 percent more accurate prediction than the previous model (Wu et al., 2009). The mean piston speed is a function of engine speed and stroke length.

\[
\omega_{e} = \frac{2 \pi \omega_{e} \text{rev/s}}{60}
\]

The specific heat ratio, \( \gamma \), of the flowing gas and can be obtained from the following empirical relationship. This value is then used along with the gas constant to determine the specific heat at constant pressure as a function of crank angle, \( \theta \).

\[
\gamma(\theta) = 1.338 - 6 \times 10^{-2} T_{sp} + 10^{-5} T_{sp}^2
\]

\[
c_{p}(\theta) = \frac{R}{1 - \frac{1}{\gamma(\theta)}}
\]

The gas turbulent velocity is approximated as half the mean piston speed and the density of the cylinder contents can then be calculated from the ideal gas relationship. From this point the Stanton number, the gas density, specific heat and gas turbulent velocity combine to form an expression for the heat transfer coefficient of the flowing gases.

\[
h(\theta) = S(\theta) c_{p}(\theta) u
\]

To develop a model for the variation in area of the internal heat transfer surface, the placement of the intake and exhaust valves was neglected to give a uniform hemispherical surface available for head transfer from the combustion chamber. The area of the cylinder walls exposed to the combustion chamber walls varies proportionally with the engine displacement.

\[
A(\theta) = \frac{\pi d^2}{2} + \frac{4(V(\theta) - V_{sp})}{B}
\]

These variables are then calculated over the engine operational cycle and inserted into the governing convection equation to give the crank specific heat flux from the flowing gas to the cylinder walls. The heat transfer rate was then integrated over the four-
stroke engine cycle to yield the coolant load as a function of engine speed.

**Results**
The results of the heat flux to the internal cylinder walls are calculations displayed graphically in Figure 3 and Figure 4.

**Figure 3: Brake power and heat load of Honda Wave NF100 over dynamometer test range**

Whilst no sensitivity analysis has been performed on the data produced by this model, the results appear comparable to those published by Wu, Chen et al. and will be used henceforth in further heat transfer analysis computations.

**Conclusions**
As Otto cycle calculations represent combustion under ideal conditions, this model represents a reasonable approximation for the extremes of operation required to quantifying coolant load under stationary, steady-state operation over a range of engine speeds. The results presented in this report will be later used to determine the heat flux through the engine block and the attached cooling fins. This conduction analysis will be used to determine the volumetric flow of ambient air required to cool the engine during stationary operation.

**References**


THE DETERMINATION OF THE GAS YIELDS FROM THE ANAEROBIC CO-DIGESTION OF ANIMAL SLURRIES, GRASS AND MAIZE SILAGE

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Abstract
Three laboratory bench scale anaerobic digestion (AD) systems (along with a unit for bubbling the produced gas through water to remove CO₂) have been constructed and are being used. The wastes being used in the digester have been collected from a farm in Kilkenny. A series of co-digestion tests have been devised and are nearing completion. These tests used a range of different biomass feedstocks; including grass, collected around UCD and maize, collected from the UCD farm in Lyons Estate. The reasoning behind these experiments is to define under what conditions there is optimum biogas production for different substrates.

Introduction

Manure residues from livestock industries have long been identified as a major source of environmental pollution. Traditionally, these wastes have been disposed of, directly or after composting, by land spreading. Since this practice results in degradation of air, soil, and water resources, new regulations for protecting the environment have been enforced to control land application of animal manure (Van Horn et al., 1994). The nitrate-directive, (91/676/EEC) regulates input of nitrate on farmland, aiming to protect ground and surface water environments from nitrate pollution, and includes rules for the use of animal manure and chemical fertilizers.

Implementation of these environmental measures has caused an increase in the cost of manure disposal for livestock farmers and this impairs the profitability of farming. As such, livestock industries and regulatory agencies are seeking alternatives for managing manure residues in an economically feasible and environmentally friendly manner. Studies have shown that anaerobic digestion (AD) of organic wastes has the potential to manage these problems in a cost effective and environmentally sustainable manner (Murphy and Power, 2008).

Anaerobic digestion is basically the break down of wastes through biological activity in the absence of atmospheric oxygen. The main outputs from this process are Methane (CH₄), Carbon Dioxide (CO₂) and the digested feedstock. The methane can be used directly in CHP units or as fuel for transport. The digestate also has many advantages. It is of low odour when compared to initial feedstock, as it comes out as a kind of “liquor” it is a lot easier to manage and doesn’t require agitation before land spreading, the nitrogen in the digestate is more available to the crops than raw slurries (Palm 2008).

Over the past decade, national and EU policy debate has highlighted the need to investigate alternative energy. The biogas produced through AD is a renewable energy source and whether used as a transport fuel or to produce electricity, it displaces fossil fuel energy production (Murphy and Power, 2006). Consequently, there is the potential for an overall reduction in emissions of greenhouse and acidifying gases, both of which Ireland has international commitments to reduce.

The objective of this project is to investigate the effect of the co-digestion of biomass with animal slurries for the optimisation of gas yields.

Materials and Methods
Experiment 1: A bench scale anaerobic digester

This experiment will be built around a 5000ml conical glass flask with an integral side arm, which is the digester (Figure 1). There are three of these digesters, into each one 3,500 ml of cattle slurry and 300ml of water are added. The water is added to make the slurry less viscous and more manageable especially when it comes to putting the digester under anaerobic conditions. Then to one digester 0.1kg of maize silage is added and mixed together, and to another 0.1kg of chopped grass is added and mixed together. The final digester is left without any substrate to act as a control.

In order to create anaerobic conditions for the bacteria to produce methane, the digester is sealed using a rubber bung and all inlet and outlet pipes are blocked using pipe clamps. To create a vacuum a filter pump is used. This device consists of a “t” fitting, one end is attached to a tap and the other end is attached to the integral side arm of the digester. When the tap is turned on a vacuum is created by means of the Venturi effect and hence providing anaerobic conditions in the digester.

The three digesters are then placed into a water bath (Figure 2); this means that the three digesters are kept at constant temperatures throughout the experiment. Experiments are done in the mesophilic temperature range and kept at a constant temperature using a heat pump. Over a 40 day retention time gas production rate and gas composition are measured.

Experiment 2: Gas Composition

In order to analyse the biogas that is produced from above digesters, a gas analysis device called the Draeger X-am 5000 is used, this has the capabilities to measure CH₄ (%lel), CO₂ (%vol), CO (ppm), H₂S (ppm) and O₂ (%vol), which are the main constituents of biogas. Each bag of captured gas is analysed using this device.
Results and Discussion:

To date results have been obtained from the 38°C and 40°C temperature range. From figures 3 and 4 you can see that there is a steady increase in Biogas production over time, this is to be expected and continue until day 60 of

![Figure 3: Biogas production at 40°C](image)

![Figure 4: Biogas production at 38°C](image)

Biogas production when it will start to level out. In Figure 4 around the day 15 mark for the grass and control digester, and day 19 for the maize digesters (maize digester was started 4 days earlier than other two), a drop in biogas production occurred, the reasons for this was that the temperature dropped to room temperature and as you can see biogas production ceased almost instantly. This shows that temperature has a big factor to play in AD.

![Figure 5: Represents total biogas production over 40 days for each substrate](image)

From figure 5 two patterns can be seen. Firstly as expected the digester with maize produced the highest amount of gas at both temperature ranges, followed by grass. Secondly and again as expected the higher temperature also causes an increase in biogas production.

Conclusions

One question that has to be raised is that, is this increase in gas production enough to justify the cost in extra energy demand that is required to heat the digester by 2°C At first glance it would appear not, but after up scaling and gas production is on an industrial level it might become more attractive.

Cattle slurry is readily available and this is why it is used as the main substrate in the digesters above, but as results have shown co-digestion causes an increase in biogas production. So how viable is co-digestion in Ireland? From figure 6 it can be seen that grass covers around 56% of Ireland’s total land area therefore there is good potential to use grass in co-digestion with cattle slurry. While arable crops including maize only cover 0.05% (O’Kiely 2009) of the total land area these might not be as good an option for co-digestion since they only offer a small increase in biogas yield per m³/t.
Acknowledgements

The author wishes to thank the Department of Communications, Marine and Natural resources for providing funding through the Charles Parsons award.

References


Figure 6: Land usage in Ireland (O’Kiely 2009)

Land area = 6.9m.ha
Agriculture
Pasture, hay & silage = 3.4m.ha
Rough grazing = 0.5m. ha


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THE RELATIONSHIP BETWEEN FIELD SOIL WATER CONTENT VARIABILITY AND SOIL MOISTURE DEFICIT PREDICTION FROM METEOROLOGICAL DATA

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Abstract

The Hybrid Soil Moisture Deficit (SMD) model (Schulte et al., 2005) was designed to predict soil moisture conditions as a function of water balance for agro-climatic regions in Ireland. It is assumed to work between the field scale (1,000 m²) and the regional scale (100 km²) and is being developed to predict runoff at the field scale. However soil physical properties that affect the water balance vary significantly at field scale. This study provides preliminary evidence of how a point estimation of SMD can be used as a predictor of a field water balance. Point SMD predictions calculated from meteorological data measured on farm were compared with continuous time series point volumetric water content (θp) and periodic observations of variation in field volumetric water content (θf) both measured by time domain reflectometry. The θp and θf trends were relatively similar.

Introduction

The Hybrid Soil Moisture Deficit (SMD) model (Schulte et al., 2005) was designed to predict soil moisture conditions as a function of water balance for agro-climatic regions in Ireland. It is a point model because it uses input data from a specific meteorological observation location; however it has always been tacitly assumed that it predicts water balance over an unspecified spatial extent thought of as a “field”. Additionally, the model is effectively dimensionless with no defined support (i.e. defined length, width and depth over which it functions). It was not designed to predict soil water contents, rather to predict when the soil was at a state of wetness, expressed relative to field capacity, with units of mm rainfall deviation from field capacity. Furthermore, the model has potential as the basis of farm decision support tools because it requires little data to run (soil classified into one of three classes, rainfall, wind speed, temperature and solar radiation), yet during development gave reliable predictions of relative soil water status for a range of grassland fields.

The SMD model is being developed as the core of a demonstration sustainable nutrient management decision support system. As part of its testing and development, it is necessary to understand more about the spatial scale over which the model applies, and how point predictions relate to field scale spatial variability on the farm. As it was not designed as a physical model, soil variations are captured via 3 operational drainage classes: well, moderate and poorly drained. Although a field is assigned to a class, two drainage classes may occur in the same field, so it is imperative to ensure that each area of a field is allocated to the correct class. Although the weather is a main factor affecting nutrient transport from the field to watercourses, the soil physical properties can also have a large impact on leaching and runoff events.

The objective of this work was to evaluate the relationship between Time Domain Reflectometry (TDR) estimates of soil volumetric water content (θp) at a fixed
location associated with the farm weather stations, spatial variability of water content in the field, and point prediction of SMD from on the farm weather stations.

Materials and methods

Sites
Ten sites representative of the three grassland soil drainage classes were selected to evaluate the SMD model and the larger decision support system as a whole. They were selected based on geographical distribution (north to south climate gradient) and the range of drainage classes they encompassed. For this paper, examples from two sites are presented representing poor and well-drained soil classes.

Soil moisture deficit calculation
Meteorological stations were installed at each site therefore weather data from synoptic stations, interpolation or Numerical Weather Prediction (NWP) were not required. Daily SMD was calculated from weather data using maximum and minimum temperature (°C), rainfall (mm), wind speed at 10m (m s⁻¹) and radiation (J cm⁻²) on a daily basis. The SMD model also requires spatial co-ordinates (latitude and longitude) and previous SMD state (the model is initialised in mid-winter to ensure wet soil conditions). In the past it has been found that the SMD model relates best to a 15 cm tensiometer, which represents rooting zone in a grassland soil.

Volumetric water content (θ)
In order to evaluate SMD predictions, the point soil volumetric water content (θₚ) was measured by a time domain reflectometer (TDR) at fixed locations relative to the weather station. Four continuously logged TDR probes were inserted into the wall of two pits. Each pit has one probe inserted at 10 cm and another one at 20 cm and at least 24 cm apart.

The spatial variation in soil water content (θₛ) was assessed on specific days by handheld TDR. Waveguides 12 cm long were used to measure the volumetric water content across the soil surface. Variation in θₛ was then compared to θₚ and maps were created to visualise how representative the fixed TDR was of the sites being used to test the DSS.

Handheld and fixed time domain reflectometers were calibrated by collecting volumetric water content samples for laboratory analysis. Soil samples (3 x 13.7 cm² at 10 cm and 20 cm depths) were taken on a monthly basis during visits to each site. These samples were dried at 65°C until the dry mass was constant and the volumetric water content was calculated as the mass of water per unit volume soil sampled.

Results

Although the volumetric water content, θₛ, has not been determined for the soil surface, the soil surface θₛ and the TDR θₚ at 10 cm depth have the same trends but slightly different absolute values (Figure 1). It can be expected that the soil surface will have a more rapid change in θ_than at 10 cm depth: on the well-drained soil, the soil surface is drier or wetter than at 10 cm depth on respectively drier or wetter periods of the year; on the poorly-drained soil, the soil surface usually remained wetter than at 10 cm depth but the θ_range was much greater at the soil surface than at 10 cm.

At a given location, SMD prediction was related to volumetric water content measurement, θ (fixed TDR or handheld TDR). On average, at a given point, the linear regression of θₚ and SMD was significant if SMD data were grouped into classes of 5 mm (Figure 2). This means that small differences in SMD were smoothed out. The linear regression of mean of θₛ and SMD was also significant (Figure 2). However, the standard deviation was much larger for the well-drained soil than for poorly-drained soil, perhaps due to
differences in soil depth or topography at the sites.

Figure 1. The volumetric water content over 13 months on a poorly-drained soil (a) and a well-drained soil (b) in Ireland. Fixed TDR time series are measured on a daily basis (-) while field observations with standard deviation of spatial variation (●) are made on a monthly basis.

Even though the SMD model is effectively dimensionless, SMD predictions were good estimates of the soil wetness. As well as comparing $\theta$ versus SMD, the spatial variation of $\theta$ was also considered. These data showed that soil moisture variations at the field scale were small (figure 1 and 2, standard deviations). However the application of the SMD model to some areas should be considered carefully. While it is recognised that these example fields do not capture all variability that might be found on grassland farms, these preliminary data do indicate that the SMD model should be able to correctly capture trends in soil water balance, thus permitting a forecast of when gravity moveable water, i.e. runoff, will occur in a field based on soil wetness.

Figure 2. Comparison of soil moisture deficit (mm) predictions with soil volumetric water content (cm$^3$/H$_2$O/cm$^3$soil) measurements (by fixed TDR (dashed line) and by handheld TDR(solid line) on a poorly-drained soil (a) and a well-drained soil (b)

Conclusions

It was found that the trend in $\theta$ was similar for the point observation and the mean of the field observations over time. This means that the point field observation is characteristic of the field it represents, but that absolute value does not necessarily reflect all that might be happening in the field.

SMD and $\theta$ were significantly related. While SMD is not a prediction of $\theta$ it is necessary that it reflects the trend in $\theta$ correctly in order to give confidence to the use of SMD to predict when a condition of gravity moveable water exists in a field.

Small changes in SMD are probably not that meaningful at the field scale. SMD classes
of 5 mm were required to clearly see trends between SMD and \( \theta \).

The relationship between SMD and \( \theta \) was different at the surface as a spatial average (as measured around the field) when compared at a given location in the field. This reflects the fact that the SMD model is a mixing bucket model that works over a non-defined depth. The trends indicate that the SMD model should work at the farm scale.

Acknowledgements

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References

Abstract

It is apparent that Miscanthus will play a vital role throughout Ireland and Europe as an alternative to fossil fuels in years to come. However, little is known about the drying habits of Miscanthus prior to harvesting, therefore it is necessary to establish the correct time of year and method of harvesting in order to achieve optimal biomass fuel quality. Different possibilities exist with respect to harvesting techniques, for example one option is to cut the crop and leave it on the ground prior to collection while direct cut/collection in one pass is the alternative option. Early indications from this study suggest an increase in moisture content in the crop that has been cut and left in the field when compared to that which is left standing and sampled directly (control).

Introduction

Over the last number of years Miscanthus has generated a lot of interest and gained a strong reputation as being an environmentally friendly substitute for rapidly depleting fossil fuels. Miscanthus is a perennial grass that produces cane-like stems and is likely to be suitable for combustion in mixed feedstock boilers (Nixon and Bullard, 2003). In terms of Miscanthus harvesting there are a number of areas that need to be addressed as Miscanthus is such a new crop. Harvesting of Miscanthus typically takes place in February/March/April (Lewandowski et al., 2000). This is when the moisture content of the crop is at its lowest after leaf senescence has taken place over the course of the winter. There are a number of issues that need to be addressed however in relation to harvest window and harvesting techniques. Finding the optimum time to harvest the crop is essential in order to achieve maximum yield of high quality biomass (Lewandowski and Heinz, 2003). Coupled with this, finding a cost effective method of harvesting is also key to ensure maximum biomass is being collected from the field. The main factor that determines harvest window is crop moisture content. This is very much dependent on weather. There are a number of options available to the grower with regards to harvesting. These include cutting the crop and placing the biomass material in a swath prior to collection, direct cutting and chipping of the crop or direct cutting and baling of the crop. Each of these techniques have their advantages, and moisture content, quality of biomass and amounts of biomass losses that occur can vary significantly depending on the system employed (Huisman, 2003). This study hopes to establish the optimum time to harvest the crop in order to achieve maximum crop yield potential as well as optimum biomass quality with respect to harvest time and harvest technique.

The objective of this study is to determine the optimum time and method to harvest Miscanthus in order to achieve maximum biomass quality and highest possible biomass yield.

Materials and Methods

The following experiments were conducted in the Teagasc Crops Research Centre, Oak Park.

Experiment 1

Moisture movement within the plant

This experiment was set out to gain an understanding of how the moisture content varies within the Miscanthus cane over the
course of the winter through to harvesting. It was carried out by taking samples of the crop from the Miscanthus stand and measuring the moisture content in the top, middle and bottom of the cane. A sample of ten canes was taken from the Miscanthus stand on a weekly basis. The leaves were removed and the canes were then divided into top, middle and bottom sections. The samples were then weighed, oven dried and re-weighed in order to determine the moisture content of three plant sections. The results from this trial were then plotted on a graph so a direct comparison could be drawn between the moisture contents of the top, middle and bottom sections of the cane.

**Experiment 2**

**Optimum harvest window and technique**

This experiment was carried out to establish the optimum time to harvest Miscanthus throughout the months January, February and March. It incorporates harvest times with a number of harvest treatments. The plot is divided into four blocks, each representing one replicate. Each block is then divided into three treatments, and each treatment is then subdivided into four sub-treatments. The three treatments used in this trial are cut in January, February, and March. The four sub-treatments are then applied which are:

1) Leave cut biomass material flat on the ground
2) Leave cut biomass material in a swath on the ground
3) Cut and place material on nets to determine dry matter loss (year 2 only).
4) Leave biomass uncut in the field (control).

A plot of the Miscanthus, measuring 56m x 15m is divided into four equal blocks, each measuring 14m x 15m (replicates). Each block is then divided into four strips measuring 3.5m x 15m (treatments) and each strip is subdivided into three sub-blocks measuring 5m x 3.5m (sub-treatments). A 1.25m strip of material is then cut and removed from the stand and placed on the clearance so that the standing crop doesn’t create a factor of error by sheltering the biomass material. In year 2 of the experiment, the material from sub-block 3 in each strip is removed to the clearance, placed in swaths on nets and weighed on a weekly basis to determine the dry matter loss that occurred to the material over the course of the experiment, using the moisture content of the material in the cut and swath treatment as a reference for the moisture content of the material on the nets.

**Results and Discussion**

**Experiment 1**

This experiment was carried out in year one of the research project and is currently being repeated in year two. When this experiment for year 1 began in October 2008, the moisture content of the plant samples varied between 71% for the top, 63% for the middle and 65% for the bottom as can be seen from the graph below (Figure 1). The general trend for the moisture content in the plant sections was to drop consistently over the course of the trial. It can be seen from the graph however that the moisture content of the top portion of the cane fluctuated considerably more than the middle and the bottom portions. It is thought this occurred due to the fact that the top section was more exposed to rain and weather conditions while the middle and bottom were not as severely affected by precipitation. However, as time progressed, the amount of fluctuation occurring in the middle section of the plant increased to a level similar to that of the top section of the plant. It is also worth noting the way in which the middle follows the same drying pattern as the bottom until approximately mid-February, at which point the moisture content of the middle began to follow a similar moisture trend to that of the top section, varying from week to week, increasing and decreasing in moisture content. It can be seen from the figure below that from the 12th February the moisture content has dropped 13-18% depending on the section of the plant in question. By April 16th moisture contents in the top middle and bottom have fallen to 29%, 30% and 41% respectively. This trial is currently being repeated in year two of the research project (2009/2010), however, recording of moisture content began at the earlier date of August 27th 2009 in order to establish when moisture loss occurs within the plant.
Experiment 2
This experiment is being carried out to establish the optimum time to harvest Miscanthus throughout the course of the spring, while also establishing if leaving the crop on the field post-mowing leads to an increase in moisture loss from the crop, or in turn results in a reduction in the quality of the biomass material as a fuel. Figure 2 below illustrates the difference in moisture contents that have occur to date. From the graph it can be seen that all three sub-treatments started off at a similar moisture content, however as time progressed, the moisture content of the control dropped slowly, reaching its lowest value of 37% by April 3rd. It can also be observed how the material cut in January and left in the field both flat and in a swath has suffered a week on week increase in moisture content once harvested until week five but reached a low of 18% by April 3rd, while crop cut in March experienced a reduction in moisture similar to that of the January treatment, but in a much shorter space of time (43% down to 17% in just 2 weeks.)

Figure 1: Crop drying data recorded from October 9th 2008 through to May 2009

Figure 2: Moisture Content data for Experiment 2
Conclusions

Experiment 1
By carrying out this experiment it is evident that the moisture trend in the top of the plant differs to that of the middle and bottom, which are quite similar to each other early in spring, however as the crop continues to wither the moisture trend in the middle of the cane tends to follow that of the top, while the bottom section tends to have a higher moisture content than that of the top and middle sections.

Experiment 2
From the results presented in Figure 2 it can be seen that cutting the crop in January and placing in a swath or flat in the field with a view to increasing the rate of moisture loss can result in an increase in moisture content when compared to that of the crop that remains standing in the field. However, cutting the crop and allowing it to wilt later in the spring, (February and March) leads to a decrease in moisture content assuming weather conditions are favourable. Therefore, it can be deduced from the first year results of this study that if early harvest (January) is desirable then cutting the crop directly is more beneficial than cutting the crop and leaving it in the field the material to wilt. However, if the material is cut and allowed to dry in the field prior to collection at a later date (February or March) then a definite reduction in moisture can be achieved when compared to the standing crop assuming weather conditions are favourable.

Further Work
The results obtained in year one and year two of experiments one and two will be analysed and compared once both trials have reached their conclusions in late spring. The moisture trend of the crop for experiments one and two for both years will also be compared to weather data obtained for the corresponding periods to determine which weather factors are most influential on crop moisture content and drying rates. Chemical and energy analysis will also be carried out on biomass material from the different treatment to determine whether harvest time/method has an effect on the quality of the biomass as a fuel.

Acknowledgements
The authors wish to gratefully acknowledge the financial support provided by Teagasc under the Walsh Fellowship Programme for this project.

References


Abstract
Organic matter is one of four constituents of soil, and plays a significant role in determining the agricultural productivity of soil. Removing agricultural products reduces the content of organic matter in soil; organic matter must therefore be replenished to maintain soil productivity. The application of organic residues has been used for decades to restore the nutrients lost through agricultural production. The EU Landfill Directive has imposed restrictions on the amount of organic waste that can be sent to landfill, thus application of organic wastes to the land has become an area of interest as an alternative means of handling biodegradable waste with the benefit of returning nutrients to the soil.

The restrictions imposed by the Landfill Directive combined with recent pressure relating to minimum organic matter thresholds for tillage soils have inspired an investigation into the efficacy of the addition of autochthonous organic material to enhance productivity of agricultural soils. Organic residues are reported to improve physical, chemical, and biological attributes of the soil, potentially increasing soil productivity. A trial has been conducted to evaluate the success of the incorporation of crop residues to an agricultural loam soil.

Introduction
The EU Landfill Directive (1999/31/EEC) has imposed strict limits on the amount of organic waste that can be sent to landfill in European Union member states (Roche, 2006), and alternative means of waste handling are encouraged such as land-spreading biodegradable waste. The application of allochthonous organic residues is beneficial for agricultural soils, as organic matter has a significant effect on soil fertility (Tan, 2000). Organic matter influences all aspects of the soil environment - physical, chemical, and biological (Doran and Parkin, 1994). Physically, organic matter affects soil structure particularly bulk density and porosity, as well as water holding capacity and water infiltration rate (Sylvia et al., 1999). Chemically, organic matter influences the cation exchange capacity and the capacity for buffering pH changes in soil, while biologically, organic matter is responsible for the supply of nutrients and energy for soil flora and fauna (Sylvia et al., 1999). It is therefore a combination of organic matter’s influence on physical, chemical, and biological characteristics that determines a soil’s productivity (Doran and Parkin, 1994).

The incorporation of crop residues into soil reduces surface water evaporation and increases water infiltration, as well as increasing the organic matter content of soil (Baldock and Nelson, 2000). In light of recent thresholds set by the Department of Agriculture, Fisheries and Food (DAFF) with regard to minimum levels of organic matter in tillage soils (Mooney, 2009) the physical and chemical impact of incorporating crop residues into a loam soil were observed on a small scale, as this is one method suggested by DAFF to remediate below-par levels of soil organic matter (Mooney, 2009).

The objective of this research is to determine the effect of incorporating chopped straw into soil with particular emphasis on improving soil productivity through enhanced physical and chemical conditioning.

Materials and Methods
Soil tests
Purpose-built soil boxes (0.6m x 0.6m x 0.45m) were used to investigate the effect
of incorporating barley straw into loam soil. Chopped straw was incorporated by hand into the top 75mm of the soil profile to replicate the presence and position of organic residues in min-till systems.

Straw was incorporated into the boxes at rates of 3 t ha\(^{-1}\) and 10 t ha\(^{-1}\) (Figure 1) to determine whether the addition of straw induced a significant change in the soil environment, with each condition replicated three times. A control condition was also used for comparison against no straw incorporated, inferring a condition of total residue removal. Half of the boxes were elevated to 20º to determine if slope induced a significant effect when combined with the presence of straw.

Weekly measurements of initial infiltration rate, bulk density, pH, nitrate-N, phosphorus, and potassium contents, and organic matter concentration were taken to determine the effect of the addition of organic residues to the soil environment. Infiltration rate was measured with an infiltrometer modified for use at this scale using the falling head technique (Gregory \textit{et al}., 2005). Nitrate-N, phosphorus, and potassium contents were determined colourimetrically using test kits purchased from LaMotte (Maryland, USA), and organic matter content was determined using the Walkley-Black method (Nelson and Sommers, 1982).

![Figure 1: Purpose-built soil boxes (0.6m x 0.6m x 0.45m) with 2 levels of straw incorporation: 3t ha\(^{-1}\) (left) and 10t ha\(^{-1}\) (right)](image1)

**Figure 1:** Purpose-built soil boxes (0.6m x 0.6m x 0.45m) with 2 levels of straw incorporation: 3t ha\(^{-1}\) (left) and 10t ha\(^{-1}\) (right)

**Figure 2:** Initial infiltration rate for the duration of the trial (February to May) for soil boxes held at an incline of 0º

**Statistical analysis**

Results were analysed using the Scheirer-Ray-Hare extension of the Kruskal-Wallis test (Sokal and Rohlf, 1995) using SPSS 15.0 (SPSS Inc., 2006).

**Results and Discussion**

There was no significant effect on the initial infiltration rate (Figures 2 and 3) or bulk density of the soil as a result of the additional straw. This is an unexpected result as Arnold \textit{et al}. (1990) report a time frame of 0.1 year required to observe a change in these properties. Similarly there was no significant effect recorded as a result of the addition of residues on the pH, phosphorus or potassium content, or organic matter concentration. It is anticipated that insufficient time could be a factor here, as Arnold \textit{et al}. (1990) report a time requirement of up to 1 year for a significant change in these properties.

![Figure 3: Initial infiltration rate for the duration of the trial (February to May) for soil boxes held at an incline of 20º](image2)

**Figure 3:** Initial infiltration rate for the duration of the trial (February to May) for soil boxes held at an incline of 20º
Nitrate-N content was the only soil attribute significantly affected by the incorporation of straw (p<0.05), however there was no distinction between the different levels of straw incorporated (Figures 4 and 5). The nitrate-N content of the soil was significantly lower when straw was present than where straw was absent. It is anticipated this is a result of cellulose degradation altering the C:N ratio of the soil environment. This result is in keeping with the time frame outlined by Arnold et al. (1990).

Conclusions
The addition of organic crop residues to a loam soil did not induce a significant change in the initial infiltration rate, despite this being reported by other authors. The only measured soil property significantly affected by the presence of organic crop residues was the nitrate-N concentration, which was lower in the presence of straw. There was no significant difference between the two levels of straw, however.

Further work
Because the results of this trial did not replicate trends reported in the literature, a subsequent investigation into the effect of incorporating biodegradable organic waste in addition to straw will be performed. This trial will investigate the benefits of organic waste diverted from landfill on the soil environment as a potential inducer of straw degradation. This trial is currently undergoing set-up.

Acknowledgements
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References


PREDICTION OF SOIL TRAFFIC DAMAGE USING SMD MODEL

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Abstract
One of the most important physical factors that determine the trafficability of the soil is the water regime. It describes the integral changes of water content in the unsaturated zone during certain periods. Soil moisture conditions are commonly quantified by the soil moisture deficit (SMD). SMD is the amount of water expressed in mm of effective rainfall required to bring the soil water content back to the field capacity, where field capacity means that macropores are air filled and all other pores are water filled (i.e. the water content to which a soil will drain due to gravity). There is a good relationship between volumetric water content and SMD over the range SMD = 0 to SMD = 20. Therefore the hybrid SMD model developed by Teagasc and Met Éireann will be used in this experiment to find the best SMD value as good indicator of soil trafficability and the SMD threshold to determine safe spreading conditions in terms of damage.

Introduction
This study proposing to investigate the level of damage caused by mechanization practices associated with different level of soil moisture deficit (SMD). The balance of the effective rainfall relative to the soil storage capacity will be the key to understand if a damaging condition is going to occur on a trafficked field at a particular forecast SMD. Taking into account that the genesis of the Irish soil cannot be captured within a restrict number of sites, the whole experiment will be run in a single field (Johnstown Castle) on three drainage classes (Well drained, Moderately drained and Poorly drained). The homogeneity of the soil enabled the study focusing on the wetting and drying cycle and it will be given that at a certain SMD the Irish soil behaves the same way across all the soil types in the country. The aim of this experiment is to find the SMD value that is a good indicator of the threshold of soil trafficability for slurry spreading in terms of potential soil damage during the field operations.

Materials and Methods
Shulte et al. (2005) developed a hybrid SMD model. The hybrid SMD model is simple by necessity because it works on a national scale by categories of soil. Shulte at al. (2005) developed a hybrid SMD model. The hybrid SMD model is simple by necessity because it works on a national scale by categories of soil. Given a standard meteorological condition, a field is subjected to Precipitation (pptn) and Evaporation (Ep). The difference between these two events determines Net rain (mm). When Net rain is negative, soil is defined as drying. Otherwise if net rain is positive, soil will be wetting. The amount of soil water present in a field is calculated as Soil Moisture Deficit (SMD). It is defined as the amount of water that must be added to soil to restore it to field capacity. Field capacity (FC) is the amount of soil water held in soil after excess water has drained away by gravity and downward movement has stopped, which usually takes place within 2–3 days after rain or irrigation in soils of uniform structure and texture. The Hybrid model for soil moisture deficits is not a physical process model. The spatial variations are captured within the differences in drainage regimes (fig.1) associated with different soil types. Therefore, the Irish soil was divided into three distinct soil drainage classes: well-drained soils, which never exceed field capacity; moderately drained soils, can exceed field capacity and have free moveable water able to drain away in 24 hours bringing the land to field capacity;
poorly drained soils which need more than 24 hours to return to field capacity.

**Figure 1.** Indicative drainage map of Ireland based on the drainage capacity of the dominant mineral type of each soil association (Schulte et al., 2005).

The SMD model is a water mass balance model with a daily time step, calculating SMD from the cumulative balance of precipitation, evaporation and drainage:

\[
SMD_t = SMD_{t-1} - \text{Rain}_t + \text{ET}_t + \text{Drain}_t
\]

Where \( SMD_t \) and \( SMD_{t-1} \) are the moisture deficits (SMD) on day \( t \) and \( t-1 \), respectively (mm). \( \text{Rain} \) is the daily precipitation (mm/day), an input variable of the model, \( \text{ET} \) the daily actual evapotranspiration (mm/day), and \( \text{Drain} \) equals the amount of water drained daily (mm/day) by percolation and/or overland flow.

The approach to this research will start from these concepts going forward in to develop the following points:

Field trials to evaluate the suitability and reliability of soil water deficit as an indicator of soil trafficability

An experiment investigating the level of damage caused by mechanization practices associated with different levels of soil moisture deficit (SMD 0, 5, 10, 15) has been set up on three drainage classes (Well drained, Moderately drained, Poorly drained) in Johnstown Castle.

There are four randomised blocks per soils type and the factors are: soil type, SMD on wetting cycle and SMD on drying cycle (fig.2).

Trafficability will be tested on different SMD values.

Soil moisture deficit (SMD) will be calculated using met data collected daily and entered into the SMD model (Schulte et al., 2005)

When the desired SMD is predicted, treatment application and soil measurements will be undertaken with one traffic event for plot (at the start of the experiment). The recovery of the soil from the traffic damage (if any) will be calculated by grass yield penalty in 30 days and by soil measurements at 30 days and 60.

Every plot will measure 4 metres width by 5 meters length. At each site, for each forecast SMD when wetting or drying, a traffic event will be run through a tractor carrying a full tanker after grass has been cut, and subsequently soil measurements will be undertaken.

**Figure 2.** Diagram of a randomised plot layout design with assigned SMD on wetting and drying cycle for the well drained soil type.

The cone penetration resistance, shear strength and bulk density before and after trafficking will be measured (Smith., 1997). The balance of the effective rainfall relative to the soil storage capacity will be the key to understand if a damaging condition is going to occur on a trafficked field at a particular forecast SMD. Therefore the SMD model will be used in this experiment to find the SMD value that is a good indicator of the threshold of soil trafficability for slurry spreading in terms of potential soil damage during the field operations.
**Results and Discussion**

For each plot, the grass will be cut prior to treatment application. The grass will be moulded by lawnmower to a height of 5 cm. In order to quantify a relative yield penalty associated with the wheel traffic, both the wheel track and an untrafficked strip (the centre) of the plot will be cut again 30 days (+/- 5 days) after the treatment application. The herbage removed will be used to calculate the Yield penalty observed in the wheel track, relative to the yield observed in the untrafficked area. The yield penalty will provide an idea of trafficking in terms of percentage of the field that gets field traffic. It will be a real output for farmers in terms of the risk effect of trafficking.

**Conclusions**

The effectiveness of the SMD model has already been shown on Irish. The success of the method used in this experiment is highly connected with the strong interaction between the model, the soil measurements and the soil type.

**References**


BIOMASS AND LIPID ANALYSIS OF 12 MICROALGAL STRAINS GROWN IN THE QUINN PILOT SCALE PHOTO-BIOREACTOR

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\textsuperscript{2}Quinn Glass Limited, Derrylin, County Fermanagh, Northern Ireland.

Abstract

Microalgae have been previously investigated as a fuel source due to their high photosynthetic efficiency and their ability to produce lipids as a biodiesel feedstock. One of the key research tasks for commercialisation of algae for energy purposes is to screen species for favourable composition and for ease of cultivation and processing. However one of the biggest challenges in producing microalgae in temperate regions is the lack of sufficient natural light for much of the year. One way to overcome this is the use of artificial light in closed production systems i.e. photobioreactors (PBRs). Lipid content is not the only potentially useful energy resource in microalgae.

Introduction

Global warming resulting from widespread CO\textsubscript{2} emissions due to human activities has become of growing concern as an environmental issue. Among the various strategies for mitigating CO\textsubscript{2}, the biological sequestration of CO\textsubscript{2} using photosynthetic microalgae has been receiving considerable attention, as microalgae have a higher CO\textsubscript{2} fixation ability and produce biodiesel and bioproducts through their biomass (Yoo et al., 2010). The biggest unknown in Ireland or other similar climates is whether it is possible to achieve reasonable productivity in view of prevailing natural light and temperatures. Nutrients and carbon are other key requirements for microalgal growth. For carbon, exhaust gas from power plants which contain significant quantities of low-cost CO\textsubscript{2} can be used (SEI, 2009). The two most common systems for producing microalgae are open ponds and closed photobioreactors. Photobioreactors are preferred over open pond systems mainly due to the control of potential contamination and the higher cell mass productivities attained. The cost of closed systems is higher than open pond systems (Brennan & Owende 2009). The successful mitigation of CO\textsubscript{2} and production of biodiesel using microalgae requires that microalgae are sorted according to their growth rate, lipid content, and tolerance of high levels of CO\textsubscript{2} (Yoo et al., 2010). The energy conversion reaction of biomass can be classified into biochemical, thermochemical and direct combustion (Amin, 2009). Algal slurry is 5-15% dry solid content after harvesting. Dry lipids are necessary for esterification and removal of water is expensive (Brennan & Owende 2009).

The aim of this work is to extract and analyse each microalgae strain available to find the resulting oil yield and potential as a biodiesel.

Materials and Methods

Microalgae Strains and Medium

Twelve microalgae strains obtained from two sources: 1) Six strains obtained from the Culture Collection of Algae and Protozoa, Centre for Coastal and Marine Sciences,
Dunstaffnage Marine Laboratory, Oban, Argyll, UK.

Table 1 Experimental strains

<table>
<thead>
<tr>
<th>Microalgae Species</th>
<th>Code</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isochrysis galbana</td>
<td>CCAP 927/1</td>
</tr>
<tr>
<td>Isochrysis sp.</td>
<td>CCAP 927/14</td>
</tr>
<tr>
<td>Nannochloropsis oculata</td>
<td>CCAP 849/1</td>
</tr>
<tr>
<td>Nannochloropsis sp.</td>
<td>CCAP 211/46</td>
</tr>
<tr>
<td>Pavlova lutheri</td>
<td>CCAP 931/1</td>
</tr>
<tr>
<td>Skeletonema costatum</td>
<td>CCAP 1077/5</td>
</tr>
</tbody>
</table>

2) Quinn Glass provided six strains of microalgae which they used to grow in their pilot-scale photobioreactor. The strains supplied by Quinn Glass Limited and the components of the culture medium are not available yet.

Photobioreactor Description
Design and specifications for the photobioreactor and harvesting process for this study are not available yet.

Biomass Measurement & Total Lipids
Yoo et al, (2010) determined the dry weight of the algal cells. The cells were measured by filtering an aliquot of the culture suspension through pre weighted GF/C filters (Whatman, England). After rinsing with distilled water, the filters were dried at 105°C for 1h, and reweighted. The total lipids were extracted from microalgal biomass using a modified method of Bligh & Dyer (1959). The lipids were extracted with chloroform-methanol (2:1, v/v), and then separated into chloroform and aqueous methanol layers by the addition of methanol and water to give a final solvent ratio of chloroform:methanol:water of 1:1:0.9. The chlorolayer was washed with 20ml of a 5% NaCl solution, and evaporated to dryness. Thereafter the total lipids were measured gravimetrically.

Biochemical Conversion
(Transesterification)
Figure 1 (Amin, 2009) shows the schematic process of biodiesel production. The first step is removing water content from the oil by increasing its temperature to 120°C for about 5-10 mins. Next it is allowed to cool and by using a catalyst tank with mixed sodium hydroxide and methanol and stirring, sodium methoxide is produced. Meanwhile, clean oil is heated to 60°C for 5 mins, mixed with the sodium methanol and the mixture transferred to ultrasonic or mixer equipment. This equipment agitates the solution for 30 mins. After the mixing process, the solution is allowed to cool and separate. The separation process takes approximately 15-60 mins. The methyl ester or biodiesel would float on the top layer, while the denser glycerine would be in the bottom layer. In the last step, the biodiesel is washed, dried and then quality tested.

Results and Discussion

Algae Growth
The six marine strains were described by the supplier Culture Collection of Algae and Protozoa. They are easy to maintain, of suitable size and they almost all contain significant amounts of the highly unsaturated fatty acids EPA 20:5 (n-3) [eicosapentanoic acid] or DHA 22:6(n-3) [docosahexaenoic acid].

Expected Results
It is difficult to give expected results as the specifications of the photobioreactor for this study are not available yet. However, Yoo et al., (2010) cultivated Botryococcus braunii, Chlorella vulgaris and Scenedesmus sp. with 10% CO₂ to
mitigate the CO₂ and produce biodiesel. The maximum biomass of *Scenedesmus* sp. was the highest at 3.13 g L⁻¹ on day 14, while its biomass productivity was 217.50±11.24 mg dw L⁻¹ d⁻¹. The total lipid content of *B. braunii* was 2-4 times higher than that for the other two strains. From these results it is suggested that *Scenedesmus* sp. is more appropriate to mitigate CO₂ due to its high biomass productivity and C-fixation ability. *B. braunii* is more suitable for production of biodiesel due to its high lipid content and proportion of oleic acid. The results from (Yoo et al, 2010) could yield similar results in this project going forward. Also the real flue gas (5.5% CO₂) experiments carried out in this same study are noted.

**Energy Production**

The result of the transesterification process is biodiesel. Transesterification is a process of exchanging the alkoxy group of an ester compound by another alcohol. It is the reaction of a fat or oil with an alcohol to form esters and glycerol. The alcohol combines with the triglycerides to form esters and glycerol. The results of the biodiesel product should be quite similar to those of conventional diesel in its main characteristics or compatible with conventional petroleum diesel and it can also be blended in any portion with petroleum diesel. Amin (2009) also compared the biodiesel from microalgal oil quality to the diesel fuel and the ASTM biodiesel standard shown in Table 3. The existing European Standard for Biodiesel (EN 14214) is compared also. The viscosity (mm²s⁻¹ cSt at 40°C) must be noted (>5.0) as it is high for microalgae biodiesel, this may become a problem for this biodiesel to meet standards.

### Lipid Content

In a study by (Mata et al, 2010) they found the lipid content (% dry weight biomass) of some of the species available from the Culture Collection of Algae and Protozoa. As shown in Table 2, the oil content of these marine microalgae range between 7 and 53% but higher productivities can be reached in other species.

<table>
<thead>
<tr>
<th>Marine microalgae species</th>
<th>Lipid content (% dry weight biomass)</th>
<th>Lipid productivity (mg/L/day)</th>
<th>Volumetric productivity of biomass (g/L/day)</th>
<th>Areal productivity of biomass (g/m²/day)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isochrysis galbana</td>
<td>7.0-40.0</td>
<td>-</td>
<td>0.32-1.60</td>
<td>-</td>
</tr>
<tr>
<td>Isochrysis sp.</td>
<td>7.1-33</td>
<td>37.8</td>
<td>0.08-0.17</td>
<td>-</td>
</tr>
<tr>
<td>Nannochloropsis oculata</td>
<td>22.7-29.7</td>
<td>84.0-142.0</td>
<td>0.37-0.48</td>
<td>-</td>
</tr>
<tr>
<td>Nannochloropsis sp.</td>
<td>12.0-53.0</td>
<td>37.6-90.0</td>
<td>0.17-1.43</td>
<td>1.9-5.3</td>
</tr>
<tr>
<td>Pavlova lutheri</td>
<td>35.5</td>
<td>40.2</td>
<td>0.14</td>
<td>-</td>
</tr>
<tr>
<td>Skeletonema costatum</td>
<td>13.5-51.3</td>
<td>17.4</td>
<td>0.08</td>
<td>-</td>
</tr>
</tbody>
</table>

### Table 3 Comparison of properties of biodiesel, diesel fuel, ASTM standard (Amin, 2009) and EU Biodiesel Standard [BASF].

<table>
<thead>
<tr>
<th>Properties</th>
<th>Biodiesel from microalgae oil</th>
<th>Diesel fuel</th>
<th>ASTM D 6751 Biodiesel Standard.</th>
<th>EN 14214 EU Biodiesel Std.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (kg L⁻¹)</td>
<td>0.86</td>
<td>0.838</td>
<td>0.86-0.90</td>
<td>0.86-0.90</td>
</tr>
<tr>
<td>Viscosity (mm²s⁻¹ cSt at 40°C)</td>
<td>5.2</td>
<td>1.9-4.1</td>
<td>3.5-5.0</td>
<td>3.5-5</td>
</tr>
<tr>
<td>Flash point (°C)</td>
<td>115</td>
<td>75</td>
<td>Min 100</td>
<td>120</td>
</tr>
<tr>
<td>Solidifying point (°C)</td>
<td>-12</td>
<td>-50 to 10</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Cold filter plugging point(°C)</td>
<td>-11</td>
<td>-3.0 (max -6.7)</td>
<td>Summer Max 0, Winter max &lt;15</td>
<td>-</td>
</tr>
<tr>
<td>Acid value (mg KOH g⁻¹)</td>
<td>0.374</td>
<td>Max 0.5</td>
<td>Max 0.5</td>
<td>Max 0.50</td>
</tr>
<tr>
<td>Heating value (MJ kg⁻¹)</td>
<td>41</td>
<td>40-45</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>H/C ratio</td>
<td>1.81</td>
<td>1.81</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
**Conclusions**

Microalgal biodiesel is the only renewable biodiesel that has the potential to completely displace liquid transport fuels derived from petroleum. Algal biomass needed for production of large quantities of biodiesel could be grown in photobioreactors, but a rigorous assessment of the economics of production is necessary to establish competitiveness with petroleum-derived fuels. Achieving the capacity to inexpensively produce biodiesel from microalgae is of strategic significance to an environmentally sustainable society. As the lipid content is not the only potentially useful energy resource in microalgae further work could include the anaerobic digestion of the algal biomass for energy conversion. Previous studies found that it is feasible to use salt adapted microorganisms for the anaerobic digestion of marine algal biomass. The physico-chemical pretreatment, codigestion or control of gross composition are strategies that were also suggested which can efficiently increase the conversion yield of algal organic matter into methane. When the lipid content does not exceed 40%, anaerobic digestion of the whole biomass appears to be the optimal strategy on an energy balance basis, for the energetic recovery of cell biomass. This study provides new motivations to more accurately identify the optimal growth conditions for microalgae species in photobioreactors and to achieve maximum biodiesel productivity and CO₂ fixation from an energetic and environmental point of view.

**References**


CASE STUDY COMPARISON ON ANAEROBIC DIGESTION AND THERMAL GASIFICATION FOR A CHOSEN SITE

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Abstract
The European economy is currently in a sharp downturn. Competitiveness, sustainability and security of supply can aid the recovery of this fallen economy. A comparison of biomass to energy technologies (Anaerobic Digestion and Thermal Gasification) was carried out in terms of the process, types of systems and limitations they hold. The purpose of this comparison is to evaluate the potential to use a CHP plant for heat and electricity for the chosen site. A further study will carry out an economical comparison of capital and operating costs of both technologies and energy balances of both processes with a known number of feedstocks. Thermal gasification is the process where biomass is gasified using partial oxidation, which creates a mixture of gases called syngas which can then be used in a CHP plant. Anaerobic Digestion is the microbial decomposition of organic matter without the presence of oxygen. A biogas with high levels of methane is created which can also be used to fuel a CHP plant.

Introduction
The European economy is at an all-time low. The Green Paper 2006 focuses on competitiveness, sustainability and security of supply (Green Paper, 2006). This will aid long-term strength and stability in the European economy. Regulation (EC) No 663/2009 addresses that for the European Economic Recovery Plan to become effective it must supply financial benefits not only to support the economic crisis but to community projects in the energy field. The gas and electricity sector has been highlighted. During recent times, the gas and electricity infrastructure has been in extremely vulnerable situations such as the gas crisis (2006 & 2009) (Regulation (EC) No 663/2009). Regulation (EC) No 663/2009 suggests that by investing in these infrastructures now, it will ensure security of supply at competitive prices when the economy overturns and energy demand at a global scale increases. Primary energy consumption has been increasing steadily for the last 10 years. In 2008, Ireland alone consumed 0.1% of the world’s primary energy (BP, 2009). This has unveiled the increasingly important need for security of supply. In minimising our dependency on oil we can contribute to sustainability on a global scale. Anaerobic Digestion and Thermal Gasification of biomass both offer an alternative to conventional systems that will address competitiveness, sustainability and security of supply.

The objective of this paper is to review Anaerobic Digestion and Thermal Gasification technologies focusing on an economical analysis, and to compare the feasibility of using these technologies on a chosen site that has a heat and power demand.

Materials and Methods

Literature Review

A review of the literature will be carried out to investigate the technologies and regulations that currently exist for Anaerobic Digestion and Thermal Gasification. Previous case studies will be assessed both in Ireland and Europe to determine the feasibility of both technologies focusing on an economical comparison.

Results and Discussion
Technologies
Biogasification can occur not only by anaerobic digestion but also by a process called thermal gasification. The process of thermal gasification of biomass through partial oxidation forms a gaseous mixture of syngas which is made up of hydrogen, carbon monoxide, methane and carbon monoxide (Wang et al., 2008). The oxidants that may be used are air, O2, CO2 and steam. The operating costs and the heating value of the oxidants in the reaction determine which oxidant is more efficient. There are three main types of gasifiers: fixed-bed, moving bed and fluidised bed. Fixed bed and moving bed produce large quantities of tar/char due to the low, non-uniform heat and mass transfer between the solid biomass and gasifying agent but are economical on a small scale and can gasify wet biomass. Fluidised bed can achieve a high heating rate, uniform heat and mass transfer which in turn results in high productivity. The main limitations related to thermal gasification are (1) Ash related problems, due to erosion, corrosion and deposition during syngas utilisation. Alkali’s such as potassium react with silica, which form a deposit on the reactors walls. A build up of this leads to sintering and de-fluidisation on the bed surface. (2) Char and Tar build-up, relating to a reduction in syngas yield. This can be minimised by choosing the optimal design and operating parameters of a gasifier. Catalysts can be used in a reaction to reform tar, which is converted into gas. High quality syngas (with minimum tar) can be directly fed into a gas-turbine or fuel cell for combined heat and power (Wang et al., 2008).

Anaerobic Digestion is the decomposition of organic matter into more volatile components by micro-organisms without the presence of oxygen (Ward et al., 2008). There are typically four stages: Hydrolysis, Acidification, Acetogenesis and Methanogenesis which is where methane is produced. The biogas produced contains <65% methane, <41% CO2, <17% nitrogen, <1% oxygen and traces of other gases. Considerations to design of an anaerobic digester are to allow a high organic load rate, short hydraulic retention time, and to produce maximum volume of methane. There are also three main types of reactors: batch-reactors, one-stage continuously fed systems and multi-stage continuously fed systems. Multi-stage systems are more expensive than single stage reactors but are more stable because of the sensitive methanogenic bacteria being buffered by the first stage. The multi-stage reactor has also shown to produce a higher yield of methane (Ward et al., 2008). The main limitations associated with anaerobic digestion are the costs. A case-study on an on-farm AD, showed costs of €17,428 per year over a period of 10 years depending on grants and indexation (Hesslop, 2009).

Case studies of AD

**BIOGEN Twinwoods AD plant, UK**
BIOGEN uses liquid manure and food chain wastes as its feedstock, therefore it is a means of disposing waste, while obtaining gate fees. The digestate from the AD process allows them to sell 30,000 tonnes/annum of biofertiliser for nearby farms. The reactor generates 1.6MWh/annum of thermal energy and electric energy generated is 10,300MWh and 5% of the electrical power consumption is used by the plant itself (SEI, 2010a).

**Gehrung, Germany**
Biogas plant Gehrung, is an on-farm AD started operation in 2006 with investment costs of €500,000. The feedstock used are maize, silage, food wastes from the farm itself and the local area. The digester is manufactured by Weltec Biopwer GmbH and has capacity of 800m³ There is an on-site fermenter for pasteurisation of food wastes and final storage space. Thermal energy generated is 788,400kWh/a and the electric energy is 650,000kWh/a. The plant utilises most of the thermal energy on site, and 30,000kWh/a of the electric energy is used on site, the rest is exported to the grid (SEI, 2010a).

**Saaz, Austria**
The Saaz biogas plant is 500kWel NAWARO which is an energy crop
process with a CHP plant. The plant produces 5000 m³ of gas/day. Investment costs were in the region of 1.5 million euro. The plant generates thermal energy of 4,897,000 kWh/year and electric energy of 4,197,000 kWh/year. The plant uses 12% of the electric energy for itself. The rest is sold to the grid and digestate is spread over 300 ha of land (SEI, 2010b).

Conclusion

Anaerobic digestion/thermal gasification linked with CHP plant offer many economical and environmental benefits such as reduced energy costs and a greater security of energy supply. A lot of research has been done on AD but further case studies will be assessed on thermal gasification technologies.

Future Work

1. To carry out an economical analysis of capital and operational costs of AD and TG
2. To choose a site of known location to carry out the case study
3. To assess energy balances of both processes with known number of feedstock.
4. To conclude which biomass to energy conversion technology are more economically viable.

References


AN ASSESSMENT OF THE FEASIBILITY OF CO-COMBUSTING BIOMASS WITH COAL AT MONEYPONT POWERSTATION

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Abstract
One of the main contributors of global warming is the combustion of fossil fuels. In recent figures published by SEI, about 93.6% of Ireland’s electrical energy in 2008 was generated from the burning of such fuels. Ireland is currently at the mercy of producing nations, and is trying to establish its own indigenous supply and also to comply with its Kyoto protocol requirements. One of the main proposed solutions to assist this is the use of biomass. The results of this study will produce an in depth analysis into the current reserves of biomass available to Moneypoint Powerstation and the economic and logistical issues which would arise. Various combustion technology solutions will also be explored.

Introduction
Moneypoint is Ireland’s second largest Powerstation with an overall output of 915MW and is Ireland’s only coal fired plant. It is located in the coastal town of Kilrush in south/west county Clare. Coal accounts for approximately 20.4% of electricity generation in Ireland (SEI, 2009). The plant consumes approximately 2 million tonnes of coal each year delivered by three 305MW steam generating boiler plants. (Station, 2009). The Irish government considered converting Moneypoint to natural gas but decided against this, as it would lead to an over reliance on thus for Ireland’s electricity generation. Instead it opted to update Moneypoint’s emissions abatement equipment via the MERP (Moneypoint environmental retrofit project) at a cost of €368million (ESB, 2010). This will enable the Powerstation to continue into the future complying with EU LCPD 2001/81/EC (Large combustion plant directive) with regard to Nitrous and Sulphurous oxides. The energy generation sector alone accounts for over 21.8% of Ireland’s GHG emissions (EPA, 2009) and with the predominance of fossil fuels, there is great potential for Ireland to find more sustainable methods for producing its electricity. The German-Irish Chamber of Industry and Commerce has calculated, “the potential at the current technical level of the whole range of renewable energy sources to be more than 728,000 GWh per annum. That is more than four times the current total Irish energy requirement (175,000 GWh per annum)”. (Reinhard, 2009). Such renewable solutions include wind, hydro, biomass and solar.

Biomass offers a realistic way for Ireland to lower its CO₂ emissions by displacement with carbon neutral biomass and create an indigenous source of raw material to aid indigenous energy production, especially with the volatile nature of Oil and Gas cost and supply. Ireland is currently falling short of its Kyoto commitments by approximately 4.40 Mt CO₂eq, bearing in mind this includes afforestation targets and EU Emissions Trading Scheme of 20.38 Mt CO₂eq per annum (EPA, 2009), biomass co-combustion could help bridge this gap.

The aim of this research is to establish the most technically suitable co-combustion solution and
biomass supply chain within a feasible proximity to Moneypoint Powerstation.

Materials and Methods

Biomass selection
Biomass can be defined as all the earth’s living matter; materials such as wood, plant and animal wastes, which unlike fossil fuels, were living matter until relatively recently. This study will deal with woody biomass only as these are currently the most abundant in Ireland and a mix of other biomasses would lead to a number of combustion issues, due to their varying chemical composition.

Combustion Method Selection
As there are a range of combustion alternatives available for co firing, there will be a number of different combustion technology solutions examined. Their various merits will be evaluated in order to establish the most technically feasible selection for the proposed biomass raw materials. Such woody materials will include waste wood e.g. from sawmill, forest residues e.g. thinnings, demolition wood reclaimed from recycling facilities etc. and finally from woody based energy crops: predominantly SRC Willow.

Logistics
This study will examine the biomass resources in the vicinity of Moneypoint Powerstation. These will include forests, sawmills, Energy crop plantations and finally waste recovery facilities. The infrastructural constraints will be investigated, to appraise how economically feasible it will be to transport the feedstock from extraction locations to the Powerstation site. When considering transporting each biomass, such variables as bulk density, calorific value and ash content will need to be taken into consideration. The potential for conversion of local agricultural land will also be assessed. The characteristics of road and rail networks will undoubtedly be of paramount importance when establishing efficient transport links. This will reveal the quantity of biomass in the vicinity of the Powerstation, the characteristics of local infrastructure, the economic viability of transporting each feedstock and establishing the potential for increasing biomass production in the locality.

This study will establish the optimum co-combustion technology solution with various levels of biomass inclusion. Economic estimates, along with existing studies will reveal the extent, if any, of the change in cost of electrical (GJ) production as a result of changing to co-combustion with biomass. The quantity of biomass required for co-combustion will be calculated to establish the demand of the Powerstation for various levels of biomass inclusion. The amount of woody based biomass in the vicinity will then be assessed to determine if a) there is enough in the region, b) if there is a shortfall, how much more needs to be produced and c) if its within an economic and technically feasible transport distance. This will involve calculating the amount of forests, sawmills, timber waste recovery facilities and willow crop production in the western to south/western region and summing their respective outputs. With the use of GIS (Geographical Information System), these aspects can be measured and will be categorised into various distance increments. In the event of there being a deficit of supply in the region, the agricultural land will be assessed for potential of increased biomass production. The rail and road networks will also be explored to find out how conducive
they would be for biomass transportation. A unique aspect of the Powerstation is its location at Moneypoint jetty port, so this could prove a valuable asset for importation from either across the Shannon estuary, from other ports in Ireland or from countries abroad if necessary, but only as a last resort due to increased cost and embodied energy. The storage requirements will be analysed to ascertain the spatial implications of storage of biomass at the site.

Ireland’s Energy Mix 2008

<table>
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<tr>
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<td>Renewables</td>
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</tr>
<tr>
<td>Electricity Imports</td>
<td>1%</td>
</tr>
<tr>
<td>Coal</td>
<td>20%</td>
</tr>
<tr>
<td>Peat</td>
<td>11%</td>
</tr>
<tr>
<td>Natural Gas</td>
<td>55%</td>
</tr>
<tr>
<td>Oil</td>
<td>7%</td>
</tr>
</tbody>
</table>

Fig. 5 Fuel mix for electricity generation (Howley et al. 2009)

**Results and Discussion**

As is clear from fig.1 results published in December 2009, Ireland is clearly over reliant on fossil fuels, thus there is ample need for diversification. The results will yield the most appropriate co-combustion solution with minimum alteration to the existing equipment. The south western region boasts some of the highest quality agricultural land in Ireland including the renowned “Golden Vale” for its green pastures. If a study of the region proves this, then energy crop production will be an option. On the other hand some of county Clare is covered in a Karst landscape, with the ‘Burren’ taking up 360km² of the north of the county (Group, 2000). This will be taken into account as this type of land would be unsuitable for biomass growing. The actual biomass demand of the plant will be quantified at various levels of feedstock inclusion. This is fundamentally important to determine how much biomass needs to be produced in the area and draw comparisons from the two. If there is a large discrepancy between supply and demand, it will be a key factor in the entire study. Should the amount of biomass available fall drastically short of requirements then co-combustion may not be feasible. As biomass and its transport cost is calculated, if it proves much more expensive to co-combust than complete coal combustion in the plant, this will invariably cease the concept of co-firing at Moneypoint Powerstation. The site is located at the south western edge of county Clare bordering the Atlantic Ocean and thus has not a very central location. This will inevitably pose a logistical hindrance as if it were surrounded by land; transportation distances would no doubt be reduced. Thus the transport distances to sawmills, wood producing forests etc. will prove interesting. The use of a software logistical model will help reveal where transport distances become unviable.

**Conclusion**

Biomass can potentially provide an indigenous energy source; however the actual feasibility of putting such a supply chain for this specific application has not yet been addressed. The barriers involved from biomass growth/source to the final stage of combustion must be first overcome to ensure the viability co-combustion. This study will produce an in depth analysis into the overall feasibility of co combusting Moneypoint Powerstation with selected biomass. All the necessary variables have been included such as, transport distances, alterations to plant equipment, cost comparisons between biomass and coal...
including transportation, potential for increase of biomass production in the localised area etc.

References


FAST PYROLYSIS OF WOODY BIOMASS AND POLYOLEFIN WASTE FOR LIQUID TRANSPORT FUEL PRODUCTION

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Abstract
Fast pyrolysis is a conversion technology which can be applied for the production of liquids from plastic wastes and biomass. This paper reports the fast pyrolysis of willow chip, wood pellets and a polyethylene/polypropylene blend in a bench-scale fast pyrolysis reactor. Maximum liquid yields (47 wt %) were achieved from the pyrolysis of wood pellets at 500°C. Application of the biooil as a fuel is limited due to poor fuel properties and upgrading is required. Pyrolysis of the polyolefin blend proved problematic due to clogging of the reactor and was discontinued. Future work will look at resolving the plastic pyrolysis problems and improving liquid yields. The experiment is currently being scaled up on a 1kg/h fluidised bed pyrolysis reactor at the University of Hamburg.

Introduction
Fast pyrolysis of woody biomass and waste polyolefins is a thermochemical conversion technology than can be used for the production of liquid transport fuel.

When carbonaceous feedstocks are subjected to pyrolysis i.e. high temperatures (~500°C) in an oxygen-free environment, they decompose to vapours, aerosols and chars (Bridgwater, 2007; Aguado et al., 2008). When applied to biomass feedstocks, the condensed liquid is called biooil. Depending on the severity of the cracking of polyolefins (e.g. polyethylene) a wax may be generated in addition to the pyrolysis liquids.

Neither pyrolysis oils from polyolefins nor biomass can be directly substituted for diesel or gasoline (Czernik and Bridgwater, 2004). Approaches to upgrade the oil product include catalytic pyrolysis (cracking), hydroprocessing, emulsification and blending (Walendziewski, 2006; Huber et al., 2006; Elliott, 2007; Corma and Huber, 2007).

A research placement at the University of Hamburg has been organised. The work will focus on investigating the feedstock characteristics and reactor operational parameters optimising the liquid yield and its fuel properties on a 1kg/h BFB pyrolysis reactor. Before this work begins, a preliminary study has been undertaken to investigate the influence of pyrolysis temperature on the liquid yield for biomass and polyolefin feedstocks. The results are reported herein.

The objective of this study is to investigate the influence of pyrolysis temperature on the pyrolysis oil yield from woody biomass and waste polyolefins.

Material and Methods

Biomass and polyolefin feedstocks
Two biomass and one polyolefin feedstock were used for this experiment. The biomass feedstocks, namely wood pellets and willow chip were dried at 150°C for 24 hours prior to pyrolysis. Willow chip was reduced to a uniform particle size 2-6mm. The purpose of these pre-treatments is to reduce experimental variability on the system that might be introduced by varying particle size and moisture content.

Bench scale flash pyrolysis reactor
Fast pyrolysis processes are characterised by high heating rates, temperatures of about 500°C and low vapour residence times (1-2s). A bench scale reactor was designed and constructed with this in mind.
(Figure 1). The main feature of the reactor is the quartz pyrolysis tube (500mm long with 50mm internal diameter). There are two zones in the reactor, a purging zone and a pyrolysis zone.

In a typical experiment, the pyrolysis zone is heated to the desired pyrolysis temperature while the oxygen is removed from the sample and the reactor by an inert Nitrogen flow (~250cm³/min). When the temperature has been reached, the basket which holds the sample is introduced to the hot zone. Under a high heating rate the feedstock devolatilises into a smoky vapour and char. The char remains in the sample basket while the volatile products are forced to the condensers by the inert nitrogen flow. The condensers are maintained at -5°C by circulating refrigerated ethylene glycol, and some of the condensable products are collected for analysis. Non-condensed vapours and aerosols exit the apparatus and are removed by an extractor.

For this experiment samples were pyrolysed at 400°C, 450°C and 500°C which is the typical temperature range which maximises liquid production. At the end of each experiment the mass of condensed liquid and char were recorded and some of the liquid products were analysed.

Results and Discussion

General Comments

While the pyrolysis of willow chip and wood pellets proceeded in a relatively stable manner, pyrolysis of the polyethylene/polypropylene blend proved to be much more problematic.

Figure 6 The bench-scale fast pyrolysis reactor used for these experiments.

Upon introduction to the heating zone the sample rapidly decomposed to a bubbling foam, immediately exiting the reactor and condensing in the condenser forming a solid waxy substance which clogged the condenser line. No further experiments were carried out with polyolefins.

Pyrolysis yield structure

Figure 2 shows bio-oil and char yields for pyrolysis of willow chip and wood pellets. Char yields were typical of fast pyrolysis experiments (20-25 wt %). The maximum liquid yield achieved was 47 wt % for wood pellets at 500°C, which is relatively low. For example, a maximum liquid yield of 69 wt % at 440°C by Mauviel et al. (2009) during the pyrolysis of beech wood with a similar experimental apparatus. This is perhaps to a better reactor design and product collection system (which included a cartridge containing adsorbents and cotton wool to trap those vapours
which had not been collected in the condenser). Oil yields from willow were lower than those from the wood pellets. This is most likely due to the development of a blockage in the reactor which may have influenced results.

Characterisation of bio-oils

The resulting bio-oil was a free-flowing dark brown/black liquid with a smoky smell. Characterisation of the bio-oils showed that they had a high water content of about 35 wt %, are quite oxygenated (Oxygen content ~ 40 wt %) and acidic (pH ~ 2). An FTIR spectrum of bio-oils from wood pellets is illustrated in Figure 8. The various stretching and deformation vibrations and absorption peaks of C-H, O-H, C=O and C=C groups indicated the presence of alkanes, single, polycyclic and substituted aromatic groups, carboxylic acids and derivatives, ketones and aldehydes, alcohols and phenols (Sensöz and Can, 2002). The bio-oils were also analysed via GC/MS, though identification of compounds was challenging because of a limited library database and no standard solutions. Nonetheless compounds belonging to chemical families typically found in bio-oils were identified: aldehydes (e.g. furaldehyde), furans (e.g. 3-methyl-Furan), ketones (e.g. 2-hydroxyl-3-methyl-2-Cyclopenten-1-one), phenols (e.g. 2-methyl phenol and 4-methyl-1,2,-benzenediol), aromatics (e.g. 1,2,4-trimethyl-Benzene), and carboxylic acids (e.g. 3-hydroxy-1-Cyclopentencarboxylic acid).

Discussion

Bio-oils contain hundreds of chemical compounds derived from the chemical cracking of the cellulose, hemicellulose and lignin fractions of biomass, and as such resemble more the biomass from which they were derived rather than petroleum products. Bio-oils are combustible but not flammable. The high quantity of water lowers the heating value and causes ignition delay. However it does reduce the viscosity which improves pumping and atomization properties. A major problem with bio-oil is its instability and poor storage characteristics. Over time, organic acids catalyse the polymerisation of hydroxyl, carbonyl and carbonyl group compounds to heavier compounds. This has the effect of increasing the viscosity and water content over time. Furthermore, if the water content of bio-oil exceeds 30-50 wt %, phase separation of the oil will occur into an aqueous phase and a heavier oily phase.

Conclusions

Willow chip, wood pellets and a PE/PP blend were pyrolysed in a bench-scale fast pyrolysis reactor. Pyrolysis of the polyolefin blend was problematic due to violent release of a white foamy substance which, upon condensation, clogged the apparatus. Maximum liquid yields (~ wt 47%) were achieved from the wood pellet feedstock at 500°C. The resulting bio-oils had a high water content (35 wt %), were highly oxygenated (~40 wt %) and quite acidic (pH= 2). Ketones, aldehydes, carboxylic acids, phenols and furans were identified in the bio-oil. The high water
and oxygen contents as well as the presence of highly reactive compounds limit the use of bio-oils as a fuel. Future work will aim to increase the liquid yields from this apparatus by improving the product collection system and overcoming problems with plastic pyrolysis. The experiment is being scaled up to a 1kg/hr laboratory fluidised bed pyrolysis unit at the University of Hamburg (Figure 9) and work is due to begin shortly.

Acknowledgements

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References


Abstract
This project investigates the productivity of eight algae strains for biomass and lipid content in a laboratory air-lift photobioreactor growth medium. An eight column glass photobioreactor with 1 litre per column medium capacity will be constructed and inoculated with eight resilient algae strains and maintained under axenic conditions in batch runs. External illumination will be implemented by three fluorescent light units operating under a 16:8 (light:darkness) cycle and providing 200 µmol m$^{-2}$ s$^{-1}$ exposure on the surface of the columns. Aeration will be effected by enhanced Air-CO$_2$ (2% CO$_2$) mixture bubbled from the bottom of the glass column growth chamber. The results will enable the identification of viable strains for further investigation into their potential for biofuel production.

Introduction
It is widely accepted that the use of fossil fuels as a primary energy resource is unsustainable in respect to depleting resources and progressive environmental degradation arising from the accumulation of greenhouse gases in the atmosphere (Schenk et al., 2008). Renewable, carbon neutral fuels are required to meet energy demands while contributing to the amelioration of climate change. Microalgae appear to be the only capable source of renewable fuels that does not conflict with food production (Chisti, 2007).

Microalgae are unicellular or multicellular microorganisms that can be found in abundance in a diverse range of ecosystems. The simple organisms use sunlight to convert carbon dioxide and nutrients into biomass, which can provide a wide range of feedstock for the production of biofuels such as biodiesel, bioethanol, biogas and biohydrogen (Schenk et al., 2008).

For biofuel extraction, microalgae offer numerous advantages over conventional energy crops, including: (1) Higher photosynthetic efficiency therefore higher yield; (2) Higher oil contents that are non-toxic and biodegradable; (3) Nearly all year round continuous harvesting potential; (4) Carbon negative fuel production when combined with CO$_2$ sequestration and biochar incorporation into soil; (5) Can be grown on marginal or waste ground; (6) Can utilise salt and brackish waters, thereby reducing the load on freshwater sources, and; (7) Can be used for treatment of organic effluents and bioremediation (Rodolfi et al., 2008).

However, there are limitations to microalgae production, harvesting and extraction of biofuel, including potential utilisation for CO$_2$ capture.

Criteria that are critical to the successful establishment of biofuel production from microalgae include high biomass productivity, high lipid contents, robust organisms and production of valuable co-products (Brennan and Owende, 2010).

This paper outlines the experimental setup to be used to determine optimal photoautrophic growth conditions for eight identified algae strains.
Materials and Methods

**Organisms and growth materials:** Eight marine algae strains have been identified (Table 1) and starter cultures will be obtained from the Culture Collection of Algae and Protozoa, of the Scottish Association of Marine Science Laboratory, Dunbeg, Scotland. These algae were chosen due to their established use in marine fish hatcheries, which requires algae that have high biomass productivity and resilient therefore easy to grow. The algae are to be cultivated in standard f/2 medium (Anderson, 2005) modified to pH 8.0 (NaNO₃ 0.882Mm; NaH₂PO₄·H₂O 0.036mM; Na₂SiO₃·9H₂O 0.106mM; FeCl₃·6H₂O 0.012mM; Na₂EDTA·2H₂O 0.012mM; MnCl₂·4H₂O 0.910 μM; ZnSO₄·7H₂O 0.077 μM; CoCl₂·6H₂O 0.042 μM; CuSO₄·5H₂O 0.039 μM; Na₂MoO₄·2H₂O 0.026 μM).

<table>
<thead>
<tr>
<th>Table 4 Identified experimental algae strains.</th>
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<tbody>
<tr>
<td><strong>Strains</strong></td>
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<tr>
<td>Isochrysis galbana</td>
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<tr>
<td>Isochrysis sp.</td>
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<tr>
<td>Nannochloris atomus</td>
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<tr>
<td>Nannochloropsis gaditana</td>
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<tr>
<td>Nannochloropsis oculata</td>
</tr>
<tr>
<td>Nannochloropsis sp.</td>
</tr>
<tr>
<td>Pavlova lutheri</td>
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<tr>
<td>Tetraselmis chui</td>
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**The photobioreactor:** The algae will be grown in batches under semi-axenic conditions in the closed photobioreactor illustrated in Fig. 1. The photobioreactor will consist of eight cylindrical glass.
columns (diameter 56mm, length 500mm with 1 litre medium each); it will be equipped with three external illumination systems composed of 7 fluorescent tubes each (Thron CAT 5), which together will supply 200 µmol m⁻² s⁻¹ (PAR) to the surface of the culture vessels. The external illumination is set to a 16:8 light:dark cycle. To provide uniform growing conditions the photobioreactor will be situated in a constant temperature room to maintain a medium temperature of 25°C. Prior to inoculation of the algae in the growth medium, the reactor will be sterilised in an autoclave (121°C at 2 atm for 1h).

Mixing and aeration are effected by bubbling ambient Air-CO₂ mixture through a glass tube located at the base of the photobioreactor. The gas mix will be processed through a WittGasetechnik KM 60 2ME Air-CO₂ mixer (WittGasetechnik Gmbh, Germany) to 2 % CO₂. The enhanced air, sterilised using filters (0.22 µm, Millipore), will be passed via an air inlet tube into the culture medium. It is envisaged that the turbulence caused by air passing up through the culture vessel will be adequate to mix the medium sufficiently to keep cells in constant suspension in the culture medium. The enhanced Air-CO₂ mixture will be pumped through at a rate of 0.25 v/v/min.

**Analytical methods:** Algal biomass productivity will be determined by daily measurement of cell growth from initial inoculation until the stationary growth phase. A 10ml sample will be extracted from each glass column at the same time each day. This is intended to maintain uniformity of samples over the growing period, due to changes in the biological composition of cells over daily growth periods. Biomass productivity will be determined by cell counting using a Sedgwick-Rafter counting slide, and by flow cytometry (FACSAria Cell sorter) to count cells. These counting methods will be correlated to produce algal growth curves over the individual observations periods. After each sample extraction, 10ml of fresh f/2 medium will be added to maintain a constant growth volume.

Growth medium temperate, dissolved oxygen, and pH changes will be monitored (Thermo Scientific Orion 5-star Portable Multimeter) daily to check the overall health of cultures.

**Expected Results**

It is anticipated that biomass and lipid contents will vary between strains. Previous studies in larger photobioreactors have shown output can range from 0.5 g l⁻¹ day⁻¹ to 3g l⁻¹ day⁻¹ (Acién Fernández et al., 2001; Camacho Rubio et al., 1999; Doucha et al., 2005; Molina Grima et al., 2001).

The constant monitoring of temperature, dissolved oxygen and pH will aid in the identification of solutions to growing problems anticipated during the investigation period. Small variations in these parameters can indicate possible negative changes occurring to the growing population over the time period.

**Conclusions and Recommendations**

This investigation should allow a preliminary evaluation of the potential of mass cultivation of eight marine algae strains for biofuel production. Biomass productivity is one of the key components in determining the viability of algal strains for production of liquid biofuel. High growth rates which results in high accumulation of biomass provide an initial indication of the strains potential for biofuel production.

After determining biomass productivity rates, further research will need to be carried out on the most promising strains to evaluate their potential for producing high amounts of lipids, another major criterion in determining the viability of algal for conversions to biofuels.

**Acknowledgements**

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References


CO2 MITIGATION AND CARBON SEQUESTRATION POTENTIAL OF NANNOCHLOROPSIS OCULATA IN A LABORATORY SCALE BATCH REACTOR

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Abstract

Electricity generation currently accounts for around 33% of worldwide carbon dioxide (CO_2) emissions. One potential method of offsetting these emissions is through biological sequestration of the emitted CO_2. This process would utilise CO_2 from the flue gases of a power plant to cultivate photosynthetic autotrophic organisms. The produced biomass can subsequently be converted into biofuels, decreasing the demand for fossil fuels. The effect of CO_2 concentration and temperature on the carbon sequestration potential of Nannochloropsis oculata was investigated.

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. If this cycle were properly managed, it could be a major contribution to mitigation of this greenhouse gas (Hughes and Benemann, 1997).

A large fraction of the anthropogenic emissions of carbon dioxide (CO_2) results from the combustion of fossil fuels for energy production. As energy needs increase, especially in the developing world, CO_2 emissions are expected to rise considerably in the coming years. Meeting energy demands without high emissions will require stringent management of CO_2 including the use of post-combustion carbon sequestration. Carbon capture and sequestration is a process of removing CO_2 from flue gases and storing it for extended periods, preventing emissions. Biological sequestration is a temporary storage of CO_2 whereby the biomass produced can be used as an energy source by converting it to biofuels. Essentially the CO_2 is being recycled while the conversion of biomass to energy displaces the use of fossil fuels in energy generation. Biological sequestration coupled with biofuel production offers great potential to meet this demand. Photosynthesis is the method of utilising anthropogenic carbon and was the original process that fixed carbon millions of years ago creating today’s fossil fuels. Using this process, captured flue gases containing high concentrations of CO_2 can be used to cultivate large amounts of biological media. In a controlled environment, this could produce large yields of valuable biomass for producing biofuels, as well as some value added by-products. Selection of the best media for carbon sequestration is crucial in achieving a high level of CO_2 removal while also ensuring an economic benefit from the process (Olaizola et al., 2004).

In this experiment, Nannochloropsis oculata, a small microalgal species, is assessed for its potential to sequester carbon from a high concentration CO_2 source. Flue gases may contain anything up to 15% CO_2 and a direct relationship between CO_2 concentration and growth rate can be seen for many microalgal strains (Chae et al., 2006). Temperature can also have a significant effect on biomass production. Therefore the optimum temperature and CO_2 concentration at which individual strains of microalgae can sequester carbon should be determined.

The objective of this study was to determine the sequestration potential of Nannochloropsis oculata under various temperature and CO_2 concentrations at laboratory scale.

Materials and Methods
Selection of microalgal strain
Initially various microalgal strains were reviewed and selected for further experimental study based on their suitability for carbon sequestration. There are a number of different species suitable for carbon sequestration. To differentiate them from one another a set of criteria for comparison was developed to facilitate selection of the most appropriate biological media. Essentially the selected media should have a rapid growth rate, be easily cultivated on a large scale, have a high CO₂ fixing rate, generate a large biomass yield and produce valuable by-products to offset the cost of carbon sequestration. Table 1 illustrates some microalgal strains which were considered for carbon sequestration. Following the selection process *Nannochloropsis oculata* was selected because it is a robust strain with good yields and it has the potential for CO₂ mitigation in a CO₂ enriched environment (Chiu et al., 2009).

Experimental design
A two-factor, fully randomized factorial design was employed. The two factors selected as independent variables were flue gas temperature and CO₂ concentration (Table 2). This was to allow for the assessment of the optimal cultivation temperature and CO₂ concentration of the algae. Light intensity and air flow rate were kept constant.

A laboratory scale batch reactor was designed for the cultivation of algae (Fig 1). Exit gases were analysed using a flue gas analyser (Applus+ Auto Logic, Sussex, UK) in order to calculate CO₂ removal and algae were analysed for carbon content after harvesting using a carbon analyser (Primacs® TOC analyser (CS22), Skalar, Netherlands). Growth rates were also monitored to calculate the biomass production rate. This information was used to calculate the total carbon sequestered and sequestration rate was quantified.

Light source
Batch cultivation was carried out on an 18/6 hr, light/dark photo period. Light for the experiment light was provided by 40W fluorescent lamps to achieve a light intensity of 300 µmol.m⁻².s⁻¹ at the surface of the culture flask (Chiu et al., 2009).

Culture mixing
Effective mixing of the culture is necessary to ensure that each cell has sufficient nutrients and is exposed to the same light intensity for effective photosynthesis (Laing, 1991). In this experiment, mixing is achieved via rigorous aeration from a combination of compressed CO₂ and air.

![Diagram of experimental setup](image)

**Figure 1** Schematic of the experimental setup for the batch cultivation of microalgae under varying temperature & CO₂ levels

Microalgae and cultivation medium
*Nannochloropsis oculata*, sourced from the Scottish Association for Marine Science’s culture collection (Argyll, Scotland), was maintained as a stock culture in the laboratory. This was prepared in 300 ml Erlenmeyer flasks utilising Erdschreiber Medium as the nutrients for the algae. The broth was transferred to a 4 L nalgene bottle for batch cultivation of the microalgae. The bottles contained filtered artificial sea water containing the following nutrients and trace elements (per litre); 75g NaNO₃, 5g NaH₂PO₄·H₂O, 4.36g Na₂EDTA, 3.16g FeCl₃·6H₂O, 180mg MnCl₂·4H₂O, 10mg CoCl₂·6H₂O, 10mg CuSO₄·5H₂O, 23mg ZnSO₄·7H₂O, 6mg Na₂MoO₄, 100mg vitamin B1, 0.5 mg vitamin B12 and 0.5mg biotin (Chiu et al., 2009).
Table 1: The carbon sequestration potential of selected microalgal strains

<table>
<thead>
<tr>
<th>Strain</th>
<th>Optimum CO₂ conc. (%)</th>
<th>Specific growth rate (µ d⁻¹)</th>
<th>Carbon reduction rate (%)</th>
<th>Carbon fixation rate (g/h)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>Euglena gracilis</em></td>
<td>10</td>
<td>0.32 x10⁶ᵃ</td>
<td>64.8ᵇ</td>
<td>0.4gᶜ</td>
<td>(Chae et al., 2006)</td>
</tr>
<tr>
<td><em>Chorella sp.</em></td>
<td>5</td>
<td>0.422</td>
<td>2</td>
<td>0.316</td>
<td>(Chiu et al., 2008)</td>
</tr>
<tr>
<td><em>Nannochloropsis oculata</em></td>
<td>2</td>
<td>0.194d¹</td>
<td>47</td>
<td>0.211</td>
<td>(Chiu et al., 2009)</td>
</tr>
<tr>
<td><em>Emiliania huxleyi</em></td>
<td>5–10 ᵍᵈ</td>
<td>0.52 – 0.97 d⁻¹</td>
<td>70</td>
<td>n/a</td>
<td>(Riebesell et al., 2000)</td>
</tr>
</tbody>
</table>

ᵃ: No µ specified. Cell density measured in cell/ml/day
ᵇ: Carbon reduction nit specified. Carbon content of produced biomass found as % of cell mass
c: Carbon fixation rate not specified. Carbon sequestration calculated as g biomass/ g CO₂
d: Optimum CO₂ concentration in gas stream not available. Dissolved CO₂ concentration specified in µmol L⁻¹ culture

Table 2: The experimental factors and levels employed in the factorial experimental design

<table>
<thead>
<tr>
<th>Factor</th>
<th>18</th>
<th>24</th>
<th>30</th>
<th>36</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (°C)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Added CO₂ (%)</td>
<td>0</td>
<td>5</td>
<td>10</td>
<td>15</td>
</tr>
</tbody>
</table>

Cultivation of microalgae
This experiment utilised a CO₂ enriched air stream (from a compressed CO₂ source) which was bubbled through the media. CO₂ concentrations levels were set according to the experimental design. The air was heated to control the temperature at the inlet also according to the experimental design. The experiment ran on a 7 day cycle. Half of the biomass was harvested daily, and replaced with fresh nutrients to keep the microalgae in the high production log phase. This was also where the algae have a high capacity for photosynthesis. The inlet concentration of CO₂ was controlled using flow meters and the exit gases were analysed on-line to assess the amount of CO₂ in the outlet gas stream (Figure 1). This determined the amount of CO₂ converted into organic carbon by the microalgae. Samples of the collected biomass were assessed in the carbon analyser to calculate the carbon content of the microalgae.

Growth Rate
Growth rate is an important factor when selecting a suitable media for carbon sequestration. High growth rate suggests that the rate of carbon mitigation is increased. Growth rate was assessed using a Sedgwick counting chamber. A sample of broth was taken and analysed under the microscope to calculate the microbial cell count per ml of medium.

Flue gas analysis
In this experiment, flue gases were simulated utilising a compressed air and CO₂ source. The flow rate of gas and concentration of CO₂ was monitored using flow meters. Exit gases from the batch reactor were analysed for CO₂ content using the flue gas analyser. This will determine the amount of CO₂ removed from the air stream by the algae.

Results and Discussion
As experimental work is on-going, only expected results are shown here. Figure 2 illustrates typical growth curves for a number of CO₂ concentrations. As shown by Chiu, et al. (2009), microalgae can achieve a 47% reduction in the CO₂ content of the gas stream having a carbon
mitigation rate of 0.211 g h⁻¹. Although the algae performed best at low CO₂ concentrations, this experiment aims to improve the cultivation techniques and operating parameters to increase the carbon mitigation rate and assess the overall potential of the strain for carbon sequestration.

![Figure 2](image-url) Growth profiles of *N. oculata* NCTU-3 cultured in the semicontinuous system aerated with 2%, 5%, 10%, and 15% CO₂. (Chiu et al., 2009)

**Conclusions**

*Nannochloropsis oculata* shows great potential for carbon mitigation from point sources. The process is to be optimised further to increase the growth rates for higher CO₂ concentrations following the identification of the challenges associated with using this strain to sequester carbon. Various experiments will now be carried out to quantify this potential. A laboratory scale boiler system will be designed and constructed. The result of varying light intensity and lighting period on carbon sequestration rate, growth rates and yield will be determined. The same results could be examined while altering the temperature of the flue gases and concentration of CO₂. The results from these experiments will allow the optimum conditions for growth to be established while sequestering the maximum amount of CO₂.

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INTEGRATED ASSESSMENT OF BIOGAS TECHNOLOGY OPTIONS

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Abstract

The German government developed an integrated energy and climate program for structured GHG reduction, in which 20% of GHG emissions shall be reduced by 2020 compared to 1990 [1]. These targets are underpinned by the European Energy Policy by need for reduction of GHG emissions by using less, cleaner, and locally produced energy, including energy recovery from waste [2].

Biogas substitutes fossil energy carriers in sectors of electricity, heat and transportation fuel, which reduces emissions like nitrogen oxides (NOₓ), hydrocarbons (HC) and particles. In particular, biogas utilization avoids 5.54 and 1.01-1.34 million tons CO₂ for electricity and heat production, respectively [3]. Application of the digestate from biogas production as fertilizer avoids production of chemical fertilizer, to further mitigate GHG emissions. The biogas production in Germany still has potential for expanded application attainable by enhancement of incentives and minimization of barriers in implementation process, for biogas production and utilization [4].

Objectives of this study are to carry out an integrated assessment of biogas technology deployment, with specific focus on (i) policy drivers determining the biogas technology deployment, and (ii) energy efficiency and environmental performance of biogas production deployment. Technical and environmental performance of biogas production systems depend on type of feedstock used, conversion technology employed, biogas utilization pathways as well as processing and handling of digestate. In the next stage of the study, environmental impact criteria for sustainable biogas production systems will be determined.

Introduction

The CO₂ neutral nature of fuels produced from renewable resources, allowing a reduced contribution to climate change, is often a strong argument in favour of renewable energies [5], however, it is not always as significant as expected due to energy and material consumed for cultivation and the transport of renewable resources. Beyond CO₂ neutral emissions, additional emissions arise during biogas production and utilization. Furthermore, digestion residues – the digestate has to be transported and disposed, which can lead to burden or release of the environment. Consequently, all this aspects have to be considered within operation of biogas production plants to state an environmental friendly and sustainable energy production [6]. Sustainable biogas production and utilization based on multiple feedstock and different energy conversion pathways encompasses a positive energy input to energy output ratio (energy efficiency) [7] and little environmental impacts effected by emissions like CO₂ and methane.

The overall objective of this project is to analyze the performance of integrated biogas production and utilization technology options. The project evaluates the prospects for expanded utilization of biogas technology in Germany, and assesses the energy efficiency and potential environmental impacts of biogas production and utilization pathways. It focuses on multiple feedstock utilization, in order to develop scope and methods to facilitate optimization of the inherent technology options.
Materials and methods

The project divided into four specific objectives. Objective 1 covered the prospects for expanded utilization of biogas in Germany. Objective 1 aimed to assess the prospects for expanded deployment of biogas technology in Germany, by identifying key factors affecting the complete chain of processes in plant implementation from the planning process, installation and commissioning, to feedstock supply, and biogas production and utilization. The associated tasks have been completed and a manuscript has been submitted to the Renewable & Sustainable Energy Reviews Journal for consideration.

Objective 2 dealt with energy audit of different biogas production systems. It covered the energy balance for different biogas system scenarios, including single and co-digestion of multiple feedstock, different biogas utilization pathways, and waste-stream management strategies. The energy balance was evaluated as Primary Energy Input to Output (PEIO) ratio, to assess the process energy efficiency, hence, the potential sustainability. Fig. 1 shows the study boundary analyzed, encompassing: feedstock resources, harvesting and transport, biogas plant operation, biogas-to-energy conversion technologies, and digestate handling. Analyses were based on literature data relevant to conditions in Germany. The associated tasks have been completed and a manuscript submitted to the Applied Energy Journal for consideration.

Objective 3 which is currently in progress, analyses the environmental performance of different biogas production systems. The specific objective is to rate individual system performance and to identify ‘hotspots’ in biogas production and utilization processes where further improvements may be achieved to enhance sustainability. Full Life cycle assessment (LCA) of the biogas production system will be carried out with SimaPro 7.1 software and results benchmarked against reference scenarios. Sensitivity analysis will be undertaken to establish the effects of a number of parameters including the use of (i) single feedstock and (ii) co-digestion of multiple feedstock in small and large-scale biogas systems, as well as, (iii) different biogas utilization pathways (iv) and various waste management options. In essence the objective seeks to determine key steps or unit processes within the life cycle of different biogas production systems with significant environmental impacts.

Objective 4 will focus on potential environmental impacts of replacing selected reference energy generation systems with biogas systems.

Results and discussion

From the concluded Objective 1, it was found that biogas technology could make a significant contribution towards meeting the national targets for renewable energy deployment in Germany. This suggests that existing technology and policy drivers and the accompanying incentives need to be enhanced.

Results of Objective 2 show that there could be significant variation in energy efficiency for biogas plants arising from feedstock resource and processes adopted, and conversion technology and digestate management technique applied.

Single feedstock digestion

Fig. 2 shows that for single feedstock digestion, the PEIO ratio ranged between 10-64%, depending on energy demand for feedstock supply logistics. Energy input was highly influenced by the characteristics of feedstock used. For example, agricultural waste, in most part,
did not require pre-treatment. Energy crop feedstock required the respect cultivation energy inputs, and processing of industrial waste streams included energy-demanding pre-treatment processes to meet stipulated hygiene standards.

Feedstock co-digestion
For co-digestion of multiple feedstocks, the PEIO ranged between 45.6–48.6% and 34.1–55% for small and large-scale biogas systems, respectively, which suggests more stable processes in co-digestion (Fig. 4).

Biogas utilization pathways
Fig. 5 presents that the recorded PEIO for small and large-scale biogas utilization pathways ranged between 4.1-43.7% and 1.3-12%, respectively, depending on efficiency of the respective energy conversion systems, degree of energy utilization and potential substitution of different fossil fuels, which indicates the inherent potential for energy efficiency enhancement. For example, most efficient utilization pathways for small and large-scale biogas plants was CHP generation with heat utilization at relatively short transmission distance (PEIO 6.2%) and upgrading of biogas specifically for gas grid injection, but using small-scale CHP to service process and biogas upgrading energy loads (PEIO 1.3%), respectively.

Sustained utilization of digestate
Energy efficiency could be enhanced by up to 6% by recovery of residual biogas from enclosed digestate storage units. Energy performance of digestate management strategy depended on whether dewatering or drying was required to enhance transportation efficiency (Fig. 6), but drying was sustainable only where surplus heat from energy conversion process was available.
enhanced handling for loading, transport and spreading

Initial Screening LCA under Objective 3, using SimaPro software and exemplar impact assessment method Eco-Indicator 99 will identify those parts of the systems (life cycle) that are important and need focus for further work. For example, preliminary results have shown, that single feedstock digestion results in significant differences in single score results, especially, if feedstocks like grass silage and wheat silage are primarily cultivated for energy production, which determine high impacts in land use. A more detailed impact assessment and interpretation of results is in progress.

Conclusion

Results of Objective 1 show that just 10% of available feedstock potential in Germany is currently used for biogas production. To realize this potential, enhancement of incentives and minimization of barriers to expansion of biogas production will be required, including: (i) simplifying the procedures in biogas plant implementation process; (ii) enhanced R&D on feedstock co-digestion, especially of agri-food industry waste and Municipal Solid Waste streams, and; (iii) enhancement of biogas utilization through provision of incentives to biogas plants, e.g., access to electricity and gas grid infrastructure.

Completed tasks under Objective 2 pointed out, that implementation of new biogas plants does not always focus on high energy output alone. Substitution of fossil fuels, additional income options for farmers or alternative waste management systems to landfilling are key determinants of viability. For example, feedstock with high biogas yield may not always be available due to seasonal availability, legal restrictions (health and environmental protection), energy demanding pre-treatment requirements (e.g. abattoirs waste), or highly unstable anaerobic digestion process control that may not support sustained utilization. However, more efficient AD process and utilization of generated gas, combined with sustained utilization of the digestate can enhance feedstock-to-energy efficiency to foster sustainability.

Acknowledgements

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FEASIBILITY STUDY FOR ANAEROBIC DIGESTION USING MUNICIPAL WASTE (MSW) IN IRELAND

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Abstract
The rate at which fossil fuels, such as oil, coal and peat are being produced cannot meet our global demands. As fossil fuels supplies dwindle they become more expensive. Ireland is now faced with the challenge of finding a method of sustainable energy that provides at least one alternative option to fossil fuels. Anaerobic digestion (AD) is currently being used as a treatment for the organic fraction of Municipal solid waste in Europe namely Germany and Denmark. The advances of AD technology have been supported by legislation. Most European countries hope to limit MSW to less then 5% of the collected material and have increases taxes on landfilling. Although these technologies are viable and successful in Europe will this process feasible in Ireland.

Introduction
Municipal solid waste (MSW) is the waste generated in a community with the exception of industrial and agricultural wastes (Tchobanoglous, 1993). Almost all of Ireland MSW ends up in landfill as there are no facilities to treat it as a biomass for sustainable energy source in Ireland. Ireland is under agreement to reduce Green House Gas emissions since the Kyoto protocol. The National Greenhouse Gas emissions in 2003 totalled 24.9% above the 1990 levels. A 13% reduction above the 1990 baseline is imperative by 2012 or serious fines will be imposed. (Acquaye & Duffy 2009) Municipal solid was amounted to 910,000 tonnes in 2009. This volume of waste can no longer be facilitated. The landfill directive (1999) states that the amount of waste going to landfill must be reduced, and thus all waste must maximise its use and value before it ends up in landfill. Landfills and old waste deposits are some of the major anthropogenic sources of methane (CH4) emissions worldwide. Germany is highly advanced in the area of AD, during the last 15 years the amount of carbon dioxide equivalent (CO2-eq.) emitted from German landfills was reduced by approximately two third. (Ritzowski and Stegmann 2007) Supportive legislation, pollution, large grants, CO2 taxes and special loans are all incorporated to reduce emissions. (Bioexell 2008) Ireland’s difficulty may lie with the lack of support from the Irish government in relation to AD projects.

The objective of this study is to investigate municipal solid waste as a feedstock for Anaerobic Digestion, developing scope and methods between previous studies and the economical impact it may have on Ireland

Procedure
The research is based on previous work, and documented examples of AD are used in this literature. Firstly, a desktop study of existing knowledge regarding anaerobic digestion and municipal solid waste...
Table 1. Feedstock Characteristic (Roa et al., 2000)

<table>
<thead>
<tr>
<th>Feedstock</th>
<th>Biogas yield m3/ Kg volatile solid</th>
<th>Methane %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fruit and Veg solid waste</td>
<td>0.429-0.568</td>
<td>50-60%</td>
</tr>
<tr>
<td>Agri waste</td>
<td>0.730</td>
<td>59.9%</td>
</tr>
<tr>
<td>Municipal waste</td>
<td>0.564</td>
<td>70%</td>
</tr>
<tr>
<td>Cattle waste</td>
<td>0.252</td>
<td>62%</td>
</tr>
</tbody>
</table>

(MSW) treatment was carried out. MSW includes waste food and paper and other waste collected by the refuse companies such as hotels and garden wastes, all wastes excluding hospital and pharmaceutical wastes can be included in this anaerobic digestion treatment. Investigations of future anaerobic digestion technologies are also reviewed. All AD plants must have an area where waste can be segregated, pre-stored, digestion and gas utilisation area. The beneficial end products are stabilized humus and methane. This biogas (methane) can then be combusted to provide heat, electricity and hot water. This conversion of heat and energy is carried out by an engine know as a CHP (Combined Heat Power). Developing technologies in CHP’s are utilized as they have a greater financial return on gas. Analysis on waste generation in Ireland shows that, it is in fact viable for anaerobic digesters to function sufficiently. The quantity of municipal waste generated in consists of almost 55% household waste and just over 40% results from commercial the remaining 2.9% is generated from the streets. Panda Waste has recently marked the ground breaking of Ireland’s first mechanical biological treatment plant which will convert over 250,000 tonnes of black bin waste (previously destined for landfill) to biogas and digestates. Legislation is a main concern when planning an anaerobic digestion site. Although anaerobic digesters do not have negative effects on the environment in anyway, the public still hold a negative perception of it. The NSW EPA Environmental Guidelines for the Use and Disposal of Biosolids Products (1997) should be consulted to determine the quality of biosolids that are suitable for use as input materials for composting. All biosolids are graded for customers to understand the safety of the products. Anaerobic digestion earns revenue, though the environmental benefits are the real advantage to AD such as energy security and displacing air emissions. There are major criticisms regarding the cost of running an AD plant by Mahony (2002).AD provide enough energy to heat and run their own plants following their start-up period. It is most likely that a diesel engine (8-10%) would be used for the digesters for ignition. A mesophilic temperature is the most commonly used temperature for AD in Ireland but Enright et al (2007) has showed
comparable results with psychrophillic temperatures following a slow start up period. Carbon and energy balances are assessed, and the potential of carbon emission savings are inspected. Biogas return on AD is usually greater than 60% methane. Municipal wastes are compared with other studies and comparable results are expected. Detailed assessment of both the environmental and the economical impact it will have on Ireland will be noted. Its advantages such as an alternative energy source, and also the disadvantages will be highlighted and explored.

Results and Discussion

The relevant literature has been reviewed, and following analysis of waste generation in Ireland at present there is an explicit need for such facilities. In the last ten years the use of AD has become a popular option for treating waste in Germany. Although there are a few small scale AD plants on farms around the country, none are functioning at a commercial level. Having researched other AD plants throughout Europe the main advantage to it, is not its profitability but that so much waste can be treated in this manner and the biogas production. Large AD facilities offer the potential to reduce 75% of municipal materials in landfill and the remaining digestates can be used for fertilizer and waste water treatments. Landfills are a source of large amounts of emissions of methane to the atmosphere and have potential of causing global warming. Although AD is increasing and being recognised as a modern waste treatment, there are problems associated with it. Such as the technical aspect, negative image surrounding it and stringent regulations. The Irish Beef Association and the Dairy Farmers Association, will not accept products from farms that use AD digestate. For this reason it is important to educate the public and divest their negative image of AD. As a result many farmers and industries are reluctant to use the technology, despite the fact it is reducing such a large percentage of our landfill waste. The environmental benefits include reduced water pollution, reduced GHG emissions and reduced odours from landfills and waste will have reach its maximum potential before reaching landfill. Gas composing of 65-75% methane is adequate to generate electrical power and heat. This not only reduces GHG’s but also averts the need for such large landfill sites. Legislation such as the European White Paper three main principles is to reduce Co2 emissions, maintain reliability of energy source and provide competitive markets in Ireland. By utilising AD technology we are meeting the demands of the white paper. The digestates may be used for high quality fertilizer and other possibilities for these digestates are currently being researched.

Acknowledgements

The authors would like to thank Anne Marie Enright and Vincent O’Flaherty.

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EVALUATION OF THE IMPACT OF ANAEROBIC CO-DIGESTION OF ANIMAL WASTE WITH AGRI-SUBSTRATES ON BIOGAS PRODUCTION AND DIGESTATE.

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Abstract
The anaerobic digestion of organic material produces a methane rich biogas and digestate. The amount of biogas and the quality of digestate obtained will vary according to the feedstock used. The co-digestion of cattle slurry with maize and grass will be evaluated in relation to biogas yield and composition. In addition, the digestate resulting from the process will be examined for fertiliser quality. Three bench scale anaerobic digestion units will be constructed to carry out the experiments.

Introduction
Anaerobic digestion is a natural process in which organic matter is decomposed in an environment devoid of oxygen. The process produces a methane rich biogas; generally in the region of 60% methane and 40% carbon dioxide. The digested material remaining after the anaerobic digestion process is known as digestate. The anaerobic digestion of animal wastes can achieve an array of benefits to the energy sector, the environment, agriculture and thus the surrounding community. The biogas produced is mostly utilised in the generation of electricity and can also be used as a renewable vehicle fuel or injection into the natural gas grid. As this is a renewable source of energy, it contributes to the reduction of GHG and mitigation of global warming. Furthermore, this also reduces the dependency on imported fossil fuels and contributes to meeting Kyoto Protocol targets. O’Rourke et al. (2009) notes that Ireland has set a target that by 2020, 33% of electricity will be generated from renewable sources. Mata-Alvarez (2000) also states that anaerobic digestion of animal slurry results in a reduction in odours, reduction of pathogens, excellent fertiliser and high quality soil amendment and a reduction in ground and surface water contaminations. Digestate as a fertiliser is significantly better than undigested slurry. The digestate can have up to 20% higher ammonium-nitrogen content than untreated cattle slurry (Mitchell and Gu 2009). Furthermore, digestate maximises plant nitrogen uptake as it is in a more available form and the risk of nitrate leaching is minimised as it has considerably less pollutant potential (Mitchell and Gu 2009). Animal slurry digested on its own produces a low biogas yield which, in most cases would not be economically viable in a large scale digester. However, the biogas productivity can be substantially enhanced if it is co-digested with an additional substrate (Cavinato et al. 2010). This project will be a continuation of a study by a Research Masters student, Matthew Hogan. The experiments will be of further support to his findings. In addition, the fertiliser quality of the digestate will be also studied.

The aim of this project is to study the effect of the anaerobic co-digestion of cattle slurry with agri-substrates on biogas yields and digestate fertiliser quality.
Materials and Methods

Experiment 1: A bench scale anaerobic Digester

This experiment is based on the construction of a bench scale anaerobic digestion unit using a 5000ml beaker sealed with rubber sheeting. Although the previous tests by Hogan used a conical flask, it was not entirely effective as the neck of the flask acted as an obstruction which inhibited the gas extraction process. A plumbing fitting will be placed through the seal which will be used to extract the gas.

The container will be made anaerobic through the use of a water vacuum. This will be attached to the extraction fitting which will draw out all of the air creating an anaerobic environment. The unit will be placed in a basin filled with water which will be heated with a heating element. There will be a series of experiments at different temperatures with a residence time of 40 days.

![Diagram of the experiment.](image)

Three bench scale models as shown in Figure 1 are planned to be assembled. The three digesters will consist of different mixtures, namely:

| Digester 1: | Cattle slurry (control). |
| Digester 2: | Cattle slurry & grass. |
| Digester 3: | Cattle slurry & maize. |

When the biogas begins to be produced, it will be collected in cellophane bags. The volume of gas will be measured using a water displacement method. The gas yield will be calculated over a given time. In addition, the amount of methane produced in the biogas will also be quantified using a gas detection instrument.

Experiment 2: Biogas composition Analysis

A ‘Draeger X-am 5000’ gas detection instrument will be used to measure the composition of the biogas. This device measures methane, carbon dioxide, hydrogen sulphide, and carbon monoxide.

Experiment 3: Digestate quality testing

The liquid fraction is usually returned to the land as a fertiliser and the solid fibre used as a soil conditioner (Holm-Nielsen 2009). By the separation of the digestate into two phases the plant nutrients are divided, so that the solid phase is used as a phosphorus fertilizer and the liquid phase as a nitrogen fertilizer (Palm 2008). Therefore the liquid fraction will be tested for N and the solid will be tested for P. Nitrogen will be determined using the Kjeldahl method and phosphorous will be evaluated using atomic absorption. Potassium will be evaluated in both using atomic absorption also.

Results and Discussion

The experiments have not yet begun and therefore, no results have been achieved. However as this will be a continuation of Hogan’s work, the results will not be expected to differ greatly.
If the project is carried out successfully and the expected results materialise, the cattle slurry and maize mixture should be the most effective in terms of biogas yield and methane composition as maize is among the most promising energy crops for biogas production (Holm-Nielsen 2009).

Figure 2: Hogan’s results at 40º celsius, which indicates the cattle slurry and maize as the most productive mixture.

The results of the proposed experiments should not deviate greatly from these results as they are replicates of Hogan’s experiments which should support his findings further.

Similarly it would be expected that the maize combination would produce the digestate with the highest fertiliser value. Moller et al. (2009), notes that the nutrient contents of the feedstock equals the digestate as nothing is lost in the process, although the nutrients are converted to a more available form. The nutrient content of the cattle slurry will be calculated prior to digestion and compared to the nutrient levels of the digestate.

The C.S.O. (2008) note that of Ireland’s total farmed area, 79% is in grassland which carries in excess of 6.7 million cattle. This indicates the volume of wastes produced which if managed effectively, can be exploited to produce biogas.

Persson et al. (2006) note that low methane levels are required for the production of heat, although biogas needs to be upgraded to over 95% methane in order to be used with natural gas. In addition, biogas has to be upgraded to natural gas quality in order to be used in normal vehicles, designed to use natural gas.

The digestate from anaerobic fermentation is a valuable fertiliser due to the increased availability of nitrogen and the better short-term fertilization effect (Weiland 2010). However the biogas quality and digestate quality varies depending on the quality of the feedstock. Furthermore the fertiliser value of digestate is of significance as over application of nutrients to land can be detrimental to the environment. The nitrogen load on farmland is regulated by the E.U. nitrates Directive (91/676/EEC) which stipulates maximum nutrient levels to be applied to land. The information obtained on the digestate will assist in meeting these limits.

Conclusions

Biogas is mainly utilized in engine-based combined heat and power plants and gas upgrading and utilisation as renewable vehicle fuel or injection into
the natural gas grid is of increasing interest because the gas can be used in a more efficient way. This project will indicate which mixtures are most effective for large scale anaerobic digestion in agriculture as the composition of methane in biogas determines its use. Upgrading of gas is very expensive which means optimising biogas yield and composition is essential. The fertiliser value obtained from the mixtures will be of benefit as the mixtures and temperatures will indicate optimum conditions in terms of the digestate quality for the anaerobic digestion of agricultural substrates.

Acknowledgements
The authors would like to acknowledge the support of Matthew Hogan and Science Foundation Ireland (SFI).

References


The objective of this study was to determine whether there was an increase in nitrate concentrations in soil water samples as a result of fertilizer nitrogen (N), in the form of cattle slurry, being applied at various rates to an establishing crop of Miscanthus; this trial was conducted during 2008/09. The crop received either no fertilizer (0-unfertilized control) or an annual application of 60, 120 or 180 kg N/ha. Soil water solution samples were collected fortnightly from porous ceramic cup samplers. Nitrate (NO$_3^-$) levels in these soil water samples were determined and monitored. In 2008, the soil water nitrate concentrations were high on all treatments, 14, 16 and 20 mg/l, respectively for 0, 60 and 120 kg N/ha. However, there was no significant difference between treatments. Soil water nitrate concentrations were again high (12-21 mg/l) in 2009, particularly at the 180 kg N/ha levels which showed significantly higher levels of nitrate leaching when compared to all other treatments. The results indicate that leaching losses were closer to those recorded under arable land than extensively managed grassland; slurry application on an establishing Miscanthus crop does not appear to contribute adversely to levels of nitrate in groundwater when compared to other more extensive cropping systems.

Introduction

Miscanthus x giganteus is a woody rhizomatous C4 grass species which originated in South-East Asia and was initially imported to Europe as an ornamental plant; it is a perennial plant with an estimated productive life span of at least 10-15 years (Jones and Walsh, 2007). The remarkable adaptability of Miscanthus to different environments (Numata, 1974) makes it suitable for establishment and distribution under a range of European and North American climatic conditions (Lewandowski et al., 2000). Energy and paper pulp production were the first end uses which were considered for Miscanthus, but the viability of other end uses are also being examined, such as, utilization in building material and in particular the suitability of Miscanthus for the bioremediation of contaminated soils; this potential use of the crop has come about as the pressures exerted on soils have increased due to intensive agriculture, industrialization, the expansion of urban areas and other factors (Visser and Pignatelli, 2007). Miscanthus is a promising non-food crop, yielding high quality lingo-cellulosic material for both energy and fibre production. It is characterized by relatively high yields, low moisture content at harvest and high water and nitrogen use efficiencies (Jones and Walsh, 2007). However, little is known about the interactions between this crop and fertilizer nitrogen management. The nitrogen requirement of grassland and most arable crops has been studied at length with the impact of agronomic practices on nitrate leaching quantified (Davies et al., 1996). However, the majority of studies on the effects of nitrogen fertilizers on Miscanthus (Lewandowski et al., 2000) focus on the effect of nitrogen on biomass yield, with fewer studies on the losses to drainage waters from this crop.

The objective of this study was to evaluate the effects of applying various rates of cattle slurry on nitrate leaching to drainage water and to measure N losses under field plots of Miscanthus.
Materials and Methods

The experiment was carried out at Lyons Research Farm, University College Dublin, Ireland (53° 18' 28" N, 6° 31' 59" W). Following harvest of the spring barley in 2006 the site was left fallow over winter (2006/07). In May 2007 soil cultivation commenced after the site had been treated with a glyphosate based herbicide. *Miscanthus x giganteus* (Greef and Deuter, 1993) was established from rhizomes in May 2007. A recommended planting density of 18-20,000 rhizomes/ha was used to obtain 10,000 plants ha or 1 plant/m. Post establishment the site was treated with a suitable sulphonyl urea based herbicide to suppress weeds. For practical reasons a conventional plot design was not possible; rather, sections of crop were divided into subplots and monitoring equipment (suction cup samplers) was installed in each sub-plot, i.e., 4 samplers per treatment. In 2008, the nitrogen treatments used were 0, 60 and 120 kg N/ha while in 2009 a rate of 180 kg N was added to give an overall treatment programme of 0, 60, 120 and 180 kg N/ha. Nitrogen was supplied in the form of cattle slurry which was applied to the crop using a side chute attached to a vacuum tanker. By using the side chute slurry was applied without driving on the crop. The slurry was collected on Lyons Farm and was agitated immediately prior to spreading to ensure uniformity. Table 1 shows the characteristics of representative slurry samples taken from each load prior to application. A portion (50 ml) of these samples was homogenized by shaking for 10 min, in keeping with Diez *et al.*, (2001) and then analyzed in the laboratory.

**Table 1: Physiochemical characteristics of cattle slurry.**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Total Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry Matter (%)</td>
<td>6.9</td>
</tr>
<tr>
<td>N (kg/t)</td>
<td>3.7</td>
</tr>
<tr>
<td>P (kg/t)</td>
<td>0.7</td>
</tr>
<tr>
<td>K (kg/t)</td>
<td>4.3</td>
</tr>
</tbody>
</table>

In January 2008, ceramic cup samplers were installed in each plot at 60 cm deep. Samplers were placed in the centre of the plot; a description of the installation and use of the ceramic cups is given in Curley *et al.* (2010). Prior to fertilizer application soil solution samples from ceramic cup samplers were extracted and samples analyzed for NO$_3^-$ to assess baseline levels. Throughout the trial period a vacuum of -80 kPa was applied to the samplers and maintained for a period of 7-10 days (Johnson *et al.*, 2002). Samples of the soil solution were then extracted using negative pressure and NO$_3^-$ determined for the extracted samples. Sampling took place on a fortnightly basis for four months post fertilizer application. Samples were analyzed for NO$_3^-$ using the zinc reduction method. All agro meteorological data (soil moisture, drainage potential, soil moisture deficit and potential evapotranspiration) was supplied by Met Éireann for Casement Aerodrome, a synoptic weather station 6 km from Lyons farm for the duration of the experiment. In addition to this, soil moisture was measured gravimetrically each autumn and volumetric soil water content was assessed using handheld Time Domain Reflectometry (TDR) probes; vertical tensiometers (capable of measuring water pressure of 0-90 kPa) were installed according to Diez *et al.*, (2001). Statistical analysis was performed by using MINITAB 15 (Minitab Inc., 2009) software. For statistical evaluations of treatment effects and sampling dates a one-way ANOVA was used. Differences between treatments and NO$_3^-$ levels in the soil solution samples were analyzed and compared by using Tukey simultaneous confidence intervals.

Results

The presence of nitrate in waterways is not a new problem (Addiscott, 1996). However, what is new is the public concern about nitrate, arising mainly from the incidence of two medical conditions that have been associated with it's presence: *methaemoglobinaemia* (blue-baby syndrome) in infants and stomach cancer in adults (Addiscott, 1996); despite both being serious conditions it must be noted that these conditions are not caused directly by nitrate but rather by nitrite to which nitrate may be reduced. This study sought to evaluate the effects of applying various rates of cattle slurry on nitrate.
leaching to drainage waters and thus, the impact on groundwater quality.

In 2008, mean soil water nitrate concentrations were high on all treatments; 14, 16 and 20 mg/l for 0, 60 and 120 kg N/ha, respectively. As fertilizer N rates increased there was a corresponding increase in soil water nitrate concentrations with the highest soil water nitrate concentration recorded in the treatment that received 120 kg N/ha. This trend follows that documented by Christian and Riche (1998), who also recorded an increase in soil water nitrate concentrations as fertilizer nitrogen rate increased. These results would suggest that the application of nitrogen fertilizer (as slurry) increased nitrate concentrations as shown in the higher concentrations on the treatments where N was applied. Nitrate levels in soil water samples peaked at 25 mg/l, 29 days post fertilizer application (Fig. 1) before consistently decreasing.

In 2008, overall levels from all treatments were still below the acceptable limit (50 mg/l) for the production of potable water, as enforced by the European Communities (Drinking water) regulations (S.I. No. 278, 2007).

In 2009 the application of nitrogen fertilizer increased nitrate concentrations in soil water, shown in the higher concentrations on the treatments where nitrogen was applied. However, despite an increase in nitrate concentrations there was no significant difference in concentration levels between the 0, 60 and 120 kg N/ha with mean soil water nitrate concentrations of 12-14 mg/l. The 180 kg N/ha level recorded a significantly higher levels of nitrate leaching when compared to all other treatments (21 mg/l). Mean nitrate levels in soil water samples peaked 24 days post fertilizer application (Fig. 2) before decreasing steadily for the remainder of the growing season.

On the whole, levels of nitrate in the soil solution did not exceed the acceptable limit for the production of potable water in either 2008 or 2009.

**Discussion**

Numerous leaching and drainage studies have consistently found that nitrate is the dominant form of nitrogen present in soil water. Whether the nitrogen source is animal manure or commercial nitrogen fertilizer, over-application or ill-timed application of either source can provide too much plant-available nitrogen and increase the potential for nitrate leaching (Hatfield and Cambardella, 2001).

Nitrate contributes to surface water degradation when it flows into subsurface drainage lines that discharge into streams and lakes or when it leaches below the active plant-root zone into shallow ground water resources that connect to surface water bodies through natural processes such as base flow (Dinnes et al., 2002).

The purpose of this study is to investigate the effects of applying various rates of cattle slurry on the degree of nitrate leaching to drainage water under newly established Miscanthus grass conducted over two years (2008/09).

In 2008, the application of nitrogen fertilizer (as slurry) increased nitrate concentrations in soil water samples, shown in the higher concentrations on the treatments where nitrogen was applied. Furthermore, during the first year nitrate concentration in soil water was high partly as a result of previous agricultural practices which probably caused higher rates of nitrogen mineralization than would be usual for arable land. Overwinter
fallowing and spring cultivation for planting of *Miscanthus* might also have contributed to mineralization and leaching, Christian and Riche (1998) reported similar findings. In 2009, there was no significant difference in soil water nitrate concentration up to 120 kg N/ha, in addition, the mean nitrate concentrations were lower, 12-14 mg/l. *Miscanthus x giganteus*, as a rhizomatous perennial grass producing an annual crop of stems has the potential to translocate nutrients to the rhizomes. This minimizes nutrient off-take and the pollution resulting from combustion of nutrient-rich material, while returning nutrients to the rhizomes for the support of the next year's growth. Moreover, *Miscanthus* should have the benefit of the higher nitrogen use efficiency which is associated with the C4 photosynthetic pathway. Simmelsgraad (1998) demonstrated that crop type was one of the most important factors affecting N loss. Thus, in year two of this trial it is assumed that soil water nitrate concentrations are lower due somewhat to the increased nutrient uptake of the crop as the total plant and root biomass increased. The lack of cultivation in the second year would have reduced mineralization of soil organic matter and therefore the change in soil management would have had a substantial effect in reducing leaching (Christian and Riche, 1998). Fertilizer application had a positive affect on nitrate concentrations in soil water samples (Fig. 3). The relationship between increasing fertilizer N rate and nitrate concentration in soil water samples in response to higher fertilizer N rates indicated a positive correlation between levels of fertilizer N and nitrate concentration with coefficient of determination (R²) values of 0.96 and 0.72 for 2008 and 2009, respectively. These results may be beneficial to meeting the European Community's (Drinking Water) Regulations recommendations for maximum levels for nitrate (50 mg/l) in potable water and suggest that the production of *Miscanthus* would have a low or beneficial environmental impact on groundwater quality.

**Conclusions**

The application of nitrogen fertiliser (as slurry) to *Miscanthus* increased nitrate concentrations in soil water samples, shown in the higher concentrations on the treatments where nitrogen was applied. However, the overall levels of nitrate in the soil solution did not exceed European Community's (Drinking Water) Regulations recommendations for maximum levels for nitrate (50 mg l⁻¹) in potable water.

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Minitab Inc., Quality Plaza, 1829 Pine Hall Rd, State College PA 16801-3008, USA.


THE QUALITY OF GROUNDWATER UNDERLYING BIOENERGY PLANTATIONS FERTILIZED WITH ORGANIC WASTES

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²Teagasc, Bio-energy Department, Oak Park Crop Research Centre, Carlow.

Abstract
Groundwater (GW) quality in Ireland is assessed using the interim guideline values (IGVs) (EPA, 2003) set out by the Irish EPA. The quality of GWs underlying small plantations of bioenergy crops where organic wastes were spread was assessed in relation to the IGVs. Biosolid Sludge (BSS) and Brewers Waste (BW) were spread onto blocks of Miscanthus X Giganteus using 3 treatment levels (0, 50, and 100%), where 100% represented the maximum load permissible based on sludge-spreading regulations SI 148 (DoE, 1998). GW was sampled monthly from GW wells in each of the treatment blocks. Samples were filtered and concentrations of nutrients N, P, and K and six major heavy metals (HMs) Cu, Cd, Cr, Pb, Ni, and Zn were determined. Results showed mean (averaged over 23 months) K levels exceeded IGV values on 100% application plots, mean NO₃ levels did not exceed IGVs, and mean P levels exceeded IGV on all BSS blocks (and on the 100% application BW block). Of the HMs studied, mean Pb concentrations regularly exceeded IGVs with highest levels being observed in samples from 100% application blocks. This indicates there may be problems related to GW pollution from the landspreading of these wastes.

Introduction
Land-spreading on bioenergy crops is a possible route for the disposal of organic wastes. However, issues related to GW pollution make research into the environmental impact of these practices a priority. Hazards include the possibility of a decline in GW quality from pollution by HMs and nutrients. The viability of landspreading of BSS and BW was investigated based on the IGVs established by the Irish government (EPA, 2003). These IGVs provide a framework for meeting the targets of the new GW directive from the EU (EC, 2006). This GW directive will be part of the larger Water Framework Directive (WFD) (EC, 2000) that sets the regulatory framework in which water-quality is assessed across the EU.

The objective of this work was to assess the quality of GWs underlying bioenergy crop plantations on which organic wastes were spread. GW quality is discussed in terms of the current IGVs.

Materials and Methods:
Spreading was conducted on an annual basis on established plantations of Miscanthus X Giganteus located in Oak Park, Co. Carlow, Ireland. The plots were 0.12 ha in size and organic wastes were applied at 3 treatment levels: heavy (100%), light (50%) and control (0%). Three plots on the Barley Field (BF) plantation were spread with BW and three on the nearby Near Avenue Meadow (NAM) plantation with BSS. The procedures and upper-limit of spreading were based on regulatory limits set out in S.I. 148 (DoE, 1998) and Teagasc nutrient management guidelines (Teagasc, 2008). BSS waste was spread on the NAM using a towed disc-spreader and BW on the BF using an irrigation system.

Prior to spreading, GW wells were inserted into each plot; 3 wells were placed on treated plots and 1 well on each control plot. Monthly samples were taken for 25 months between Oct 2007 and Oct 2009. Samples collected from plots with multiple wells were bulked before analysis each month. All GW samples were collected in accordance with guidelines published by the US EPA (EPA, 1996).

GW samples were filtered using a Sarstedt 0.45um micropore filter, sent to the Teagasc Water Lab in Johnstown Castle, (Co. Wexford) and analyzed for the major nutrients NO₃, P and K and 6 HMs (Ni, Cd, Pb, Zn, Cu,
and Cr) using atomic absorption spectroscopy. Conductivity and pH analysis were conducted on all samples and monthly rainfall and GW well levels were recorded, (but are not presented here). Nutrient and HM levels were assessed in relation to waste-spreading quantities applied; mean and max concentrations recorded over the 24 month monitoring period and compared with the IGVs for each of the species.

Results and Discussion

Tables 1-6 show the mean and maximum concentrations for three major nutrients N, P and K; for six HMs Cr, Cu, Cd, Zn, Ni, and Pb; as well as pH and conductivity. IGV values for each of these parameters are provided and percentage exceedence of the maximum and mean concentrations is included (the IGV level = 100%). The number of samples where concentrations were higher than IGVs, as well as the total percentage of samples exceeding IGVs, from a total of 23 samples taken from Oct 07 to Aug 2009 is included.

Observed pH and conductivity levels did not exceed IGVs in any case. The mean P, K and Pb, concentration rates were higher than permissible IGVs (Tables 1, 2, 4, 5, 6). In terms of nutrients, concentrations of K and P exceeded limits where 100% and 50% BW was spread (Tables 1 and 2) but not on the control block (Table 3). For the blocks where BSS was spread, the K of 5/mgK/l IGV was exceeded in the 100% application block (Table 4), but not on 50% or 0% blocks (Tables 5, 6). The mean N and P levels were under IGV on all blocks spread with BSS (Tables 4-6).

For HMs on blocks spread with BSS, mean Pb concentrations exceeded IGVs on all blocks (Tables 4-6), though whether this had a link to treatment is unclear. For BSS blocks, the only HM for which mean concentration was significantly higher than IGV was Pb, and this was the case for all blocks regardless of treatment.

For maximum concentration values, more instances occurred where species concentration exceeded the IGV. The observed range between the mean and max concentrations was large in many cases. This demonstrates the variability of the species concentrations being studied. For maximum HMs, significant one-off exceedences were recorded (with Pb again being the most significant pollutant both in terms of the max concentration levels recorded and the number of times where concentration rates exceeded IGVs). HM concentrations in GWs samples from the blocks spread with BSS waste were higher than for the blocks spread with BW. This suggests a possible link between waste treatment level and HM concentration, as the HM concentration of BSS is generally much higher than the HM concentration of BW. In general, the pattern of IGV exceedence indicated that waste treatment level was linked to some observed concentration rates. The level of some species such as Pb and P on control plots were unexpectedly high and more research is required to establish both the significance of the results and the correlation between treatment level and GW concentrations.

Conclusions

Results indicate that some potential pollution issues may arise from the landspreading of organic wastes on bioenergy plantations. In terms of the major nutrients, nitrate concentrations remained within IGV values; however, mean concentrations of P and K were higher than IGV values where wastes were spread. For HMs, only Pb showed consistent exceedence of IGV by mean concentrations and this occurred on all plots (including controls). Concentration variability was high for all blocks, thereby making assessing significance difficult. Mean values were high on control plots for Pb and K concentrations. Based on current results, further work needs to be done to establish the significance of the results presented here and also to establish correlation between treatment levels and species concentration in GW.

Acknowledgements

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Table 5: Summary of ground-water quality data for 0.12 ha block spread with (100 %) Brewer's Waste

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Limit&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Mean&lt;sup&gt;b&lt;/sup&gt;</th>
<th>% limit (mean)&lt;sup&gt;c&lt;/sup&gt;</th>
<th>Max&lt;sup&gt;d&lt;/sup&gt;</th>
<th>% limit (max)&lt;sup&gt;e&lt;/sup&gt;</th>
<th>SE&lt;sup&gt;f&lt;/sup&gt;</th>
<th>% SE&lt;sup&gt;f&lt;/sup&gt;</th>
</tr>
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<tbody>
<tr>
<td>pH</td>
<td>&gt;6.5 -&gt; 9.5</td>
<td>7.80</td>
<td>Na</td>
<td>8</td>
<td>Na</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Cond&lt;sup&gt;f&lt;/sup&gt; (mS/gm3)</td>
<td>1.0</td>
<td>0.583</td>
<td>58</td>
<td>0.780</td>
<td>78</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>NO3 (mg/l)</td>
<td>25</td>
<td>7.0</td>
<td>28</td>
<td>57.7</td>
<td>231</td>
<td>2</td>
<td>8</td>
</tr>
<tr>
<td>K (mg/l)</td>
<td>5</td>
<td>40.8</td>
<td>816</td>
<td>894.6</td>
<td>17893</td>
<td>8</td>
<td>32</td>
</tr>
<tr>
<td>P (mg/l)</td>
<td>0.03</td>
<td>0.048</td>
<td>160</td>
<td>0.427</td>
<td>1423</td>
<td>4</td>
<td>16</td>
</tr>
<tr>
<td>Cd (ug/l)</td>
<td>5</td>
<td>1.4</td>
<td>29</td>
<td>13.5</td>
<td>271</td>
<td>2</td>
<td>8</td>
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<tr>
<td>Cr (ug/l)</td>
<td>30</td>
<td>2.2</td>
<td>7</td>
<td>12.9</td>
<td>43</td>
<td>0</td>
<td>0</td>
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<tr>
<td>Cu (ug/l)</td>
<td>30</td>
<td>16.3</td>
<td>54</td>
<td>85.4</td>
<td>285</td>
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<td>12</td>
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<tr>
<td>Pb (ug/l)</td>
<td>10</td>
<td>42.7</td>
<td>427</td>
<td>356.3</td>
<td>3563</td>
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<td>28</td>
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<tr>
<td>Ni (ug/l)</td>
<td>20</td>
<td>9.9</td>
<td>50</td>
<td>175.1</td>
<td>875</td>
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<td>4</td>
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<tr>
<td>Zn (ug/l)</td>
<td>100</td>
<td>13.5</td>
<td>14</td>
<td>154.9</td>
<td>155</td>
<td>1</td>
<td>4</td>
</tr>
</tbody>
</table>

(1) (EPA, 2003); <sup>b</sup>Mean recorded value; <sup>c</sup>Mean as % of limit; <sup>d</sup>Maximum recorded value; <sup>e</sup>Max as % of limit; <sup>f</sup>Samples (i.e. months) in exceedence; <sup>g</sup>Conductivity.

Table 6: Summary of ground-water quality data for 0.12 ha block spread with (50 %) Brewer's Waste

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Limit&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Mean&lt;sup&gt;b&lt;/sup&gt;</th>
<th>% limit (mean)&lt;sup&gt;c&lt;/sup&gt;</th>
<th>Max&lt;sup&gt;d&lt;/sup&gt;</th>
<th>% limit (max)&lt;sup&gt;e&lt;/sup&gt;</th>
<th>SE&lt;sup&gt;f&lt;/sup&gt;</th>
<th>% SE&lt;sup&gt;f&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>&gt;6.5 -&gt; 9.5</td>
<td>7.80</td>
<td>Na</td>
<td>8</td>
<td>Na</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Cond&lt;sup&gt;f&lt;/sup&gt; (mS/gm3)</td>
<td>1</td>
<td>0.524</td>
<td>52</td>
<td>0.72</td>
<td>72</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>NO3 (mg/l)</td>
<td>25</td>
<td>4.9</td>
<td>19</td>
<td>27.2</td>
<td>109</td>
<td>1</td>
<td>4</td>
</tr>
<tr>
<td>K (mg/l)</td>
<td>5</td>
<td>8.7</td>
<td>173</td>
<td>74.2</td>
<td>1484</td>
<td>9</td>
<td>36</td>
</tr>
<tr>
<td>P (mg/l)</td>
<td>0.03</td>
<td>0.18</td>
<td>14</td>
<td>0.042</td>
<td>9483</td>
<td>4</td>
<td>16</td>
</tr>
<tr>
<td>Cd (ug/l)</td>
<td>6</td>
<td>1.5</td>
<td>30</td>
<td>11.9</td>
<td>238</td>
<td>2</td>
<td>8</td>
</tr>
<tr>
<td>Cr (ug/l)</td>
<td>30</td>
<td>2.1</td>
<td>7</td>
<td>12.2</td>
<td>41</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Cu (ug/l)</td>
<td>30</td>
<td>13.1</td>
<td>44</td>
<td>33.6</td>
<td>112</td>
<td>4</td>
<td>16</td>
</tr>
<tr>
<td>Pb (ug/l)</td>
<td>10</td>
<td>42.2</td>
<td>427</td>
<td>356.3</td>
<td>3563</td>
<td>7</td>
<td>28</td>
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<tr>
<td>Ni (ug/l)</td>
<td>20</td>
<td>16.5</td>
<td>83</td>
<td>208.2</td>
<td>1041</td>
<td>4</td>
<td>16</td>
</tr>
<tr>
<td>Zn (ug/l)</td>
<td>100</td>
<td>4.8</td>
<td>5</td>
<td>22.4</td>
<td>22</td>
<td>4</td>
<td>16</td>
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</tbody>
</table>

<sup>a</sup>-<sup>g</sup>See Table 1 footnote

Table 7: Summary of ground-water quality data for 0.12 ha block spread with (0 %) Brewer's Waste

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Limit&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Mean&lt;sup&gt;b&lt;/sup&gt;</th>
<th>% limit (mean)&lt;sup&gt;c&lt;/sup&gt;</th>
<th>Max&lt;sup&gt;d&lt;/sup&gt;</th>
<th>% limit (max)&lt;sup&gt;e&lt;/sup&gt;</th>
<th>SE&lt;sup&gt;f&lt;/sup&gt;</th>
<th>% SE&lt;sup&gt;f&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>&gt;6.5 -&gt; 9.5</td>
<td>7.70</td>
<td>Na</td>
<td>8.1</td>
<td>Na</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Cond&lt;sup&gt;f&lt;/sup&gt; (mS/gm3)</td>
<td>1</td>
<td>0.465</td>
<td>46</td>
<td>0.730</td>
<td>73</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>NO3 (mg/l)</td>
<td>25</td>
<td>8.7</td>
<td>35</td>
<td>104.2</td>
<td>417</td>
<td>1</td>
<td>4</td>
</tr>
<tr>
<td>K (mg/l)</td>
<td>5</td>
<td>8.7</td>
<td>173</td>
<td>74.2</td>
<td>1484</td>
<td>9</td>
<td>36</td>
</tr>
<tr>
<td>P (mg/l)</td>
<td>0.03</td>
<td>0.004</td>
<td>14</td>
<td>0.042</td>
<td>9483</td>
<td>4</td>
<td>16</td>
</tr>
<tr>
<td>Cd (ug/l)</td>
<td>6</td>
<td>0.7</td>
<td>15</td>
<td>5.4</td>
<td>107</td>
<td>1</td>
<td>4</td>
</tr>
<tr>
<td>Cr (ug/l)</td>
<td>30</td>
<td>1.5</td>
<td>5</td>
<td>5.6</td>
<td>19</td>
<td>0</td>
<td>0</td>
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<tr>
<td>Cu (ug/l)</td>
<td>30</td>
<td>8.0</td>
<td>27</td>
<td>26.2</td>
<td>87</td>
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<td>0</td>
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<tr>
<td>Pb (ug/l)</td>
<td>10</td>
<td>48.8</td>
<td>488</td>
<td>367.7</td>
<td>3677</td>
<td>6</td>
<td>24</td>
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<td>Ni (ug/l)</td>
<td>20</td>
<td>13.9</td>
<td>70</td>
<td>238.9</td>
<td>1194</td>
<td>1</td>
<td>4</td>
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<tr>
<td>Zn (ug/l)</td>
<td>100</td>
<td>3.1</td>
<td>3</td>
<td>12.0</td>
<td>12</td>
<td>1</td>
<td>4</td>
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</tbody>
</table>

<sup>a</sup>-<sup>g</sup>See Table 1 footnote

Table 4: Summary of ground-water quality data for 0.12 ha block spread with (100 %) biosolid sludge

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Limit&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Mean&lt;sup&gt;b&lt;/sup&gt;</th>
<th>% limit (mean)&lt;sup&gt;c&lt;/sup&gt;</th>
<th>Max&lt;sup&gt;d&lt;/sup&gt;</th>
<th>% limit (max)&lt;sup&gt;e&lt;/sup&gt;</th>
<th>SE&lt;sup&gt;f&lt;/sup&gt;</th>
<th>% SE&lt;sup&gt;f&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>&gt;6.5 -&gt; 9.5</td>
<td>7.70</td>
<td>Na</td>
<td>8.1</td>
<td>Na</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Cond&lt;sup&gt;f&lt;/sup&gt; (mS/gm3)</td>
<td>1</td>
<td>0.538</td>
<td>54</td>
<td>0.800</td>
<td>80</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>NO3 (mg/l)</td>
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<td>8.7</td>
<td>35</td>
<td>74.2</td>
<td>297</td>
<td>1</td>
<td>4</td>
</tr>
<tr>
<td>K (mg/l)</td>
<td>5</td>
<td>8.7</td>
<td>173</td>
<td>74.2</td>
<td>1484</td>
<td>9</td>
<td>36</td>
</tr>
<tr>
<td>P (mg/l)</td>
<td>0.03</td>
<td>0.14</td>
<td>474</td>
<td>2.85</td>
<td>9483</td>
<td>4</td>
<td>16</td>
</tr>
<tr>
<td>Cd (ug/l)</td>
<td>5</td>
<td>1.5</td>
<td>31</td>
<td>17.9</td>
<td>358</td>
<td>2</td>
<td>8</td>
</tr>
<tr>
<td>Cr (ug/l)</td>
<td>30</td>
<td>4.0</td>
<td>13</td>
<td>16.7</td>
<td>56</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Cu (ug/l)</td>
<td>30</td>
<td>11.2</td>
<td>37</td>
<td>57.8</td>
<td>193</td>
<td>2</td>
<td>8</td>
</tr>
<tr>
<td>Pb (ug/l)</td>
<td>10</td>
<td>33.6</td>
<td>336</td>
<td>445.0</td>
<td>4450</td>
<td>7</td>
<td>28</td>
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<tr>
<td>Ni (ug/l)</td>
<td>20</td>
<td>11.5</td>
<td>57</td>
<td>62.5</td>
<td>312</td>
<td>2</td>
<td>8</td>
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<tr>
<td>Zn (ug/l)</td>
<td>100</td>
<td>8.4</td>
<td>8</td>
<td>62.5</td>
<td>62</td>
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<td>8</td>
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<sup>a</sup>-<sup>g</sup>See Table 1 footnote
Table 5: Summary of ground-water quality data for 0.12 ha block spread with (50 %) biosolid sludge

<table>
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<tr>
<th>Parameter</th>
<th>Limit a</th>
<th>Mean b</th>
<th>% limit (mean) c</th>
<th>Max d</th>
<th>% limit (max) e</th>
<th>SE f</th>
<th>% SE</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>&gt;6.5 &gt;9.5</td>
<td>7.7</td>
<td>Na</td>
<td>8.1</td>
<td>na</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Cond (mS/gm3)</td>
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<td>53</td>
<td>0.730</td>
<td>73</td>
<td>0</td>
<td>0</td>
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<tr>
<td>NO3 (mg/l)</td>
<td>25</td>
<td>6.2</td>
<td>25</td>
<td>22.7</td>
<td>91</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>K (mg/l)</td>
<td>5</td>
<td>1.0</td>
<td>20</td>
<td>3.0</td>
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<td>0</td>
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<td>P (mg/l)</td>
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<td>0.061</td>
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<td>11</td>
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<td>Cr (ug/l)</td>
<td>30</td>
<td>1.7</td>
<td>6</td>
<td>4.6</td>
<td>15</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Cu (ug/l)</td>
<td>30</td>
<td>8.1</td>
<td>27</td>
<td>49.1</td>
<td>164</td>
<td>1</td>
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<td>Pb (ug/l)</td>
<td>10</td>
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<td>4436</td>
<td>5</td>
<td>20</td>
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<tr>
<td>Ni (ug/l)</td>
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<td>152.9</td>
<td>764</td>
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<tr>
<td>Zn (ug/l)</td>
<td>100</td>
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<td>5</td>
<td>35.4</td>
<td>35</td>
<td>1</td>
<td>4</td>
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</table>

See Table 1 footnote

Table 6: Summary of ground-water quality data for 0.12 ha block spread with (0 %) biosolid sludge

<table>
<thead>
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<th>Parameter</th>
<th>Limit a</th>
<th>Mean b</th>
<th>% limit (mean) c</th>
<th>Max d</th>
<th>% limit (max) e</th>
<th>SE f</th>
<th>% SE</th>
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</thead>
<tbody>
<tr>
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<td>&gt;6.5 &gt;9.5</td>
<td>7.7</td>
<td>Na</td>
<td>8.3</td>
<td>na</td>
<td>0</td>
<td>0</td>
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<tr>
<td>Cond (mS/gm3)</td>
<td>1</td>
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<td>73</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>NO3 (mg/l)</td>
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<td>26</td>
<td>78.3</td>
<td>313</td>
<td>2</td>
<td>8</td>
</tr>
<tr>
<td>K (mg/l)</td>
<td>5</td>
<td>1.2</td>
<td>25</td>
<td>4.9</td>
<td>98</td>
<td>0</td>
<td>0</td>
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<tr>
<td>P (mg/l)</td>
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<td>0.051</td>
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<td>16</td>
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<td>Cd (ug/l)</td>
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<td>95</td>
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<td>0</td>
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<td>Cr (ug/l)</td>
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<td>10</td>
<td>19.0</td>
<td>63</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Cu (ug/l)</td>
<td>30</td>
<td>8.7</td>
<td>29</td>
<td>40.7</td>
<td>136</td>
<td>2</td>
<td>8</td>
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<tr>
<td>Pb (ug/l)</td>
<td>10</td>
<td>12.5</td>
<td>125</td>
<td>149.1</td>
<td>1491</td>
<td>5</td>
<td>20</td>
</tr>
<tr>
<td>Ni (ug/l)</td>
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<td>13.4</td>
<td>67</td>
<td>161.6</td>
<td>808</td>
<td>2</td>
<td>8</td>
</tr>
<tr>
<td>Zn (ug/l)</td>
<td>100</td>
<td>5.1</td>
<td>5</td>
<td>39.7</td>
<td>40</td>
<td>2</td>
<td>8</td>
</tr>
</tbody>
</table>

See Table 1 footnote

References


OPTIMIZATION OF EXTRACTION METHOD AND CHROMATOGRAPHY CONDITIONS FOR THE NON–POLAR FUNGICIDE CHLOROTHALONIL

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1 UCD School of Agriculture, Food Science and Veterinary Medicine (Biosystems Engineering), University College Dublin, Belfield, Dublin 4
2 Teagasc, Johnstown Castle, Wexford

Abstract
An analytical method for non-polar fungicide using gas chromatography with electron capture detection (GC-ECD) was optimised. The limit of detection (LOD) achieved was 5 ppb and the mean method recovery was 97.3% (SD ± 9.1). A solid phase extraction (SPE) of chlorothalonil from a water matrix was developed. The mean recovery was 79.4% (SD ± 6.1).

Introduction
Chlorothalonil (2, 4, 5, 6- tetrachloro-1, 3–benzenedicarbonitrile) is an organochlorine, non-polar, non–systematic foliar fungicide, applied for the control of fungal diseases in different commodities, including agricultural crops, turf and ornaments (Tomlin, 2006). In Ireland, chlorothalonil can be applied to arable crops at 2000 g/ha active substance and between 3000 – 12000 g/ha to vegetables and fruits. The most common plant protection product used in Ireland is Bravo 500 with 500 g/L active substance. The transport and toxicity of chlorothalonil is of concern, especially in aquatic systems since it is considered “very highly toxic” to fish and invertebrates with acute toxicity levels of 10 – 80 µg/L (Caux et al., 1996). Some properties and characteristics of chlorothalonil are presented in Table 1.

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular formula</td>
<td>C₈Cl₄N₂</td>
</tr>
<tr>
<td>Molecular weight</td>
<td>265.9</td>
</tr>
<tr>
<td>Melting point (°C)</td>
<td>252.1</td>
</tr>
<tr>
<td>Vapour pressure (mPa at 25 °C)</td>
<td>0.076</td>
</tr>
<tr>
<td>Henry constant (Pa m³ mol⁻¹ at 25 °C)</td>
<td>2.50 x 10⁻²</td>
</tr>
<tr>
<td>Water solubility (mg/L at 25 °C)</td>
<td>0.61</td>
</tr>
<tr>
<td>Structural formula:</td>
<td><img src="image" alt="Structural formula" /></td>
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</table>

Conventionally pesticides are extracted and pre-concentrated from aqueous media using liquid – liquid extraction (LLE) before gas chromatographic determination (USEPA 508.1). The LLE employs large amount of toxic solvents and is time consuming. An alternative approach is to use off - line solid phase extraction (SPE) that offers shorter extraction time, lower cost and the consumption of low volumes of organic solvents. Normal phase or reversed phase SPE cartridges are available commercially to extract pesticides from aqueous samples but they require a suitable elution solvent and pH for extraction. There is not much information in the literature on extraction methods for chlorothalonil from aqueous samples, but Oasis HLB cartridges followed by sample acidification (Chaves, 2008) and AccuBOND C-18 cartridges (Agilent application notes) have been used. The objective of this study was to establish the best solid phase extraction procedure for chlorothalonil from...
aqueous samples and to optimize chromatography conditions for its quantification using GC-ECD.

Materials and Methods

Chemicals
Chlorothalonil as an analytical grade (97.5% purity) was obtained from Dr. Ehrenstorfer GmbH, Germany. The grade was used to prepare stock solutions of chlorothalonil in three different solvents: isooctane, methanol and n-hexane in order to select the best solvent for the GC performance. A chlorothalonil standard (98.9 % purity, 100µg/mL; AccuStandard, New Haven, USA) was also obtained. All solvents used were pure analytical GC grade solvents (Pestiscan, Lab Scan) and had a purity at least of 99.5 %. Isopropanol (2-propanol) was purchased from Sigma-Aldrich and had purity above 99.8%. All stock solutions were kept in amber glass flasks and stored below -20°C. All aqueous samples were prepared in MQ water (Millipore, USA).

Solid phase extraction method development
The LLE published in the standard method (USEPA 508.1) was replaced with solid phase extraction (SPE). The extraction procedure was performed using a vacuum manifold (Phenomenex) attached to a vacuum pump (Laboport, 240 mbar abs). The SPE cartridges used were 60 mg/ 3 mL polymeric reversed phase Strata X (Phenomenex). The advantage of Strata X was it could be used with any solvent for elution step and there was no sample pH dependency. This facilitated the overall extraction procedure and reduced additional analytical cost.

Water samples (25 mL) were spiked with chlorothalonil stock (500 ng/mL) prepared in methanol. The sample concentrations were 5 ng/mL. Methanol was used due to the low solubility of chlorothalonil in water (0.61 mg/L at 25 °C) and also because is miscible with aqueous media. For all extractions, methanol (2 mL) was applied for conditioning and MQ water (2mL) for equilibration at flow rates at 6 mL/min. Samples were loaded at a flow rate of about 2 mL/min and washed with MQ water (2mL) at the same rate. Drying time (10, 15 and 40 min), elution solvent (isooctane, isooctane + 2 – propanol) and elution volumes (2 mL and 4 mL) were tested to obtained acceptable (70 – 110 %) recoveries and good GC performance. The flow rate for elution was 1 mL/min.

GC instrumentation
A Varian CP – 3800 gas chromatograph (GC) equipped with an electron capture detector (ECD) was used. The instrument was also equipped with an autosampler (CP-8400) and a capillary column ZB-MR2 (CL Pesticide Proprietary Phase), 30m x 0.32mm i.d., film thickness 0.25 µm (Phenomenex). Helium was used as carrier gas and nitrogen was the make-up gas supplied by a N2 generator (Dominick Hunter).

GC method comparison, optimization and separation check for non-polar pesticides
The ZB-MR2 column was tested with a standard USEPA 508.1 method and a method similar to one provided by Phenomenex (GC application notes). The method by Phenomenex used on-column injection of 1µL at 123 ºC to avoid fast decomposition and volatilisation of chlorothalonil with the ECD temperature of 340 ºC. Due to the lack of on-column module, the method by Phenomenex was optimised. The oven temperature programme was 120 ºC held for 0.5 min to 210 ºC with no hold, then at 30 ºC/min to 300 ºC with no hold and at 6 ºC/min held for 2 min; the flow rate was 1.2 mL/min, giving a total reaction time of 20.50 min. The injector temperature was set at 250 ºC. The modifications were made to detector temperatures (300, 320 and 340 ºC), injection type (split/splitless), sample volume (1 and 2 µL), detector range (1 and 10) and solvent type (isooctane, methanol, n-hexane). Recoveries from the methods were calculated at 2 standard concentrations (50 and 100 µg/L) in 3 replicates. The USEPA standard method (508.1) injection volume was 2 µL, injected as splitless for 45 seconds at injector temperature of 250 ºC and 320 ºC detector temperature. The oven temperature programme stared at 40 ºC
held for 1 min and after raised at 20 °C/min to 160 °C held for 3 min, at 3 °C/min to 275 °C with no hold and after at 20 °C/min to 310 °C with no hold at flow rate of 1.2 ml/min, giving the total reaction time of 50.08 min.

Results and Discussion

Solid phase extraction method
The best recoveries were obtained when eluting with a mixture of 2-propanol + isoctane (200 µL alcohol + 800 µL solvent) in 2 loads and 1000 µL of isoctane in additional 2 loads (4 ml total elution) with drying step of 10 min. Mean extraction recovery was 79.4% and SD ± 6.1 (n = 7). In comparison, the elution with 2 mL (200 µL alcohol + 800 µL isoctane and 1000 µL isoctane) gave recovery of 56.1 % and SD ± 7.0 (n = 7) when drying at 10 min. The GC performance of extracted sample is shown in Figure 1.

Table 2 Results of recovery experiment

<table>
<thead>
<tr>
<th>Concentration (µg/L)</th>
<th>Detector (ºC)</th>
<th>Recovery (%) mean ±SD, n=3</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>300</td>
<td>92.9 ± 8.9</td>
</tr>
<tr>
<td>50</td>
<td>320</td>
<td>91.9 ± 7.5</td>
</tr>
<tr>
<td>50</td>
<td>340</td>
<td>106.3 ± 6.8</td>
</tr>
<tr>
<td>100</td>
<td>300</td>
<td>103.5 ± 6.9</td>
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<td>100</td>
<td>320</td>
<td>102.7 ± 7.9</td>
</tr>
<tr>
<td>100</td>
<td>340</td>
<td>110.4 ± 10.9</td>
</tr>
</tbody>
</table>

Method comparison
Both methods provided good separation of chlorothalonil on the ZB-MR2 column, although the “optimised” method had a shorter reaction time which reduced the overall time required for sample analysis. The retention of chlorothalonil with the optimised method was 7.162 min and the retention time with the standard 508.1 method was 24.886 min (Figure 5).

GC method performance
Isooctane appeared to be the best solvent for chlorothalonil separation (Figure 2) in comparison to i.e. n-hexane which gave very unclear baseline and high noise (Figure 3). The best baseline and low noise was obtained in detector range 10 (Figure 4, a) but it reduced the sensitivity of the ECD. Better detector sensitivity was achieved in range 1 (Figure 4, b and c) combined with detector temperature of 340 °C that reflected in method recovery (Table 2) but the noise became higher, bringing difficulties to quantitative measures of chlorothalonil in samples injected as extracts, and thus the “optimised” method was set as follows: sample injection volume of 1 µL injected as splitless for 75 seconds at 250 °C injector and 320 °C detector temperatures. Although, all recoveries gained (Table 2) were in acceptable range.

Figure 1 82.3 % recovery of sample injected (62.5 ng/mL) to the GC-ECD with the “optimised” method

Figure 2 Chlorothalonil run with “optimised” method. Concentrations at 50 (µg/L) and 100 (µg/L) in isoctane
Figure 3 n-hexane run at 250 °C injector and 340 °C detector temperatures

Figure 4 Isooctane run in range 10 (a) and 1 at 300 °C (b) and 320 °C (c) detector temperatures

Figure 5 “Optimised” (a) and standard USEPA 508.1 method (b) performance. Concentration 400 (µg/L)

Conclusions
The SPE extraction method from the aqueous samples was successful and can be used for chlorothalonil in an aqueous matrix. This approach reduced the expected analytical cost and the consumption of organic solvents. The optimised GC method could separate chlorothalonil without use of an on-column module. Isooctane gave the best performance and thus will be used for future GC-ECD analysis.

Acknowledgements
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Authors also wish to acknowledge Elementec Ltd (Ireland) for GC technical support and Phenomenex (UK) for free samples of Strata X for method testing.

References


Appendix 1
(Research projects in progress which have not been included in the Research Review)


Askari M and N Holden. Hyperspectral Sensing of Soil Properties for Soil Resources Management (PhD)


Bergin D, U G Barron and F Butler. A meta analysis of the effect of chilling on prevalence of salmonella spp on pig carcasses (PhD) SafeFood, The food Safety Promotion Board/Food Institutional Research Measure (FIRM)

Deverell R, K McDonnell. A review of bioethanol fiscal support strategies (PhD) Irish Department of Agriculture, Fisheries and Food /Research Stimulus Fund

Doyle P and F Butler. Utility of HACCP to minimise risk of pathogenic bacteria in farm milk (PhD)

Emenike A and C O'Donnell. Predicting Irish wheat quality characteristics using near infrared spectroscopy (PhD). Teagasc Walsh fellowship

Farrell L and T P Curran. Raw material impact on condensate production within an animal rendering facility as predicted using neural network forecasting (PhD) Enterprise Ireland Innovation Partnership/College Proteins

Hennessy M and N M Holden Development of a Farm Scale Sustainable Nutrient Management Decision Support System (PhD) Irish Department of Agriculture, Fisheries and Food /Research Stimulus Fund

Herbin T and N Holden. Effects of dairy technology management on soil structure and nitrogen content (PhD) Irish Environmental Protection Agency

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.

Lynch D, B Bowen and K McDonnell. On farm combustion and energy recovery from poultry litter (MAgriSe) Department of Agriculture, Fisheries and Food


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
Prieto Lage M A, J Bartlett and T Curran. Sustainable Water Supply and Consumption in County Sligo (MSc) Sligo County Council

Soumpasis I and F Butler. Deterministic and stochastic simulation of a filed experiment on salmonella typhimurium propagation at pig farms (PhD) Qporkchains, EU 6th Framework project.

Valous N A, F Mendoza and D W Sun. Characterisation of visual texture of pork ham images using normalised lacularity (PhD) Food Institutional Research Measure (FIRM) as administered by the Irish Department of Agriculture, Fisheries and Food.

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
Appendix 2

(Profiles of Postdoctoral Research Scholars only includes: Dr Gonzales Barron, Mr. Bowen, Drs Connolly, Delgado, Devlin, ElMasry, Everard, Fagan, Gowan, Li, Mendoza, O’Rourke, Redmond, Shanahan, Tansey, Tang, Woodcock, Zhang).

Ursula Andrea Gonzales-Barron, BSc, Eng, PhD

Project Title: Microbial Risk Assessment Network of Ireland

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

Abstract:

Current poultry litter management practices are seen as unsustainable and alternative solutions are required. This project is addressing some outstanding regulatory and technical issues required to overcome problems encountered by waste management problems through the combustion of poultry litter. The project will determine the litter fuel quality and optimise combustion through the monitoring of flue gas emissions including potential for dioxin formation. This will facilitate establishment of best practices to meet the regulatory requirements of Integrated Pollution Control (IPC) licensing. The project will optimize the thermal efficiency and reduce maintenance requirements by matching heat exchanger output with heat load and through the use of buffer tanks. The monitoring of flue gas emissions including dioxin, building a dispersion model based on local topography and meteorology which will be included in an environmental impact study to assist compliance national IPC regulations. Funded by the Department of Agriculture, Fisheries and Food, this project is been carried out in conjunction with University of Limerick (UL). UCD’s responsibilities for this project are focused on the development of a dispersion model to predict pollutants, risk assessment of storage and management practices and the assessment of health and welfare for the birds and local environment.

Background, skills and Qualifications:

My thesis examined the crucial areas that were involved in the installation of a 1MW biomass boiler in UCD. Through monitoring the plans revolving around the installation of the boiler a computer program was designed and produced to aid decision making for similar projects. The computer program also doubled up as a decision support system for domestic users examining the possibility of converting to indirect (biomass) heating applications.

Through my involvement in the Bioresources Research Centre (BRC), I was editor of the BRC Energy and Commodities Bulletin and also update the BRC website regularly.

Recent Research:


Project Title: Mapping, Assessment and Quantification of the effects disturbance on the peat soil C stock in Ireland

Project Leader: Professor Nicholas Holden and co PI Dr. John Connolly

Abstract
Peatlands in Ireland contain between 53 % and 62 % of the national soil carbon (C) stock. Many peatlands throughout the country have been and are currently disturbed. Peatland disturbance impacts on the resource’s ability to sequester C. It is essential that disturbance of peatlands be examined and quantified in order to manage this critical C resource. This project will use high resolution satellite imagery along with ground based indicators to develop a method to quantify the effect of disturbance and climate change on peatland C stock. This research will enable policymakers to identify critical peatland areas requiring management intervention.

Background, Skills & Qualifications
Since January 2007, I have been employed as a post doctoral researcher in the Bioresources Research Centre in Biosystems Engineering. My main interests lie in the application of GIS and remote sensing to examine the interaction between terrestrial ecosystems and the atmosphere and the assessment of terrestrial carbon pools and their sensitivity to climate change. I am currently examining ways to determine the extent and severity of disturbance to the peatland carbon pool in Ireland, funded by an EPA STRIVE Postdoctoral Fellowship. My PhD. focused on using GIS for mapping the spatial extent of peatlands in Ireland and using remote sensing to examine various biophysical parameters associated with peatlands. In 2001 I completed a M.Sc. (Geography) at the University of Sheffield. The focus of that work was on the environmental monitoring and assessment of dryland environments. My Bachelors degree was in Arts (Geography) within this degree I primarily focused on physical and environmental geography.

Grants
- EPA STRIVE Doctoral Scholarship: Remote sensing of grasslands for evaluating compliance with key environmental legislation (£95,000)
- EPA STRIVE Post Doctoral Research Fellowship: Identification, mapping assessment and quantification of the effects disturbance on the peat soil C stock in Ireland (£277,664)
- EPA STRIVE Doctoral Scholarship: Assessing and monitoring vegetation disturbance on Irish peatlands using satellite remote sensing (£95,000)

Recent publications
Adriana Delgado, Eng., M.Sc., PhD

Project Title: Method for improving the quality of frozen foods by assisting the freezing process and reducing the size of the ice crystals (MINICRYSTAL).

Project Leader: Professor Da-Wen Sun

Abstract
Past research has shown that high power ultrasound (HPU) can initiate ice nucleation and control crystal size distribution during the freezing process, leading to frozen products of better quality. As quality issues take increasing precedence among EU consumers, a key challenge facing frozen food manufacturers is how to reposition their frozen products so consumers can consider them as health-friendly and also of good quality. In response, this project will design and develop a prototype HPU system for its industrial validation in food freezing facilities. It will be cost-effective and easy to operate and easily integrated with commercially available freezing equipment.

Background, Skills & Qualifications
After obtaining a degree in Food Engineering I was working in the Institute of Technological Development for the Chemical Industry (INTEC, Santa Fe, Argentina), from 1986 to 1998. From 1988 to 1989 I attended a course in the Economy of Agricultural and Food Systems in Viterbo (Italy), and joined INTEC later, after completion of this course. When working in INTEC I was involved in projects related to the preservation of fruits and vegetables by freezing, took part as lecturer in undergraduate and postgraduate courses and obtained a Master in Food Technology in 1997. In 1999 I came to Ireland to pursue doctoral studies. From 2002 to 2004 I was working as research officer in a joint project between the Ashtown Food Research Centre and UCD related to the use of chilling in HACCP systems for beef. In 2005 I completed the PhD degree in Biosystems Engineering Department, UCD, and since then I am working as postdoctoral researcher.

Recent Publications
Dr. Ger J Devlin, BSc., PhD.

Project Title: GIS Feedstock Energy Mapping (GIS FM) and Optimal Route Biomass Logistics (Bio Trans)

Project Leader: Dr. Kevin McDonnell

Abstract
ArcLogistics Routing is a platform for complementing FITPAC model to model routes for biomass for transportation, optimal supply chain logistics, annual variations in crop responses/yields, crop quality, physical location of supplies and end-users, transport routes (their quality, and extent), transport costs, LCA and sustainability.

Background, Qualifications and Skills
Obtained primary BSc. in Applied Physics from Dublin City University in 2001. In 2007 was awarded my PhD degree from the Department of Biosystems Engineering, UCD. The project to date addresses the issues of incorporating technology advancements into the haulage sector for increased efficiency in terms of revenue per km VS cost per km. From his recent appointment as Charles Parsons research fellow, Dr Devlin's other research interests also include the monitoring and modelling of exhaust emissions from articulated trucks together with engine, driver and fuel performance within the area of increased GHG emissions in the transport sector in Ireland. The core area of research involves using GIS and Remote Sensing for Feedstock Energy Mapping (GIS FM) and the logistical economic assessments in the supply chain of biomass feedstocks and the carbon footprint of such an optimised logistical haulage sector. Dr. Devlin also teaches the module "Alternative Biofuels and Renewable Energies" in conjunction with Dr. Kevin McDonnell.

Peer-reviewed Publications
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 will be working in Biosystems Engineering Department, UCD, as a postdoctoral researcher under the guidance of Prof. Da-Wen Sun.

Selected Peer reviewed journal articles


Colm Everard, B.Eng., PhD

**Project Title:** Development of non-destructive sensors for optimisation of biofuel production.

**Project Leaders:** Dr. Colette Fagan and Dr Kevin McDonnell

**Abstract**

The objective of this project is to develop rapid, non-destructive, on-line sensors which could be used to optimise production of biofuel pellets from agricultural biomasses and residues, such as spent brewer’s grain. Optimisation of the production process and greater consistency in final product quality will assist in the uptake of such biofuels and in particular those from novel sources such as industrial waste biomass. Sensing technologies, near infrared spectroscopy and hyperspectral imaging will be developed to characterise incoming raw material (biomass) and outgoing final product, and elucidate the relationship between biomass quality, processing parameters and final quality. If biofuel production from novel agricultural biomasses and residues is to be optimised this fundamental information is required. Successful development of a sensor technology that is able to control pellet production would have a significant impact on product quality and consistency and hence play a role in achieving the goals of a low-carbon, high-efficiency and sustainable biomass-to-energy system.

**Background, Skills & Qualifications**

I obtained a BE in Biosystems Engineering at University College Dublin. My PhD thesis, concerning the determination of quality characteristics of process and Cheddar cheeses using rheological, sensory and dielectric measurement techniques, was completed in 2005 under the supervision of Dr. Colm O’Donnell, Biosystems Engineering, UCD and Dr. Donal O’Callaghan, Teagasc, Moorepark Food Research Centre. I spent three years as a research officer with Teagasc (Moorepark Food Research Centre) developing cheese syneresis control technologies for improved product consistency. These control technologies included in-line and on-line mid infrared, near infrared and computer vision sensor systems for process control. Presently I am working within the Bioresources Research Centre (BRC) continuing my research in process analytical technologies (PAT). The aims of this research are to develop non-destructive sensors for the optimisation of biofuel production from novel sources of agricultural biomasses and residues with the ultimate objective of increasing the contribution of biomass to the energy supply of Ireland and the EU.

**Recent Peer-reviewed Publications**

Colette Fagan, BSc, MSc(Agr), PhD.

Project Title: Environmental impact assessment of biomass-to-energy systems

Project Leaders: Prof. Shane Ward and Dr. Kevin McDonnell

Abstract
Holistic assessments of energy balances associated with biomass utilisation systems are required which take account of issues such as agricultural production systems and land-use change impacts. Rapid sensing techniques could assist in the reduction and assessment of the environmental impact of biomass-to-energy (B2E) systems. Conversion of B2E is influenced by the type of feedstock, its physical characteristics and chemical composition. Energy crops and agricultural residues are inherently heterogeneous. Robust analytical methods are therefore required to support/enable and optimize B2E conversion processes. The development of rapid sensing technologies for in-field feedstock characterisation, feedstock monitoring during storage and environmental impact assessment of B2E should increase overall conversion efficiency, reduce environmental impacts and enhance process reliability.

Background, Skills & Qualifications
I graduated in 2002 from the Faculty of Science, UCD with a BSc(Hons) in Industrial Microbiology and in 2003 from the Faculty of Agriculture, UCD with a MSc(Agr) in Engineering Technology. My PhD in Biosystems Engineering, concerning the development of process analytical technology (PAT) tools to improve control of key processing steps in cheese manufacture, was awarded in May 2007 by UCD. It involved the development of PAT tools (infrared, dielectric spectroscopy, computer vision and image analysis) in conjunction with multivariate data analysis for quality characterization and process control of cheese manufacture. Following my PhD I took up a postdoctoral position in Biosystems Engineering (2006-2008) working on the development of a NIR sensor for control of syneresis during cheese processing. I joined the UCD Bioresources Research Centre in 2008 as a Charles Parsons Research Fellow working in the area of sustainable utilisation of bioresources, with a particular focus on environmental impact assessment of B2E systems.

Peer-reviewed Publications
Aoife Gowen, BA M.Sc., PhD

**Project Title:** Hyperspectral imaging system for the non-destructive assessment of mushroom quality and shelf-life prediction

**Project Leader:** Dr. Colm O’Donnell

**Abstract**

Hyperspectral imaging (HSI) combines conventional imaging and spectroscopy to simultaneously acquire both spatial and spectral information from an object. This technology has recently emerged as a powerful process analytical tool for rapid, non-contact and non-destructive food analysis. In this study, the potential application of HSI, combined with novel multivariate analysis and image processing techniques, is investigated for damage detection and shelf life prediction of white mushrooms (*Agaricus bisporus*). The aim of this work is the development of a non-destructive shelf life monitoring system to identify sub-standard mushroom batches in the logistic chain.

**Background, Qualifications and Skills**

I joined UCD in 2007 as a postdoctoral fellow, working on hyperspectral imaging for nondestructive assessment of food quality. My main research interest is the application and development of multivariate analysis and image processing techniques for hyperspectral image data mining. I obtained a PhD from the Dublin Institute of Technology in 2006 for my work concerning the development of quick-cook legumes using innovative processing techniques, such as combined microwave-hot air dehydration. This work included development of nonlinear models to predict the effects of hydration and dehydration processes on legume quality characteristics. Prior to this I worked as a Clinical Imaging Scientist with the Epilepsy department of Beaumont Hospital, Dublin. I was awarded an MSc in Financial Mathematics from Dublin City University (2001) and a BA in Theoretical Physics from Trinity College Dublin (2000).

**Recent Publications**

Dejun Li, B.Sc., M.Sc., PhD

Project Title: Quantification of the potential of white clover to lower GHG emissions from Irish grassland-based dairy production

Project Leader: Dr. James Humphreys and Prof. Nicholas Holden

Abstract
This project aims to quantify the change in greenhouse gas (GHG) emissions from Irish dairy production when mineral fertilizer N (MFN) is replaced by white clover-biologically fixed N (BFN). This will be quantified using lifecycle assessment (LCA) on a whole farm basis, initially using existing data sets of N flows within both MFN-based and white clover-BFN-based systems of dairy production measured over the last four (2003-2007) years at Teagasc Research Farm at Solohead. Gaps in existing knowledge in terms of nitrous oxide and ammonia emissions will be filled by on-site measurements and compared with model predictions. An appropriate LCA methodological framework will be developed and questionnaire detailing the key inputs needed to conduct the LCA of dairy farms will be drawn up. This questionnaire, which will include indicators of economic performance, will be used in the collection of data from approximately 20 farms on a range of soil types around the country that have switched from MFN-based to white clover-BFN-based grassland in recent years. This will give a broad-based interpretation of the likely change in GHG emissions associated with the wider use of white clover for dairy production that can be linked into the national emissions inventory. This study may provide justification for payments for white clover in rural environment protection schemes.

Background, Skills & Qualifications
I obtained my PhD in environmental science in 2007 under the supervision of Prof. Xinming Wang at Guangzhou Institute of Geochemistry, Chinese Academy of Sciences. The PhD thesis is about soil nitric oxide emissions from forests and vegetable fields in the Pearl River Delta, China. This involved field measurements and modelling of soil nitric oxide emissions from these ecosystems. Also my thesis involved the first direct measurement of N isotopic signature of soil derived nitric oxide. I obtained an MSc. in ecology in 2004 and a BSc. in biology in 2001.

Recent publications:
Project title: Development of a Novel Non-contact and Rapid Computer Vision System for Quality Evaluation and Control of Pre-sliced Cooked Hams

Project Leader: Professor Da-Wen Sun

Abstract

The production of high quality ham products with an attractive appearance and premium eating quality is an important goal for the meat industry. The digital image of a ham slice contains a large number of image features that can be easily extracted to be read quantitatively by a computer; this is analogous to a real ham slice that has quality attributes (such as colour and texture) which can be qualitatively perceived by human vision. The main goal of this project is to search and identify the most suitable image features that are linked to the quality attributes of ham, and can be also useful for objective quality control in real time. It considers the implementation of a colour calibrated computer vision system based on the CIE colour standard.

Background, skills & Qualifications

I have graduated from the National Agricultural University (Perú) in the Faculty of Food Engineering (1993). My MSc (1999) and PhD (2005) were carried out in Catholic University in Chile. During my PhD, I developed computer vision systems and image analysis techniques for quality characterization of food surfaces based on pattern recognition methods. The first part of this project was completed in Chile and the second one at Lund University (Sweden). In 2005, I worked as a Postdoctoral researcher in the Postharvest Technology Lab at KU Leuven (Belgium) for two years. In this project I investigated the 3D microstructure of apple tissues using X-ray CT. Currently, I work in Biosystems Engineering, UCD, as a postdoctoral researcher under the guidance of Prof. Da-Wen Sun.

Recent publications


Sharon O’Rourke, BAgrSc, PhD

Project Title: Optical sensing and chemometric analysis of soil properties

Project Leader: Prof. Nick Holden

Abstract
High resolution soil sampling can be prohibitive on a large scale due to associated costs. Recently attention has moved to optical sensing which combined with multivariate modelling techniques offer a rapid, low-cost alternative to the traditional wet chemistry analysis of soils. The main objective of this project is to evaluate the potential of hyperspectral imaging to determine a range of soil nutrient and geochemical properties in representative Irish soils. Soils are inherently heterogeneous due to variation in soil parent material and different land management regime resulting in contrasting mineralogy and organic matter inputs. The effect of soil type and land use management situation on calibration development will determine the scale (regional or national) to which prediction models can be applied. Employing optical sensing and chemometric analysis as routine in the future will depend on a play off between the improvement in sampling resolution and prediction accuracy.

Background, Skills and Qualifications
I obtained a BAgrSc in Agriculture and Environmental Science from UCD in 2004. My PhD thesis was completed in 2009 at Queens University Belfast under the supervision of Dr. Bob Foy and Dr. Catherine Watson. This evaluated a number of mitigation options for controlling phosphorus loss in intensive dairy production systems. Strategies examined were the timing of manure applications to grassland in relation to first rainstorm event and lowering manure phosphorus content by manipulation of the phosphorus in the dairy cow diet or amendment with waste water treatment residuals. My current role in this department is to develop a national research capacity for applications of optical sensing for soil properties and a set of protocols to permit higher spatial resolution in data acquisition for applications such as soil survey, precision agriculture and soil carbon monitoring.

Recent Publications

Grainne Redmond, B.Sc., PhD

**Project Title:** Quantitative Microbial Risk Assessment Network of Ireland

**Project Leader:** Prof. Francis Butler

**Abstract**
The overall objective for the network is to develop a high calibre, internationally recognised, multidisciplinary network of national experts on the application of microbial quantitative risk assessment as a tool to underpin risk management actions. The network facilitates the generation of scientific knowledge in this emerging area of risk analysis and addresses 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**
Grainne Redmond graduated from the Dublin Institute of Technology with a BSc in Applied Science. After obtaining a MSc in Food Science from UCD she then went on to be awarded a PhD in Agriculture from UCD in 2000. She is currently the Network Manager of the Irish Quantitative Microbial Risk Assessment Network of Ireland (www.ucd.ie/microbialrisknetwork)

**Recent publications**


Conor Shanahan, BE, M.Sc., PhD

Project Title: Quantitative risk assessment of microbial hazards to maximise beef safety

Project Leader: Prof. Francis Butler

Abstract:
Quantitative microbiological risk assessments are used to model the risk from pathogens present in the beef slaughter chain. Four pathogens are being modelled, Campylobacter, Salmonella, Listeria monocytogenes and VTEC. The models will estimate the prevalence and counts of the particular pathogen to the boxed beef stage of the slaughter process. The models can then be used to highlight areas of potential infection and to assess the effectiveness of intervention strategies.

Background, Skills and Qualifications:
My PhD thesis was concerned with the development of a traceability system for cattle from farm to slaughter utilising radio frequency identification as data carriers and biometric data for identity verification. It was completed in 2008 under the supervision of Dr. Kevin McDonnell in UCD. I obtained an M.Sc (Agri) in Environmental Protection from UCD in 2005 and BE in Agricultural and Food Engineering from UCD in 2001.

Recent publications:

Fergal Tansey B.Sc., Ph.D.

Project Title: SigmaChain - developing a stakeholders guide on the vulnerability of food and feed chains to dangerous agents and substances.

Project Leader: Prof. Francis Butler

Abstract
The main objective of the SigmaChain (ΣChain) project (contract no. FP6-518451) is to develop systems that will optimize food chain traceability with respect to minimizing vulnerability to contamination. The SigmaChain website can be accessed at http://www.sigmachain.eu/. The project is based around four case studies: drinking water (rapid contamination chain), milk powder (batch mixing chain), and both poultry meat and farmed salmon (long geographic chains).

Workpackage 1: Development of a conceptual framework to identify and prioritise critical links in the total chain (leader SINTEF Fiskeriog, Havbruk AS, Norway). The contaminant database for the four products, covering microbial/chemical/other (physical/toxins/viruses), was completed.

Workpackage 2: Case studies of four products which are highly vulnerable to contamination (leader Max Rubner-Institut (MRI), Kulmbach, Germany). Chain maps for the four products were completed using Microsoft Visio, each consisting of start/end/main process/process/input/output steps. A review of electronic tracking and tracing systems was completed, covering PGIs, RFID (EPC Class 1, Generation 2) and electronic data interchange.

Workpackage 3: Risk modelling and ranking (leader UCD, Dublin, Ireland). A review of risk assessment models from literature and a report on risk ranking criteria for microbial (Risk Ranger) chemical (ADIs) contaminants were completed. The contaminant database for the four products is complete and risk ranking of selected high risk microbial and chemical contaminants for poultry and milk powder was carried out.

Workpackage 4: Validation of the framework developed in WP1 and development of stakeholders’ guide (leader TNO, Netherlands). Virtual (on-line) workshops using the Delphi method were performed and progress is continuing on consumer focus groups to the end of the project. A preliminary draft of the contents of the Stakeholder’s Guide was prepared and will be finalized by April 2009.

Workpackage 5: Demonstration (leader Biosystems Engineering Ltd., NovaUCD, Dublin, Ireland). A workshop with legislators was held in Dublin in June 2008 and a risk manager’s forum was also held in Dublin in September 2008, with the objective of refining the Stakeholders’ Guide for industry use.

Background, Qualifications and Skills
After obtaining a B.Sc. Degree (1989) in industrial microbiology from University College Dublin, I joined Unilever Research, Bedford, England (1989-1997) as assistant research scientist and was involved in one to three-year multi-disciplinary research projects in both the meals and meal components and ice cream groups. These activities produced one peer-reviewed paper and 13 company research and business reports. I then joined Glanbia Meats, Ruskey (1997-2000) as cannery quality assurance manager and was responsible for ensuring the safety, quality and legality of all canned meat and pasteurised meat products. I then joined Ashtown Food Research Centre, Dublin (2001-2004) as research officer and was involved in a three-year FIRM funded project in which I was awarded a Ph.D. Degree (2007) from University College Dublin on ‘Effect of freezing on the texture, quality and ultra-structure of sous vide ready-meal components.’ I am now working with Biosystems Engineering Ltd., NovaUCD, University College Dublin since 2006 and I am currently involved in project management of the above project and I also carry out thermal process validation studies for Irish food companies to BRC and USDA requirements.

Recent Publications
Jialiang Tang, BA, M. Sc., PhD

Project Title: Cryptosporidiosis Network Ireland: Development of Skills and Knowledge to Predict Cryptosporidiosis Risk in Catchment Water

Project Leader: Prof. Nicholas Holden and Dr. Tom Murphy

Abstract
In order to assess risk of Cryptosporidiosis in humans, the role the environment plays in regulating the exposure of the human population to oocysts must be considered. There is limited information in the scientific literature on the efficacy of various soil and catchment systems for filtering and inactivating oocysts. An increased understanding will aid in epidemiological investigations of outbreaks and in predicting spatial and temporal variability of risk to human populations. The scientific objective of Crypto net.ie is to develop a Cryptosporidium spp. specific Microbial Risk Assessment (MRA) model for catchment waters that can be used to identify when potable water is at high risk of being contaminated. The project involving two ungauged small Irish farming catchments selected for Cryptosporidium transport modeling using SWAT 2005 is still ongoing. My temporal work is the first trial using SWAT bacteria module to predict this persistent protozoan pathogen transport in farming catchments on daily base.

Background, Skills and Qualifications
My PhD thesis work was concerning eco-hydrological processes in small agricultural catchment and completed in 2005 supervised by Prof. Taolin Zhang and Prof. Bin Zhang at ISSAS, CAS (Chinese Academy of Sciences). I obtained an MSc and a BA about Soil and water conservation at Southwest University of China in 2002 and 1999 respectively.

Recent Publications
Tony Woodcock, BE, MEngSc, PhD

Post doc researcher on the Bioresources Research Centre Charles Parsons Project; Biomass Conversion Technologies

Project Leader: Dr Kevin McDonnell

Abstract: A small-scale down-draft fixed-bed gasifier experimental kit was purchased. Currently in the process of reviewing and sourcing available and appropriate biomass feedstocks for gasification purposes (focusing mainly on 2<sup>nd</sup> generation feedstocks). Gas samples will be analysed for energy content, presence of tar or other hazardous compounds. Ultimately, it is hoped to study the entire process from producing the biomass feedstocks to creating the synthetic gas, including transport of biomass, to determine the economic and environmental feasibility of such a system.

Background, skills & qualifications: I am a postdoctoral fellow at UCD. My main research interests are in the area of renewable energies, specifically the role of biomass feedstock, conversion technologies etc. I was awarded a PhD in Biosystems Engineering from UCD in 2009 which I completed under the supervision of Dr Colm O'Donnell. My thesis concerned the development of fingerprinting techniques for the prediction of geographical origin of food using chemometric analysis of near infrared spectroscopic data. I graduated in 2005 from the Faculty of Engineering, UCD with a MEngSc and in 2003 I was awarded a BE(Hons) in Biosystems Engineering, UCD.

Publications:


Zhihang Zhang, BEng., PhD

**Project Title:** Use of Power-Ultrasound in the Acceleration of Ice Nucleation and Control of Ice Crystal Distribution during Freezing of Foods.

**Project Leader:** Prof. Da-Wen Sun

Abstract
Freezing is a very widespread process within the food processing industry, as a very important means of preserving fresh foodstuffs. However, ice crystal formed in the frozen foods can causes many irreversible physical and chemical changes within the food matrix, often leaving the final product with lower eating quality than when it was in the fresh state. This project will build upon promising research in the ability of high powered ultrasound (HPU) to initiate ice nucleation and to control crystal size distribution in the frozen product during solidification of liquid food. Past research has also shown promise for HPU to shorten the freezing process and lead to a product of better quality. This project will design and develop a prototype HPU system for its industrial validation in food freezing facilities. It will be cost-effective and easy to operate and easily integrated with commercially available freezing equipment.

**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”. I am currently working as a postdoctoral researcher on the above mentioned project.

**Recent publications**


Appendix 3

Biosystems Engineering, UCD School of Agriculture Food Science and Veterinary Medicine : Postgraduates 2009/10 as photographed by Sean Kennedy
Appendix 4

Biosystems Engineering, UCD School of Agriculture Food Science and Veterinary Medicine: Staff 2009/10 as photographed by Sean Kennedy