FOREWORD

The Sixteenth Annual Research Review describes the ongoing research programme in Biosystems Engineering at University College Dublin from over 94 researchers (10 academic staff, 2 technicians, 23 postdoctoral researchers and 59 postgraduates). The research programme covers three focal areas: Food and Process Engineering; Bioresource Systems; and Bioenvironmental Engineering. Each area is divided into sub-areas as outlined in the Table of Contents which also includes the name of the research scholar (in bold); the research supervisor(s); the title of the research; the nature* of the research programme; and the research sponsors. It also includes the noting of four awards for presentational excellence at the Sixteenth Annual Biosystems Engineering Research Seminar held in University College Dublin on Thursday 10th March 2011.

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 2011

*MEngSc1, MSc1, MAgrSc1 = Research Masters (Mode 1)
MEngSc2, MSc2 = Taught Masters (Mode 2)
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Appendix 4  Biosystems Engineering UCD: Staff Complement 2010/2011 as photographed by Sean Kennedy
FREEZING PROCESS EFFECTS ON PORK QUALITY FEATURES

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Abstract
The effects of frozen storage on pork quality properties will be investigated. Thawing loss, pH and colour measurements will be performed to determine differences between fresh and frozen-thawed pork. Spectral information will be used to distinguish differences between fresh and frozen-thawed meat. The purpose of this study is to evaluate how the freezing process affects pork quality. The results will be used to investigate how damage in the meat structure caused by freeze-thawing cycles can be identified through physical tests.

Introduction
Meat products are an important component of the human diet and its quality is of concern to consumers, governmental control authorities and retailers. Nevertheless, meat can be a target for adulteration in many ways and one very obvious kind is to illegally sell thawed meat as fresh. The attractiveness is obvious since fresh meat is more valuable than frozen meat (Ballin and Lametsch, 2008). Freezing is an easy and effective way to extend the meat shelf life. Many studies have shown that frozen food quality depends on the ice crystal size, quantity, distribution and drip loss during thawing. The frozen meat interior will form bulk ice crystal during the freezing process, and these ice crystals not only disrupt cell membrane, but also damage fibre structure (Sanza et al., 1999) and speed up protein denaturation (Shenouda, 1980) leading to increased drip loss during thawing which will decrease the quality of meat, causing lost of flavour, lower water holding capacity, lipid oxidation, dehydration, decreased tenderness, decreased protein solubility, etc. This means that the frozen meat quality not only depends on the freezing technology but also the thawing process (Martino et al., 1988).

The cold chain refers to the transportation of temperature sensitive products along a supply chain through thermal and refrigerated packaging methods and the logistical planning to protect the integrity of these shipments (Rodrigue et al., 2009). But generally, there are probably some flaws in the meat cold chain leading to meat temperature fluctuation and causing a freezing-thawing cycle. Many investigations have shown freeze-thawing cycles increased ice crystal size in the space between fibre, torn and confused muscle fiber bundles, and breakdown muscle structure. Moreover, the higher multiple freeze-thawing cycles, the more recrystallization phenomena in meat which make the meat texture structure and freshness great worse (Sigurgisladottir, et al., 2000).

The objective of this study is to investigate if thawing loss, pH, colour and spectral features can be used determine the extent of damage caused by the freezing process on pork.
Material and methods

Pork Samples
A set of 20 pork samples from the loin (*longissimus dorsi*) muscle will be selected at the meat factory by trained inspectors. The samples will be cut into chops with 1 inch thickness before being vacuum-packed and sent to the Computerized Food Technology Laboratory at UCD Belfield, Dublin, Ireland.

Preparation and storage condition
The same set of samples will be used for the entire study. Quality features will be measured in the fresh slaughtered samples. The samples will be vacuum packed in polyethylene bags, frozen and stored at -18°C for 1-4 weeks. The frozen meat samples will be thawed at room temperature until the meat temperature reaches 0-2°C. This study will comprise a total of 20 samples divided into 4 groups named A, B, C, D, with 5 samples per group.

Experiments design
Drip loss after thawing, colour measurement, pH measurement will be performed. After that, spectral information will be investigated. Group A will be thawed every week and refreeze for 4 weeks to emulate temperature variations during the frozen storage along the cold chain. Samples from groups B, C and D will be thawed after 2, 3 and 4 weeks of storage respectively (Table 1).

<table>
<thead>
<tr>
<th>Week</th>
<th>A</th>
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Test 3: Colour measurement, pH test, hyperspectral imaging
Test 4: Thawing loss, colour measurement, pH test, hyperspectral imaging

Thawing loss
The exudation caused by freezing process will be performed using a balance to weight each sample before freezing and after thawing. The thawing loss will be determined as percentage of the sample weight (Equation 1):

\[
\frac{(W_{bf} - W_t)}{W_{bf}} \times 100\% \tag{1}
\]

where \(W_{bf}\) is the Weight of sample before freezing and \(W_t\) is the Weight of sample after thawing.

Colour and pH measurements
Colour (*CIELab*) and pH will be measured for each sample after a 30 minute blooming period. \(L^*\) is a correlate of lightness, while parameters \(a^*\) and \(b^*\) represents “redness” and “yellowness”, respectively. Colour features will be obtained as the average of ten measurements performed on the surface of each sample with a Minolta Chromameter (CR-400, Konica Minolta Corp., Japan). Ultimate pH will be calculated.
as the average of 2 pH measurements using a portable pH-meter (AB15, Fisher scientific Inc., USA).

*Spectral analysis*
Spectral information will be extracted from images acquired in reflectance mode using a pushbroom hyperspectral system (Figure 1). The system consists of a linescan spectrograph, a charged couple device (CCD) camera, illumination unit, a translation stage, data acquisition software, and a computer. The spectrograph and camera collect spectral images in the wavelength range of 897-1752 nm. One average spectrum will be acquired for each sample before freezing and after thawing.

![Illustrative diagram of a pushbroom hyperspectral imaging system and with a representative spectrum obtained from meat sample.](image)

**Figure 1.** Illustrative diagram of a pushbroom hyperspectral imaging system and with a representative spectrum obtained from meat sample.

*Statistical analysis*
The results from colour measurement will be analyzed using the statistical program. To investigate the effect of frozen storage on the response variables (colour L*, a*, b*, pH and thawing loss) an analysis of variance (ANOVA) will be performed. Principal component analysis (PCA) will be performed on the spectral data to verify differences caused by the frozen storage.

**Results**
The expected result is to verify to which extent frozen storage conditions will affect pork colour, pH and drip loss. Recently, it has been proved the viability of spectroscopic methods for identification of frozen and thawed beef in the NIR and visible range (Thyholt and Isaksson, 1997; Downey et al., 1997a, b). Spectral information will be investigated to determine differences between fresh and frozen-thawed pork.

**Acknowledgements**
The author would like to thank Professor Da-Wen Sun and Mr. Douglas Barbin, and some PHD Students and Senior Technician Officer.
References


SPECTRAL TECHNIQUES FOR DETECTING MICROBIAL SPOILAGES AND BACTERIAL PATHOGENS IN FOOD: A REVIEW

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Abstract

Detection of bacterial pathogens and spoilage organisms is critical in food surveillance. Several methods are available. Culture and colony counting method and polymerase chain reaction are powerful but strongly restricted by their intrinsic drawbacks. More promising vibration spectroscopy techniques have been applied in the identification of microbes, but efforts are still needed to establish robust models for industrial application. Moreover, as an emerging method, hyperspectral imaging is also suggested a worthy of further study.

Introduction

Global concerns over food safety are rising due to increasing reports of food-borne outbreaks. Food safety problems arise mainly because of food contaminations including physical, chemical and microbiological contaminations. Out of these three, the most confronted is microbiological contamination, which is closely related with bacterial pathogens and spoilage organisms. Specifically, researchers found that the majority of food-borne outbreaks are caused due to pathogens such as Campylobacter, Salmonella, Listeria monocytogenes, and Escherichia coli O157:H7 (Al-Qadiri et al., 2008). These bacterial pathogens can cause a wide range of symptoms. For example infections by E. coli O157:H7 can lead to gastrointestinal disorder (e.g., bloody diarrhoea and abdominal pains). Possible complications (including Haemolytic uremic syndrome as well as some neurological problems) and sometimes death may also happen especially to immune-compromised patients, such as young children and the elderly (Duffy et al., 2006). In addition, the occurrence of food contamination can result in great economic losses (Yang and Bashir, 2008). Therefore, effective measures are urgently required to reduce the occurrence of diseases from eating unsafe food, where identification of these pathogens and spoilage bacteria is the first critical step. Various approaches available for the detection of bacterial contamination include routine culture and colony counting, PCR, vibration spectroscopy and hyperspectral imaging etc (Davis, 2010a; Velusamy et al., 2010; Yoon et al., 2010). However, there are many advantages and disadvantages within these approaches in terms of selectivity, sensitivity and rapidity (Lazcka et al., 2007). Hence, the objective of this review is to give an introduction and comparison of various methods utilized in the detection of bacterial pathogens and spoilage organisms with emphasis on infrared spectroscopy.

Traditional methods

Culture and colony counting method

Conventional culture methods are the most commonly used technologies for food-borne pathogen detection because of their high accuracy, and they are considered as standard methods. However, they are normally quite time-consuming and laborious, since these technologies rely heavily on complex experimental procedures which aim to facilitate the growth of single bacteria into colonies so that counting will become quite easy (generally, at the final stage of incubation, a colony usually origin from the same bacterium) (Velusamy et al., 2010). Furthermore, some experimental conditions such as sampling, media preparation and incubation do affect the results obtained (Amamcharla et al., 2010).

Polymerase chain reaction (PCR)

As a nucleic acid amplification technology, PCR has been successfully employed to detect a single bacterium almost 20 years ago (Velusamy et al., 2010). In one round of PCR, stranded
DNA is first denaturised by heat, and then the two separated strands will serve as substrates for the added specific primers to locate target gene sets. Later, by polymerization, the two sets will develop into another two new identical DNA strands. Thus, by running a number of cycles, DNA sequences of target bacteria are isolated, amplified and finally quantified. Apart from previous enrichment, PCR takes from 5 to 24 h to produce a confirmed result according to the PCR method used (Lazcka et al., 2007).

**Vibration spectroscopy**

Vibration spectroscopy discussed here includes infrared (IR) spectroscopy and Raman spectroscopy (RS). Vibration spectroscopy screens food components based on their molecular vibrations which are reflected in the spectra at certain wavelengths.

**Raman spectroscopy**

Raman Spectroscopy is based on the low inelastic scattering of monochromatic light that interacts with molecular vibrations. Yang and Irudayaraj (2003) employed Fourier transform Raman spectroscopy with 1064 nm excitation to classify six different microorganisms. However, the signals of excitation in the near infrared region are often submerged by the more intense fluorescence emission (Gremlich and Yan, 2001). To overcome this problem several Raman signal enhancement methods such as resonance Raman spectroscopy or surface enhanced Raman scattering (SERS) were applied. Among these studies, ultraviolet resonance Raman was successfully utilized to classify *Bacillus* and *Brevibacillus* to species level (López-Díez and Goodacre, 2004). By introducing silver colloidal nanoparticles, Chen et al. (2007) used SERS to identify *E. coli* and *L. monocytogenes* cultures with a simple ratio algorithm, and they achieved 100% accuracy. However, Raman spectroscopy is naturally prone to disturbance from parameters of the optical systems.

**Infrared (IR) spectroscopy**

IR spectroscopy is sensitive to the variation of the chemical components and structure of the bacterial cells, which enables IR spectroscopy to be an effective method for differentiation of bacteria and food spoilage (Burgula et al., 2007). One of the earliest reports on the application of IR-based microbial classification was reported on discrimination of 72 strains by using a spectral library consisting of 90 strains (Helm et al., 1991). Fourier transform infrared (FTIR) spectroscopy is able to detect closely related spoilage bacteria (Lin et al., 2005) and has potential for monitoring spoilage. Ellis et al. (2002) studied the spoilage of unvarnished chicken, and predicted the microbial loads successfully and rapidly. In their work, effective wavebands which were claimed to be related with free amino acid were chosen by the application of an genetic algorithm and genetic programming. A similar method was also implemented on comminuted beef (Ellis et al., 2004). In another research on minced beef, principal component analysis was also reported in identifying the important wavelengths concerned with spoilage, and the authors found that these results were consistent despite different storage conditions (Ammor et al., 2009).

As an emerging new technology, near infrared spectroscopy (NIRS) together with versatile chemometric methods has been widely employed in food quality and safety control. In spoilage analyses, Horvath et al. (2008) developed a good quantitative model based on NIRS and partial least square (PLS) with a correlation coefficient of 0.977. In a qualitative study, ground pork tenderloin samples were classified into two groups as fresh and spoiled against three main indexes for meat freshness and finally the accuracy gained was up to 90% (Chou et al., 2010).

Much work has been done to investigate the feasibility of infrared spectroscopy in differentiation, classification and identification of pathogenic bacteria. Lin et al. (2004) recorded the FTIR spectra of *Listeria* after extracting bacterial cells by centrifuge and filtering, and they demonstrated distinctive fingerprints for discrimination of intact and sonicated bacteria. Separation of bacteria from food prior to spectral acquisition has proved to be effective in recognition of live and heat-injured/dead cells (Davis et al., 2010a, 2010b).
Moreover, Al-Qadiri et al. (2008) also managed to demonstrate that infrared spectroscopy is useful in determining the extent of injury in heat-treated pathogens, both gram-positive and gram-negative. On the other hand, direct classification of food products based on the population of pathogens such as *Salmonella* in packaged meat was also accomplished by using gas-phase FTIR spectroscopy with high accuracy (Amamcharla et al., 2010).

**Hyperspectral imaging (HSI)**

Hyperspectral imaging is a novel method that combines NIRS and computer vision to acquire both spectral and spatial information of samples (Sun, 2010). In detecting bacterial pathogens and spoilage organisms, Yong et al. (2010) discriminated poultry-origin *Campylobacter* and non-*Campylobacter* species in Petri dishes in tandem with algorithms of thresholding and spectral feature fitting. While Peng et al. (2011) pioneered the application of HSI for beef spoilage determination using scattering parameters. In these work, HSI is verified as being promising in both qualitative and quantitative analysis of bacterial microorganisms.

**Conclusions**

Various methods were reviewed including their applications in detecting bacterial pathogens and spoilage organisms. Within these approaches, culture and colony counting methods have been most widely accepted as standard methods, and PCR is also employed for food safety inspection by authorities. However, these methods require skilled professionals and usually take a long time. On the contrary, spectroscopic techniques are capable of detecting microbes in a non-destructive and rapid way. Therefore, more research on vibration spectroscopy is needed to establish robust and precise models which can be applied in the food industry. Furthermore, the great potential of hyperspectral imaging is noted, future work for the detection of pathogenic and/or spoilage bacteria on food should also be well appreciated.

**Acknowledgements**

This PhD study is supported by Chinese Scholarship Council (CSC) and University College Dublin (UCD) via CSC-UCD Scholarship Scheme. The authors would also like to acknowledge Dr. Amalia Scannell for her kind suggestions.

**References**


PREDICTION OF PORK SENSORY ATTRIBUTES USING NIR HYPERSPECTRAL IMAGING TECHNIQUE

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Abstract

In this study, a hyperspectral imaging based technique was investigated for objective determination of pork sensory attributes. Near-infrared hyperspectral images (900-1700 nm) were obtained for pork samples from the \textit{longissimus dorsi} muscle, and representative spectral information was extracted from the loin eye area. Spectral information was related to sensory characteristics by partial least-squares regression (PLSR) models. The results showed that pork meat could be discriminated into tender and tough categories with a coefficient of determination ($R^2$) of 0.78. Results indicated the potential use of NIR hyperspectral technique for rapid assessment of pork quality.

Introduction

“Lean quality” in fresh pork refers to a wide range of factors that directly affect raw product attractiveness to potential customers and influence sensorial properties for fresh products. Overall acceptance of pork is associated to several sensory attributes such as tenderness, flavour and juiciness, and how these attributes are influenced by technological features. Instrumental measurements of tenderness are rather simplistic in comparison to the intricate set of interactions that occur in the mouth. Hence, there are some concerns regarding the level of correlation between instrumental measurements and sensory responses of meat texture (Perry \textit{et al.}, 2001; Watson \textit{et al.}, 2008). Sensory quality of the muscle \textit{longissimus dorsi} is of special interest, because this part of the carcass is usually destined for fresh consumption (Van Oeckel \textit{et al.}, 1999). Experienced panellists are usually trained to score the specific attributes of eating quality of meat, requiring exhaustive procedures for sample preparation and training of experienced panellists. Therefore, the meat industry could benefit from a fast and non-destructive method for identification and quantification of pork quality features.

Previous studies have investigated the capability of spectroscopic methods to predict beef sensory attributes (Hildrum \textit{et al.}, 1995). More recent studies on beef samples reported $R^2$ values of 0.50 and 0.58 for juiciness and chewiness, respectively, using PLS calibration models from spectral information in the visible/NIR range (400-1100nm) (Liu \textit{et al.}, 2003). The near-infrared spectral region (800 to 2500nm) consists of overtones and combination bands of the molecular absorptions found in this range, and can be useful for applications where multi-component molecular vibration analysis is required in the presence of intrusive substances.

The main objective of the present study was to investigate the potential of using NIR hyperspectral imaging technique as a fast and non-invasive method to predict pork sensory attributes.

Materials and Methods

Sample preparation

Fresh pork samples from the loin (\textit{longissimus dorsi}) muscle at 24 h post-mortem were selected from different quality categories by trained inspectors to include a wide range of variation for the quality attributes. All samples were cut into chops with a thickness of 1 inch in the pilot scale abattoir (Meat Industry Development Unit, Teagasc Food Research Centre Ashtown, Dublin) before being vacuum packed and sent to the Computerized Food
Technology Laboratory at UCD Belfield, Dublin, Ireland for image acquisition. Pork chops were imaged, vacuum-packed, frozen and stored at −18°C for approximately 5 months before sensory analysis.

Sensory panel testing
The loin samples were removed from the freezer approximately 24 h before cooking. Sensory evaluation was performed on 30 thawed samples in four separate sessions conducted during 2 days. Eight trained panellists from Teagasc Food Research Centre (Ashtown, Dublin) tasted samples from distinct pork classes. The design was exactly the same in each case with each panellist tasting 8 samples per session in two sets of 4 samples. The steaks for sensory panel analysis were grilled (Silesia Velox UK Ltd, Oxfordshire, UK) for 5 min to a 72°C core temperature. Eight 15 mm by 15 mm squares were cut from the cooked steak, labelled with a three digit code and served to eight experienced in-house panellists. The panel rated tenderness, juiciness on a scale from 1–8. A scale of 1–6 was used for flavour and overall acceptability (AMSA, 2005). Panellists were instructed to cleanse the palate between samples with a bite of an unsalted cracker and a sip of water. Testing took place in individual booths under red lighting.

Hyperspectral imaging system
Spectral images were acquired in the reflectance mode using a pushbroom hyperspectral imaging system (Figure 1). The system consisted of a spectrograph (ImSpector, N17E, Spectral Imaging Ltd, Finland), a charged couple device (CCD) camera along with C-mount lens (Xeva 992, Xenics Infrared Solutions, Belgium), illumination unit comprising of two tungsten-halogen lamps (V-light, Lowel Light Inc, USA), a translation stage (MSA15R-N, AMT-Linearways, SuperSlides & Bushes Corp., India), a data acquisition software (SpectralCube, Spectral Imaging Ltd., Finland), and a computer. The system collected spectral images in the wavelength range of 897-1752 nm with a spectral increment of about 3.34 nm between the contiguous bands producing a total of 256 bands.

![Figure 1. Schematic diagram of a pushbroom hyperspectral imaging system](image)

Image acquisition and pre-processing
During image acquisition, each pork sample was laid in the translation stage and conveyed to the field of view (FOV) of the camera. Upon entering the FOV, a hyperspectral image of the sample was acquired and the image in raw format was sent to the computer for storage and further processing. The complete image acquisition process was controlled by the SpectralCube software. The acquired hyperspectral image is a 3-D image called 'hypercube’ with two spatial dimensions (x, y) and one spectral dimension (λ).

A white image (100% reflectance) was acquired from a white reference ceramic tile, and a dark image (0% reflectance) was obtained with the light source off and the camera lens completely covered with its opaque cap. A relative reflectance image (R) was then calculated:

\[ R = \frac{R_s - D}{W - D} \]

(1)
where R was the relative reflectance of an image; R₀ was the original raw image; D was the dark image, and W was the white image.

**Prediction method**

Partial Least Squares is a regression procedure that relates a set of independent variables (predictors) to response variables (observations) by reducing a large number of original descriptors to a new variable space based on small number of orthogonal factors (latent variables) (Wold et al., 2001a,b). Calibration models were calculated for the original raw spectral data with a full cross validation approach (leave one out). The optimal number of latent variables (LV) for establishing the calibration model was determined using the minimum value of predicted residual error sum of squares (PRESS). Later on, samples were classified into two groups for tenderness and juiciness attributes (namely tender or tough, and juicy or dry), and new PLS models were built to classify the samples into these categories.

**Results and Discussion**

**Sensory tests**

Table 1 summarizes the experimental results for pork sensory attributes. Panellists identified a wide range of tenderness, as expected, since there was variation in quality grades among samples. However, flavour and overall acceptability changed very little.

<table>
<thead>
<tr>
<th>Sensory attribute</th>
<th>Max</th>
<th>Min</th>
<th>Mean±SD*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Juiciness</td>
<td>6.50</td>
<td>3.75</td>
<td>4.75±0.63</td>
</tr>
<tr>
<td>Tenderness</td>
<td>7.50</td>
<td>4.25</td>
<td>6.10±0.64</td>
</tr>
<tr>
<td>Flavour</td>
<td>5.13</td>
<td>3.88</td>
<td>4.43±0.29</td>
</tr>
<tr>
<td>Overall Acceptability</td>
<td>5.13</td>
<td>3.38</td>
<td>4.46±0.34</td>
</tr>
</tbody>
</table>

*SD = Standard Deviation

**Prediction of sensory characteristics from NIR spectra**

The average intensity of each pixel in the selected ROI comprising the loin-eye area of each sample was extracted and used to build prediction models for sensory attributes.

<table>
<thead>
<tr>
<th>Attribute</th>
<th>LV</th>
<th>C R²</th>
<th>CV R²</th>
<th>SEC</th>
<th>SECV</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Prediction</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Juiciness</td>
<td>4</td>
<td>0.60</td>
<td>0.49</td>
<td>0.40</td>
<td>0.50</td>
</tr>
<tr>
<td>Tenderness</td>
<td>7</td>
<td>0.81</td>
<td>0.54</td>
<td>0.28</td>
<td>0.52</td>
</tr>
<tr>
<td><strong>Classification</strong></td>
<td>8</td>
<td>0.89</td>
<td>0.67</td>
<td>0.15</td>
<td>0.27</td>
</tr>
<tr>
<td>Juiciness</td>
<td>8</td>
<td>0.93</td>
<td>0.82</td>
<td>0.12</td>
<td>0.52</td>
</tr>
</tbody>
</table>

Table 2 shows the PLS calibration statistics for sensory juiciness and tenderness, respectively. Pork flavour and overall acceptability could not be properly predicted by the PLS models. A quite clear trend is that sensory attributes with broader range of response resulted in better prediction models. Hence, the difficulty in building prediction models for flavour and overall acceptability are possibly due to the small variety of response values. Better models were later obtained for classification of samples into two groups. Tenderness is the most important factor affecting consumer perception of eating quality of meat. Sensory tenderness results are similar to previously reported findings. The samples used for sensory analysis were frozen, thawed and cooked. To prompt the application of NIR spectral analysis for this purpose, it is necessary further studies about the relationship between chemical/physical properties of fresh and frozen/thawed meats and the NIR spectra.
Conclusions

Results obtained in this study have shown the potential of NIR hyperspectral imaging system for fast and non-destructive assessment of pork quality features. Results for tenderness prediction were slightly better compared to other sensory features. PLSR models were not successful for prediction of all the sensory attributes, probably because linear models are rather simplistic compared to the complex combination of factors that influence tasting. The pork industry can benefit from the possibility of performing this non-destructive technique at an early stage of processing without additional laborious analysis. This study illustrated the potential use of hyperspectral imaging for determination of pork sensory attributes by using fast and non-destructive method.

Acknowledgements

The authors gratefully acknowledge the financial support from the Food Institutional Research Measure (FIRM) strategic research initiative administered by the Irish Department of Agriculture, Fisheries and Food.

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NIR hyperspectral imaging and partial least squares for the prediction of pH, colour and drip loss of lamb muscles

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Abstract

The potential of near-infrared (NIR) hyperspectral imaging was evaluated for the prediction of pH, colour (L* value) and drip loss of different lamb muscles. Hyperspectral images of lamb muscles were obtained using a pushbroom NIR hyperspectral imaging system in the spectral range of 900-1700 nm. Muscles from semitendinosus (ST), semimembranosus (SM), Longissimus dorsi (LD) of Suffolk, Telex, Blackface and Charollais breeds were used for the study. Partial least squares regression (PLSR) models were developed to build a relationship between spectral data and the various quality attributes measured. The models performed well for predicting colour, pH and drip loss with the coefficient of determinations (R²) of 0.92, 0.58 and 0.66, respectively. The study demonstrated that NIR hyperspectral imaging can be used for rapid evaluation quality attributes of lamb.

Introduction

The requirements of reliability, expeditiousness, accuracy, consistency and simplicity for quality assessment of food products encouraged the development of non-destructive technologies to meet the demands of consumers to obtain superior food qualities. Hyperspectral imaging is an emerging, non-contact, cutting-edge analytical technology that combines conventional digital imaging and spectroscopy in a single system. The system provides images in a three-dimensional form called “hypercube” which provides spatial information along with spectral information. The combined nature of imaging and spectroscopy in a hyperspectral imaging enabled this system to simultaneously provide physical and chemical characteristics of an object as well as their spatial distributions.

Recently, hyperspectral imaging techniques have received much attention for the quality and safety assessment of meat. It has been successfully implemented for predicting beef tenderness (Naganathan et al., 2008), classification and prediction of marbling, colour, texture and exudation, drip loss, pH in pork (Qiao et al., 2007a,b,c), contaminants and tumour detection in chicken (Lawrence et al., 2004; Kong et al., 2004) and assessment of water and fat contents in fish fillets (ElMasry & Wold, 2008). However, no research endeavours have been reported yet on quality evaluation of lamb meat by hyperspectral imaging. Therefore, it is of our priority to implement this technology for the quality evaluation of lamb. In our previous work (Kamruzzaman et al., 2011), the potential of NIR hyperspectral imaging technique was successfully evaluated for the discrimination of lamb muscles.

The objective of this study was to evaluate the potential of near-infrared (NIR) hyperspectral imaging technique for the prediction of some quality attributes of lamb muscles.
Materials and Methods

Sample preparation and measurement of quality attributes
Lamb samples for this study were collected from Ashtown Food Research Centre (AFRC), Teagasc, Dublin 15, Ireland. Three muscles: ST, LD and SM were selected for the experiment. Each Muscle was cut to slices of 1 inch in thickness using a scalpel and cutting machine. Each sample was individually vacuum packed and shipped to the laboratory in ice boxes and then kept at 2°C. The samples were bloomed for 30 min and surface moisture was wiped by paper towels before image acquisition and quality measurements. Three quality parameters (pH, drip loss and colour) were measured and used as indicators of quality attributes. The value of pH was measured at three different locations in each muscle with a pH meter (AB15, Fisher scientific Inc., USA) and then averaged to give only one pH value for each muscle. Colour (L* Value) was measured using Minolta Chroma meter (CR-400, Konica Minolta Corp., Japan) in three different locations in each muscle, and then averaged for each muscle. Drip loss was determined as a percentage of weight loss after 2 days of storage at 4°C.

NIR hyperspectral imaging system
A laboratory NIR hyperspectral imaging system (900-1700 nm) was assembled to acquire hyperspectral images of the lamb muscles in the reflectance mode. The hyperspectral imaging system consists of a 12-bit CCD camera along with a standard C-mount lens, a spectrograph, an illumination unit of two 500-W tungsten halogen lamps, a translation stage and a computer supported with data acquisition software.

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

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

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

Image segmentation
The images were segmented to separate only the lamb meat from the background and adjoining fat portion of the sample. Firstly, the background was removed from the lamb muscle image by subtracting a low-reflectance band from a high-reflectance band followed by a simple thresholding with a value of 0.09. This step produced a segmented image for the whole muscle including the lean and fat portions of the muscle. Again, segmentation was performed for detecting fat by simple thresholding at a value of 0.055 to produce a binary image of fat pixels only. Then, the lean portion was isolated by subtracting fat pixels from the first segmented image containing both lean and fat portions to produce a mask containing only the lean part in a black background. The isolated lean portion was then treated as the main region of interest (ROI) to be used for extracting spectral data from each sample.

Analysis of spectral data
Full cross validation PLSR models were build for each quality attributes using the Unscrambler software v9.5 (CAMO AS, Trondheim, Norway). The precision and the predictive capabilities of the models were evaluated by the root-mean-square error of calibration (RMSEC), root-mean-square error estimated by cross-validation (RMSECV), and the coefficient of determination (\( R^2 \)).
Results and Discussion

Statistics of measured quality attributes
The descriptive statistics such as mean, range, standard deviation (SD) for pH, drip loss and colour for each muscle determined by reference methods are summarised in Table 1. It should be noted that a wide range of variability present in the reference data are beneficial to produce stable calibration models, whereas a narrow range of variability can negatively affect predictability of any parameter.

Table 1: Statistics of colour, pH and WHC in the tested muscles

<table>
<thead>
<tr>
<th>Parameter</th>
<th>No of samples</th>
<th>Mean</th>
<th>SD</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>200</td>
<td>5.49</td>
<td>0.15</td>
<td>5.24-5.84</td>
</tr>
<tr>
<td>Drip loss (%)</td>
<td>131</td>
<td>1.38</td>
<td>0.59</td>
<td>0.59-3.09</td>
</tr>
<tr>
<td>L* value</td>
<td>200</td>
<td>36.73</td>
<td>4.91</td>
<td>27.97-49.97</td>
</tr>
</tbody>
</table>

Prediction of the quality attributes by PLSR
A critical step in the creation of an accurate PLSR model is choosing the correct number of latent variable (LV). The optimal number of latent factors for PLSR models for the prediction of each quality parameter was estimated at the lowest value of predicted residual errors sum of squares (PRESS) as shown in Fig 1. The number of latent factors to predict pH, drip loss and colour were 12, 13, and 9, respectively. To visualise graphically the performance of the PLSR calibration models, the measured values obtained from the laboratory test (destructive) for the different quality attributes and its predicted values resulting from the optimal PLSR models are plotted as shown in Fig 1.

Figure 1. Prediction of pH, drip loss and L value using PLSR models: predicted residual error sum of squares (PRESS) for predicting (a) pH, (c) drip loss and (e) L* value as a function of number of latent variables. (b) Measured versus predicted values of pH, (d) measured versus predicted values of drip loss and (f) measured versus predicted values of L*.

The most accurate model was obtained for predicting the L* value than those for pH and WHC. This was expected, because this characteristic is directly related to the optical
reflectance properties of the muscle. The L* value could be predicted accurately with an $R^2$ of 0.92, RMSEC of 1.19, and RMSECV of 1.29. The model has good prediction ability as revealed by the higher value of $R^2$ as well as smaller difference between RMSEC and RMSECV. The least successful model was obtained for predicting pH with an $R^2$ of 0.58, RMSEC of .085 and RMSECV of .095. The drip loss was predicted with an $R^2$ of 0.66, RMSEC of 0.29%, and RMSECV of 0.34%.

Conclusions

A hyperspectral imaging system in the NIR region of 900-1700 nm was developed to evaluate some quality attributes of lamb muscles. The PLSR models were developed to relate reflectance spectra and the lamb quality attributes. The delineated results indicated that NIR hyperspectral imaging has a great potential to be a non-destructive tool for predicting the lamb meat quality attributes.

Acknowledgements

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.

References


ANALYSIS OF INDICATIVE ORGANISMS FOUND ON LAMB CARCASS

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Abstract

Food safety is the most important aspect for the food industry. Food microbiology is one of the methods used to monitor the safety of food. TVC’s and Enterobacteriaceae are indicator organisms found on lamb and are analyzed in this study to determine if there is any association or trend between the presence of each in the meat. The results show the presence of both indicator organisms on the carcass and it is possible to see a relationship between the trend lines, a large increase in the TVC readings shows a corresponding increase in the Enterobacteriaceae readings.

Introduction

The food industry is one of the largest industries worldwide. A major focus of food manufacturing plants is whether a food is safe for human consumption i.e. is the product free from harmful levels of pathogens? To enforce and monitor these levels government and regulatory bodies were established worldwide and regulations were set in place to ensure uniform safety of foodstuffs. The Food Safety Authority of Ireland (FSAI) first came into effect in January 1999 and was set up to govern the safety of food produced in Ireland, in turn they have contracted the Department of Agriculture, Fisheries and Food to monitor the food safety in the food manufacturing facilities. Regulations state that foodstuffs should not contain microorganisms, their toxins or metabolites in quantities that present a risk to human health. To ensure this preventative measures such as good manufacturing process (GMP), continuous risk assessment and HACCP are employed by companies (FSAI 2009). High levels of pathogens present in foodstuffs can cause outbreaks of foodborne illness, symptoms of which can be nausea, fever, diarrhea abdominal cramps, etc. (CDC 2011). Food microbiology is a very important aspect of quality control in food manufacturing. The general principles of food microbiology are: (i) the protection of the consumers against food-borne microbial disease and (ii) prevention of food spoilage due to microbial activities (McMeekin and Ross 2002). Storage conditions, as well as process conditions, must also be closely monitored to prohibit/limit the amount of microbial growth during the storage time e.g. temperature.

By law (EC 2005) manufacturing facilities are required to test for the presence of TVC (total viable count), Enterobacteriaceae and Salmonella. This report will focus on the presence of TVC and Enterobacteriaceae indicator organisms present in lamb meat from several commercial abattoirs in Ireland. Indicator organisms are used to signal a microbiological problem that could impact the quality or safety of a food ingredient, finished product or the production/processing/handling environment. They can also indicate a potential hygiene problem (Jaykus and McClure). TVC’s give a quantitative suggestion of the presence of microorganisms in a sample, i.e. TVC represents the number of colony forming unit (cfu) per gram/milliliter of a sample. Enterobacteriaceae have a high spoilage potential if found in food products (Brightwell et al. 2007). They are Gram negative, rod-shaped bacteria which are facultative anaerobes. Many members of this family are found in the gut flora of humans and animals therefore it is an important bacterium to monitor in food products. The most widely studied bacteria in this family, one that is used as an indicator organism in many tests, is Escherichia coli.

The objective of this paper is to conduct an analysis of indicative microorganisms in lamb and to establish trends and associations between the organisms using data collected in commercial abattoirs over a two year period.
**Materials and Methods**

The data collected for this study came from several commercial lamb abattoirs in Ireland. It reports on enterobacteriaceae and TVC counts. The tests are performed on a daily basis in the abattoir and boning hall and the results are pooled at the end of the week to give an average reading for the seven day period. Each sample is duplicated when plated to give a better overall view of the results and to account for any human error that occurs during testing.

**Results and Discussion**

As the analysis is an on-going process the results represented here are limited to only one abattoir over a set period of time. Figure 1 represents the data collected over a 13 week period between April and July 2008. Table 1 shows the limits for TVC and Entero’s present on the carcass. The TVC results show a higher microflora count than the Enterobacteriaceae count. The reason for this is the TVC test measures all microorganisms that are viable whereas Enterobacteriaceae is a specific species of bacteria tested for by using a selective media (Violet Red Bile Glucose Agar). The readings found in the marginal range mean that the meat is safe for consumption, however the counts are nearing the unacceptable range and actions must be undertaken to reduce these numbers back down to the acceptable range. These actions may include more stringent hygiene regulations for workers.

![Figure 1. TVC and Entero swab sample results for a 13 week period between April and July 2008](image-url)
Table 1. Limits for the quantity of TVC and Enterobacteriaceae permitted in lamb meat (EC 2005)

<table>
<thead>
<tr>
<th>Bacteria</th>
<th>Acceptable Range</th>
<th>Marginal Range</th>
<th>Unacceptable Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Viable Count</td>
<td>&lt;3.5 Log</td>
<td>3.5 - 5 Log</td>
<td>&gt; 5 Log</td>
</tr>
<tr>
<td>Enterobacteriaceae</td>
<td>&lt;1.5 Log</td>
<td>1.5 – 2.5 Log</td>
<td>&gt; 2.5 Log</td>
</tr>
</tbody>
</table>

The TVC readings in Figure 1 show 2 readings in the unacceptable range, 3 readings in the marginal range and 8 readings in the acceptable range. The Enterobacteriaceae show 2 readings in the unacceptable range, 9 readings in the marginal range and 2 readings in the acceptable range. It is possible to see a relationship between the trend lines, a large increase in the TVC readings shows a corresponding increase in the Enterobacteriaceae readings.

The Enterobacteriaceae readings in this analysis are high. Measures need to be taken and procedures reassessed to improve the processing conditions and reduce contamination. The high results could also be associated with external factors, for example the position of the swab taken. The areas of the carcass that are most likely to come in contact with the fleece during fleece removal i.e. the brisket and the flanks, are more inclined to have higher contamination levels than lower risk areas such as the hindquarter, however because the results are pooled an overall higher microbial reading is observed during the analysis. Also the working conditions and the hygiene of the workers can be of concern. The working area, as well as the workers attire (apron, gloves and boots) must be maintained at the highest level of hygiene possible at all times.

Conclusions

Food safety is the most important parameter in the food industry. The food products must be suitable for human consumption without causing any illness or other harmful effects. The above graph shows the importance of monitoring foods for indicator organisms to ensure there is no contamination of the products during processing or storage. This monitoring helps companies to comply with EU regulations.

Acknowledgments

The author would like to thank Prof. Francis Butler and the companies that supplied the results for their time and help.

References


PREDICTION OF *STAPHYLOCOCCUS AUREUS* GROWTH IN HAM DURING CHILLING USING PATHOGEN MODELLING PROGRAM

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**Abstract**

Whole meat after cooking should be chilled as quick as possible to eliminate the potential hazard of bacteria growth. As it is required by Food Safety Authority of Ireland, the time spent between 50°C to 12°C during chilling time must be ≤ 4 hours. A computer-generated model (Pathogen Modeling Program, U.S. Department of Agriculture) was used to examine the growth of *Staphylococcus aureus* in ham during chilling. The prediction is based on the actual time and temperature data of a commercial ham chilling process.

**Introduction**

According to Food Safety Authority of Ireland, whole, non-reformed or non-restructured meat products must be chilled to ≤ 3°C within six hours, with a final storage temperature of ≤ 3°C. The time spent between 50°C to 12°C during chilling time must be ≤ 4 hours. (Gaze et al., 1998) The temperature range (5°C to 63°C), at which surviving pathogens can readily multiply, must be traversed as quickly as possible to minimise growth during chilling, after cooking. Most non-sporing non-pathogenic bacteria will not multiply readily at < 10°C. A temperature of ≤ 5°C is required primarily to reduce the growth of spoilage organisms and achieve extended storage life. (Food Safety and Authority of Ireland, 2006) Slow chilling after cooking of meats or meat products represents a hazard as it may result in the growth of *Staphylococcus aureus* and further production of staphylococcal enterotoxin.

There is an association between ham and outbreaks of *Staphylococcus aureus* intoxication. As is reported in the US, 680 foodborne illness outbreaks were caused by pathogenic bacteria during the 3-year period from 1999 to 2001. Among them, 63 were caused by *S. aureus*, with 11 involving ham. There are two plausible ways in which hams could be contaminated with *S. aureus* before cooking. First the surface of the ham could be contaminated as a result of slaughter, fabrication, or handling. The second possible route of contamination is via the brine solution that is pumped throughout the ham using long needles. If the brine solution or pumping apparatus was contaminated with *S. aureus*, the organism could be introduced into the ham interior. (Ingham et al., 2004)

An initial evaluation of the potential for *S. aureus* growth during chilling is possible using actual product time and temperature data and *S. aureus* growth values from a computer-generated predictive model. In US, the Department of Agriculture (USDA) Food Safety Research Unit has developed such a model, known as the Pathogen Modelling Program, which can be used for foodborne pathogen growth predictions. However, the model can only predict the growth of bacteria under static conditions while during chilling the temperature is dynamic. To adjust the model to reflect the actual situation, it is assumed that the temperature is constant during small time internals and the growth is calculated during each time internal, and then add them together to get the total predicted growth over the entire time-temperature range. The objective of this project is thus to evaluate the growth conditions of *S. aureus* in ham during chilling using the Pathogen Modelling Program from the U.S. Department of Agriculture.
Materials and Methods

Evaluate the temperature change during chilling

To use the model to predict the growth of *S. aureus* during a time that temperature is decreasing, it must know how the temperature changes exactly during a commercial process. Figure 1 gives the core temperature changes in ham during air-blast chilling process. As it is required to traverse between 50°C to 12°C during chilling time within 4 hours, the start time is set at 100 mins with corresponding temperature 52 °C and the end point is 340 mins with corresponding temperature 12°C. This 4 hours is divided by half an hour time interval. Table 1 is the reading of the temperature of each 0.5 hour interval from Figure 1.

![Temperature Changes](image)

**Figure 1:** Ham core temperature with experimental data during air-blast chilling process (Hu & Sun, 2001)

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Actual Temp (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100(0hr)</td>
<td>52</td>
</tr>
<tr>
<td>130(0.5hr)</td>
<td>42</td>
</tr>
<tr>
<td>160(1hr)</td>
<td>34</td>
</tr>
<tr>
<td>190(1.5hr)</td>
<td>28</td>
</tr>
<tr>
<td>220(2hr)</td>
<td>24</td>
</tr>
<tr>
<td>250(2.5hr)</td>
<td>19</td>
</tr>
<tr>
<td>280(3hr)</td>
<td>16</td>
</tr>
<tr>
<td>310(3.5hr)</td>
<td>13</td>
</tr>
<tr>
<td>340(4hr)</td>
<td>10</td>
</tr>
</tbody>
</table>

**Table 1:** Corresponding of temperature of each 0.5 hour time interval

Data input

To obtain the growth values, the following environmental conditions were used in the model: aerobic growth (chosen because aerobic growth is more rapid than anaerobic and most ham are not vacuum packed), pH 6.5 (typical prepumping value for hams), 2.5% water-phase sodium chloride (calculated from worst case values of 1.8% sodium chloride and 68% moisture), and 100 ppm added sodium nitrite (max residual level published by Food Safety Authority of Ireland in 2009). The initial level of *S. aureus* is set at 3.0 log (CFU/ml). The
model covers the temperature range of 10 to 42°C. For each time interval with temperatures below the optimum for \textit{S. aureus} growth (37°C), the maximum temperature for the interval was assumed to have occurred for the entire interval. For time intervals between 37°C and the maximum temperature for \textit{S. aureus} enterotoxin production (46°C), the lowest growth temperature in the interval was assumed to have occurred for the entire interval. This is because for each time period the most suitable temperature condition is assumed to overestimate \textit{S. aureus} growth to maximise the safety. It was assumed that \textit{S. aureus} was initially in growth phase (no lag phase), which is plausible because the temperature is continuous decreasing. The changes of environmental condition are quite small so that bacteria do not need too much time to adjust to the new conditions. The logs of growth predicted during each time interval is determined from the corresponding isothermal model information and the cumulative logs of growth was calculated.

\textbf{Results and Discussion}

\textit{Predictive Results}

Predictions made for maximum \textit{S. aureus} growth from the PMP 7.0 computer-generated model was 2.57 log units (table 2), when exposed to the temperature conditions experienced during the chilling of ham. According to Downes & Ito (2001) food in which the level of \textit{S. aureus} has reached 10^6 per gram may cause illness. Thus, this level of growth, which is about 3 \times 10^5 cells, would not result in enterotoxin production sufficient to cause illness if \textit{S. aureus} numbers prior to growth were in the 3-log range.

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|c|c|c|}
\hline
Time elapsed (hr) & Length of interval (hr) & Actual temp (°C) & Assigned temp (°C) & Generation time from model (hr) & Log CFU/ml & Logs of growth \tabularnewline
\hline
0.5 & 0.5 & 52-42 & 42 & 0.5 & 3.50 & 0.50(0.50) \tabularnewline
1 & 0.5 & 42-34 & 34 & 0.6 & 3.52 & 0.52(1.02) \tabularnewline
1.5 & 0.5 & 34-28 & 34 & 0.6 & 3.52 & 0.52(1.54) \tabularnewline
2 & 0.5 & 28-24 & 28 & 1.0 & 3.48 & 0.48(2.02) \tabularnewline
2.5 & 0.5 & 24-19 & 24 & 1.5 & 3.25 & 0.25(2.27) \tabularnewline
3 & 0.5 & 19-16 & 19 & 3.1 & 3.12 & 0.12(2.39) \tabularnewline
3.5 & 0.5 & 16-13 & 16 & 5.2 & 3.10 & 0.10(2.49) \tabularnewline
4 & 0.5 & 13-10 & 13 & 9.5 & 3.08 & 0.08(2.57) \tabularnewline
\hline
\end{tabular}
\caption{Use of \textit{Staphylococcus aureus} growth values from the PMP predictive model to estimate \textit{S. aureus} growth during chilling of ham.}
\end{table}

\textsuperscript{a} Core temperature for a commercial ham.

\textsuperscript{b} Increase logs of growth for the given time interval with cumulative logs of growth in parentheses based on \textit{S. aureus} start level is 3.0 log (CFU/ml).

\textsuperscript{c} Growth parameters obtained for the following environmental conditions: aerobic growth, pH 6.5, 2.5% water-phase sodium chloride, and 100 ppm added sodium nitrite. Time and temperature data used were based on actual commercial conditions.

\textbf{Conclusions}

The prediction result shows critical limits for ham chilled during a 4 h period with internal temperature between 50°C and 12°C will not allow growth of \textit{S. aureus} to levels where enough toxin is produced to cause illness. Thus, the critical limits are safe and could be validated for use in HACCP plans. The future challenge for the Pathogen Modelling Program is to validate predictions in the actual food matrix rather than in lab media. In addition future challenges include evaluating the cumulative effect of any temperature fluctuation that
regularly occurs in the distribution, and to take in account the fact that the pathogen initial count is usually unknown, and may be below the detection limit. (Shimoni & Labuza, 2000)

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Food Safety and Authority of Ireland. (2006). Guidance Note No. 15 Cook-Chill Systems in the Food Service Sector (Revision 1), Dublin.
DETECTION OF SYNTHETIC MILK ADULTERATION IN NATURAL MILK

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Abstract

The objective of this work is to evaluate the ability of conventional milk quality tests to detect various levels of synthetic milk in cows’ milk. Milk adulteration is a major issue in India where the use of urea combined with vegetable oils, salt, sugar and detergent is frequently used to adulterate cows’ milk. The conventional milk quality tests to be evaluated are the classical compositional and quality tests conventionally applied at raw milk intake and will include, protein and fat determination, freezing point depression, acidity.

Introduction

Milk is an excellent source of energy, protein, minerals and vitamins (Noyhouzer et al., 2009) making it an essential nutritional food for infants as well as the elderly. Among compounds found in milk, urea is a normal constituent. The typical concentration of urea in milk is 18–40 mg/dL (Jonker et al, 1998). A cut-off limit for urea concentration in milk is normally accepted at 70 mg/dL. It also forms a major part (55%) of the nonprotein nitrogen of milk (Sharma et al, 2008). Urea being relatively cheap and rich in nitrogen is an economical choice to adulterate the milk. Adulteration of milk with urea decreases the nutritive value of the milk. The effect of urea above the cut-off limit in milk may cause indigestion, acidity, ulcers, cancers, malfunctions of kidney, etc. (Trivedi et al, 2009). Hence, urea estimation in milk is of great significance. With the annual production of milk reaching 70 million tons, India is poised to become the world’s leading milk producer but adulteration of natural milk with a chemically synthesized milky liquid (synthetic milk) is a matter of serious concern. The dairy industry employs various checks, these tests commonly include determination of fat and total solids by chemical or physical analyses; estimation of sediment by forcing milk through filter pads and noting the residue left; determination of bacterial count, determination of freezing point etc. (Trivedi et al, 2009). However, most of these measurements are expensive and time consuming, as the milk samples need to be taken to the laboratory for testing. Synthetic milk is an excellent imitation of natural milk. Milk fat is mimicked by vegetable oil; the nitrogen component in milk is mimicked by urea; detergents are added to make it frothy. This mixture is so expertly prepared that the specific gravity of the synthetic milk is the same as natural cows’ milk. This mixture is then mixed with natural milk in varying proportions. Such milk can be processed into “value added” products which bring in a bigger profit.

Several chemical analysis methods have been developed for urea analysis in milk, but all chemical and analytical practices are time consuming and may require highly skilled workers and expensive equipment (Trivedi et al, 2009). The food and dairy industries needs rapid, reliable and affordable techniques for quality control. The application of thermal biosensors in food analysis is a growing field with increasing demand for reliable sensors (Mishra et al, 2010). Numerous biosensors have been reported in recent years for milk urea analysis, such as manometric biosensor (Jenkins & Delwiche, 2002) and potentiometric biosensor (Trivedi et al, 2009). Some of these reported biosensors have a very low detection limit and low operational stability, which renders them unfit for routine analysis. There is a need for economical, reliable, robust and reproducible biosensors specifically for urea analysis in milk.

The objective of this work is to evaluate the ability of conventional milk quality tests to detect various levels of synthetic milk in cows’ milk and the conceptual development of biosensors for detecting synthetic milk in natural milk.
The conventional milk quality tests to be evaluated are the classical compositional and quality tests conventionally applied at raw milk intake and will include protein and fat determination, freezing point depression, acidity. For development of biosensor concept of Potentiometric biosensor (Trivedi et al, 2009) and immobilising Urease enzyme on DEAE – Cellulose paper strip (Reddy et al, 2004) technique on modified glucometer will be tested.

**Materials and Methods**

**Biochemical and Reagents:**
Urea [CO(NH2)2], Detergent, salt, sugar, skimmed milk powder and water are used to manufacture a synthetic milk. The reagents were mixed in the correct proportions and then homogenised in a Silverson mixer. Synthetic milk is prepared by mixing adequate amounts of Urea, Detergent Powder, Skimmed Milk Powder, Salt/sugar to water and mixing it well in a container. The preparation is visually very similar to natural milk and approximates the total nitrogen, fat content and specific gravity of natural milk. Detection of synthetic milk is very easy and it can be even detect under a microscope as it does not contain any somatic cells. But when the mixture is added to natural milk in 10%-20% to natural milk then detection of the adulteration becomes very difficult.

In the present work varying concentrations of synthetic milk will be added to cow’s milk and the milk mixture subsequently analysed for fat, protein (total nitrogen), acidity, urea concentration, freezing point. In each case a limit of determination will be established, at which point the test method can reliably identify the adulterated milk and the similar samples will be tested with the indigenously developed Urease enzyme biosensor strips as well as a glucometer modified with urease enzyme and the critical limits and working of such portable biosensor will be tested.

**Results and Discussion**

Synthetic milk is not a very well defined product as even different research papers have their different views over its production and it is mixed in varied proportions (Mishra et al, 2010; Trivedi et al, 2009). But the researches have show that biosensor methods are highly reproducible, cost effective, reliable and robust. But biosensor technology has shown strong ability of detecting such adulterations (Mishra et al, 2010). (Mishra et al, 2010) developed a Flow injection analysis biosensor for urea analysis in adulterated milk using enzyme thermistor, method is based on detection of heat produced when a biological reaction takes place. Whereas a Potentiometric biosensor has been developed by (Trivedi et al, 2009). So, a very similar approach can be utilized to develop a urea detection sensor for household purpose.

![Figure 1](image1.jpg) Synthetic milk before Boiling.  
![Figure 2](image2.jpg) Synthetic Milk after boiling
A boiling test was conducted to determine effects of boiling on 100% synthetic milk. Before boiling, the milk preparation looks very similar to natural milk but after boiling the preparation turns light yellowish brown and coagulation was observed.

Conclusions

In the current scenario and looking at the unorganised milk market in the developing world it is very necessary to develop a sensor based technology which is economical, reliable, robust, and reproducible to tackle the problem of milk adulteration. The sensor should be sturdy enough to bear the heavy fat and solute load of Milk and other solute load.

Acknowledgements

I would like to thank my supervisor and mentor Professor Francis Butler for his guidance and support.

References

A Study of the Effect of Chilling on Prevalence of Campylobacter on Poultry carcasses by Meta-analysis

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Abstract

Meta-analysis is commonly used to combine results of prevalence studies of pathogens at critical stages within the food processing chain. Food processors can access reliable information on the effectiveness of interventions for preventing and controlling foodborne illness in humans. Meta-analyses confirmed that the chilling operation has a significant beneficial effect on the reduction of Campylobacter prevalence on poultry meats. Because of the systematic approach of meta-analysis and its reliance on actual data, the output distribution of the relative effect size merits consideration in quantitative risk assessments of the prevalence of Campylobacter in the chilling stage along.

Introduction

The definition of meta-analysis is (DeCoster, 2004): The statistical analysis of a large collection of analysis results for the purpose of integrating the findings. Meta-analysis is a statistical procedure that integrates the results of several independent studies considered to be ‘combinable’ with the basic purpose of providing the same methodological rigor to a literature review that we require from experimental research. As different studies were taken out with different designs, population sizes, experiments and amount of study-effect factors, researchers suggested that combing the studies will produce an estimate that has more complex information than any single study. With meta-analysis, it may be possible to explain the differences between results from individual studies by defining coding variables or moderators that contain information specific to the individual studies, such as theoretical constructs, population samples, data collection procedures, research designs, and other basic study characteristics (Noble, 2006). In food safety research, meta-analysis may be used to determine the effect of interventions pre- and postharvest, disease incidence and pathogens prevalence.

Carcasses can be contaminated with fecal material during slaughtering and other carcasses can be cross-contaminated. Contamination of poultry meat with foodborne pathogens remains an important public health issue, because it can lead to illness if there is malpractice in handling, cooking or post cooking storage of the product. The most commonly identified bacterial cause of diarrheal illness in the EU is Campylobacter (EFSA, 2008). Raw poultry meat is often contaminated with Campylobacter since these bacteria can live in the intestines of healthy birds. Eating undercooked chicken, or ready-to-eat food in contact with raw chicken, is the most common food-borne source of this infection. It causes fever, diarrhoea and abdominal cramps. This study was carried out to investigate whether there is support in the sampled population of studies for the causal inference that the chilling stage within pork production significantly decreases Campylobacter prevalence on poultry meats and, if so, to estimate the overall effect of the chilling operation on the studied outcome. The objective of this study is to demonstrate the applicability of a parametric approach of meta-analysis to determining the overall effect of chilling on Campylobacter prevalence on poultry meats.
Materials and Methods

For binary outcomes, meta-analyses are generally centered on the relationship between one explanatory and one response variable. This relationship, ‘the effect of X on Y’, defines the analysis. The two models developed are the fixed-effects meta-analysis model and random-effects meta-analysis model. The five basic steps to perform a meta-analysis (DeCoster, 2004) are: (1) Define the theoretical relationship of interest, (2) Collect the population of studies that provide data on the relationship, (3) Code the studies and compute effect sizes, (4) Examine the distribution of effect sizes and analyze the impact of moderating variables, (5) Interpret and report the results. It is suggested that a systematic review and meta-analysis begins with the formulation of a focused study question (Sargeant, 2005). When forming the question, three important factors should be considered: population, intervention and outcome. The question in this study is the estimation of the overall effect of chilling on the prevalence of Campylobacter on poultry carcasses during poultry production.

Electronic and non-electronic literature searches were carried out to identify all references reporting prevalence data for Campylobacter on poultry carcasses before chilling and after cold storage in slaughterhouses, following the systematic review protocol presented by Sargeant et al. Data are collected among a number of completed and on-going studies undertaken by EFSA/FAO/WHO on Campylobacter in broilers in EU and other published articles relative to the prevalence of campylobacter on poultry carcasses. All the information presented in these studies was assessed and considered for inclusion in the meta-analysis.

After the problem statement formulation and data collection, a parameterization or measure unit of the intervention’s effect size was determined. The effect size ($\theta$) refers to the degree to which the hypothetical phenomenon (i.e., decrease in Campylobacter prevalence due to chilling) is present in the population (i.e., poultry carcasses during processing). Consequently, meta-analysis proceeds by converting the effect size into a parameter or common metric that permits direct comparison and summation of the independent studies (Noble, 2006). It is important to decide which parameter measuring effect size will be used to describe and summarize the data in the meta-analysis (Sargeat et al, 2007). In this study, two parameters may be chosen, relative risk (RR) and risk difference (RD), thus these separate effect size ($\theta$) measures will produced two distinct meta-analysis by two different models: fixed-effects meta-analysis model and random-effects meta-analysis model. RR is defined as the probability of the outcome in the treatment group relative to the probability in the control group, and RD is defined as the difference in probabilities between the treated and control group. Then mathematic method was used to calculate the effect size of individual studies ($\theta_i$) for the first meta-analysis and then to the second meta-analysis,

$$\theta_i = \ln RR$$

or $\theta_i = RD$

and two further values, the standard error of the effect size (SE($\theta_i$)) and the inverse variance weight($\omega_i$)

$$\omega_i = \frac{1}{SE(\theta_i)^2}$$

Further steps of this study involve calculation of different values following the two different models, plotting and comparing the parameters RR and RD to answer the question formulated for this study (the overall effect of chilling on the prevalence of Campylobacter on poultry carcasses).
Results (expected)
As this mathematic work is on-going, only expected results are shown here. According previous studies, after slaughtering, the final products are stored as chilled (<4°C) or frozen products (-18 to -20°C), causing a further reduction of the Campylobacter contamination of the chicken meat. Chilling reduces numbers by between 0.6 and 1.0 log10 cfu/g (Oosterom et al., 1983b; Yogasundram and Shane, 1986), especially when dry air is used for chilling (Salvat and Laisney, 2002). Thus, we can deduce the effect size parameterization of RR and /or RD will be highly significant, providing strong evidence for the reduction of Campylobacter prevalence on poultry carcasses due to chilling. The effectiveness of chilling may be observed among different chilling methods and different countries in EU.

Conclusions (expected)
Meta-analysis will allow food safety researchers to synthesize the current body of knowledge on targeted issues along the complex continuum of agricultural-food production and will provide increased credibility for findings in the field. Meta-analysis can reduce the delay between research discoveries, implementation and identify reasons for heterogeneity, and increase the precision of the overall results. This study will confirm the effectiveness of chilling on the prevalence of Campylobacter in poultry carcasses. Chilling is one of the process operations reported to cause the greatest changes (decreasing) in the contamination of campylobacter.

Acknowledgements
The author would like to thank Prof. Butler for his help.

References
Nanoparticle migration and exposure assessment from food packaging

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Abstract

Nanotechnology is the manipulation of matter at the nanoscale, generally between 1 – 100 nm. Discoveries of unique nanomaterial properties have lead to novel applications in the food industry, one of which is antimicrobial food packaging materials. Human exposure to nanoparticles may be influenced by the consumption of meat subjected to such packaging conditions. Chicken samples were wrapped in silver nanoparticle antimicrobial food packaging materials and analysed with inductively coupled plasma mass spectrometry (ICPMS). A worst case scenario of a 4 day storage period resulted in 1.01 mg of silver per 100 g of chicken breast meat. When chicken consumption is considered, the corresponding silver intake would only reach 2.6% of a provisional human limit value. Both the initial concentration and the storage temperature were found to significantly impact particle migration (p<0.05).

Introduction

For the food industry, where competition is intense and innovation is vital, nanotechnologies have emerged as aids to advancements in producing improved quality food with functionalised properties. Nanotechnologies have been applied in the food sector from primary production to stock monitoring at a retail level. One emerging and promising application of nanotechnologies 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. The vacuum packaging of large meat cuts prior to being displayed at the butcher counter would benefit from this type of technology. It is perishable high value food products that are the most likely food category to use these technologies. In addition, appropriate disposal of potentially hazardous packaging waste would be considerably easier to control once limited to retailer use only. Vacuum packaging of this kind uses primarily LDPE. This supports the need to focus on other packaging materials to obtain a commercially viable end product.

Concerns have been raised with regard to potential human exposure to nanoparticles as a result of the future use of these materials in industry. 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). Any of these exposure routes 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 or environmental health (Chau, Wu and Yen, 2007). As with other new technologies, the rush to market may outpace the investigation into possible health and environmental implications (Morgan, 2005). It is important to fully assess risks of all new materials before their use is widespread.

In this study, the particular exposure route of concern is via unintentional transfer of nanomaterials from antimicrobial food packaging into foods. Such migration depends on many factors (see figure 1.) 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.
Materials and Methods

Experimental Design for Migration Tests
64 Chicken breasts, weighing approximately 120 g each, were wrapped in one of 4 types of plasticised polyvinyl chloride (PVCP) which incorporated different percentages of silver nanoparticles; 5% and 0.5% and different sizes of nanoparticles; 10 nm and 50 nm. 4 chicken breasts, weighing approximately 120g each, were wrapped in blank PVCP films containing no nanoparticles. The PVCP films were made by project partners to the specification illustrated in Table 1. The chicken/film samples were kept at one of 4 storage scenarios. In the first, the samples were kept at 20°C for 4 days, the second; 20°C for 2 days, the third; 5°C for 4 days and the fourth; 5°C for 2 days (see figure 2).

Preparatory Protocol
The chicken breast cuts were wrapped in 120 cm² of these nanofunctionalised films on the breast bone side of the chicken. Tin foil was wrapped around these to eliminate a possible effect of light. The samples were then vacuum packaged in standard polyethylene vacuum packaging bags. Vacuum packing was carried out on the samples to ensure maximum contact between the antimicrobial packaging and the chicken. For such active packaging materials, sharing a common interface or physical contact with the food surface is essential for them to impart the desired effect (Vermeiren, Devlieghere and Debevere, 2002). Each sample was done in quadruplicate. One blank was included for each time/temperature combination. Samples were kept in constant temperature rooms for the duration of the experiment.

Figure 1. Factors effecting nanoparticle migration from nano packaging to food

Figure 2. Experimental Design
ICPMS Analysis

Analysis was carried out using inductively coupled plasma mass spectrometry (ICPMS) equipment. ICPMS analysis is a quantitative technique which combines a high temperature ICP source with a mass spectrometer. It is commonly used to detect ultra trace metals in complex matrices such as foods. Matrix interferences are minimized due to the high temperature of the ICP source. The sample was homogenized and 1-2 g of this underwent a microwave digested with 10 ml of concentrated nitric acid. Isotope 107 with rhodium was used as an internal standard. Samples were analysed according to protocol assigned the ISO number: DIN EN ISO 17294-2-E29.

Table 1. Films made to suit factorial design experiment

<table>
<thead>
<tr>
<th>Concentration of nanoparticles in PVC: 5%</th>
<th>Diameter of nanoparticles:10 nm</th>
<th>Diameter of nanoparticles:50 nm</th>
<th>No nanoparticles (blank)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration of nanoparticles in PVC: 0.5%</td>
<td>16</td>
<td>16</td>
<td>-</td>
</tr>
<tr>
<td>No nanoparticles (blank)</td>
<td>-</td>
<td>-</td>
<td>4</td>
</tr>
</tbody>
</table>

Results and Discussion

Laboratory Tests

Following storage at 5°C for 4 days in contact with a PVCP film containing 5% nanoparticles of a diameter of 50 nm, a mean silver level (n=4) of 7.7 mg/kg of chicken breast meat was detected. As shown in table 1, there were two levels of nanoparticle % fill (5% and 0.5%). This parameter was found to be significant (p<0.05) in the laboratory tested samples. Storage temperature was also found to significantly impact particle migration from packaging to the meat (p<0.05), although the migration increased at the lower temperature (5°C) compared to the higher temperature (20°C). This may be due to unusual thermal behavior exhibited by the particular polymer used; PVCP. The results of this analysis were used to assess likely exposure to silver particulate nanomaterial that could potentially arise from the use of such packaging in the mainstream food industry.

Exposure

Credible relatable toxicity values for toxicity values for the consumption of nanoparticles for humans are unavailable. So a provisional ingestion limit value (0.482 mg of silver/kg(body weight)/day) was obtained from scientific literature (O’Brien and Cummins, 2010). This was generated using oral toxicity studies using a model organism and interspecies allometric distribution factors. Chicken consumption data for Ireland was sourced, (0.022 kg per person per day) (IUNA, 2001). An assumption was made that all chicken consumed in Ireland was packaged in PVCP containing 5% nanoparticles of a diameter of 50 nm and stored at 5°C for 4 days. Therefore the exposure incurred = \( \frac{\text{(Silver level in chicken)} \times \text{(Irish chicken consumption)}}{\text{Average body weight}} \)

\[
\frac{(7.7 \text{ mg/kg}) \times (0.022 \text{ kg/pp/pd})}{71.5} = 0.0024 \text{ mg/day/kg(body weight)}
\]
This would amount to 0.49% of the provisional ingestion limit for silver nanoparticles.

Conclusions

Eating foods packaged with PVCP which incorporates silver nanoparticles is not likely to lead to the consumption of silver levels which exceed provisional ingestion limit values.

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 negative perception of a technology can lead to consumer rejection (e.g. G.M. foods). A probable 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.

PVCP appears to be becoming less popular as a high value perishable foods’ packaging, with only a few supermarket own brand cheeses still using it. Polyethylene, either low density polyethylene (LDPE) or high density polyethylene (HDPE) would be a more suitable food packaging matrix to incorporate nanoparticulate materials into because of their popularity as food packaging materials.

Acknowledgements

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

References


Coagulase-positive Enterotoxins of Staphylococcus aureus isolates from Milk used in Raw Milk Farmhouse Cheese

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Abstract

Coagulase positive Staphylococcus aureus can produce a range of emetic proteins known as Staph enterotoxins (SEs) which can be present in raw milk and therefore in cheese made from raw milk. To determine the number and types of SE present, 117 raw product samples were enumerated for Staphylococcus aureus. Isolates were characterised for SE. From the 81 raw product samples that were positive for coagulase positive S. aureus, characterisation included analysis for SE by Reverse Passive Latex Agglutination for SEA, SEB, SEC and SED production, and by multiplex PCR for the SEA, SEB, SEC, SED and SEE genes.

Introduction

S. aureus is a gram positive, facultative anaerobe that is ubiquitous in nature. Some, but not all strains produce pyrogenic, pepsin-resistant Staphylococcus Enterotoxins (SE’s) which are potent emetic agents causing Staphylococcus Food poisoning (Dinges et al. 2000; Le Loir et al. 2003). The relevance of S. aureus in relation to risk in raw milk and raw milk food is its ability to produce SE.

The production of the classical SEs by SEA, SEB, SEC, and SED producing S. aureus strains in raw milk is variable. In Italy 55% of isolates were found to be positive for these SEs (Normanno et al. 2007). In Turkey 25.5% of isolates were positive for SEs (Boynukara et al. 2008). When S. aureus strains that are SE producers reach between 10⁵ to 10⁸ cells per gram, the SE levels are thought to reach the toxic dose levels (100ng/ml) which can cause food poisoning (Le Loir et al, 2003).

Farmhouse raw milk cheese is potentially a high risk food (André et al. 2008). S. aureus may occur in raw milk as a result of contamination by bovine, food handlers or the processing environment. Foods that are handled such as Artisan Cheese are thought to have higher risks associated with S. aureus and there is a need to assess this perception. Many Artisan raw milk cheese producers do not use pasteurization and therefore have a higher risk of S. aureus contamination.

In this study we enumerated and characterised S. aureus isolates from raw milk, and from curds, whey, fresh cheese and ripe cheese made from that milk. The study included five milk suppliers of raw milk cheesemakers.

The objective of this study was to study the supply of raw milk to farmhouse cheeses with respect to S. aureus and to use this data as part of a risk assessment.
Materials and Methods

Sample collection
In the south of Ireland, from March to June 2010, a total of 117 samples at various stages in manufacture were aseptically collected from 5 bovine milk suppliers and their 4 raw milk cheese producers. 10 raw milk samples was collected from all 5 suppliers. Extra samples were taken from Suppliers 2, 3, and 4 as described in detail in Table 1.

Table 1. The bulk raw milk sampled and products from 3 of the suppliers of raw milk cheese and products were analysed. Number of coagulase positive S. aureus samples in brackets.

<table>
<thead>
<tr>
<th>Product</th>
<th>Supplier 2</th>
<th>Supplier 3</th>
<th>Supplier 4</th>
<th>Sample Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk Raw Milk</td>
<td>10(3)</td>
<td>11(9)</td>
<td>10(10)</td>
<td>31</td>
</tr>
<tr>
<td>Vat Raw Milk</td>
<td>10(6)</td>
<td>2(1)</td>
<td>0</td>
<td>12</td>
</tr>
<tr>
<td>Curds</td>
<td>10(9)</td>
<td>6(6)</td>
<td>2(2)</td>
<td>18</td>
</tr>
<tr>
<td>Whey</td>
<td>10(0)</td>
<td>6(0)</td>
<td>2(2)</td>
<td>18</td>
</tr>
<tr>
<td>Fresh Cheese</td>
<td>5(5)</td>
<td>2(0)</td>
<td>5(4)</td>
<td>12</td>
</tr>
<tr>
<td>Ripe Cheese</td>
<td>0</td>
<td>0</td>
<td>2(0)</td>
<td>2</td>
</tr>
<tr>
<td>Totals</td>
<td>45</td>
<td>27</td>
<td>21</td>
<td>93</td>
</tr>
</tbody>
</table>

Enumeration of S. aureus from raw milk and raw milk products
Coagulase positive S. aureus were enumerated using ISO 688-2-1999 on Baird Parker Rabbit Plasma Fibrinogen selective agar (oxoid) with the deviation that the limit of detection for whey was 1 cfu/g and some cheeses was 100 cfu/g due to the nature of their viscosity and background flora, respectively. All other samples had a detection limit of 10 cfu/g.

Strains Isolates of S. aureus from raw milk and raw milk products
Bulk raw milk, the same raw milk from the cheese vat prior to cheesemaking, fresh curds and whey were all collected when available at the day of manufacture. Fresh cheese and ripe cheese were also collected from the same batches, fresh cheese was taken during the following weeks. Ripened cheese was taken after the product had ripened fully and was ready for sale.

Bulk raw milk was sampled from the farm dairy bulk tank, (using a 50ml sterilised dipper) which was either fresh from the animal or cooled from the previously milking period for no longer than 3 days.

All samples were immediately placed on ice, returned to the laboratory at 4°C, and analysed within 24hrs of receipt. When present, at least 2 strains were isolated from each sample and subcultured on tryptic soy agar, (one hundred and fifty five isolates, representing up to 2 isolates from each of the 81 positive samples for S. aureus were used in this study). Isolates were stored in cryovials at -20°C.

SET-RPLA:
The 155 Isolates were analysed (by reverse passive latex agglutination [RPLA]) by the Toxin detection kit for the detection of staphylococcal enterotoxin A, B, C and D, as per the manufacturers instructions (Oxide product Code: SET TD0900).

Multiplex PCR
The Primers used for the 5 classical S. aureus enterotoxins (A, B, C, D, E) were used as described by Mehrotra et al. (2000), Peles et al. (2007) and Gonano et al. (2009). The DNA of the 155 isolates were extracted using Prepman ultra™ (Applied Biosciences code 4318930). Quantities for PCR mix; 1ul of a 0.5uM/ul dilution concentration for all Primers, 2ul DNA
with a concentration range of 50-200ng/ul measured using a Nanodrop 1000 spectrophotometer (Thermo Scientific), 12.5ul ImmoMix™ Red (Bioline BIO25021) made to 25ul total reaction volume with PCR grade water. PCR; Amplicons were produced from subjecting samples to the following amplification conditions; Initial heat treatment of 95°C for 10min, 30 cycles of 94°C for 30sec, 54°C for 45sec and 72 for 30sec, followed by final degradation step of 72 for 10min. The Amplicons was visualised in UV light with the addition of SyBr® (invitrogen™) 1kb with a Ladder (Bioline Hyperladder IV) and positive controls (supplied by Lund University).

**Results and Discussion**

The number of samples positive for *S. aureus* is shown in Table 1. The *S. aureus* enumeration results (Table 2) showed that all samples were within the limits set by EC regulations for colony count.

Milk samples had relatively low counts while fresh cheese gave the highest counts. Whey samples gave the lowest counts.

**Table 2.** Enumeration; Range of cfu/ml for raw milk and associated products.

<table>
<thead>
<tr>
<th>Product</th>
<th>Supplier 1</th>
<th>Supplier 2*</th>
<th>Supplier 3</th>
<th>Supplier 4</th>
<th>Supplier 5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk Raw Milk</td>
<td>80-900</td>
<td>&lt;10-35</td>
<td>10-110</td>
<td>140-700</td>
<td>15-330</td>
</tr>
<tr>
<td>Vat Raw Milk</td>
<td>-</td>
<td>&lt;10-60</td>
<td>&lt;10</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Curds</td>
<td>-</td>
<td>&lt;100-3100</td>
<td>17-800</td>
<td>780-7200</td>
<td>-</td>
</tr>
<tr>
<td>Whey</td>
<td>-</td>
<td>&lt;1&lt;</td>
<td>&lt;1</td>
<td>24-38</td>
<td>-</td>
</tr>
<tr>
<td>Fresh Cheese</td>
<td>&lt;100</td>
<td>&lt;100-6700</td>
<td>-</td>
<td>1800-14000</td>
<td>-</td>
</tr>
<tr>
<td>Ripe Cheese</td>
<td>-</td>
<td>-</td>
<td>&lt;10</td>
<td>&lt;10</td>
<td>-</td>
</tr>
</tbody>
</table>

Of the 5 raw milk supplies tested, SEC was isolated from products originating from only one supplier. These SEC isolates were negative for all other SE genes tested. None of the isolates from any of the other four suppliers produced SEA, SEB SEC or SED toxin nor did they harbour the SEA, SEB, SED or SEE genes (Table 3).

**Table 3.** Results of 151 isolates tested for SE production and gene.

<table>
<thead>
<tr>
<th>S Enterotoxin</th>
<th>SET-RPLA</th>
<th>PCR</th>
</tr>
</thead>
<tbody>
<tr>
<td>SEA</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>SEB</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>SEC</td>
<td>26</td>
<td>26</td>
</tr>
<tr>
<td>SED</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>SEE</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

**Conclusions**

The SEC positive isolates were epidemiologically related as they were all from the one supplier over a short time period of less than 12 weeks and found in milk, curds and whey and cheese batches. None of the isolates from any of the four suppliers produced SEA, SEB SEC or SED nor did they harbour the SEA, SEB, SED or SEE genes. The results indicate that, from a perspective of staphylococcal enterotoxin, milk used for raw milk cheese production in Ireland poses a limited risk to public health.
Acknowledgements

This work was supported by the EU 6th Framework Programme under the project BIOTRACER, and by the Food Institutional Research Measure, project.

References


RESIDUES OF QUATERNARY AMMONIUM COMPOUNDS IN FOOD PLANT ENVIRONMENT: THEIR IMPORTANCE AND ANALYSIS METHODS

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Abstract
Quaternary ammonium compounds (QACs) have been used frequently in food processing plants as antimicrobial agents. Their residues remain after the cleaning process and may affect the safety of food materials with the risk of product contamination. Therefore, it is important to evaluate the sanitation process with regard to the sanitizer residues. In this study, a review of analytical methods and sampling procedures for the residue evaluation of QACs is provided. Several analytical methods have been reported for the quantification of QACs including gas chromatography, capillary electrophoresis, high performance liquid chromatography (HPLC). Almost all existing studies have shown that the HPLC method provides more reliable and accurate results due to its high sensitivity, selectivity and automation characteristics. It should be also noted that, because of the very low concentration of QAC residues after the cleaning process, an accurate sampling procedure is necessary before setting up the analytical technique.

Introduction
Disinfection is regarded as a critical step in achieving desired hygienic conditions in food processing and production areas. However, the contamination of the product with the disinfecting agent should be avoided. Hence, principle knowledge about the selection of the appropriate disinfectants and the related methods of application and residue quantification is necessary.

Quaternary ammonium compounds (QACs) have been shown to have good antimicrobial activity and therefore are widely used in food processing plants to minimise bacterial growth and subsequent biofilm formation (Oulahal et al., 2008). They are a class of salts derived from ammonium in which nitrogen atom is attached to four aryl or alkyl groups (Jia et al., 2001). QACs are positively charged cations, hence, their mode of action is related to their attraction to negatively charged materials such as bacterial proteins. Their antimicrobial activities depend on the alkyl chain length.

Alkylbenzyldimethylammonium chloride known as Benzalkonium chloride (BAC), is the most widely used QACs, is a mixture of homologue compounds with various even-numbered alkyl chain lengths from n = 8 to n = 18. This disinfectant provides effective protection in low concentrations (< 1 mg/l) against bacteria, yeast, mould and viruses with long term durability and environmentally friendly performance (Sütterlin et al., 2008).

The wide use of QACs on food or feed contact surfaces may result in residues in human food originating from treated surfaces, such as equipment and appliances. The residues can migrate to food and can be consumed as a part of the final product by the consumer. Moreover, in accordance with the European Union policy of maintaining a ‘high protection level’ for consumers, residue levels of disinfectants should be kept ‘as low as reasonable achievable’ (ALARA) following the principles of Good Manufacturing Practice in using disinfectants (Dornseiffen, 1998).

Reliable analytical methods for the determination of quaternary ammonium biocides are required for the effective monitoring of occupational and environmental exposure as well as in the quality control of manufactured products (Núñez et al., 2004).

The objective of this paper is to provide a brief overview of the application and importance of QACs as antimicrobial and disinfectant agents, and finally, evaluate different analytical techniques used for their recovery and quantification.
Methods for the quantification of QACs
Various studies have been carried out focusing on the analysis of QACs. The first and the most common method of evaluation have consisted of using the Disulphine Blue Active Substance (DBAS) method and two phase titration before the development of novel methods. Emergence of more sophisticated instrumental analysis using gas chromatography (GC), nuclear magnetic resonance, thin-layer chromatography coupled with flame ionization detection, liquid chromatography (LC) and capillary electrophoresis (CE) led to better precision of quantification of these compounds (Martínez-Carballo et al., 2007). Each analytical method possesses some advantages and disadvantages when employed for the evaluation of QACs. Therefore, for achieving accurate and reliable results, the most useful and sophisticated instrumental technique should be selected and set up.

HPLC is a well established method for the evaluation of residues in food materials. Ion-pair HPLC with direct UV detection is usually employed for the determination of QACs, since they are polar, easily soluble in water and have low volatility. Liu and Ding (2004) observed that HPLC is the most promising method for analyzing alkyl benzyl cationic surfactants. LC–MS and LC–MS–MS methods using an electrospray ionisation source and an ion trap analyser have also been developed for the analysis of biocides such as BAC homologues and didecyldimethylammonium chloride (DDDMAB). The LC–MS–MS method provided limit of detections in the low ppb range with a very good linearity and therefore seems to be a very efficient method (Núñez et al., 2004). Figure 1 illustrates a mass chromatogram recorded for a standard mixture of BAC C12, BAC C14, BAC C16 and DDDMAB (Ford et al., 2002).

![Figure 1: A mass chromatogram acquired for a standard mixture of BAC C12, C14, C16 and DDDMAB; peaks are annotated with the appropriate molecular structure (adapted from Ford et al. (2002).)](image)

Results from the analysis by GC showed that, since QACs have high molecular weight with extremely low vapour pressure in GC injector, they may undergo thermolysis and elude analysis (Wulf et al., 2010).
CE is another method employed for the analysis of QACs in a number of studies. Heinig et al. (1997) discovered that because of the relatively long alkyl chain of QACs they have the tendency to sorb onto the capillary surface and form micelles in the capillary column which may affect their separation by CE. They suggested that excessive consumption of organic solvent and buffer pH may enhance separation by CE (Heinig et al., 1997). Liu and Ding (2004) also confirmed this observation. Other studies on QACs analysis in drinking water samples showed that CE has a less-than-desirable sensitivity based on concentration, as compared to HPLC. Hence, to fulfil the maximum legally permitted levels of QACs in drinking water, enrichment procedures such as solid phase extraction (SPE) prior to determination have to be used (Núñez et al., 2004).

Discussion for sampling method selection
The majority of the analysis methods mentioned above have been notably applied for measuring QACs in drinking water, waste water, effluents or sludge. It is evident that the techniques for isolation and recovery of QACs from the primary sources play an importance role in the final results. Based on some studies, isolation and pre-concentration of QACs in water or effluent samples is preferably performed by SPE via a cartridge whereas recovery of target compounds from surfaces in manufacturing environments by SPE may be lost during the process. Therefore, before the selection of chromatographic conditions, a defined extraction procedure should be applied. Different studies on the recovery of drug residues from surfaces in the processing environments have been carried out following roughly similar extraction procedure which can be applied for QACs residues isolation and analysis.

In the first step, different solutions of the target compounds are applied to the surface, letting them dry. Recovery of these residues can be applied by cotton swab moistened with the appropriate mobile phase solvent. In different studies, a couple of solvents with a defined gradient have been used for the separation of QACs, i.e. acetonitrile/Formic acid-ammonium formate buffer (50 mM, pH = 3.5); acetonitrile/water with 10 mM ammonium acetate/isopropanol with 0.1% formic acid; HFBA solution (15 mM, pH 3.3)/acetonitrile (Bester and Lamani, 2010; Castro et al., 2000; Martínez-Carballo et al., 2007)

After wiping the surface with cotton swabs vertically and horizontally, they should be immersed into a tube containing the mobile phase. The tube containing cotton swabs and mobile phase is then sonicated in a bath for 5 to 10 min. Sonication lets the moistened cotton swab releasing the residues of QACs recovered from the surface into the mobile phase solution. Then, the test solutions will be ready to be injected into the chromatograph. Once the chromatographic conditions had been selected and developed, the method should be validated paying attention to the linearity, precision, accuracy, selectivity, limits of detection and quantitation and stability of standards and samples (Klinkenberg et al., 2003; Nozal et al., 2001; Qin et al., 2010)

Conclusions
Different sophisticated instrumental analysis methods have been used for the measurement QACs. QACs have specific physico-chemical properties resulting in a number of difficulties during their quantification including low sensitivity of the instrument toward QACs, thermolysis of target compounds when analysed by GC, micelle formation in the capillary column and excessive consumption of solvent in CE. Experiences obtained in different studies for the evaluation of QACs have revealed that the HPLC method when coupled with UV detector or MS is the most efficient method. Recovery of the residues before the final step of quantification by the chromatograph has also a considerable effect on the accuracy and precision of the final results. Swabbing techniques followed by sonication seem to be helpful for the best possible recovery of QACs residues from surfaces.

Acknowledgements
The author would like to thank Mr. Hossein Kiani, PhD student in Biosystem Engineering, for all his help and advice for preparing this paper.
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THE DEGRADATION OF PHYTO-OESTROGEN IN SOYA INFANT FORMULA USING SONICATION

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Abstract

Soya infant formula has been used for the last 40 + years as an alternative to breast milk and bovine infant formula to feed infants. Soya beans are well recognised for containing high levels of phyto-oestrogen. This paper will investigate the use of sonication for the degradation of phyto-oestrogen compounds in soya infant formula. This work follows previous studies on the use of sonication in waste water treatment plants for the removal of oestrogens from an aqueous solution. The proposed work will be conducted on soya infant formula at specified treatment time points (0, 10, 20, 30, 40, 50 and 60 min), amplitudes (24.4, 30.5, 42.7, 54.9 and 61 µm) and varied with pulse durations of 5 s on and 5 s off. The samples will be analysed under HPLC conditions.

Introduction

Soya infant formula (SIF) has been consumed by millions of infants worldwide and holds a third of the American market. SIF is usually the third choice for infants after breast milk and bovine milk respectively (Patisaul and Jefferson 2010). Soya products contain heat stable phyto-oestrogens from the isoflavone class (Bhatia and Greer 2008). Many studies on the effects of isoflavone in adults have found that the phyto-oestrogen’s: genistein and daidzein, have been associated with the alteration of the female reproductive cycle, as potent inhibitor of tyrosine kinases, interfering with cell signal-transduction pathways and anti-carcinogenic properties (Setchell, Zimmer-Nechemias et al. 1998). Bhatia and Greer (2008) found that the main diets of infants with strict vegan parents, lactose intolerance and congenital galactosemia consisted of soya infant formula. Infants on SIF ingest approximately 6 to 9 mg isoflavone per kg body weight per day. This is up to seven times higher than for adults meeting the FDA soya consumption guideline. Total isoflavone concentration in SIF varies due to environmental and genetic differences between batches and sources; nonetheless it is consistently higher than in most other food sources (Patisaul and Jefferson 2010). Setchell, Zimmer-Nechemias et al. (1998) conducted a study on SIF of which the findings showed that SIF contains 32 - 47 mg/L of total isoflavone concentration; therefore, exposing the infant to 22 - 45 mg isoflavone/day. This is significantly higher than human breast milk where the level of phyto-oestrogen is negligible (< 0.01 mg isoflavone/day) with a total isoflavone concentration of 5.6 ± 4.4 µg/L (Setchell, Zimmer-Nechemias et al. 1998). There are limited studies on the relationship between phyto-oestrogen such as genistein and daidzein and their effects on infants. However, there are concerns about the long term effects of these phyto-oestrogens on sexual development and reproduction, neurobehavioural development, immune function, and thyroid function (Irvine, Fitzpatrick et al. 1998; Bhatia and Greer 2008; Badger, Gilchrist et al. 2009).

Until the full impact on the consumption of phyto-oestrogenic compounds has been fully established, it is necessary to examine the potential removal techniques that may be employed to render SIF safe for consumption. Phyto-oestrogens and oestrogen have been found in waste water treatment plants due to a number of potential sources, such as human and livestock waste products and discharges from food (Fu, H., Suri, et al. 2007; Suri, Nayak et al. 2007; Kang and Price 2009). Studies have found the degradation of oestrogen in waste water to reduce significantly when sonicated. The oestrogen degradation rates increase with an increase in power intensity (Suri, Nayak et al. 2007). The structural similarity of phyto-oestrogen and 17- oestradiol has prompted this study using sonication as a method of degrading phytoestrogen’s in SIF (Bhatia and Greer 2008).

The objective of this study is to investigate the potential of using sonication to degrade phyto-oestrogen in soya infant formula at the laboratory scale.
Materials and Methods

Measurement of Isoflavone in SIF
The proposed methods will be carried out in accordance with the procedures used by Frank et al. 1994 and Irvine, Fitzpatrick et al. (1998).

Samples
Samples of soya infant formula were purchased from a local supermarket.

Chemicals
Acetic acid, Acetonitrile, Methanol, Genistein, Daidzein

Extraction of isoflavone
To determine the distribution of isoflavone, samples were extracted in 80:20 methanol:water for 4 hr. The extract was cooled and immediately passed through a 0.45 μ filter before 20 μl it was injected onto the HPLC system.

Instrumentation and Chromatographic condition
Chromatography was performed on a HPLC equipped with a 20 μl injection loop and a UV/Vis detector. A 3.9 x 300 mm C18 reverse phase column, connected to a C-18 pre-column insert was used. Elution was carried out as described by Frank et al. (1994). Mobile phase 20:80 acetonitrile: 10% acetic acid for 15 min and then 70:30 acetonitrile: 10% acetic acid for 15 min at a flow rate of 0.8 ml/min. Analyte was monitored at 260 nm during each run.

Degradation of Isoflavone in SIF
The proposed methods will be carried out in accordance with the procedures used by Suri et al. (2007) and Adekunte, et al. (2010).

Ultrasound treatment
A 1500W ultrasonic processor (VC 1500, Sonics and Materials Inc., Newtown, USA) with a 19 mm diameter probe was used for sonication at a constant frequency of 20 kHz. 50 ml reconstituted SIF was placed in a 100 ml jacketed vessel and samples of 20 μl of SIF were taken at specified treatment time points (0, 10, 20, 30, 40, 50 and 60 min), amplitudes (24.4, 30.5, 42.7, 54.9 and 61 μm) and varied with pulse durations of 5 s on and 5 s off. The ultrasound probe was submerged to a depth of 25 mm in the sample. All treatments were carried out in duplicate.

Results and Discussion
The experiment is ongoing. The results obtained by Irvine et al. (1998) and Setchell et al. (1998) reported the concentrations of individual isoflavone; genistein and daidzein, measured by HPLC. These results give a guideline for the concentrations of Isoflavone in SIF that are expected to be obtained in this experiment. They are summarized for different commercial infant formulas in Table1.

Ultrasound treatment
Suri, Nayak et al. (2007) found that the ultrasound degradation of individual oestrogens in an aqueous solution, in the 0.6, 2 and 4 kW sonication unit, respectively, show in Figures 1-3. Destruction of the individual oestrogens varied from 87 to 99% for batch sonication time of 60 min in the 0.6kW reactor in Figure 1. Figure 2 shows that 66–98% destruction of the individual oestrogens observed in 40 min of sonication in the 2 kW batch system. Figure 3 results obtained shows that in the 4 kW continuous flow-through system, 64–90% removal of the oestrogens was observed in 35 min of residence time.
Table 1: Isoflavone composition of soya infant formula.

<table>
<thead>
<tr>
<th>Product type</th>
<th>Product</th>
<th>Total Genistein (µg/g, mg/L)</th>
<th>Total Daidzein (µg/g, mg/L)</th>
<th>Total Isoflavone (mg/g, g/L)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Powder</td>
<td>Nursoy</td>
<td>6.2 ± 2.1</td>
<td>7.4 ± 1.0</td>
<td>307.3 ± 27.8</td>
<td>Setchell, et al. (1998)</td>
</tr>
<tr>
<td>Powder</td>
<td>Isomil</td>
<td>8.7 ± 1.2</td>
<td>10.9 ± 2.1</td>
<td>316.9 ± 13.1</td>
<td>Setchell, et al. (1998)</td>
</tr>
<tr>
<td>Liquid</td>
<td>Prosobee conc</td>
<td>1.0 ± 1.0</td>
<td>2.2 ± 0.6</td>
<td>91.0 ± 18.2</td>
<td>Setchell, et al. (1998)</td>
</tr>
<tr>
<td>Liquid</td>
<td>Isomil ready to feed</td>
<td>1.0 ± 0.1</td>
<td>1.0 ± 0.1</td>
<td>43.5 ± 0.7</td>
<td>Setchell, et al. (1998)</td>
</tr>
<tr>
<td>Liquid</td>
<td>Allsoy conc</td>
<td>1.2 ± 0.3</td>
<td>0.9 ± 0.3</td>
<td>63.7 ± 9.2</td>
<td>Setchell, et al. (1998)</td>
</tr>
<tr>
<td>Powder</td>
<td>Formula A</td>
<td>92</td>
<td>55</td>
<td>NA</td>
<td>Irvine et al. (1998)</td>
</tr>
<tr>
<td>Powder</td>
<td>Formula B</td>
<td>81</td>
<td>50</td>
<td>NA</td>
<td>Irvine et al. (1998)</td>
</tr>
<tr>
<td>Powder</td>
<td>Formula C</td>
<td>91</td>
<td>48</td>
<td>NA</td>
<td>Irvine et al. (1998)</td>
</tr>
<tr>
<td>Powder</td>
<td>Formula D</td>
<td>83</td>
<td>44</td>
<td>NA</td>
<td>Irvine et al. (1998)</td>
</tr>
</tbody>
</table>

Figure 1: Oestrogen degradation profile. Sonication reactor: 0.6kW; batch system; initial oestrogen concentration: 10g/l (Suri, Nayak et al. 2007)

Figure 2: Oestrogen degradation profile. Sonication reactor: 2 kW; batch system; initial oestrogen concentration: 10g/l (Suri, Nayak et al. 2007).

Figure 3: Oestrogen degradation profiles. Sonication reactor: 4 kW; continuous flow system; initial oestrogen concentration: 10g/l. (Suri, Nayak et al. 2007).
Conclusions

Suri et al. (2007) found that sonication was observed to be efficient for destruction of oestrogen hormones in aqueous solutions. The sonication process produced 80–90% destruction of individual oestrogens at initial concentration of 10 g/l within 40–60 min of contact time. Bhatia and Greer (2008) found phyto-oestrogen have structural similarities with 17- oestradiol, indicating that it is possible to degraded the levels of phyto-oestrogen in soya infant formula. This project proposes to carry out experimentation on the destruction of phyto-oestrogen in soya infant formula by sonication.

Acknowledgements

The author would like to thanks Prof. Colm O Donnell for his encouragement and guidance and Pfizer Ireland Pharmaceuticals, t/a Wyeth Nutritionals Ireland for access to their facilities and guidance.

References


Coupled spectrophotometric and in vitro microbial assessment of pyocyanin production in *Pseudomonas aeruginosa*

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Abstract

*Pseudomonas aeruginosa* is an opportunistic pathogen causing both acute and chronic lung disease. *P. aeruginosa* exerts many of its patho-physiological effects by secreting virulence factors; pyocyanin is one of the main metabolites of *P. aeruginosa* that can be produced from 90 to 95% of isolates. Spectrophotometric methods will be used for the rapid assessment of pyocyanin production. This investigation will allow the development of a proof of concept for rapid assessment of the microbial metabolism of *P. aeruginosa* based on a carefully selected metabolic indicator and will provide correlations between growth stage and pyocyanin levels.

Introduction

*Pseudomonas aeruginosa* is a Gram-negative, aerobic rod belonging to the Gamma Proteobacteria class of bacteria. The bacterium has become increasingly recognized as an emerging opportunistic pathogen of clinical relevance (Todar, 2011). The microorganism occurs in soil, animal faeces, water and also in foods and is possibly involved in enteritis, transmitted by water and foods. It can be isolated from respiratory and urinary tract infections, wounds, and burns. Microbiological examination of foodstuffs often reveals the presence of *P. aeruginosa* (Szita, et al., 1998).

Pyocyanin (PCN) is a blue, chloroform-soluble, redox-active secondary metabolite that is produced by *P. aeruginosa*. PCN is readily recovered in large quantities in sputum from patients with cystic fibrosis who are infected by the microbe. PCN allows *P. aeruginosa* to kill cells, disrupts cilia actions, inhibit lymphocyte proliferation, and alter phagocytic function. Due to its redox-active properties, pyocyanin generates reactive oxygen species that induce oxidative stress in bacterial and mammalian cells (Lau et al., 2004). The synthesis of this pigment also appears to be under the control of iron concentration since the addition of iron to a medium containing low phosphate stimulates the synthesis of pyocyanin (Cox, 1986). Spectrophotometry is based upon measurement of light transmission through appropriate solvents and analyte solutions, and is a well known widely applicable instrumental technique in analytical chemistry in which chemical analysis information is required. A spectrophotometer consists of two instruments, namely a spectrometer for producing light of any selected wavelength, and a photometer for measuring the intensity of light. The instruments are arranged so that liquid in a cuvette can be placed between the spectrometer beam and the photometer. The amount of light passing through the tube is measured by the photometer. The photometer delivers a voltage signal to a display device, normally a galvanometer. This signal changes as the amount of light absorbed by the liquid changes. Spectrophotometry can be used as a simple and rapid method for pyocyanin quantitation assays (Kong et al., 2005).

The objective of this study is to develop a rapid instrumental tool for assessing the microbial production of PCN from *P. aeruginosa* using UV-Vis spectrophotometry. Conventional in vitro microbial techniques will be used for validating the physical method.
Materials and Methods

*Overall workflow*

The overall workflow that will be followed for the microbiological and spectrophotometric analysis is shown in Figure 1.

![Workflow for microbial and spectrophotometric analyses](image)

**Microbial analysis**

The frozen culture of *P. aeruginosa* will be inoculated in Pseudomonas broth under controlled temperature (37°C). The growth evolution studies of the strain will cover lag phase, log phase, and stationary phase under controlled incubation conditions. Samples will be taken at frequent time intervals and until the stationary phase is reached. The culture sample (1 ml) taken from different growth phase will be diluted to 1/10, 1/100, 1/1000, 1/10000, etc. to obtain the appropriate colony number that can be counted on the agar plates. General nutrient agar and Pseudomonas agar will be used for performing plate counting. Hereafter, the number of *P. aeruginosa* colonies will be counted and multiplied by the dilute factors (e.g. 10, 100, 1000, 10000, etc.) to get the number of CFU per ml of the original sample.

**Pyocyanin quantitation assay**

*P. aeruginosa* (Figure 2) strains will grow with aeration at 37°C in Pseudomonas broth to maximize pyocyanin production. Each culture will be inoculated from a fresh colony and
adjusted to an optical density at 600 nm of 0.02 before incubation. Quantitation of pyocyanin production will be done by extracting a 5 ml of culture with 3 ml of chloroform followed by mixing with 1 ml of 0.2 N HCl to give a red solution (Xu et al., 2005). The absorbance at 520 nm of this solution is a measure of the amount of extracted pyocyanin. Concentrations, expressed as micrograms of pyocyanin produced per millilitre of culture supernatant, will be determined by multiplying the optical density at 520 nm \( (\text{OD}_{520}) \) by 17.072 (Essar et al., 1990).

![Figure 2: Scanning electron micrograph (x15000 magnification) of \textit{P. aeruginosa}](image)

The instrument that will be used for the analysis is the SHIMADZU UV MINI 1240 (Figure 3). This is a single beam spectrophotometer with a silicon photodiode detector, a wavelength range of 190.0 to 1100.0 nm and a 0.1nm step. Glass cuvettes will be used in the experimental protocol.

![Figure 3: Single beam UV-Vis spectrophotometer for pyocyanin determination](image)

**Results and Discussion**

In our study, it is expected that the spectrophotometric method for PCN determination will provide rapid responses that will allow us to correlate the PCN production with the \textit{P. aeruginosa} growth stage. It is known that the microbial activity expressed as population levels per time, rather than the activity of microbial enzymes, influence the accumulation of metabolic by-products (Nychas et al., 2008). PCN is one of the major metabolites produced during the growth of \textit{P. aeruginosa}. It is well established that the actual concentration of the media (in our case Pseudomonas broth) can affect the type and the growth rate of microbial population (\textit{P. aeruginosa}) and, moreover, seems to be the principal precursor of this microbial metabolite. Therefore, we expect to observe that PCN will be influenced by the changes in the levels of \textit{P. aeruginosa} population.
Conclusions

Spectrophotometric analyses might prove to be a useful tool for the rapid determination of PCN production from *P. aeruginosa* and will give information on the correlation between growth stage and PCN levels.

References


COOLING OF COOKED CARROT CUBES OF DIFFERENT SIZES WITH THREE COOLING METHODS
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Abstract

Three different cooling methods: air blast cooling, immersion cooling, and vacuum cooling were evaluated based on their cooling losses and cooling times for different sizes of cooked carrot cubes. For the same sizes of samples, results revealed the shortest cooling time, however, with the highest cooling loss were obtained when carrots cubes were cooled using vacuum cooling, compared to the other cooling methods. For the same cooling method, different sample sizes exerted a small impact on the cooling loss while shorter cooling time was obtained when the size was smaller. It was concluded that, irrespective of the sizes of carrot cube, vacuum cooling was the most efficient cooling method in comparison with the other cooling methods but it caused the highest cooling loss; on another hand, the impact of a larger size on cooling time for vacuum cooling was much smaller than for the other cooling methods, even though a larger size resulted in longer vacuum cooling time.

Introduction

Carrots play an important role in peoples’ daily diet. On the other hand, they are recognized as one of the most important sources of β-carotene amongst various fruits and vegetables present in western diets (Torronen Lehmusaho et al., 1996), and β-carotene is an important nutrient for the human body. Studies have demonstrated that high blood levels of β-carotene can effectively decrease the risk of cancer (Torronen Lehmusaho et al., 1996). There is no doubt carrots are an important part in maintaining peoples’ healthy life. Cooked carrot not only appears in peoples’ homemade foods, but also is a common component in ready meals. For the manufacturing of ready meals, the cooling rate of hot foods, after cooking, should be as quickly as possible since opportunities for microbial growth will be greatly reduced with the rapid cooling rate (Anon., 1991; Zhang and Sun, 2006). Strict regulations regarding cooling times also drive manufacturers to find innovative methods to reduce cooling time. As a rapid cooling method, vacuum cooling has been widely studied in the food industry (Sun and Zheng, 2006). Some papers have investigated the application of vacuum cooling on cooked carrots, however, the effect of carrot size on vacuum cooling, to the best of the authors knowledge, has not yet been studied.

The objective of this work was to study the effect of carrot cube size on cooling time and cooling loss following vacuum cooling by comparison with other cooling methods.

Materials and Methods

Samples preparation
Carrots of Fontana from Germany were used in the present experiments. The carrots were preserved at about 4 °C before using. The similar size carrots were selected to cut into cubes of 1 × 1 × 1 cm or 2 × 2 × 2 cm. The average weight for the former was 1.1 ± 0.2 g and 9.5 ± 0.3 g for the latter. The carrot cubes of each size were divided into three groups with 6 carrot cubes in each group. Cubes were wrapped in tin foil and stored at 1 °C in a refrigerator before further process to prevent moisture evaporation from the cubes.

Cooking and cooling procedures
Samples were cooked individually in boiling water in a stainless steel pot, using an electric cooker (9934-10, Russell Hobbs, Ireland) until the core temperature of the samples reached
around 90 °C. After cooking, the cooked cubes were immediately moved into different chillers for cooling until the sample core temperature got to below 10 °C.

Three cooling methods were used: namely vacuum cooling, air blast cooling and immersion cooling. A cooked sample was vacuum cooled using a laboratory vacuum cooler (Autec Ltd., UK), by moving the sample into the chamber, closing the chamber door, followed by immediately fully opening the vacuum pump valve with the main valve completely closed. When the chamber pressure was reduced to 12.2 mBar (the corresponding saturated pressure of water at 10 °C), it was precisely maintained by adjusting the bleeding value. Sample cooled by air blast cooling was performed using an air blast chiller (CBF 20, Foster refrigerator Ltd., UK) at air temperature 0 ± 3 °C, and air velocity of 1.078 ± 0.020 m s⁻¹. As for immersion cooled samples, they were immersed in a large tank of water at 5 ± 2 °C without any package. For each cooling method and each size of carrot cube, 6 replicates were carried out, with one sample in each replicate.

Data acquisition during cooling
The core temperature of each sample during cooling was measured using a thermocouple (T-Type, Radionics, Ireland). The chamber pressure was measured by a pressure transducer (PR4000, MKS, Germany). Data acquisition systems (SCXI1000, National Instrument, USA) and programs based on LabView (v4.2, National Instrument, USA) were used to record the measured pressure in the vacuum chamber and the temperatures from both the air blast chiller and vacuum cooler. A data logger (TC-08, Pico Technology, UK) was used to collect the temperature data during immersion cooling. All the data was collected at an acquisition interval of 1 s.

Weight loss
Weights before and after cooling were measured, and the cooling loss was calculated using the following formula:

\[
\text{Cooling Loss (\%) } = \frac{(W1 - W2)}{W1} \times 100\% \tag{1}
\]

Where W1 was the weight of the cooked sample and W2 was the weight of the cooled sample.

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

Results and Discussion

Cooling losses of carrot cubes
As presented in Table 1, vacuum cooling caused significant moisture loss (14.80%) for 1 × 1 × 1 cm samples, compared with 7.6% cooling loss for air blast cooling and 1.39% cooling gain for immersion cooling \((P < 0.01)\). For the larger size of 2 × 2 × 2 cm, the significant differences still exist: 15.16% cooling loss for vacuum cooling whilst 8.26% cooling loss for air blast cooling and no cooling loss for immersion cooling. This is due to unavoidable water evaporation during the vacuum cooling procedure: water evaporation will cause considerable latent heat to be absorbed from the product itself and its surroundings for phase change, and the temperature of the products will then drop (Sun, 2001; Wang and Sun, 2001; Sun, 2005; Mutlu and Kemal, 2009). The reason for little cooling loss or even weight gain in immersion cooled samples may be that the chilled water surrounding the cooked sample not only prevented water evaporation from the sample but also dispersed into the sample due to the osmotic pressure caused by the sugar in the carrot.
Table 1: Cooling loss and time of cooked carrot cubes

<table>
<thead>
<tr>
<th>Sizes</th>
<th>Cooling loss (%)</th>
<th>Cooling time(s)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>vacuum cooling</td>
<td>air blast cooling</td>
<td>immersion cooling</td>
</tr>
<tr>
<td>1 × 1 × 1 cm</td>
<td>14.80&lt;sup&gt;Aa&lt;/sup&gt;</td>
<td>7.60&lt;sup&gt;Ab&lt;/sup&gt;</td>
<td>-1.39&lt;sup&gt;Ac&lt;/sup&gt;</td>
</tr>
<tr>
<td>2 × 2 × 2 cm</td>
<td>15.16&lt;sup&gt;Aa&lt;/sup&gt;</td>
<td>8.26&lt;sup&gt;Ab&lt;/sup&gt;</td>
<td>0.00&lt;sup&gt;Ac&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

Note: Means with different upper case letters within a column are significantly different (P<0.01); Means with different lower case letters within a row are significantly different (P<0.01); The minus sign in this table means the sample weight gain.

Cooling time of carrot cubes

In respect of size of 1 × 1 × 1 cm, the cooling times for air blast cooling sample (226.8 s) were almost twice of those for vacuum cooling (120.0 s). Immersion cooling showed comparative cooling time (138.5 s) with vacuum cooling and less cooling time than air blast cooling (226.8 s) (as shown in Table 1). This may be explained by the different heat transfer modes of the cooling methods. Vacuum cooling relies on evaporative cooling, while air blast cooling achieves a temperature reduction mainly based on heat conduction or convection during their cooling processing, and usually the heat conduction inside the food is the controlling step for the cooling. The ratio of evaporative to conductive heat transfer is between 8 and 16 (Sun, 2001). Vacuum cooling, therefore, represents substantial faster cooling rate than other cooling treatment (Zheng and Sun, 2004). It was found that cooling rate of immersion cooling is faster than that of air blast cooling. This may be attributed to the higher heat-transfer coefficient in immersion cooling, which is 20 times higher in liquid media than in air. Furthermore, the chilling liquid contacts product surface and promotes heat-transfer characteristics (Sun, 2001).

According to the curves in Fig. 1, there were substantial differences between different sample sizes for the same cooling methods. As for vacuum cooling, the cooling time for 2 × 2 × 2 cm (397.2 s) was considerably longer than that for 1 × 1 × 1 cm sample (120.0 s) (shown in Table 1), which indicates that size impacts on the vacuum cooling time for carrot cube. This may be due to the different porosities for carrots. Unlike other vegetables such as lettuces and mushrooms, carrot is less porous, indicating less evaporation and hence less evaporative heat transfer inside the food, resulting in a greater role of heat conduction in heat transfer inside the carrot during vacuum cooling. Therefore, the vacuum cooling rate decreased with sample size.

However, the size of carrot cube did not negatively impact the cooling rate for vacuum cooling as for the other cooling methods, as shown in Fig. 1. The prolonged cooling times caused by the increase of size were approximate 277 s, 474 s and 406 s for vacuum cooling, air blast cooling and immersion cooling, respectively. This resulted from the combined cooling effect of evaporation and heat conduction inside the carrot cube during vacuum cooling, and only heat conduction inside the carrot during air blast cooling and immersion cooling.
Conclusions

It was found that in relation to sample sizes, vacuum cooled samples achieve the highest cooling rate, followed by immersion cooling and air blast cooling. However, as was expected, vacuum cooling caused the highest cooling loss. As far as the effect of sample sizes is concerned, vacuum cooling rate was reduced with the increase of size, nevertheless, the cooling rate is still much more rapid than the other methods studied. It was concluded that vacuum cooling was the most efficient cooling method for cooling of different sizes of carrot cubes.

References


INNOVATIVE WINE AGEING TECHNOLOGIES FOR PRODUCING FINE WINES DURING A SHORT AGEING PERIOD

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Abstract
Wine ageing is an important process to produce high-quality wines. Traditionally, wines are aged in oak barrel ageing systems. However, due to the drawbacks of the traditional ageing technology, including time consumption, high cost, etc, innovative ageing technologies have been developed. The technologies introduced in this paper can produce fine wines during a short ageing period. Therefore, they are regarded to greatly benefit the modern winemaking industry.

Introduction
Wines play an important role in people’s life. It is widely recognized that fresh wine is undrinkable due to its harsh taste, pungent smell and some possible harmful side-effects. Thus, the fresh wine should be aged until it is drinkable and marketable.

During wine ageing, groups of reactions occur which tend to improve the taste and flavor of wine over time. Traditionally, oak barrels are used in the ageing of wine because of the positive effects they have in sensory characteristics and in volatile compounds. However, there are some disadvantages in this traditional ageing method. Firstly, the ageing process in barrels normally takes from 3-5 months to 3-5 years, which is time-consuming. Secondly, barrels are expensive, take up a lot of space in wineries and their lifetime is not long. In addition, as the barrel becomes older, it might become populated with undesirable microorganisms such as *Brettanomyces*, which can produce sensorially significant concentrations of ethylphenols with their unpleasant medicinal and horsy aromas (Suárez et al., 2007). Considering the negative effects of barrels on ageing, current researches were focused on developing new ageing technologies and improving present technologies. One of these involved putting small pieces of wood into wine in order to provide a woody aroma and taste on wines (Morales et al., 2004). Micro-oxygenation is also employed to introduce small and measured amounts of oxygen into wines (Guerrero et al., 2011). For some wines, ageing on lees could improve their organoleptic characteristics (Doco et al., 2003). Furthermore, some physical methods have been developed to accelerate the ageing process, which involved ultrasonic wave (Chang, 2005), gamma rays (Chang, 2003), electric field (Zeng et al., 2008) and nanogold photocatalysis (Lin et al., 2008). These technologies are promising to artificially accelerate the ageing process and enhance the sensory quality of wine.

The objective of this article is to review the recent developments of wine ageing technologies and the innovative technologies which can produce high-quality wines during a short ageing period.

Improvement of Barrel Ageing System for Accelerating Ageing Process
In the traditional barrel ageing system, oxygen from the atmosphere diffuses in through the
semi-permeable walls of the barrel and chemical reactions occur in a region near the interface of inner barrel wall. As a result, a concentration gradient of the products builds near the barrel wall, and the accumulation of these products forms a reaction barrier, which inhibits fresh wine from reaching the reaction region. Consequently, the ageing reaction of wine is slowed and the ageing technology is considered to be time-consuming.

Recently, a non-deleterious barrel ageing system was developed to breach the reaction barrier and accelerate ageing (Eustis, 2010). In this semi-permeable wine ageing container, either an internal device or an external device can be fitted, such as an internal circulating pump and an external pump, so that a liquid motion is induced mechanically and fresh wine is brought continually to the reaction region to accelerate ageing. Furthermore, it is believed that the oxygen transfer from barrel surface to the inner barrel is increased by the mechanical motion of liquid.

**Wine Ageing Using Wood Fragments**

To save money and shorten ageing time in barrels, alternative ageing systems that add wood fragments, such as oak chips and oak staves into wines have been considered. In this alternative ageing system, the small size of wood fragments allows wines to be absorbed quickly while only the layer closest to the liquid is soaked in the barrel in traditional ageing systems. The liquid penetrates and soaks wood fragments totally, which improves the compounds diffusion from the wood fragments into the wine. On the other hand, since wood is being put into wine and not wine into wood, the entire surface area of the wood is usable and not just 40% of it (Stutz et al., 1999). Therefore, the extraction rate of oak-related compounds is enhanced in the ageing system in the presence of wood fragments and the length of contact time can be reduced.

In the application of wood fragments, several factors, including pretreatment, size, botanical characters, and geographical provenances of wood should be taken into account since these factors can affect the quality of final wines.

**Combination of Micro-oxygenation and Wood Fragments during Ageing**

Micro-oxygenation is a technique that consists of introducing small and measured amounts of oxygen into wines with the objective of improving wine colour, aroma and texture and involves the use of specialized equipment to regulate the oxygen doses applied.

The application of micro-oxygenation alone cannot accelerate the ageing process. However, the combination of micro-oxygenation and wood fragments can be regarded as an effective tool to shorten the ageing time. Guerrero et al. (2011) proposed a method of ageing using 5 g/L of oak chips and a dose of oxygen around 70 mL/L month. With the proposed method, and according to their sensorial and analytical results, the authors concluded that Sherry wine vinegars similar to those traditionally aged could be obtained by the combination of micro-oxygenation and oak chips addition in 14 days against 105.

**Novel Wine Ageing Technologies on Lees**

Ageing on lees can benefit the quality of wines. During ageing, the autolysis phenomenon undergone by yeast lees is of paramount importance in determining the composition and quality of final wines. To shorten the ageing time on lees, the autolysis process should be
accelerated.
There are two strategies which can accelerate the autolysis process. One is selecting the strains that undergo rapid autolysis. Among all the used yeast species, the osmophilic yeast genera *Schizosaccharomyces* and *Saccharomyces* show very positive polysaccharide release kinetics and rapid autolysis (Palomero et al., 2009). The other strategy is adding commercial enzyme preparations. These products are mixes of several enzymes such as β-glucanase and pectinase that considerably increase the polysaccharide concentration in both white and red wines (Pellerin and Tessarolo, 2001). It should be taken into account that the addition of the enzymes directly to the wine in the presence of lees increases the glucose concentration, which as a source of carbon may stimulate the growth of undesirable microorganisms such as *Brettanomyces*.

Wine Ageing Using Some Novel Physical Technologies
The physical technologies which can be applied for ageing involve ultrasonic waves, irradiation, electric field and nanogold photocatalysis. Wine ageing using ultrasound is a good example of enhanced oxidation. The acoustic cavitation, which consists of the formation, growth and violent collapse of small bubbles or voids in liquids, can provide high temperature and high pressure for the modification of chemical reactions. 20 kHz and 1.6 MHz ultrasonic waves were used to accelerate the ageing of rice wine (Chang, 2005). It was found that rice wine could potentially be aged to a quality taste of market rice wine within 1 week by using 20 kHz ultrasonic waves while the 1.6 MHz ultrasonic wave treated ones could not achieve expected taste. Combined with the study of Lindley and Mason (1987), it could be concluded that the proper ultrasonic frequency used for accelerating wine ageing reactions is mainly divided between 20 and 100 kHz.

Besides the study of ultrasonic waves for wine ageing, Chang (2003) also found that the application of γ-irradiation at a suitable dosage can improve some defects of rice wines in one hour instead of the one-year ageing time required for the market product of grain alcoholic beverage, without the presence of irradiation residues. Therefore, γ-irradiation can be potentially used for accelerating wine ageing.

Electric field treatment is also considered as an effective method to accelerate young wine ageing and this technique has been used in Chinese wine factories. Zen et al. (2008) found that a treatment with electric field 600 V/cm for 3 min can accelerate red wine ageing, which made the harsh and pungent raw wine become harmonious and dainty.

Nanogold catalysts, which have a particle size ranging from 80-120 nm, can react with water and oxygen to produce free hydroxyl radicals on exposure to a light source of an approximately 245 nm (Lin et al., 2008). Nanogold photocatalysis has been used to accelerate the maturation of young sorghum spirits in the study of Lin et al. (2008). In this study, the process successfully accelerated maturity of young sorghum spirits with pleasant sensory feeling within 120 min at ambient temperature. In addition, the matured product was identified to be non-toxic by acute toxicity test.

Conclusions
Ageing is an essential operation in the whole winemaking process in order to produce high-quality wines. Nowadays, the winemaking industry is greatly concerned with manufacturing
high-quality wines in a short ageing period. This paper reviews some innovative ageing technologies. Although all these technologies are promising to accelerate ageing process, the quality of wine should always be the first consideration.

Acknowledgements
The authors would like to thank the financial support from the European Commission, 7th Framework Programme Theme Capacities.

References

Very interesting: Grade C+
ACTIVE CONTROL OF NUCLEATION AND ICE CRYSTAL SIZE IN AGAR GELS BY ULTRASOUND IRRADIATION: PROCESS EVALUATION AND MICROSTRUCTURAL ANALYSIS

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Abstract
Nucleation of ice during freezing is an important phenomenon affecting the probability distribution of the ice crystal size and crystal growth rate. Power ultrasound has been proven to be useful in promoting the nucleation of ice in water-based solutions and different theories have been proposed to describe the mechanism of this phenomenon. In the present work, the use of ultrasound waves to induce nucleation in agar gel samples was studied. The samples were put into tubing vials and were frozen in an ethylene glycol-water mixture (-20 °C) in an ultrasonic bath system. Ultrasound (25 kHz, 0.45 W cm\(^{-1}\)) was applied continuously for 3 s at different sample’s temperatures. Results indicated that ultrasound irradiation at different temperatures was able to initiate nucleation in agar gel samples after a short delay. Microstructure evaluation of the samples revealed that the size distribution of ice crystals was affected by ultrasound induced nucleation temperature. Decreasing the nucleation temperature resulted in smaller ice crystals created in the sample. In conclusion, the use of ultrasound as a means to control the crystallization process offers promising application in food freezing but further investigations to understand the mechanisms is required before it can be adopted, especially for solid foods.

Introduction
The crystallization of water occurs during the phase transition stage of the freezing process and is a key step in determining the efficiency of the freezing process and the quality of final product. The crystallization of water consists of two stages namely nucleation and crystal growth. The morphology, size and distribution of ice crystals are strongly related to nucleation (DeMan, 1999; Petzold & Aguilera, 2009). However, ice nucleation occurs spontaneously and stochastically within a wide range of temperatures and is affected by several factors such as impurities, asperities, surface properties, etc. that in general cannot be easily monitored and manipulated (Nakagawa, Hottot, Vessot & Andrieu, 2006). Therefore, a method to control the nucleation phenomena and turn its stochastic behaviour into a repeatable and predictable manner can be valuable and promising for the food freezing industry.
Ultrasound waves have been shown to be able to initiate nucleation in different supersaturated solutions (Chalmers, 1964) and supercooled aqueous solutions (Chow, Blindt, Chivers & Povey, 2003, 2005; Chow \textit{et al.}, 2004; Inada, Zhang, Yabe & Kozawa, 2001). In most of the experiments carried out on ultrasound assisted nucleation, fluid samples have been employed while solid foods have not been widely considered.

The objective of this article is to study the effect of ultrasound waves on the nucleation of ice and the microstructure of the frozen samples of a solid model food composed of water (90%), agar (2%) and sucrose (8%) at different temperatures.

Materials and Methods
Preparation of model food samples
The model food samples were prepared by melting the mixture of deionised water (Sigma-Aldrich, Dublin, Ireland), sucrose (Fischer Scientific UK Ltd, Leicestershire, UK) and agar powder (VWRInternational, Fontenay-sous-Bois, France) (90%, 8% and 2%, w/w) with
gentle heat, followed by filling the melted mixture into tubing vials (1.2 mL, 0.9 mm diameter). The samples were cooled to room temperature before they were frozen. They were freshly made each day.

**Freezing experiments**
An ultrasonic bath system was employed (CQBF-1025, 726 Research Institute, China Shipping Company, China). Unidirectional ultrasound waves (25 kHz) could be delivered to a freezing medium of ethylene glycol - water mixture (1:1, v/v) in the tank of the system. The freezing medium was maintained at -20ºC by a low temperature circulator (Grant Instrument Ltd., Cambridge, UK).

In each freezing run, one sample in a tubing vial was frozen in the freezing medium at the fixed chosen location at the bottom of the tank, with a fixed sample holder. The temperature of the freezing process was monitored precisely with a T-type thermocouple (Radionics Ltd., Ireland) at the centre of the vial and a data logger (SQ-2040, Grant Instruments, UK) connected with a laptop. Ultrasound was radiated for 3 s continuously onto the sample when the monitored sample temperature reached a given temperature (from just below 0 to -5ºC). The intensity of ultrasound in tubing vials was fixed at 0.45 W cm⁻², measured using the calorimetric method (Li & Sun, 2002) with a tubing vial full of deionised water.

**Microstructural evaluation**
Frozen samples were cut perpendicular to the longitudinal axis of the tubing vials and the cross section (0.9×0.1 mm) at the middle of the samples were obtained as microstructure observing specimens. The specimens were dehydrated in gradually increasing concentrations of alcohol from 40%, finally reaching to 100% (Merck, Germany). Then the specimens were rinsed in xylene (Fisher Scientific, Ireland) three times, for 12 h each time. Then the specimens were passed through a series of paraffin wax (Sigma-Aldrich, Ireland) at 65ºC three times, for 6 h each time. The samples were thereafter embedded in wax and cut to thin slices (5 microns) using a microtome (Leitz 1512, Germany). Then the slices were de-waxed with a series of xylene and alcohol and covered with DPX (Cellpath Ltd., UK) and slide covers after staining with alcian blue (Sigma-Aldrich, Germany) and dried. A series of images of each specimen were taken alongside the diameter of the specimen using a light microscope (Labophot-2, Nikon, Japan) equipped with a digital camera (Micropublisher 3.3 RTV, QImaging, Canada) and a PC. The images were processed and analysed for ice crystal size measurements by using software Adobe Photoshop 11 (Adobe Systems Inc., CA, USA) and Image pro plus 6.1 (Media Cybernetics, Inc., MD, USA). The area of the ice crystals in the images were measured and used for the interpretation of the ice crystal size.

**Results and Discussion**
**Effect of ultrasound irradiation on nucleation: evaluation of the freezing curve**
The model food samples, frozen without ultrasound irradiation, nucleated in a range of temperature after a supercooling stage (-7.5 ± 0.92 ºC). Fig. 6 shows the effect of ultrasound irradiation triggered at different sample temperatures on the nucleation of ice in the solid model food samples. As it is observed in the figure, irradiation of ultrasound at any studied temperature resulted in nucleation of ice in the samples after a short delay from the trigger of ultrasound. It can be concluded that ultrasound can induce nucleation in solid foods, as it does in water and some fluid model food samples (Chow, Blindt, Chivers & Povey, 2003, 2005; Chow et al., 2004; Inada, Zhang, Yabe & Kozawa, 2001). The observation in the present study confirmed the possibility of the extension of the results obtained previously for fluid samples to a solid model food.
**Figure 1:** Nucleation temperatures of agar gel samples affected by ultrasound irradiation triggered at different sample temperatures. Arrows indicate the irradiation trigger points.

**Effect of ultrasound assisted freezing on ice crystal size distribution**
The size distribution is revealed in Fig. 2a. Fig. 2b, c & d display the processed images of agar gel nucleated at different temperatures by ultrasound irradiation.

**Figure 2:** Ice crystal size distribution (a) in ultrasound assisted freezing of agar gels nucleated at different temperatures: -2°C: ■ and b, -3°C: ▲ and c, -4°C: ● and d.
Ultrasound irradiation affected the ice crystal size distribution within frozen agar gel samples by controlling nucleation. As mentioned above, irradiation at any temperature resulted in the trigger of nucleation. Lower irradiation temperatures resulted in lower nucleation temperatures and caused the crystals to become smaller, as can be observed in Fig. 2.

Conclusions

Ultrasound was irradiated into agar gel samples which were being frozen. Results indicated that ultrasound can be used to trigger and to control the nucleation of ice. Results also revealed that nucleation of ice assisted by ultrasound, always commenced only a short while after the irradiation. Since the nucleation is a stochastic phenomenon and its control is difficult, these results can be of great value in the freezing industry and other related processes. Ultrasound triggered nucleation at different temperatures resulted in different ice crystal sizes in the model food samples. Lower nucleation temperature caused the ice crystals to become smaller.

Acknowledgements

Authors wish to thank the University of Tehran and the Iranian Ministry of Science, Research and Technology for supporting this PhD study.

References

A COMPARISON OF SMD(SOIL MOISTURE DEFICIT) RECORDINGS BETWEEN 3 DIFFERENT DRAINAGE CLASS SITES TO THE SITES NEAREST SYNOPTIC WEATHER STATION.

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Abstract

Most farms in Ireland do not have their own weather recording stations. Fundamental to the development of the farm scale nutrient management decision support system is to know the soil moisture status of the farm site. This paper looks at using the nearest synoptic weather station data for the non weather recording farm site to determine the SMD state for the site. Sites of the three different soil drainage class are studied, well, moderately and poorly drained. Each location has been instrumented with weather stations and soil moisture probes. Comparing their recorded weather data to the nearest synoptic weather station data has shown that the synoptic weather station determines the presence of a transport vector (free flowing water) 82% (well), 89% (moderately) and 97% (poorly) of the time.

Introduction

In Ireland, the greatest threat posed to water quality status at present is eutrophication. Preventing poorly timed and excessive application of artificial and organic fertilisers to land is essential to reducing this threat and ensuring best management practice for farmers (Schulte et al., 2006). Current regulation in Ireland of nutrient application to farmland is enforced through closed periods for spreading during the winter season based on historical weather patterns and farmer discretion during other periods (Minister for the Environment and Government, 2009). This farm-scale decision support system aims to provide the farmer with more relevant information to help them make sustainable nutrient management decisions for their farm. Using soil drainage classification, soil nutrient state and incorporating real-time meteorological data enables the system to determine when it will be environmentally safe to apply fertilizer along with maximising the fertilizer replacement value. One of the elements the system looks at to determine if it is environmentally safe is the presence of a transport vector – free flowing water. The system always assumes the presence of a target - that all farmland in Ireland is connected in some way to surface or ground water. Hence, if a source of nutrient is applied (slurry/fertilizer spread) and a transport vector is present a pollution event occurs (Holden et al., 2007). When the SMD (soil moisture deficit) of the field is at or below 0 the transport vector is present (Schulte et al., 2005). It is important for the system to be able to determine with accuracy if the current SMD state is at, above or below 0. Here we look at 3 sites, one of each drainage class, well, moderately and poorly. The objective of this paper is to look at how well a synoptic weather stations data would be applicable to a non weather recording farm site in calculating its SMD state, the actual recorded SMD at the site is compared to the nearest synoptic weather station recorded SMD.
Materials and Methods

Site location and instrumentation
Each weather station records, rainfall in mm, windspeed sample in m/s, windspeed in km/hr, temp in °C, relative humidity %, solar radiation in kW/m², evapotranspiration ET₀, solar radiation in MJ/m² each averaged and recorded on the hour. The soil moisture probes are CS616 water content reflectrometers. They consist of 2 stainless steel rods at a +/− 0.7 volt square wave output with a frequency that depends on water content. The rods are 300 mm long and 3.2 mm in diameter with a 32 mm spacing. Each probe site has 2 probes spaced at 1 m apart inserted horizontally at 10 cm and 2 probes at 20 cm depth. The datalogger records a measured pulse from each and records the volumetric water content (VWC) which is a function of the period for each hour.

The well drained site’s weather station is installed on a south facing slope of the field at an elevation of 58 m with the probes at an elevation of 73 m. The moderately drained site’s weather station is installed at a 91 m elevation with the 4 soil moisture probes are installed alongside the weather station at the same altitude. The poorly drained site’s weather station and probes installed at an 87 m elevation.

Each month the data is collected at each site along with 6 soil samples at each of the soil moisture probe pits. 3 cores are taken at the 2 depths 10 cm and 20 cm. Each of the probes are calibrated to the soil samples volumetric water content measured. On the well drained site one of the probes at 20 cm depth had to be replaced on the 26th Feb.

Meteorological data
The nearest synoptic weather station to the well drained site in Slane is Mullingar, 54 km south west of the site. The synoptic weather station nearest to the moderately and poorly drained sites is Ballyhaise, 38-40 km south west of the moderately and poorly drained sites. The weather stations data looked at are recorded SMD and forecasted SMD (the 3 day deterministic ECMWF data) to compare to the sites actual measured SMD.

Results and Discussion
The time period looked at was from 1st September 2008 to 30th June 2009 a 302 day period. Firstly the wetting trend is looked at, in terms of number of days of matched trend — the calibrated VWC readings are compared to the SMD wetting trend. The trend is one of three different states wetting, drying or constant. When SMD recorded a constant trend, as there was no change in the SMD value, if it also was in a constant state at 0 for the well drained and -10 for the moderately or poorly drained (the minimum the SMD model will calculate at) the VWC was reading was set to be matched to the SMD state. The trends for the Synoptic weather stations and their forecast are also compared to the measured SMD values. The actual presence of the transport vector compared to the determined presence of the transport vector at the synoptic station and the forecast of the transport vector is then looked at.

Table 1. A comparison between on‐site recorded soil moisture state (volumetric water content) to calculated SMD from on‐site recorded weather data, to nearest synoptic
The well drained site

The relationship between the soil moisture state measured by the soil moisture probes (the volumetric water content (VWC)) and the SMD calculated from the weather data gave correlation of 0.71. The soil moisture probes recorded the same soil wetting trend as the SMD recorded 267 days of the 302 or 88% of the time, see figure 1. If this well drained site in Slane was to use the Mullingar synoptic weather station data it would have had the correct wetting trend 211 days or 70% of the time and correctly predicted the presence of the transport vector 248 of the 302 days or 82% of the time. Out of these 54 days 41 had a transport vector at the synoptic station and not on site with 13 days having a transport vector on site and not at the synoptic weather station. The forecast data for the Mullingar synoptic station if used for the well drained Slane site would have predicted the presence of a transport vector 63% for the 24 and 61% for the 48 and 72 hour forecast of the time see table 1.

The moderately drained site

The relationship between SMD and VWC returned a correlation of 0.81 with most of the soil moisture states fluctuating in around soil moisture capacity. The soil moisture probes recorded the same soil wetting trend for 248/302 days as the on-site recorded SMD. When looking the periods when the soil moisture probes and SMD recordings trends differed, the moisture fluxes are small for most of the time periods, 0.3 mm, 0.03 mm, 0.33 mm and 0.6 mm of rainfall. The 2 exceptions are the 19th-20th Dec with the on-site weather station recording a drying of 3.72 mm and the soil moisture probes recording a constant soil moisture state, and the 20th-21st Jan where the on-site weather station is recording a soil wetting of 2.25 mm and the soil moisture probes are recording a constant soil moisture state. If this moderately drained site in Monaghan were to use the Ballyhaise weather station data it would have predicted the correct wetting trend 237/302 days 78% of the time and correctly determined the presence of the transport vector 89% of the time (269 days). There were 15 days where there was a transport vector present at the synoptic station and not on site and 18 days a transport vector was present on site but not at the synoptic weather station. If the Ballyhaise deterministic ECMWF forecast data were used for the moderately drained site it would have predicted the presence of the transport vector correctly 69% for 24 and 48 hour forecast and 64% for the 72 hour forecast of the time see table 1.

The poorly drained site

This site remained quite wet throughout this time period. When the model had reached maximum wetness at -10 the VWC probes continued to record further wetting. It can be seen that using the synoptic weather station the trend would have been correct 242 days 80% of the time and that more importantly using that data for the site would have predicted the presence of the transport vector.
correctly 97% of the time. Looking at the 3 day forecast data it predicted the presence of the transport vector with an accuracy of 91% for 24 and 48 hour forecast and 88% for the 72 hour forecast, see table1.

Discussion
The 302 day period looked at was a wetter than average year, the transport vector was present for 92 days on the well, 125 days on the moderately and 249 days on the poorly drained soils. Looking at the days where the soil moisture probes wetting trend truly differed to the SMD recorded from the weather data shows that lateral flow would need to be taken into account to determine the true SMD of the soil, although this is a very small percentage of the time. Using the synoptic weather station data for the 3 sites the correct determination of the presence of the transport vector was 82% for the well, 89% for the moderately and 97% of the time for the poorly drained sites. The weather data from the synoptic station wasn’t interpolated, it was taken directly, if it had been interpolated to the farm site location the correct determination of the presence of a transport vector would be even better.

Conclusions
The soil moisture probe readings, while they are weighted towards the wetter end of their scale, are in good correlation with the recorded SMD on site. It looks like it would be possible to use synoptic station weather data for a non weather recording farm site, the assumption would be that interpolating the data would even make it more accurate in determining the presence of the transport vector.

Acknowledgements
This project is funded by Department of Agriculture, Fisheries and Food, Research Stimulus Fund 2007, Farm-scale decision support system: a DSS for sustainable nutrient management. RSF 07-502.

References
THE INFLUENCE OF HARVEST TRAFFIC, BEFORE AND AFTER SHOOT EMERGENCE AND IN WET AND DRY SOIL CONDITIONS ON SOIL COMPACTION, CROP RESPONSE AND YIELD POTENTIAL IN AN ESTABLISHING MISCANTHUS CROP.

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3Teagasc Crops Research Centre, Oak Park. Co. Carlow.

Abstract

An experiment was conducted in Spring 2010 in which establishing Miscanthus plants (sown in 2007) were trafficked with harvest machinery (simulated) at two stages of crop regrowth – four weeks before shoot emergence (Early Traffic) and four weeks after shoot emergence (Late Traffic), in order to determine the effects on soil compaction, crop response and yield potential. Two levels of soil moisture were also used – below field capacity (Dry Soil) and at field capacity (Wet Soil).

Soil penetration resistance (SPR), bulk density (BD) and water infiltration (WI) were measured to assess the level of soil compaction. Crop response was assessed throughout the growing season by monitoring stem numbers and stem height while harvest samples were taken in January to assess the yield potential. SPR and BD values were significantly higher and WI values were significantly lower in all treatments when compared to the control. There were significant differences in values for stem numbers and stem height between the control plots and some of the other treatments with the control plot values being higher in all cases. Yield potential was considerably higher in the control plots when compared to the other treatments.

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 (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).

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. Field trials have shown that Miscanthus is capable of producing dry matter yields in excess of 20 tonnes per hectare annually in suitable sites (Price et al., 2004).

The objective of this research was to investigate the influence of harvest traffic, before and after shoot emergence and in wet and dry soil conditions on soil compaction, crop response and yield potential in an establishing Miscanthus crop in Ireland.
Materials and Methods
Experiments were conducted at UCD Lyons Research Farm, Newcastle. Co. Dublin in February and April 2010 in a silty clay loam soil. The existing crop in the trial area was removed in a manner that avoided applying wheel traffic on the trial plants in advance of applying treatments. The experimental plots were arranged in a randomised, complete block design with four replications. The experiment consisted of five treatments:

1. Control – No Traffic
2. Early Traffic – Dry Soil
3. Early Traffic – Wet Soil
4. Late Traffic – Dry Soil
5. Late Traffic – Wet Soil

The equipment used in this experiment was selected to simulate the Baler System of Miscanthus harvesting. Simulated Baler System Traffic applied combined axle loading in excess of 50 tonnes on the surface of the soil and consisted of trafficking the following components and individual axle loads on the appropriate plots:

1. Tractor and Mower/Conditioner (Axle loads - 2810 kgs, 3230 kgs, 1850 kgs)
2. Tractor and Baler (Axle loads – 3640 kgs, 6560 kgs, 9370 kgs)
3. Tractor and Front-End-Loader with bale (Axle loads - 3360 kgs, 2650 kgs)
4. Tractor and Loaded Bale Trailer (Axle loads - 3640 kgs, 6560 kgs, 9370 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 travelling at 40 kph forward speed.

The Early Traffic experiments were conducted on February 20th 2010 while Late Traffic experiments were conducted on April 24th 2010. These dates were determined by a combination of two factors:

1. Soil moisture content on the day (Dry Soil)
2. Estimated date of shoot emergence (mid March)

Wet soil conditions were achieved by adding water to the appropriate plots until they were saturated and then allowing them to drain until they were at field capacity. Essentially, this experiment examined the effects of harvesting Miscanthus before and after shoot emergence in wet and dry soil conditions. Crop response was assessed on a weekly basis throughout the growing season by monitoring stem numbers per square metre and stem height while plots were harvested on January 29th 2011 and yield potential was calculated on the basis of tonnes per hectare of dry matter.

Volumetric soil moisture content was measured to a depth of 20 cm using a HydroSense TDR Soil Moisture Tester. The crop was treated with a herbicide but received no inputs with regard to fertiliser. All data was analysed by means of a one-way analysis of variance (ANOVA) using MINITAB 15 (Minitab® Statistical Software). Significance was set at the 5% level.

Results and Discussion
Soil penetration resistance results (Figure 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 all trial treatments when compared to the control (no traffic) at depths of approximately 5 - 35 cm but there was very little variation in SPR values when the trafficked trial treatments were compared. SPR values in all treatments to a depth of 30 cm never reached levels that would represent a compact soil condition likely to impede crop growth (Taylor, 1971). Bulk density values of the soil (Figure 2) in grams per cubic centimetre (g/cc) were in agreement with the SPR results as were water infiltration results (Figure 3).

Crop regrowth results (Figures 4 and 5) show average stem numbers per square metre (stems/m²) and average stem height respectively. Stem numbers were significantly higher in the control and both Early Traffic treatments throughout the growing season when compared to the Late Traffic treatments. When stem numbers stabilised in August, the control plots averaged 64.5 stems/m² while the Early Traffic treatments (Numbers 2 and 3) averaged 60.25 stems/m² and 56.0 stems/m² respectively. The Late Traffic treatments (Numbers 4 and 5) averaged 50.25 and 49.25 stems/m² respectively.
Stem height was significantly higher in the control plots when compared to both Early Traffic treatments and Late Traffic Wet Soil. The stem height of Late Traffic Dry Soil was noticeably lower than the control, however, the difference was not statistically significant. When growth ceased in mid-October, stem height in the control plots averaged 251.25 cm while stem heights in the trafficked treatments (Numbers 2 to 5) averaged 233.75 cm, 238.13 cm, 243.13 cm and 240.0 cm respectively.

Figure 1: Soil Penetration Resistance

Figure 2: Bulk Density

Figure 3: Water Infiltration

Figure 4: Stem Numbers

Figure 5: Stem Height

Yield Potential results (Figure 6) show yield potential in tonnes per hectare of dry matter (t/ha d.m.). Yield potential was higher, though not statistically significant, in the control plots when compared to all other treatments. A yield potential of 28.09 t/ha d.m. was recorded in the control plots while treatments 2 to 5 yielded 25.99 t/ha d.m., 25.88 t/ha d.m., 24.85 t/ha d.m. and 24.32 t/ha d.m. respectively.
Conclusions

Miscanthus harvest traffic significantly increased soil compaction as evidenced by increased soil penetration resistance and bulk density along with reduced water infiltration in all trafficked treatments when compared to the control – no traffic. There was very little difference in compaction levels between each of the trafficked treatments which suggests that it was the repeated trafficking at high axle load rather than soil moisture content that was most influential in causing soil compaction. This is in agreement with Alakukku (1996).

The crop regrowth results show that stem numbers and stem height were reduced in treatments that were trafficked and there was a consequent reduction in yield potential when compared to the control. Of the trafficked treatments, Early Traffic Dry Soil gave the highest yield potential followed by Early Traffic Wet Soil. Both Late Traffic treatments had reduced yield potential when compared to the Early Traffic treatments. Therefore, since the crop has to be trafficked in order to get it harvested, the results of this experiment suggest that harvesting should take place in advance of new shoot emergence and in dry soil conditions.

The Baler System of Miscanthus harvest applies wheel traffic to approximately 43% of total field surface area. A harvest system that involves reduced traffic intensity and increased working widths (e.g. The Forager System) is likely to impact less negatively on yields if stubble height is kept to a minimum. The yield potential of Miscanthus will only be realised if the target of establishing 10,000 plants per hectare is achieved in suitable sites. Any reduction in the establishment rate will most likely result in a proportional reduction in yield.

Acknowledgements

The authors gratefully acknowledge the provision of funding for this project by Science Foundation Ireland. Equipment, facilities and human resources provided at the UCD Lyons Research Farm, Newcastle. Co. Dublin is also greatly appreciated as is the co-operation of the Principal and Staff of Mountbellew Agricultural College, Co. Galway. Many thanks also to Ms. Fionnuala Cuffe UCD and Mr. James Curley for statistical assistance.

References

Cross calibration of satellite based multispectral data over peatlands

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Abstract
In Ireland, frequent cloud clover means that any change detection study with a high temporal and spatial resolution must use multiplatform imagery. This study illustrates the use of difference image masks with spectral and spatial thresholds in the extraction of homogeneous targets for multiplatform cross calibration using linear regression. Analysis of SPOT 4 data from May 2000 against a TM master image from July 2006 show a 7.25% increase in mean EVI2 with a 72.9 ha decrease in the resulting change detection image due to the cross calibration process. Regression analysis shows high correlation ($R^2$) of TM data against Aster VNIR (0.9346), IRS P6 LISS III (0.9487), SPOT 4 (0.7846) and SPOT 5 (0.9641), demonstrating that this technique is a viable method for the cross calibration of EVI2 derived multispectral data over peatlands in Ireland.

Introduction
One of the main goals of satellite remote sensing is to monitor vegetation and its dynamics (Martinez-Beltran et al., 2009). In Ireland, average cloud cover between 1984 and 1994, calculated from satellite imagery in spring, summer, autumn and winter was 78%, 75%, 77% and 83% respectively (Palle and Butler 2001). Such high levels of cloud cover have a significant impact on the temporal resolution of a single sourced optical sensor for use in a change detection study. A multi-platform based study reduces the issue of frequent cloud cover by increasing the possibility of unobstructed image acquisition due to the varying orbits and overpass times of the different satellites. However, spectral responses from different sensors can differ by up to -25% to +12% in the red, and -2% to +4% in the near infrared, even with detailed sensor calibration and atmospheric correction (Teillet et al., 2007). Cross calibration aims to develop linear/non-linear relationships to facilitate the transfer of reflectance data from one sensor to another (Steven et al., 2003, Wulder et al., 2008).

The objective of this study was to create a protocol for the cross calibration of multispectral data from various satellite based platforms using linear regression of ground based targets. This study was part of an overall project on detecting vegetation disturbance on Irish peatlands with a 16 to 25 day return period.

Methods

Study Sites
The Slieve Bloom Mountains Special Protection Area (SPA) (Figure 1) was selected as the study site due to the high frequency of image coverage, as well as having access to auxiliary data (e.g. landcover, disturbance records, aerial photography, vegetation surveys). The SPA covers 3845 ha, encompassing areas of upland blanket bog, dry heath and over 60% conifer cover.

Figure 1: Location map for Slieve Bloom Mountains SPA.
Data
Satellite imagery was collected from five multispectral sensors; SPOT 4/5, Landsat TM, Aster VNIR and IRS P6 (Table 1). Cross-sensor response to ground properties is not uniform and can be affected by variation in spectral resolution, atmospheric conditions, field of view and sun and azimuth angle (Steven et al., 2003). Histograms of the five platforms over the Slieve Bloom Mountain during 2005/2006 (Figure 2) show clear differences. There is a shift in spectral distribution across platforms, illustrating the importance of cross calibration of sensors in a change detection study.

Table 1: Imagery used in cross calibration analysis. Sun and azimuth angle are in degrees (°) and the master image is in bold.

<table>
<thead>
<tr>
<th>Platform</th>
<th>Sensor</th>
<th>Sun Angle</th>
<th>Sun Azimuth</th>
<th>Image Acquisition</th>
</tr>
</thead>
<tbody>
<tr>
<td>EOS Terra</td>
<td>Aster VNIR</td>
<td>53.64</td>
<td>163.61</td>
<td>10/05/2005</td>
</tr>
<tr>
<td>EOS Terra</td>
<td>Aster VNIR</td>
<td>54.96</td>
<td>161.48</td>
<td>16/05/2004</td>
</tr>
<tr>
<td>EOS Terra</td>
<td>Aster VNIR</td>
<td>27.66</td>
<td>173.34</td>
<td>16/10/2002</td>
</tr>
<tr>
<td>IRS-P6</td>
<td>LISS III</td>
<td>56.41</td>
<td>158.14</td>
<td>17/07/2006</td>
</tr>
<tr>
<td>Landsat</td>
<td>TM</td>
<td>54.89</td>
<td>147.83</td>
<td>17/07/2006</td>
</tr>
<tr>
<td>SPOT 5</td>
<td>HRG 1</td>
<td>56.92</td>
<td>156.26</td>
<td>16/07/2006</td>
</tr>
<tr>
<td>SPOT 4</td>
<td>HRVIR 2</td>
<td>57.20</td>
<td>156.00</td>
<td>01/06/2006</td>
</tr>
<tr>
<td>SPOT 4</td>
<td>HRVIR 2</td>
<td>40.80</td>
<td>158.60</td>
<td>05/04/2006</td>
</tr>
<tr>
<td>SPOT 4</td>
<td>HRVIR 2</td>
<td>57.90</td>
<td>150.90</td>
<td>16/06/2004</td>
</tr>
<tr>
<td>SPOT 4</td>
<td>HRVIR 2</td>
<td>46.90</td>
<td>168.80</td>
<td>18/04/2003</td>
</tr>
<tr>
<td>SPOT 4</td>
<td>HRVIR 2</td>
<td>50.80</td>
<td>157.50</td>
<td>30/05/2000</td>
</tr>
</tbody>
</table>

Figure 2: Histograms for the five multispectral sensors over the Slieve Bloom Mountains. Dates in the legend indicate the time of image acquisition.

Preprocessing
All data was initially geo-rectified and converted from digital number (dn) to top-of-atmosphere reflectance, with dark object subtraction applied in accordance with O Connell, et al. (submitted). Once all data has been converted to EVI2 vegetation index, an overall master image was selected (Figure 3).

Cross Calibration
The master image (Table 1) was used as the basis for all cross calibrations, and was selected based on its temporal position in the database, as well as its image quality. All other data (slaves) were subsequently geo-synchronised to the master image, and pixel based image subtraction applied. The resulting difference image was then used as a mask to extract spectrally homogeneous pixels from the
original master and slave image, with the resulting pixels plotted on a xy scatter plot (see Figure 3). Pixel selection was limited by spectral and spatial thresholds, which were set in Erdas Imagine using the AOI Seed tool (Lecia 2006). Pixels from across the spectra of the study site were extracted, ensuring a stable set of data for cross calibration analysis. The slope and intercept of the linear regression were then calculated and used in an Erdas Imagine spatial model to cross calibrate the slave image to the same radiometric scale as the master (Figure 3).

Results and Discussion
The calibration parameters (Table 2) indicate the different response of the four slave images against the TM master image. Correlation values were generally high, with the temporally tandem images (i.e. IRS and SPOT 5) producing the highest R² values. SPOT 4 and Aster showed some shift in values when plotted against the master image, with the SPOT 4 vs TM producing the lowest correlation (Table 2). The overlap of the SPOT 4 and TM is small by comparison to the other images (30% overlap), coupled with temporal offset of 47 days, resulting in an R² value of 0.7846. The Aster image on the other hand, has considerable cloud cover present (over 35%), thereby limiting the number of homogeneous pixels between it and the master image. The distribution of pixels values for the TM master image as well as the original and cross calibrated SPOT 4 image from May 3rd 2000 (Table 1; Figure 4) indicated a shift from original to cross calibrated data, with mean EVI2 changing from 0.359 (original) to 0.385 (cross calibrated) with respect to a mean of 0.409 for the TM data. This shift in values resulted in a 72.9 ha reduction in the area of vegetation change between the original and cross calibrated data, using a change threshold of 1 standard deviation.

Table 2. Shows slope, intercept and R² values in the cross calibration of SPOT 4/5, Aster and IRS images to the TM master image in the Slieve Bloom Mountains.
Figure 4: Image histograms of TM, SPOT 4 cross calibrated and SPOT 4 for upland blanket bog in the Slieve Bloom Mountains.

Conclusion
This study has shown that multiplatform based difference images can be used in the extraction of homogeneous ground based targets for the cross calibration of imagery through linear regression. Spatial and spectral thresholds ensured a strong correlation between master and slave data by eliminating the inclusion of spectrally heterogeneous pixels. The cross calibrated data will provide a more suitable database of multiplatform imagery for change detection and monitoring of Irish peatlands. Further work needs to be done on examining the effect of including anthropogenic targets such as pasture in the cross calibration process; as such targets may not be representative of the radiometric variation between master and slave images.

Acknowledgements
The authors wish to thank the Environmental Protection Agency (EPA) for their financial support under the STRIVE fellowship, the European Space Agency (ESA) for the SPOT 4/5 and IRS data as well as the US Geological Survey (USGS) for the Aster and TM data.

References
FOOD VS. FUEL – RISK ANALYSIS

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Abstract
Growing concerns on greenhouse gas emissions, climate change and energy security has lead to increased focus on the delivery of renewable energy sources from biomass. Production of energy crops is rapidly becoming an important segment in Irish and EU agriculture. To date tillage production in Ireland has focused mainly on food crops such as barley, wheat and oats. However, with the introduction of the EU Energy Crops Scheme the production of willow, miscanthus and oil seed rape has become an alternative tillage production option. Production systems and inputs for such crops are significantly different to those employed in the conventional tillage production. These variations in production highlight the need to examine and compare the effects of both systems on the natural environment. This study aims to utilise risk analysis techniques to assess the environmental impacts on soil, air and water resulting from the production of both fuel and food crops. This will ultimately highlight potential environment risks associated with growing fuel crops rather than food crops and assist in addressing social and environmental concerns.

Introduction
In early 2009 the European Union implemented a number of targets for member states to reach regarding renewable energy generation (European Commision, 2011). Under these new regulations, Ireland is obliged to meet 16% of its energy requirements using power from renewable sources by 2020 (Dept. Agriculture, 2009). A large part of this can be fulfilled by the bioenergy market. The current percentage of arable land in Ireland being used for tillage is approximately 10% (Smyth et al., 2009). However, only ~0.2% of tillage land is being used for non-food crops. It is paramount that in order to meet Ireland’s bioenergy targets for 2020, a significant portion of the land currently used to grow barley, wheat and oats needs to be converted to energy crop production. Many people are morally opposed to this idea; however, energy crops may be beneficial to ecological areas while also reducing carbon emissions. Production can also impact on the use of fertiliser and pesticides in various cropping systems. Excessive use of such inputs in crop production can have a detrimental effect on the environment (Tilman et al., 2002). It has been estimated that of the 2.5 million tons of pesticide applied to growing crops worldwide per annum, only around 0.3% actually reached the target pest (Werf,1996). Problems can occur if these contaminants remain in soil, reach water sources or threaten air quality. Concerns regarding the fate of potential contaminants from crop production in surface waters date back as far as the 1960’s and have been directly linked to a decrease in aquatic life (Carson 2002). Contaminants from crop production can also enter the atmosphere where they can travel long distances. Evidence of long range pesticide migration includes the identification of pesticides in ocean fog and arctic snow (Schomburg, 1991; Gregor and Gummer, 1989). They can also persist in soils, bound to soil colloids for long periods of time depending on their stability (Edwards 1975). They can then be taken up by plants and from there accumulate in humans and animals. The risks of this are not fully understood yet, but concerns have been raised. In turn, any contaminants that accumulate in soils have the potential to pollute surface water and groundwater (Carpenter et al. 1998).

The objective of this study is to use risk analysis techniques to compare potential environmental risks (soil, water and air components) resulting from the growth of traditional food crops as opposed to fuel crops.
Materials and Methods

Crop Selection and Production Systems
Currently, there is just under 280,000 hectares of land planted with crops in Ireland as illustrated in tables 1 and 2. After potatoes, the main food crops sown in Ireland are barley, wheat and oats. Currently Ireland produces over half of its domestic requirements of wheat, and almost all our requirements for barley and oats (CSO, 2008). The corresponding tonnage can be seen in table 1 below. The environmental risks associated with the production of these food crops will be assessed in the study.

Table 1: Quantities of Food Crops being cultivated in Ireland in 2007

<table>
<thead>
<tr>
<th>Crop</th>
<th>Area (ha)</th>
<th>Production (tonnes)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Barley</td>
<td>167,700</td>
<td>403,100</td>
</tr>
<tr>
<td>Wheat</td>
<td>84,400</td>
<td>801,800</td>
</tr>
<tr>
<td>Oats</td>
<td>19,700</td>
<td>139,870</td>
</tr>
</tbody>
</table>

(source: Dept. Agriculture, 2009)

Growing energy crops is a relatively new enterprise in Irish agriculture. Oil seed rape was originally grown as an intermediate during rotation of food crops, and for this reason is the more abundant biofuel crop (Venendaal et al., 1997). Only two other energy crops are currently grown in Ireland, Miscanthus and Willow. As seen in table 2, the land area dedicated to growing these crops is increasing steadily on an annual basis.

Table 2: Quantities of Non-Food crops being grown in Ireland

<table>
<thead>
<tr>
<th>Year</th>
<th>Willow (ha)</th>
<th>Miscanthus (ha)</th>
<th>Oilseed Rape (ha)</th>
<th>Total Hectares</th>
</tr>
</thead>
<tbody>
<tr>
<td>2006</td>
<td>67</td>
<td>122</td>
<td>4267</td>
<td>4456</td>
</tr>
<tr>
<td>2007</td>
<td>65</td>
<td>630</td>
<td>7959</td>
<td>8744</td>
</tr>
<tr>
<td>2008</td>
<td>127</td>
<td>780</td>
<td>3087</td>
<td>4131</td>
</tr>
<tr>
<td>2009</td>
<td>170</td>
<td>740</td>
<td>2300</td>
<td>3310</td>
</tr>
</tbody>
</table>

(source: Dept. Agriculture, 2009)

Figure 1 displays the relationship between crop production systems and potential environmental contaminants. The factors influencing optimal production will ultimately influence the surrounding environment. The main factors identified which affect the environment are:
(a) Crop type: input requirements, rooting depth etc.
(b) Production stage 2: pesticides/fertilisers-application volumes/methods etc.
(c) Contaminant transport: weather, soil structure, site specifics etc.

Qualitative Risk Assessment

Qualitative risk assessment is normally carried out initially, to assess the risk of a hazard and use words to describe the level of a risk (e.g. high, low, medium etc.), thus a ranking or categorising system results. Conducting a qualitative risk assessment for the natural environment identifies the contaminant pathways throughout the production chain and examines potential control points. Factors that may reduce/increase contamination are identified along the pathway. After conducting a qualitative assessment, it must be decided if conducting a quantitative risk assessment is necessary. The qualitative risk assessment will be developed using Microsoft Excel and will focus on the production systems of the aforementioned food and fuel crops, and the agricultural inputs into each. A general overview of these can be seen in figure 1. Critical points will be identified in each of the systems and the risk increase/decrease to the environment, associated with these points will be evaluated.
It is expected, that following on from this step a quantitative risk assessment will be carried out.

**Figure 1: Pathways and contaminants from crop production systems**

*Quantitative Risk Assessment*

In contrast to qualitative risk assessment, quantitative risk assessment produces numerical estimates of risk. Conducting a quantitative risk assessment requires more time and resources than a qualitative one. The quantitative risk assessment will give a numerical value of the risk the environment from growing each crop. Risks posed by fertilisers and pesticides will also be influenced by variables such as weather. The assessment will consider dispersion of fertilisers/pesticides in the environment and potential concentrations to which the environment will be exposed. It will also be used to verify if fertiliser and pesticide limits are within or exceeding those required by law.

**Results and Discussion**

A framework model has been developed for the study (Figure 1). Work on this model is ongoing with qualitative estimates being put on risks. It is hoped to create models for four types of hazard: (a) Fertiliser (b) herbicide (c) fungicide (d) insecticide. As can be seen in figure 1, four production stages are involved in the production of all the crops. These are
cultivation, sowing, the growth period, and post harvest. At each of these points agrichemical practices and inputs will be examined. Dispersion of pollutants will be influenced by weather and management practices, and will be characterised in the model to assess their influence on potential environmental contamination. A qualitative approach will initially be used to further develop this framework. Following completion of this and depending on available data, a quantitative risk assessment will be developed including sensitivity and scenario analysis.

Growing energy crops is generally considered a less intensive form of agriculture than the cultivation of cereals. This is due to energy crops requiring lower inputs of fertilisers and no requirements for fungicides. They also have deeper roots, allowing them to intercept fertilisers deeper into the soil, thus further preventing long term contamination (Dept. Agriculture, 2009). It is anticipated that results will verify such scenarios and indicate that food crops will present a higher risk to the environment. Quantitative risk assessment will be used to determine numerical estimates of contaminant levels. These estimates will be assessed/compared with EU and Environmental Protection Agency (EPA) legislation and will indicate whether fuel or food crops are exceeding limits and conditions that are required by law.

Conclusions

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

References


THE STUDY OF SOIL QUALITY, CARBON AND NITROGEN STOCK UNDER GRASSLAND AGRICULTURE SYSTEMS

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Abstract
A series of experiments is being planned to better understand the interactions of soil quality indicators and C and N stock in soil under different agricultural management. Sampling and analysis will focus on soil organic Carbon (SOC), soil organic matter (SOM), particulate organic matter (POM) and soil Nitrogen (SN) and their relationships with soil physical properties. Field sampling will be based on a design using a range of sward ages and management. Laboratory experimentation will use controlled change in organic matter input rates and physical perturbation rates to obtain empirical data about C/N dynamics.

Introduction
Global atmospheric concentrations of CO₂, CH₄ and N₂O have increased markedly and it is very likely that the observed increase in CH₄ concentration is predominantly due to agriculture and fossil fuel use. The increase in N₂O concentration is primarily due to agriculture (IPCC Climate Change 2007). Hungate et al., (1997) found that up to 98% of total C is sequestered below ground. Grasslands probably contribute >10% of the total biosphere store (Eswaran et al., 1993; Nosberger et al., 2000). In Ireland, grass provides 70-90% of animal feed requirements on land ranging from extensive to intensive managements. According to the Ireland 2020 vision (EPA:2020 Vision protecting and improving Ireland’s environment), agriculture is the largest source for GHG and the challenge agriculture faces is how to cope with climate change and sustainably utilize the soil resource. SOC and SN content are important indicators of soil quality as well as soil physical properties such as soil bulk density, soil water holding capacity, soil compaction and so on. Numerous researchers have shown that proper N management is a key to reducing C losses from soil and the balance of C and N is essential for maintaining soil quality. Moderately enhanced N fertilization increases the organic matter input to the soil proportionally more than it increases the process of C mineralization. Furthermore, although intensive N fertilization increases production, it is also shown to stimulate mineralization and therefore enhance C losses. Guo & Gifford (2002) demonstrated that conversion from crop to pasture leads to large increases in soil C of up to nearly 30%. In addition, management methods that increase forage production, such as fertilization, irrigation, inter-sowing of grasses and legumes, intensification of grazing, and introducing earthworms, also have the potential to increase SOM (Conant et al., 2001). Bruce et al. (1999) have proposed that, over the next two decades, intensively managed pastures in North America have the potential for further C gains of 0.2 Mg ha⁻¹ yr⁻¹ through the use of improved grazing regimes, fertilization practices and irrigation management as well as the introduction of more productive species. Watson and Poland (1999) concluded that past management history can play an important role in determining soil NO₃⁻ -N content and hence potential losses of N to the environment. Consequently the practices that most favor C sequestration are those that involve a reduction in the intensification of highly fertilized grasslands and a moderate intensification of poor grasslands (Jones and Donnelly, 2004). However, the magnitude of the effects varied, depending on the soil type, grass species and duration of grass establishment.

This background knowledge raises some interesting questions: (1) what is the interaction between SOC, SN and managements? (2) how to stabilize SOC, permit N availability and have a productive agricultural system through modifying management and (3) how to maintain grassland productivity in high level while maintaining soil quality?

The objectives of the project are to develop experiments to collect empirical data that will contribute to our understanding of sustainable grassland management. It will focus on understanding soil quality and the role of soil in GHG management as well as agricultural production. It is also envisaged that data on soil quality under different grassland management will contribute to improve Life Cycle Assessment of dairying production.
Material and Methods

Field sampling
Soil samples will be collected nationwide over a range of different grassland managements and durations. The locations of sampling sites will be determined according to GIS analysis of field survey and linked to the national soil database. Samples will be analyzed for texture, bulk density, macro-porosity, total porosity, SOC, POM, SOM and SN to obtain a "snap-shot" of grassland soils under different management states in order to identify C/N trends (as opposed to sampling a site over time, for reference soil is important in the research of grassland management).

Laboratory experimentation
Using controlled conditions, change in organic matter input rates and physical perturbation rates will be applied to soil samples taken from a range of sites used for the field survey. These samples will be analyzed for soil structure properties (e.g. Dexter, 2004; Holden, 2001). S theory and indices based on pore structures will be related to the biochemical properties quantified. Statistical models relating soil properties will be developed. These will be used to form the basis of an improved understanding of the mechanisms of SOM/SOC/POM/N interaction with soil structure under grassland management.

Land use data for LCA
The findings will be generalized as a series of database values for land use management in Life Cycle Assessment studies.

Results

Soil quality assessed by visual method
It is expected to obtain a general understanding of soil quality using a common, easy way called Visual Soil Quality Assessment method.

Distribution of SOC and TN
A series of results on SOC and TN content in soil profile under different pasture ages and managements will shown in this section and we are planning to get a further relationship between SOC, TN and management.

C/N dynamic
This part of results is mainly focus on C/N dynamic though controlling organic matter input rates and physical perturbation rates by soil laboratory incubation experiments. It is expected to get a further understanding of C cycle. New carbon input maybe accelerate “old” C stability and then C cycle based on varied C:N ratios in soil. Physical perturbation possibly plays a key role on C cycle due to (1) redistribution of carbon and nitrogen in soil profile and (2) cracking of soil aggregates.

Conclusion
The research will help us to get a series of results of soil carbon and nitrogen distribution in Irish grassland under different managements though “snap-shot” soil collection nationwide and laboratory assays. C/N dynamic and the mechanism of carbon stability will be better understood in soil incubation experiments. Soil quality is expected to be decreased in intensive management and C/N content will be varied from extensive to intensive grazing with the higher concentration will be found in extensive or medium management while lower ones will be in extremely grazing. From laboratory experiment, C cycle will be accelerated by new organic matter input and redistribution of carbon and nitrogen in soil profile while SOC stability, especially subsoil SOC will be decelerated by physical perturbation. Biological enzyme activities will be useful in understanding the mechanism of C cycle and SOC stability.
References
Ranking the risks from pesticides used in Irish agriculture

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Abstract
This study quantitatively ranks pesticides (and degradation products), used in Irish agriculture, according to their risk to human health and groundwater contamination. A risk based approach is developed which includes the leached quantity combined with an exposure estimate and the No Observed Adverse Effect Level (NOAEL) as a toxicity ranking endpoint, resulting in a chemical intake risk ratio statistic (R) for each pesticide. 34 active substances, and their metabolites, registered and used in the agricultural field were evaluated. MCPA obtained the highest rank, followed by Desethyl-terbuthylazine and Deethylatrazine (R value of 1.2 × 10⁻⁵, 9.7 × 10⁻⁶ and 6.3 × 10⁻⁶, respectively). A sensitivity analysis revealed that the soil organic carbon content (SOC) and soil sorption coefficient (Koc) were the most important parameters which affected model predictions (with correlation coefficient values of -0.61 and -0.58, respectively), highlighting the importance of soil and pesticide properties in both influencing risk estimates. Other parameters such as water consumption (C), interception fraction (fint) and groundwater level (Gi) also influenced human exposure levels. The analysis highlights the importance of taking a risk based approach (i.e. including level and severity of exposure) for ranking of pesticides. The risk ranking procedure identified pesticides of potential human health risk concern which may have been neglected if leachability was the only ranking criteria.

Introduction
According to the Statistical Office of the European Commission, around 327,642 tons of pesticides were sold in 2001 on the European market and 2,874 tons in 2006 in Ireland alone (EC, 2011). At the European level, legislation such as Council Directive 91/414EEC established the requirement for the risk assessment of pesticides before their use (CEC, 1994). Given the significant number of products on the market chemical ranking models can be used as initial screening tools to identify potentially harmful pesticides. Most pesticide risk ranking tools are hazard based and rely on either an appropriate toxicity endpoint (such as lethal dose, effect concentration, etc) or exposure indicators, or a combination of both. A risk based ranking approach has been recognized as an alternative to traditional hazard based chemical screening methods as this can include probability of exposure and the subsequent effect of active substances on non target organisms (Benfort, 2008). In this paper, a quantitative risk ranking approach is developed to compare the potential risk of groundwater contamination and subsequent human health risks resulting from the use of pesticides. The model differs from previously reported risk based approaches for pesticides which were hazard based (i.e. comparisons with legislative guidelines), by virtue of the fact that human exposure and human risk characterisation is considered culminating in an intake risk ratio (R) statistic which can be used to identify chemicals of human health concern.

The objective of this study is to rank pesticides, and their degradation products, used in Irish agriculture and to identify those posing the greatest threat to groundwater and to human health.

Materials and Methods
The model encompasses three steps: evaluation of the predicted leached quantity (LQ) estimation of the level of chemical intake (I) and calculation of the chemical intake toxicity ratio (R). A flow diagram of the model process is given in Figure 1. The predicted environmental concentration was estimated by developing a leaching potential model which
considers soil properties, meteorological conditions, crop type and pesticide properties. Uncertainty in input variables was modeled using probability density distributions. The model inputs and calculations are provided in Table 1. Effects of pesticides on human health are included in the model by using an appropriate toxicological indicator (i.e. No Observed Adverse Effect Level: NOAEL).

<table>
<thead>
<tr>
<th>INPUTS</th>
<th>STEPS</th>
<th>ENVIRONMENTAL CONCENTRATION</th>
<th>CHEMICAL INTAKE</th>
<th>MODEL OUTPUT</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_{oc}$: Soil sorption coefficient</td>
<td>$R$: Retardation factor</td>
<td>$E$: Leached quantity</td>
<td>$I$: Chemical intake</td>
<td>Ranking of pesticides</td>
</tr>
<tr>
<td>$S_{oc}$: Soil organic carbon content</td>
<td>$F$: Effective rainfall</td>
<td>$H$: Soils half life</td>
<td>$r$: Chemical intake/toxicity ratio</td>
<td></td>
</tr>
<tr>
<td>$A$: Air content</td>
<td>$D$: Henry's law constant</td>
<td>$C$: Chemical intake</td>
<td>$r$: Chemical intake/toxicity ratio</td>
<td></td>
</tr>
<tr>
<td>$B$: Bulk density</td>
<td>$E$: Effective rainfall</td>
<td>$F$: Soil field capacity</td>
<td>$I$: Chemical intake</td>
<td></td>
</tr>
<tr>
<td>$C$: Water consumption</td>
<td>$D$: Henry's law constant</td>
<td>$F$: Soil field capacity</td>
<td>$I$: Chemical intake</td>
<td></td>
</tr>
</tbody>
</table>

**Figure 1**: Flow diagram of the quantitative risk ranking approach for pesticides

**Results and Discussion**

**Leached quantity**

Based on the leached quantity value, the results indicate that, from 34 of the most active substances used (DAFF 2003), the highest leached quantity was obtained by 2,4-D (95th percentile 0.52 µg/l). This was followed by MCPA and Atrazine (95th percentile 0.36 and 0.34, respectively).

**Human health risk**

According to the human health risk based approach developed in this study, the top 10 pesticides were ranked in order of decreasing human health risk as follows: MCPA, Desethyl-terbuthylazine (metabolite of Terbuthylazine), Deethylatrazine (metabolite of Atrazine), Terbuthylazine, Atrazine, 2,4 D, Simazine, Mecoprop, Triclopyr and Mecoprop-P, (with R values of $1.2 \times 10^{-5}$, $9.7 \times 10^{-6}$, $6.3 \times 10^{-6}$, $4.9 \times 10^{-6}$, $2.9 \times 10^{-6}$, $2.6 \times 10^{-6}$, $2.4 \times 10^{-6}$, $1.4 \times 10^{-6}$, $4.6 \times 10^{-7}$, and $4.2 \times 10^{-7}$, respectively).
### Table 1: Model inputs and distributions

<table>
<thead>
<tr>
<th>Steps</th>
<th>Symbols</th>
<th>Description</th>
<th>Model/distribution</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Retardation</td>
<td>$S_{oc}$</td>
<td>Soil organic carbon</td>
<td>Cumulative (min 1.4, max 55.8, 2.86, 3.56, 4.92, 7, 14.26 40.82, 48.0)</td>
<td>%</td>
</tr>
<tr>
<td></td>
<td>$K_{oc}$</td>
<td>Soil sorption</td>
<td>Cumulative, Uniform or Duniform$^a$</td>
<td>cm$^3$/g</td>
</tr>
<tr>
<td></td>
<td>$K_H$</td>
<td>Henry’s constant</td>
<td>Fixe value$^a$</td>
<td>g/cm$^3$</td>
</tr>
<tr>
<td></td>
<td>BD</td>
<td>Bulk density</td>
<td>Uniform (1.14, 1.64),</td>
<td>cm$^3$/g</td>
</tr>
<tr>
<td></td>
<td>FC</td>
<td>Soil field capacity</td>
<td>0.3486 - 0.018 × Sand + 0.0039 × Clay + 0.228 × OM - 0.0738 × BD</td>
<td>cm$^3$/cm$^3$</td>
</tr>
<tr>
<td>PD</td>
<td></td>
<td>Particle density</td>
<td>Fixed value</td>
<td>kg/m$^3$</td>
</tr>
<tr>
<td>P</td>
<td></td>
<td>Porosity</td>
<td>1 - (BD × 1000/PD)</td>
<td>-</td>
</tr>
<tr>
<td>AC</td>
<td></td>
<td>Soil air content</td>
<td>FC – P</td>
<td>-</td>
</tr>
<tr>
<td>Retardation</td>
<td>RF</td>
<td>1 + (BD × $S_{oc}$ × $K_{oc}$/FC) + (AC × $K_H$/FC)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Attenuation</td>
<td>AF</td>
<td>Fraction intercepted by the crop</td>
<td>Uniform (0,0.89)</td>
<td>%</td>
</tr>
<tr>
<td></td>
<td>f$_{int}$</td>
<td>Thickness of water table</td>
<td>Uniform (1,2)</td>
<td>m</td>
</tr>
<tr>
<td></td>
<td>H</td>
<td>Application rate</td>
<td>Pesticide specific$^b$</td>
<td>g/m$^2$</td>
</tr>
<tr>
<td>Leached</td>
<td>LQ</td>
<td>Model output 1</td>
<td>$\left[2.739 \times AF \times A \times (1 - f_{int}) \right]/(1 - f_{drip})/(P \times H)$</td>
<td>µg/L</td>
</tr>
<tr>
<td>quantity</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>Water consumption</td>
<td>Lognormal (0,258,0,368)</td>
<td>l</td>
</tr>
<tr>
<td></td>
<td>BW</td>
<td>Body weight</td>
<td>Uniform (67.75,81.75)</td>
<td>kg</td>
</tr>
<tr>
<td></td>
<td>I</td>
<td></td>
<td>C × LQ/BW</td>
<td>µg/kg</td>
</tr>
<tr>
<td>Chemical</td>
<td>NOAEL</td>
<td>NO Observed Adverse Effect Level</td>
<td>Pesticide specific$^a$</td>
<td>µg/kg</td>
</tr>
<tr>
<td>intake</td>
<td>R</td>
<td>Model output 2</td>
<td>I/NOAEL</td>
<td></td>
</tr>
</tbody>
</table>

$^a$Labite and Cummins 2011; $^b$DAFF 2003

**Sensitivity analysis**

A sensitivity analysis (Figure 2) based on the Rank Order Correlation Coefficient was conducted for MCPA, as it was the highest ranking pesticide. The results revealed that $S_{oc}$ and $K_{oc}$ were the most important parameters which affected model predictions and highlighted the importance of soil quality and pesticide properties. Other parameters such as water
consumption and interception fraction (representing plant growth stage) also influenced human exposure level.

![Figure 2: Sensitivity analysis of input parameters on R ratio for MCPA](image)

**Figure 2:** Sensitivity analysis of input parameters on R ratio for MCPA

**Conclusions**
A robust risk ranking tool was developed during this study which has a human health based approach, as opposed to the hazard based approach used by previous models. The highest rank was obtained by MCPA (Risk ratio $= 1.2 \times 10^{-5}$). A sensitivity analysis indicated that $S_{oc}$ and $K_{oc}$ are the key parameters in reducing the risk associated with the use of active substances. The model can be used as an initial screening tool to highlight pesticides of environmental and human health concern while also directing future research needs.

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

**References**


Assessing the vulnerability of groundwater to pollution using hydrochemical data and multivariate statistical methods

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Abstract

This project investigated the potential of employing hydrochemical data to characterise different geographical locations in terms of groundwater intrinsic vulnerability to pollution. The analysis aims to identify groundwater constituents which could be used as tracers of water residence time. Water residence time is a good indicator of groundwater intrinsic vulnerability and therefore may be used in characterising vulnerable zones. “Principal Components Analysis” (PCA) was used to classify the groundwater constituents according to their origin (autogenic or allogenic) and residence time in the aquifer system. In the multivariate analysis the following variables were assessed: major anions (chlorine, carbonate and bicarbonate as alkalinity, and sulphate), major cations (calcium, sodium, magnesium and potassium), temperature, nitrate (NO₃) and total organic carbon (TOC). Based on the outcome of PCA four groundwater constituents, namely Mg, TOC, NO₃, and Cl were identified as potential tracers introduced into the aquifer system by infiltration. Additionally, the analysis showed that NO₃ and TOC could be used to classify the zones of contribution of each spring according to groundwater vulnerability.

Introduction

Water residence time has been the subject of much research in groundwater vulnerability assessment studies and is considered an appropriate indicator of the intrinsic vulnerability of groundwater. This is due to the fact that longer residence time (or longer transit time) indicates lower vulnerability while shorter residence times are related to higher vulnerability. In karstic regions different techniques have been used to assess the vulnerability of groundwater based on water residence time. Batiot et al. (2003) advocated that TOC is a more sensitive tracer to infiltration than other chemical elements of external origin such as Cl⁻, thus it is a more suitable proxy for fast infiltration. Garry et al. (2008) used Mg²⁺ and TOC to classify a karstic system in the catchment area of Fontaine de Vaucluse in France, into three families of water according to the degree of karstification (i.e. highly karstified, intermediate, fractured). Little has been done in Ireland to characterise groundwater vulnerability using such hydrochemical data. The objective of this work is therefore to investigate the suitability of hydrochemical data (on a national scale) to characterise the intrinsic vulnerability of groundwater in Ireland.

Materials and Methods

Data selection and database editing

Hydrochemical data for the period 2000-2008 were collated from the national network of groundwater monitoring of the Irish EPA which consists of 246 locations, mostly springs and boreholes. The data were stratified according to aquifer lithology. For this purpose a dataset of rock units distributed by the Geological Survey of Ireland (GSI) was used. The “rock units” dataset depicts generalised bedrock formations based on their expected hydrogeological characteristics. The dataset is being used by local authorities and environmental organisations in Ireland to distinguish areas according to groundwater transmissivity and degree of bedrock fracturing (Fitzsimons et al., 2005).
In this study hydrochemical data for the “Dinantian pure bedded limestones” rock unit was selected. The selection was based on data availability; the aforementioned rock unit is the most densely monitored in the country. Additionally, this rock unit should be expected to be karstified to some degree and therefore to provide an interesting area of study in terms of groundwater vulnerability. Finally, it was decided that only springs should be included in the analysis due to the fact that the inclusion of borehole data would introduce an additional parameter, the borehole depth, which was unknown for many of the boreholes.

Most of the variables had only a few missing or censored (below the detection limit) values, with the exception of TOC. In order to proceed with the analysis it was attempted to estimate the missing values. To accomplish this objective, hydrochemical relationships among the variables were used. For example for the calculation of missing values of magnesium and calcium, the concentration of total hardness was used according to the following formula:

$$\text{Hardness} \left( \frac{mg}{l} \right) = 2.497 \times (Ca, \frac{mg}{l}) + 4.118 \times (Mg, \frac{mg}{l})$$

**Exploratory Data Analysis**

Exploratory data analysis (EDA) was the first step in the statistical analysis of the hydrochemical data. EDA can be considered as an approach in statistical analysis that focuses on exploring the structure and properties of the data at hand. To carry out the EDA, bivariate and multivariate graphical techniques were used and summary statistics of the data were calculated.

The Kaplan-Meier (K-M) non-parametric method was used to calculate the median value for each parameter of the hydrochemical data set. The K-M method is frequently used in survival analysis and can be used where there is right censored data (i.e. have a fixed upper limit). In environmental studies, left censored data (i.e. fixed lower limit) are mostly encountered and, therefore, the data have to be transformed by flipping their order before the method can be applied. The selection of the K-M method was based on the fact that the number of detected values was relatively small (~15 per station) and there were also potential outliers that would introduce significant error to the output if distributional methods were used. Additionally, the K-M method can be used with data that have multiple detection limits and with detection limits that are greater than some of the detected values (Singh et al., 2010), of which both conditions are true for the dataset. Based on the K-M method the median value of the explanatory variables was calculated, which is considered to be a more robust estimate of the central location than the mean, especially in the presence of potential outliers (Reimann et al., 2008). The median value of the hydrochemical data was used to carry out the PCA method.

**Principal Components Analysis**

The next step in the process of EDA was to apply the PCA method using all the available explanatory variables from the dataset. PCA is used to reduce the dimensions of the data in a few principal components that explain most of the data variability. In hydrochemistry and specifically for hydrochemical data analysis the method has been frequently used to stratify the explanatory variables according to undergoing processes (e.g. mineralisation).

Before the PCA method could be applied, however, it was necessary to examine the correlations among the explanatory variables. This is because PCA is affected by highly correlated variables, a condition that is known as collinearity. Pearson correlation analysis was used which showed that electric conductivity (EC) and alkalinity were highly correlated (>0.95). For that reason EC was subsequently removed from the analysis. The variables were additionally centred and standardised to prevent the outcome being influenced by the variable with the greatest magnitude. This is a standard practice in multivariate statistical analysis.
because these methods are highly sensitive to the variance of the variables being used (Reimann et al., 2008). In figure 1 is depicted the outcome of the PCA method. Ca, alkalinity and SO\textsubscript{4} load is on the first axis (x). These are groundwater constituents of internal origin. Ca dissolute from carbonate minerals, similarly for the constituents of alkalinity, bicarbonate (HCO\textsubscript{3}) and carbonate (CO\textsubscript{3}). SO\textsubscript{4} dissolute from evaporite formations but it can be also introduced from the surface with fertilisers (Hunkeler and Mudry, 2004).

On the other hand, TOC, NO\textsubscript{3} and Mg load on the second axis (y). On the positive side of the second axis TOC and Cl have the highest loading values, while on the negative side Mg and NO\textsubscript{3} load more heavily than the other variables.

**Results and Discussion**

Based on the PCA results for the selected study area and for the dataset used, four groundwater constituents were identified as originating primarily from the surface, namely TOC, Cl, Mg and NO\textsubscript{3}. Additionally, PCA showed that the former two could be potentially used as indicators of short residence time, while the latter two appear to be promising indicators of long residence time. To verify this initial assumption, the selected variables were plotted on a matrix scatterplot depicted in figure 2. It can be seen that there is a negative relationship between Cl and Mg, as well as between TOC and Mg, TOC and NO\textsubscript{3} while there is no relationship between Cl and NO\textsubscript{3}. Therefore, based on the graphical representation of the target variables it may be possible that Mg and NO\textsubscript{3} concentrations decrease slower than that of TOC and Cl. Additionally, no relationship was observed between TOC and Cl on one hand and elements of internal origin (Ca, alkalinity). Further, the effect of potential outliers on the output of the analysis was investigated. By removing from the TOC–Mg plot the biggest outlier, the slope of the fitted line changed from -0.5493 to -0.2613, while repeating the same procedure for the TOC–NO\textsubscript{3} scatterplot the slope of the fitted line changed from -0.5334 to -0.3811. Considering additionally the possibility that the former outlier might represent an unmapped location of dolomite limestone – and therefore it should be removed – it was concluded that TOC and NO\textsubscript{3} are good indicators of water residence time.
Figure 2.: Matrix scatterplot of the hydrochemical variables plotted as log mg/L with a fitted line to help discern the underlying relationships between the pairs of variables. Clockwise from top-left to bottom-left, (x, y) TOC ~ Mg slope = -0.5493, Cl ~ Mg slope = -0.3373, Cl ~ NO₃ slope = 0.0089, TOC ~ NO₃ slope = -0.5334.

Conclusions

The outcome of PCA showed that TOC and Cl⁻ were good indicators of short residence time, whereas Mg and NO₃ could potentially be used as indicators of long residence time. In the analysis only springs for the Dinantian Pure Bedded Limestone (DPBL) rock unit were included and therefore the initial assumption was that Mg was introduced to the aquifer system through water infiltration, an assumption that was substantiated by the analysis. This is because Mg of autogenic origin is derived by the dissolution of dolomite limestone, which according to the selected rock unit should not be present in the areas of study. Groundwater data availability and the fact that the locations underlain by DPBL are in general karstified, additionally weighted the selection of that particular rock unit.

Based on the statistical analysis, NO₃ and TOC could be used to classify the zones of contribution of each spring according to groundwater vulnerability. In addition, spatial correlation analysis between the dependent variables (Mg and TOC) and the independent variables (e.g. degree of karstification, soil and subsoil type) could be carried out to identify the most important parameters controlling groundwater vulnerability.

Acknowledgements

The authors would like to acknowledge funding by the Department of Agriculture Fisheries and Food, as administered under the Research Stimulus Fund.

References


RISK RANKING ANTIMICROBIAL PRESENCE IN THE ENVIRONMENT

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Abstract

The presence of pharmaceuticals in the environment poses a potential risk for environmental toxicity and resistance formation. A mechanistic model is presented for determination of antimicrobial presence in the environment. The model was used to evaluate six main groups of antimicrobials consumed in Europe: penicillins (PEN), β-lactams (BET), tetracyclines (TET), macrolides (MAC), quinolone/fluoroquinolones (Q/F) and sulfonamides/trimethoprim (S/T). The model simulates the release of antimicrobials into the environment by integrating the effects of antimicrobial use, metabolism, degradation, and dilution. Each input variable was assigned a probability density to represent inherent uncertainty and variability in the parameter. The Monte Carlo simulation model resulted in a probability distribution of the predicted environmental concentrations (PECs) for each antimicrobial group. The resulting PECs were ranked in relation to resistance potential, chronic and acute toxicity and hazard quotient (HQ).

The model simulated the mean PEC of PEN, BET, TET, MAC, Q/F and S/T (0.43, 0.14, 0.05, 0.05, 0.02 and 0.07 mg/m³/day, respectively. Degradation was the main input influencing PEN environmental concentrations, usage was foremost for BET and S/T, while metabolism was the most critical input for TET, MAC and Q/F. Q/F expressed the highest rate of resistance formation potential (57%). BET expressed a moderate HQ (within the range 1.1 - 10) with all remaining antimicrobials expressing a low HQ (between 0.01 - 1). No antimicrobial group was predicted to exhibit toxicity at the predicted concentrations but may lead to levels in the environment which can increase resistance formation. The sensitivity analysis indicates a possible role for considering metabolism during regulation of new antimicrobials as this can greatly influence the PEC value. The results and limitations presented here accentuate the need for further research into antimicrobials in the environment and the development of antimicrobial resistant strains.

Introduction

Pharmaceuticals, and their metabolites, are present in the environment as a result of human, agriculture and veterinary usage. Their presence can lead to the formation of resistance among environmental bacteria populations. As antimicrobial compounds are used daily and are continuously being released into the environment, given their persistence the compounds are deemed pseudo-persistent. Thus, it is critical to identify the contributing factors which lead to antimicrobial residues in the environment and to identify antimicrobial groups which pose the greatest risk. The emergence of antimicrobial resistance, which potentially leads to therapeutic failure, has become a major health concern and is related to increased morbidity in humans. Wastewater treatment plants (WWTP) are considered to be the main contributing source of antimicrobial residues in the environment. However, the contributing factors and leading mechanism of resistance formation remain uncertain. Identifying the leading factors involved in resistance formation is fundamental to understanding the processes involved and to identify possible mitigation measures. Hence, there is a need for a quantitative risk analysis of antimicrobials in the environment to assess the potential risk to humans through direct toxicity and resistant bacteria infection.

The primary objective of this study was to determine leading factors influencing the presence of antimicrobial residues in the environment and to rank their predicted environmental concentrations (PEC), using a number of ranking endpoints.

Materials and Methods

In this study Monte Carlo simulation was used to estimate a distribution for each input factor (metabolism, degradation and dilution) for the defined risk (antimicrobial presence in the environment). Currently there is no defined acceptable limit for antimicrobial residues in the waste
water system, effluent from hospitals or wastewater treatment plant effluent. A simulation model of probable events was created to estimate the PECs of antimicrobial residues. A succession of events was identified to analyse the pathway from human consumption of antimicrobials to their release into the environment. Foremost, a simulation model was built in EXCEL 2003 (with @Risk 5.0 add-on) to characterise the fate of pharmaceuticals in the environment from patient consumption to concentration in the environment. Antibiotic consumption data was calculated using the ESAC database (Ferech et al., 2006), the 2007 ambulatory consumption for Ireland, according to ATC/DDD classification (2008 version) (ESAC 2010). Literature was examined to identify human metabolism of antimicrobials, metabolism was estimated through identification of human excretion of metabolites and parent compounds. Metabolites were considered in the model and included in the model equivalent to the parent compound as increased toxicity and de-conjugation of antimicrobial metabolites is possible (Kümmerer, 2008). Literature was examined to identify compound degradation; the ability for the compound to survive in the environment (half-life, days). Dilution was incorporated into the model to represent the presence of antimicrobials within the WWTP system. An undisclosed WWTP provided influent flow data which was converted to create a standardised value of average influent (m³) per 1000 inhabitants. The average population equivalent (PE) was calculated for each inflow data point and converted to represent 1000 inhabitants. This was repeated for a year’s data and a probability density was created to represent dilution.

Probability densities were created for each parameter discussed above. Data was collected for the six main groups of antibiotics; PEN, BET, TET, MAC, Q/F and S/T. Each variable was assigned a parametric distribution. The variables were combined to estimate the PEC of each antimicrobial entering the environment (Table 1). The model was run for 10,000 iterations and the Monte Carlo simulation resulted in a probability distribution for each antimicrobial. Subsequently, a sensitivity analysis was carried out to identify the relationship between the variables by calculating a correlation coefficient (Le and Boen, 1995). Correlation is the degree to which one variable is dependent on another (Vose, 2008).

The resulting values were ranked in accordance with three factors, resistance potential, acute and chronic toxicity and hazard quotient. Antimicrobial resistance potential was based on concentrations being released below the minimum inhibitory concentration (MIC). The lower limit of a sub-inhibitory concentration acting as a selector for resistance has been poorly explored (Acar and Rostel 2001). It is questioned whether the lower limit of the MIC will affect resistance formation. The evidence for a cut off concentration to which no resistance can form is nonexistent. Toxicity was calculated using effect concentration (EC₅₀) and lethal concentration (LC₅₀) measurements. ECOSAR software was used to identify the toxicity levels of antimicrobials to green algae, daphnia and fish. The most toxic data was recorded in each category (in accordance with the precautionary principle recommended in the EU white paper (EU, 2001)) and were averaged to find an overall toxicity value (Solomon et al. 2000); the same technique was applied to chronic toxicity data. This was repeated for each antimicrobial group and probability densities were created. It is argued that this method of toxicity testing (EC/LC₅₀ value analysis) is not significant for antimicrobials agents, as the organisms which are affected by antimicrobials are phylogenetically distinct from the cyanobacteria (algae) used in the testing. The hazard quotient (HQ) or risk quotient (RQ), a commonly used risk ranking criteria (Solomon et al., 2000; Sanderson et al., 2004; Zhao et al., 2010), was applied as a measure of concern (Tannenbaum et al., 2003) to rank antimicrobial groups. The HQ is often used as a tool to indicate the necessity for remedial action and can be used for screening and eliminating chemicals from further consideration in environmental risk assessment. A HQ value < 0.01 equates no existing hazard, 0.1-1.0 hazard is low, 1.1-10 hazard is moderate and >10 hazard is high (Lemly 1996).

**Results and Discussion**

Inputting the data (Table 1) into the EXCEL model resulted in the predicted environmental concentrations of PEN, BET, TET, MAC, Q/F and S/T (0.45, 0.14, 0.05, 0.05, 0.02 and 0.02 mg/m³/day, respectively (Table 2)). To discover a possible relationship between multiple continuous variables, the strength of the relationship was characterised by calculating the coefficient of correlation. Degradation was the main input influencing PEN environmental concentration, usage was foremost for BET and S/T, while metabolism was the most critical input for TET, MAC and Q/F.
The resistance formation potential indicated that optimal conditions for resistance occur most often for Q/F. BET expressed a moderate HQ (within the range 1.1 - 10) with all remaining antimicrobials expressing a low HQ (between 0.01 - 1) (Table 2). No antimicrobial group was predicted to exhibit toxicity at the predicted concentrations but may lead to levels in the environment which can increase resistance formation.

### Table 1: Model input parameters and equations

<table>
<thead>
<tr>
<th>S</th>
<th>Description</th>
<th>Model</th>
<th>Units</th>
<th>R</th>
</tr>
</thead>
<tbody>
<tr>
<td>$U_P$</td>
<td>PEN Use</td>
<td>11.51</td>
<td>DDD/1000inh./day</td>
<td>1</td>
</tr>
<tr>
<td>$U_B$</td>
<td>BET Use</td>
<td>1.96</td>
<td>DDD/1000inh./day</td>
<td>1</td>
</tr>
<tr>
<td>$U_T$</td>
<td>TET Use</td>
<td>3.32</td>
<td>DDD/1000inh./day</td>
<td>1</td>
</tr>
<tr>
<td>$U_M$</td>
<td>MAC Use</td>
<td>4.05</td>
<td>DDD/1000inh./day</td>
<td>1</td>
</tr>
<tr>
<td>$U_{Q/F}$</td>
<td>Q/F Use</td>
<td>1.04</td>
<td>DDD/1000inh./day</td>
<td>1</td>
</tr>
<tr>
<td>$U_{S/T}$</td>
<td>S/F Use</td>
<td>0.87</td>
<td>DDD/1000inh./day</td>
<td>1</td>
</tr>
<tr>
<td>$D_{OP}$</td>
<td>PEN Dose</td>
<td>Pearson5(2.125,3568,RiskName)</td>
<td>mg</td>
<td>2</td>
</tr>
<tr>
<td>$D_{OB}$</td>
<td>BET Dose</td>
<td>BetaGeneral(1.3814,2.3742,0.6723,3)</td>
<td>mg</td>
<td>2</td>
</tr>
<tr>
<td>$D_{OT}$</td>
<td>TET Dose</td>
<td>Triang(0,1000,1000)</td>
<td>mg</td>
<td>2</td>
</tr>
<tr>
<td>$D_{OM}$</td>
<td>MAC Dose</td>
<td>Loglogistic(0,868,84,2.981)</td>
<td>mg</td>
<td>2</td>
</tr>
<tr>
<td>$D_{OQ/F}$</td>
<td>Q/F Dose</td>
<td>Loglogistic(0.551,81.2.6799)</td>
<td>mg</td>
<td>2</td>
</tr>
<tr>
<td>$D_{OS/T}$</td>
<td>S/T Dose</td>
<td>Lognorm(2087,3098.3)</td>
<td>mg</td>
<td>2</td>
</tr>
<tr>
<td>$M_{EP}$</td>
<td>PEN urine excretion</td>
<td>Triang(0.75,93.047)</td>
<td>%</td>
<td>3;4</td>
</tr>
<tr>
<td>$M_{EB}$</td>
<td>BET urine excretion</td>
<td>Triang(0.62,5,87.639)</td>
<td>%</td>
<td>3;4</td>
</tr>
<tr>
<td>$M_{ET}$</td>
<td>TET urine excretion</td>
<td>Uniform(0,77)</td>
<td>%</td>
<td>3;4</td>
</tr>
<tr>
<td>$M_{EM}$</td>
<td>MAC urine excretion</td>
<td>Lognorm(24.139,50.322)</td>
<td>%</td>
<td>3;4</td>
</tr>
<tr>
<td>$M_{EQ/F}$</td>
<td>Q/F urine excretion</td>
<td>BetaGeneral(1.5642,2.0887,0.106.06)</td>
<td>%</td>
<td>3;4</td>
</tr>
<tr>
<td>$M_{ES/T}$</td>
<td>S/T urine excretion</td>
<td>Loglogistic(0.63,402,6.602)</td>
<td>%</td>
<td>3;4</td>
</tr>
<tr>
<td>$D_{EGP}$</td>
<td>PEN degradation</td>
<td>Invgauss(8.276,0.20736)</td>
<td>$t_{1/2}$ (days)</td>
<td>3;5</td>
</tr>
<tr>
<td>$D_{EGB}$</td>
<td>BET degradation</td>
<td>Expon(37.829,RiskName)</td>
<td>$t_{1/2}$ (days)</td>
<td>3;5</td>
</tr>
<tr>
<td>$D_{EGT}$</td>
<td>TET degradation</td>
<td>Loglogistic(0.43,414,1.0282)</td>
<td>$t_{1/2}$ (days)</td>
<td>3;5</td>
</tr>
<tr>
<td>$D_{EGM}$</td>
<td>MAC degradation</td>
<td>Pearson6(0.57885,9.4463,346.49)</td>
<td>$t_{1/2}$ (days)</td>
<td>3;5</td>
</tr>
<tr>
<td>$D_{EQ/F}$</td>
<td>Q/F degradation</td>
<td>Triang(0.04,348.31)</td>
<td>$t_{1/2}$ (days)</td>
<td>3;5</td>
</tr>
<tr>
<td>$D_{ES/T}$</td>
<td>S/T degradation</td>
<td>Expon(66.944)</td>
<td>$t_{1/2}$ (days)</td>
<td>3;5</td>
</tr>
<tr>
<td>$D_i$</td>
<td>WWTP influent volume</td>
<td>Pearson5(3.0937,50810)</td>
<td>m$^3$/day/1000inh.</td>
<td>6</td>
</tr>
<tr>
<td>$D$</td>
<td>Antimicrobial use</td>
<td>$(U_x)(D_{ox})$</td>
<td>mg/1000inh./day</td>
<td>n/a</td>
</tr>
<tr>
<td>$f_1$</td>
<td>Effect of metabolism</td>
<td>$(D_x/100)(Met_x)$</td>
<td>%,mg/1000inh./day</td>
<td>n/a</td>
</tr>
<tr>
<td>$f_2$</td>
<td>Effect of degradation</td>
<td>$(f_1)(0.5)^{1/(Deg_x)}$</td>
<td>mg/1000 inh.</td>
<td>n/a</td>
</tr>
<tr>
<td>$E_{conc}$</td>
<td>PEC</td>
<td>$(f_2)/Di$</td>
<td>m$^3$/day/1000inh.</td>
<td>n/a</td>
</tr>
</tbody>
</table>

Where; S is symbol; R is reference; x is the antimicrobial agent; PEC is predicted environmental concentration; 1. ESAC (2010); 2. WHO (2011); 3. Boxall (2005); 4. Bryskier (2005); 5. Kümmerer (2008); 6. Groom and Healy (2001).

### Table 2: Monte Carlo simulation and regression analysis results of six main antimicrobial groups consumed in Europe.

<table>
<thead>
<tr>
<th>Antimicrobial Group</th>
<th>PEC* (mg/m$^3$/day)</th>
<th>Leading contributing factor</th>
<th>$R^2$</th>
<th>Resistance formation potential (%)</th>
<th>Chronic/Acute toxicity (%)</th>
<th>HQ*</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEN</td>
<td>0.43</td>
<td>Degradation</td>
<td>0.87</td>
<td>11</td>
<td>0</td>
<td>0.31</td>
</tr>
<tr>
<td>BET</td>
<td>0.14</td>
<td>Use</td>
<td>0.66</td>
<td>47</td>
<td>0</td>
<td>2.02</td>
</tr>
<tr>
<td>TET</td>
<td>0.05</td>
<td>Metabolism</td>
<td>0.67</td>
<td>10</td>
<td>0</td>
<td>0.02</td>
</tr>
<tr>
<td>MAC</td>
<td>0.05</td>
<td>Metabolism</td>
<td>0.71</td>
<td>3</td>
<td>0</td>
<td>0.03</td>
</tr>
<tr>
<td>Q/F</td>
<td>0.02</td>
<td>Metabolism</td>
<td>0.58</td>
<td>57</td>
<td>0</td>
<td>0.86</td>
</tr>
<tr>
<td>S/T</td>
<td>0.07</td>
<td>Use</td>
<td>0.82</td>
<td>5</td>
<td>0</td>
<td>0.08</td>
</tr>
</tbody>
</table>

*PEC, Predicted environmental concentration
Conclusions
Pharmaceutical use and excretion into the environment leads to their ubiquitous presence in the environment. Due to the low PECs, toxicity is not likely, but resistance dissemination is possible. The issue of mixture toxicity was not assessed here and as some antimicrobials may have similar effects on environmental organisms the toxic effect may be extrapolated. Similarly, the use of ECOSAR® for antimicrobial toxicity reference values is limited as the bacteria targeted by antimicrobials are phylogenetically distinct from the cyanobacteria used to calculate the EC/LC50 values. Risk ranking was identified as a useful method which can be used to identify the leading contributing factors of an event, such as antimicrobial residues in the environment, and can be used to identify the relationship between variables. Experimental data and in depth understanding of the environmental stability of pharmaceuticals and their removal by STP are still lacking; specifically, the ability for PECs to act as selectors for resistance formation. The results and limitations presented here accentuate the need for further research into antimicrobials in the environment and development of antimicrobial resistant strains.

Acknowledgements
The authors would like to acknowledge the Irish EPA for the funding of this project, Under the STRIVE programme (2007-2013).

References
TACKLING THE GREENHOUSE GAS EMISSIONS FROM IRISH DAIRY PRODUCTION: IMPLICATIONS FROM LIFE CYCLE COMPARISONS

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

Abstract
The objective of this paper was to undertake a life cycle assessment (LCA) 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 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 2001-2006, the GHG (CO₂, CH₄ and N₂O) emissions from clover-based (WC) and mineral-N-fertiliser-based (FG) dairy production were compared using LCA methodology. Compared with the FG system, the overall GHG emissions for producing 1 kg ECM from WC was reduced by 14.7%. Fertilizer input per ha and milk yield per cow were found to be the most sensitive parameters for the LCA modelling.

Introduction
There is an established concern about the effect of greenhouse gas (GHG) emissions on global climate change. In Ireland agriculture is the single largest contributor to overall emissions at 26% (EPA, 2010). The Intergovernmental Panel on Climate Change (IPCC) has provided methodologies for inventorying GHG from agricultural sector at national scale. However, those methodologies do not fully capture the GHG profile of agricultural products along the production chain. A holistic method, Life Cycle Assessment (LCA), can better reveal the environmental impacts of an agricultural system. A recent study by the Joint Research Centre (JRC) of European Commission evaluated livestock contribution to the EU GHG (GGELS, 2010) and found that compared to the LCA results, the ‘agriculture’ sector defined by IPCC guidelines estimates only 57% of total GHG emissions caused by EU-27 livestock production up to the farm gate. This finding highlighted the importance of the life cycle view-point when addressing the environmental impact of agricultural production. The main GHG from agricultural production are 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 et al., 2005) found that white clover had a marked effect (22% lower per kg milk) on the GHG emissions.

The objective of this paper was to develop a LCA model of two contrasting dairy systems in Ireland (with and without white clover), to evaluate change in GHG emissions as a result of introducing white clover.

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

Goal and Scope
The goal was to develop a LCA model of two contrasting management strategies for a dairy system in Ireland (with and without white clover) to evaluate changes in GHG emissions as result of introducing white clover.
The production system evaluated was low-cost, grass-based rotational grazing as implemented as research trials at the Teagasc Solohead Research Farm, Co Tipperary, Ireland (52°51’ N, 08°21’ W) between 2001 and 2006 (Humphreys et al., 2008, 2009; Table 1). All cows were Holstein-Friesian. The soil was a clay-loam and the ten-year average rainfall was 1005 mm (Humphreys et al., 2009). The functional unit (FU) was defined as 1 kg energy corrected milk (ECM, Casey and Holden, 2005), defined as:

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

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

**Life Cycle Inventory and Impact Assessment**

The foreground, primary data describing the variations in low-cost, grass-based, rotational grazing were obtained from research records from the Teagasc Solohead Farm (Table 1. See also Humphreys et al., 2008; 2009). A few assumptions had to be made to translate the research trial data into a workable farming system (data not shown). The GHG inventory was made by multiplying life cycle activity data by emission factors (EF, Table 2). In the on-farm sector, enteric CH₄ from cows was estimated according to IPCC Tier 2 (O’Mara et al., 2006). All livestock were calculated in terms of a calendar year. CH₄ emissions for manure management and soils were estimated using relevant EFs derived from literature. N₂O emissions from manure management and soils were estimated with IPCC Tier 2 (EPA, 2010). No appropriate EF was found for CH₄ or N₂O emission from dirty water storage and spreading so it was not included in the LCA model. Indirect N₂O emissions from atmospheric deposition and leaching were estimated using IPCC Tier 2 (EPA, 2010). Diesel combustion due to the field work on-farm was included in the on-farm sector as was estimated from Kramer (1999). In the pre-farm sector, GHG emissions from fertilizer production and ingredients of concentrate production were taken from relevant Ecoinvent v 2.1 datasets in SimaPro 7.2. Emission from electricity production was taken from report on energy in Ireland during 1990-2007 (Howley et al., 2008). Emissions form diesel production, road and water transportation were taken from Casey and Holden (2005). Fertilizer was assumed to be transported from Germany and concentrates from their origin to Ireland.

**Table 1**: System characteristics at Solohead averaged over 2003 to 2006

<table>
<thead>
<tr>
<th>Classification</th>
<th>WC 01-02</th>
<th>FN 03-06</th>
<th>WC 03-06</th>
</tr>
</thead>
<tbody>
<tr>
<td>Year of experiment</td>
<td>01-02</td>
<td>03-06</td>
<td></td>
</tr>
<tr>
<td>Stocking rate (LU ha⁻¹)</td>
<td>1.75</td>
<td>2.10</td>
<td>2.50</td>
</tr>
<tr>
<td>Synthetic fertilizer N (kg ha⁻¹)</td>
<td>80</td>
<td>180</td>
<td>248</td>
</tr>
<tr>
<td>Concentrate feed (kg cow⁻¹ yr⁻¹)</td>
<td>536</td>
<td>536</td>
<td>536</td>
</tr>
<tr>
<td>Milk delivered at farm gate (kg cow⁻¹)</td>
<td>6550</td>
<td>6275</td>
<td>6242</td>
</tr>
<tr>
<td>Milk fat (%)</td>
<td>4.1</td>
<td>4.2</td>
<td>4.1</td>
</tr>
<tr>
<td>Milk protein (%)</td>
<td>3.5</td>
<td>3.6</td>
<td>3.5</td>
</tr>
<tr>
<td>Biological-N fixation (kg ha⁻¹ yr⁻¹)</td>
<td>87.4</td>
<td>9.1</td>
<td>3.2</td>
</tr>
</tbody>
</table>

¹The stocking rate (LU = livestock unit) were 2 in 2003 and 2.2 during 2004-2006
Life Cycle Impact Assessment (LCIA) was restricted to Global Warming Potential assuming CO₂ equivalence of 25 for CH₄ and 310 for N₂O.

| Table 2: Emission factors for Solohead LCA during 2001-2006 |
|---------------------|---------------------|---------------------|
|                      | CO₂                | CH₄                | N₂O                |
|                      | On-farm            |                    |                    |
| Enteric fermentation | Dairy cows         | DMI * 21.96 g / cow | 0.1% kg N₂O-N /(kg N-kg NH₃-N) |
|                     | Replacement unit   | 90% that of cows / replacement unit | |
| Manure management   | Slurry storage     | 0.0082 kg/(m³,d)   | 2% kg N/(kg N-kg NH₃-N) |
|                     | FYM storage        | 0.0059 kg/(m³,d)   | 2% kg N/(kg N-kg NH₃-N) |
|                     | Collecting yard    | 4.3*10⁻⁷ kg/(m²,h) | 7.5*10⁻⁹ kg N/(m²,h) |
| Emission from soil  | Excreta in field   | 0.001683 kg/(cow, d) | 2% kg N₂O-N /(kg N-kg NH₃-N) |
|                     | Slurry spreading   | 0.00007-0.0123 kg/m³ | 1% kg N₂O-N/(kg N-kg NH₃-N and N₂O-N) |
|                     | FYM spreading      | 0.0027kg/kg        | 2% kg N₂O-N/(kg N-kg NH₃-N and N₂O-N) |
|                     | Fertilizer spreading | 0.2 t C/t urea | 1% kg N₂O-N /(kg N-kg NH₃-N) |
| Indirect N₂O emission | EF₄=0.01, EF₅=0.025, Frac_LEACH=0.1 |
| Diesel combustion   | 3.56kg/kg          | 0.00052kg/kg       | 0.0007kg/kg       |

| Pre-farm            |                      |                    |                    |
| Fertilizer production | 8.2 kg CO₂ eq/kg CAN-N, 3.07 kg CO₂ eq/kg urea-N |
| Concentrate production | 0.375 kg CO₂ eq/kg concentrate |
| Electricity production | 0.68 kg CO₂ eq/kWh |
| Diesel production   | 0.6 kg CO₂ eq/kg    |
| Road transportation | 0.32 kg/10⁳ tkm     | 207.8 kg/10⁶ tkm   | 0.045 kg/10⁶ tkm  |
| Water transportation | 0.014 kg/10⁶ tkm    | 9 kg/10⁶ tkm       | 0.002 kg/10⁶ tkm |

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

Results and Discussion
The overall GHG emissions from the average WC and FG systems were 0.84 and 0.98 kg CO₂/kg ECM, which was dominated by the on-farm section, 0.71 and 0.78 kg CO₂/kg ECM respectively. When divided into the three GHGs, the difference between the two systems arises from the contributions from N₂O and CO₂ emissions (P < 0.001), while the CH₄ emissions are similar. When divided into the major contributors to the GHG emissions, enteric CH₄ is the largest single contributor for both systems (56.5% and 48.4% in WC and FG, same below), followed by manure management (18.5%, 15.5%), fertilizer (7.2%, 19.3%), energy (7.7% and 6.7%), indirect N₂O (5.5%, 6.2%) and concentrate feeds (4.1%, 3.5%). Significant correlation was found between fertilizer N input and GHG emissions (P < 0.001). For example, at the same stocking rate of 2.2 LU/ha during 2004-2006, the average WC system had 60.2% lower fertilizer N per ha and 13.3% lower GHG emissions per kg ECM compared with the average FG system. This highlighted the sensitivity of GHG emission per
kg ECM to the fertilizer N input per ha. A 10% increase of stocking rate from 2.0 to 2.2 LU/ha resulted in almost no change in the GHG emissions per kg ECM for both FG and WC systems during 2003-2006. However, a steady increase of GHG emissions per kg ECM with an increase in stocking rate was found over the six years of trials. No correlation was found between milk output per cow and GHG emissions per kg ECM (P > 0.05). However, 1% increase of milk output per cow (with no change in concentrate feed and small increase in enteric fermentation) was found to result +2.3% and -1.0% change of GHG emission per kg ECM in WC and FG systems on average, and the difference between which dropped to 11.8%. On the other hand, 1% decrease of milk output was found to result +0.5% change in both systems, but the difference between them remained at 14.8%. This was similar to the findings of Basset-Mens et al. (2009) where the on-farm dry matter intake was ranked as the most influential parameter for GWP of 1 kg average New Zealand milk. In addition, the different response from FG and WC output seemed to suggest that the GHG emissions from the less intensive WC system may be more sensitive to the milk output.

Conclusions
A recent LCA study found that the GHG emissions per kg milk from Irish pasture based milk production ranked as the lowest among EU-27 member states (GGELS, 2010). The result in this paper show that compared with the FG system, the overall GHG emissions for producing 1 kg ECM from WC was reduced by 14.7%, which suggests that there is more potential for GHG reduction. Fertilizer input per ha and milk yield per cow were found to be the main sensitive parameters for the LCA modelling.

Acknowledgements
The work was supported by the Department of Agriculture and Food research Stimulus Fund Programme (RSF07-516) funded by the Irish Government National Development Plan.

References


Field calibration of Time Domain Reflectometers

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Abstract

A Soil Moisture Deficit Model (SMD) will be quantitatively tested using Time Domain Reflectometry measurements. Volumetric Water Content (VWC) has been measured on a wide range of sites, representative of the SMD model drainage classes. Site-specific calibration is required as soils show large variations in physical properties. Results have shown that fixed TDR slightly underestimated actual VWC (averaged bias = 0.032cm$^3$/cm$^3$). A correction ratio was applied and was found to significantly reduce both bias and Root Mean Square Error (RMSE). Linear regressions appeared to be impractical for site-specific calibration. Although spatial variations in VWC were assessed across the soil surface and actual VWC were measured at various depths, for practical purposes it was concluded that corrective ratios provided the best estimation with an improved RMSE related to the estimator.

Introduction

A Soil Moisture Deficit Model has been proposed to predict soil water status expressed as millimetres of rainfall relative to soil field capacity for Irish conditions. The model had been tested, calibrated and validated using soil water potential measurements. Although essential parameters (saturation, field capacity and wilting point) have been shown to perform correctly on both well-drained and poorly-drained soils (Schulte et al., 2005), quantitative variations in soil water content within drainage classes may differ significantly both within a site and between sites. A third drainage class (moderately-drained soils) has also been defined but not yet calibrated.

Time Domain Reflectometers have been widely used for estimating accurately and cost-efficiently soil volumetric water content, following careful calibration of the apparatus (Robinson et al., 2003). Unique calibration equations have been proposed by several authors (including manufacturers) to adjust volumetric water content for different soil types. Stangl et al. (2009) reported that such moisture sensors could be highly affected by ambient conditions (electrical conductivity and temperature) and soil properties (clay, organic matter, bulk density and ion concentration). In-situ calibration may be challenging due to site diversity and the time required to accumulate a sufficient dataset.

The objective of this paper was to examine the calibration of TDR soil moisture sensors, taking into consideration variations in situ and between sites.

Materials and Methods

Sites

Ten sites representative of the three grassland soil drainage classes were selected to evaluate the SMD model. They were selected based on geographical distribution (north to south climate gradient) and the range of drainage classes they encompassed.

Volumetric water content ($\theta$)

Point soil volumetric water content ($\theta_p$) was measured by a time domain reflectometer (TDR) waveguides installed at fixed locations relative to on site weather stations. Four continuously logged TDR probes (CS616; Campbell Scientific, Inc.) 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.
Spatial variations in volumetric water content (θs) were repeatedly assessed across the field on a monthly basis, using a handheld TDR (Hydrosense; Campbell Scientific, Inc.). 12 cm rods were inserted across the soil surface; the measured VWC, estimate by the manufacturer’s default equation, was converted into 10 cm depth VWC using actual volumetric water content (θa).

In situ TDR were calibrated by collecting VWC samples for laboratory analysis. Soil samples (3 × 13.7 cm³ at 10 cm and 20 cm depths) were taken on a bi-monthly basis during visits to each site. These samples were dried at 65°C until the dry mass was constant and the actual volumetric water content (θa) was calculated as the mass of water per unit volume soil sampled. Fixed TDR probes were calibrated using actual VWC taken at respective depths while handheld TDR used 10 cm deep samples.

Equations and statistics

Three calibration procedures have been tested and compared to actual volumetric water content (θa) to find the most accurate and the most representative estimation of soil moisture content for each site. The first θp estimation used the manufacturer quadratic equation:

$$θ_p = -0.0663 - 0.0063 \times \text{velocity} + 0.0007 \times \text{velocity}^2$$

(1)

Then site-specific linear regressions were performed to compare VWC estimations:

$$θ_a = s \times θ_p + o$$

(2)

where s is the slope of the linear regressions and o is the y-intercept of the intersection point through the y-axis. Finally, corrective ratios are applied to estimated moisture values (θp and θs):

$$θ_{1a} = R_1 \times θ_p \quad \text{and} \quad θ_{2a} = R_2 \times θ_s$$

(3)

where the ratio, R, is respectively:

$$R_1 = \frac{\sum θ_a}{n_1} \quad \text{and} \quad R_2 = \frac{\sum θ_a}{n_2}$$

(4)

with n1 and n2, the total numbers of samples. Bias (B) and Root Mean Square Errors (RMSE) were calculated for all samples and all estimators using the following equations:

$$B = θ_a - θ_e$$

(5)

$$RMSE = \sqrt{\frac{\sum (θ_a - θ_e)^2}{n}}$$

(6)

where θe is the estimated VWC (θp, θs, θ1 or θ2)

Results

Fixed TDR calibration

The efficiency of the manufacturer equations differ extensively from one site to another. The observed bias from actual VWC ranged from -0.002 to +0.077 cm³/cm³ with an averaged bias of 0.032 cm³/cm³ (Table 1), highlighting an underestimation of TDR measurements. Variations in bias between sites illustrate the necessity for site-specific adjustments. Linear regressions performed best on homogeneous fields such as Cork 2 and Carlow 1 where the averaged coefficient of determination was 0.8 for both fields. Furthermore slight bias of 0.002 and 0.005 cm³/cm³ was observed. The manufacturer noted that the sensor performs best on sandy loam soils with bulk density (BD) less than 1.55 g cm⁻³ and clay content less than 30%. In all cases soil properties were similar to the manufacturer’s stated optimum (e.g. Table 2); the combination of
clay content, organic matter content and bulk density may have caused some of the bias. Further laboratory and statistical analyses are required to understand the impact of each parameter. General equations using soil information on particle-size distribution and temperature, as described Rüdiger et al. (2010), may be tested in the near future.

Table 1: Statistical results of calibration procedures for fixed TDR

<table>
<thead>
<tr>
<th>Site</th>
<th>Coefficient of determination ($r^2$)</th>
<th>Manufacturer estimations ($\theta_p$)</th>
<th>Ratio estimations ($\theta_r$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>10 cm</td>
<td>20 cm</td>
<td>bias</td>
</tr>
<tr>
<td>Monaghan 1</td>
<td>0.24</td>
<td>0.10</td>
<td>5.2E-02</td>
</tr>
<tr>
<td>Monaghan 2</td>
<td>0.85</td>
<td>0.64</td>
<td>2.9E-02</td>
</tr>
<tr>
<td>Meath 1</td>
<td>0.66</td>
<td>0.68</td>
<td>-1.6E-03</td>
</tr>
<tr>
<td>Meath 2</td>
<td>0.66</td>
<td>0.53</td>
<td>7.7E-02</td>
</tr>
<tr>
<td>Carlow 1</td>
<td>0.73</td>
<td>0.88</td>
<td>4.6E-03</td>
</tr>
<tr>
<td>Carlow 2</td>
<td>0.65</td>
<td>0.44</td>
<td>1.3E-02</td>
</tr>
<tr>
<td>Kilkenny 1</td>
<td>0.56</td>
<td>0.27</td>
<td>5.4E-02</td>
</tr>
<tr>
<td>Kilkenny 2</td>
<td>0.70</td>
<td>0.33</td>
<td>5.0E-02</td>
</tr>
<tr>
<td>Cork 1</td>
<td>0.18</td>
<td>0.69</td>
<td>3.9E-02</td>
</tr>
<tr>
<td>Cork 2</td>
<td>0.76</td>
<td>0.85</td>
<td>2.4E-03</td>
</tr>
<tr>
<td>Average</td>
<td>0.60</td>
<td>0.54</td>
<td>3.2E-02</td>
</tr>
</tbody>
</table>

Table 2: Soil bulk densities (g/cm³) at probes depths for each site

<table>
<thead>
<tr>
<th>Location</th>
<th>Monaghan</th>
<th>Meath</th>
<th>Carlow</th>
<th>Kilkenny</th>
<th>Cork</th>
</tr>
</thead>
<tbody>
<tr>
<td>Site</td>
<td>1</td>
<td>2</td>
<td>1</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>Depth</td>
<td>10cm</td>
<td>1.20</td>
<td>1.35</td>
<td>1.33</td>
<td>1.28</td>
</tr>
<tr>
<td></td>
<td>20cm</td>
<td>1.21</td>
<td>1.38</td>
<td>1.41</td>
<td>1.24</td>
</tr>
</tbody>
</table>

The poorest correlations were observed on Cork 1 and Monaghan 1. Cork 1 contained large amount of charcoal residues, which explained the difficulty of obtaining homogenous samples, while Monaghan 1 was a poorly-drained soil. Soil shrinkage, clay content, seasonal temperature variations and lateral movement of water were suspected to have influenced the representativeness of actual VWC. The functioning of the device is not questioned as previous work has shown that the VWC was well-correlated with SMD predictions. Sampling error was also minimised, as the procedure, the equipment used and the operator remained unchanged over the sampling period.

As biases were observed using the manufacturer’s equation, and site-specific linear regression performed poorly for most soils, it was decided to apply a corrective ratio to the estimated TDR data. Results have shown that this method reduced the bias by a factor of 20. The RMSE related to the estimator has been reduced from 0.06 to 0.038 cm³/cm³ (table 1) which approaches desirable values (<0.03 cm³/cm³) found by Western and Seyfried (2005).

Handheld TDR calibration

The bias related to the manufacturer’s calibrations varied between -0.22 and -0.06 cm³/cm³ with an averaged value of -0.11 cm³/cm³ (table 3). While a slight difference between actual soil moisture content and handheld TDR estimation may be due to soil properties, the apparent overestimation showed that the soil surface was wetter than deeper layers. Indeed TDR measurements were taken across the soil surface (0 - 12cm deep) while actual VWC was measured at 10 cm deep. Capillarity forces are believed to attract water, as a result of greater root density and organic matter content. The objective of the overall project is to evaluate the SMD model which calculates soil moisture status for the rooting zone (~30 cm). It was therefore necessary to convert soil surface VWC into 10 cm deep VWC. Linear regressions showed similar performance as observed with the fixed TDR and would be impractical for calibration. Again a
proportional ratio was applied and was found to reduce the bias from $-1.1 \times 10^{-1}$ to $-1.8 \times 10^{-3}$ (Table 3). RMSE related to the estimator was also significantly reduced from $1.4 \times 10^{-1}$ to $6.2 \times 10^{-2}$. Difference in sampling depths justify the fact that the RMSE related to the handheld TDR measurements was slightly higher than the RMSE related to fixed TDR measurements.

### Table 3: Statistical results of calibration procedures for handheld TDR

<table>
<thead>
<tr>
<th>Site</th>
<th>coefficient of determination ($r^2$)</th>
<th>Manufacturer estimations ($\theta_p$)</th>
<th>Ratio estimations ($\theta_r$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Bias</td>
<td>RMSE</td>
<td>Bias</td>
</tr>
<tr>
<td>Monaghan 1</td>
<td>0.48</td>
<td>-0.11</td>
<td>1.2E-01</td>
</tr>
<tr>
<td>Monaghan 2</td>
<td>0.60</td>
<td>-0.12</td>
<td>1.3E-01</td>
</tr>
<tr>
<td>Meath 1</td>
<td>0.48</td>
<td>-0.19</td>
<td>2.2E-01</td>
</tr>
<tr>
<td>Meath 2</td>
<td>0.88</td>
<td>-0.06</td>
<td>1.2E-01</td>
</tr>
<tr>
<td>Carlow 1</td>
<td>0.54</td>
<td>-0.08</td>
<td>1.0E-01</td>
</tr>
<tr>
<td>Carlow 2</td>
<td>0.61</td>
<td>-0.06</td>
<td>1.1E-01</td>
</tr>
<tr>
<td>Kilkenny 1</td>
<td>0.55</td>
<td>-0.09</td>
<td>1.2E-01</td>
</tr>
<tr>
<td>Kilkenny 2</td>
<td>0.51</td>
<td>-0.22</td>
<td>2.4E-01</td>
</tr>
<tr>
<td>Cork 1</td>
<td>0.06</td>
<td>-0.10</td>
<td>1.4E-01</td>
</tr>
<tr>
<td>Cork 2</td>
<td>0.64</td>
<td>-0.06</td>
<td>9.1E-02</td>
</tr>
<tr>
<td>average</td>
<td>0.54</td>
<td>-0.11</td>
<td>1.4E-01</td>
</tr>
</tbody>
</table>

### Conclusion

Biases were observed between TDR estimations and actual volumetric water content and soil properties probably accounted for most of the impact. As TDR estimations of Volumetric Water Content have been shown to strongly correlate with Soil Moisture Deficits in previous work, TDR performance would not be questioned. Poor linear regressions may therefore be justified by field heterogeneity. Proportional ratios applied to TDR estimations significantly reduced the biases and improved the RMSE related to the estimator.

### Acknowledgements

This project is funded by the Department of Agriculture, Fisheries and Food.

### References


ESTABLISHMENT OF AN OPTIMUM HARVEST WINDOW AND PRE-HARVEST TREATMENT OF Miscanthus Giganteus

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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. Delaying the harvest date of Miscanthus giganteus from the conventional harvest time of autumn until spring has been found to improve the combustion quality of the fuel while also aiding the storability of the biomass material by reducing the moisture content (MC) of the material. Different possibilities exist with respect to harvesting techniques. For example it is possible to cut the crop and leave it on the ground either in a swath or spread flat on the ground prior to collection while direct cut/collection in one pass is an alternative option. The results of this experiment show that cutting the crop and leaving it to dry prior to harvesting can lead to a higher rate of moisture loss when compared to crop left standing (control) when cut in February and March, however lower moisture contents were observed in the control earlier in the harvest window (January).

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 investigated however in relation to harvest window and harvesting techniques. Establishing 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 experiment was conducted in the Teagasc Crops Research Centre, Oak Park, Carlow. 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 does not 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.

The following figure is an illustration of the plot and the treatments applied for the purposes of this experiment.

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Block 1</th>
<th>Block 2</th>
<th>Block 3</th>
<th>Block 4</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2</td>
<td>3</td>
<td>4</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>Feb</td>
<td>Mar</td>
<td>Jan</td>
<td>Cont</td>
</tr>
<tr>
<td></td>
<td>Strip A</td>
<td>Strip B</td>
<td>Strip C</td>
<td>Strip D</td>
</tr>
<tr>
<td>N Trial</td>
<td>swath</td>
<td>DM</td>
<td>flat</td>
<td>cont</td>
</tr>
<tr>
<td>Clearance</td>
<td>flat</td>
<td>swath</td>
<td>DM</td>
<td>flat</td>
</tr>
<tr>
<td>DM</td>
<td>flat</td>
<td>swath</td>
<td>DM</td>
<td>swath</td>
</tr>
<tr>
<td>Flat</td>
<td>cont</td>
<td>swath</td>
<td>flat</td>
<td>swath</td>
</tr>
</tbody>
</table>

Figure 1: Plan of Miscanthus stand

**Results and Discussion**

This experiment was 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. Figures 2 and 3 illustrate the difference in moisture contents recorded in the two years of the trial. A significant difference in MC was observed between treatments \( p < .05 \). Cutting the crop in March was found to result in a more rapid loss of moisture than cutting the crop in January. No significant difference was observed however between sub-treatments flat and swath while the control was found to behave significantly different to the flat and swath sub-treatments \( p < .001 \), showing harvest method and cutting time influence the rate of moisture loss of the crop.

In 2009, from initial MC of 53%, after 5 weeks of the January trial, both flat and swath sub-treatments had increased in moisture to 60% compared to the control which dropped in moisture to 49% by week 5. 2010 also saw an increase in MC in the Cut January treatment, though slight, however the MC of the control in 2010 reduced by 10% over the same period. Cut February treatment in 2009 saw a 10% reduction in MC from an initial MC of approximately 40% after 1 week of the treatment. Although an increase of 5% was observed between weeks two and three of the treatment, the MC subsequently dropped by almost 30% from the MC recorded at the start of the treatment, 23% lower than that of the control.

In 2010 the Cut February treatment also experienced an increase in MC after one week, however, dropped to a MC of 32% after 5 weeks on a par with that of the control.
Cut March treatment had an initial MC of 43% and 38% in 2009 and 2010 respectively, after one week, 2009 saw a reduction in MC of approximately 15% while week 2 saw the MC reduce by a further 20%. Cut March 2010 however, from an initial MC of 38% experienced an increase in MC of 6% after one week before concluding the trial at 32% MC, just 3% higher than the control.

In 2009 the initial MC of the control in January was 54% which experienced a 17% reduction by week 12 of the trial when a MC of 37% was recorded. Compared to this, the control in 2010 reduced in MC from an initial content of 64% to 29% by the conclusion of the trial. The results of the trial show that while the time of harvest can significantly affect the rate of moisture loss from the biomass material, no difference was observed between flat and swath subtreataments. However, a significant difference in MC and rate of moisture loss was observed between the aforementioned subtreataments and the control (uncut) material.

**Figure 2:** Moisture Content data for year 1

**Figure 3:** Moisture Content data for year 2
Conclusion

From the results presented in the figures, 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) can be seen to accelerate the rate of moisture assuming weather conditions are favourable. Therefore, it can be deduced from the 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 notable reduction in moisture can be achieved when compared to the standing crop assuming weather conditions are favourable.

Further Work

While the results of this trial show how the drying of the crop varies as a result of different cutting times and cutting methods, to what extent the various weather factors responsible for the drying and wetting of the crop are unknown. Therefore further analysis will be carried out to establish to what extent the various weather parameters are responsible for change in moisture content of the biomass material.

Acknowledgements

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

References

MEASURING THE INFILTRATION RATE OF SOIL: INFLUENCE OF METHOD

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Abstract
The recorded rate at which water infiltrates into soil is influenced by soil physical conditioning, current and previous management practices, and the method used to determine infiltration rate. The inherent variability of soil and the potential inaccuracy associated with the method and equipment employed can overestimate the infiltration rate of soil. Small-scale box trials were conducted to determine the influence of the particulars of the method used on the infiltration rate recorded for a medium clay-loam soil which has cropping history of maize-winter wheat-grass-grass-grass. No significant difference was observed for saturating the soil prior to infiltration rate determination, and there was no significant difference between the rates recorded using a single ring infiltrometer and a double ring infiltrometer, indicating that these methods are equally suitable when working at this scale.

Introduction
The rate at which water enters and moves through the soil profile is influenced by the physical conditioning of the soil (Hemmat et al., 2007). The type, texture, structure, and moisture content of the soil all influence the infiltration capacity of a soil at any time (Foth, 1990; Lowery et al., 1996). The incorporation of organic material into soil can increase water infiltration into soil by improving soil structure which facilitates air and water transmission (Brady and Weil, 2008). The organic fraction of the soil skeleton has a significant impact on the rate of water infiltration both through its influence on the soil physical environment and through its effect on soil moisture content (Foth, 1990): organic matter actively adsorbs water particles, holding them in the soil profile. The moisture content of a soil has a significant effect on the infiltration capacity of soil: the higher the soil moisture content, the lower the observed infiltration rate (Lowery et al., 1996).

Obtaining an accurate measurement of the rate at which water infiltrates into soil has proven difficult as the rate is variable both temporally and spatially as a result of being dependent on multiple variable attributes of soil (Chowdary et al., 2006). The specifics of the method used to record infiltration rate also has an effect on the observed rate. An ideal infiltrometer measures the mean infiltration rate taking into account the shortcomings of the infiltrometer itself, without affecting the actual infiltration rate (Shouse et al., 1994). It has been suggested that a single ring infiltrometer is the simplest technique to measure infiltration, however the influence of lateral flow into soil can not be controlled in a single ring infiltrometer, and can lead to overestimating infiltration capacity (Tricker, 1978). One of the most widely used equipment modifications to overcome this overestimation is the implementation of an outer buffer ring, which is used to reduce the influence of lateral flow by flooding the soil surrounding the inner cylinder and forcing the water in the inner cylinder to flow vertically through the soil (Gregory et al., 2005). The benefit of using a buffer ring was reported by Chowdary et al. (2006) and Marshall and Stirck (1950), however Bouwer (1986) found no benefit of using a buffer ring when ring diameter is small.

The objective of this work was to determine the influence of method used to measure infiltration rate when working at a scale which facilitates extensive replication.

Materials and Methods
The influence of method was evaluated on a medium clay-loam soil which had been in maize-winter wheat-grass-grass-grass rotation. This trial was conducted at Lyons Estate research...
farm using purpose-built boxes of size 0.6 m x 0.6 m x 0.4 m. The boxes were designed to minimize edge effects from the box walls during infiltration rate measurement. To simulate the retention of crop residues within the soil, chopped barley straw was incorporated into the uppermost 75 mm of the soil profile at a rate of 3 t ha\(^{-1}\). To isolate the influence of crop residues on the rate of infiltration and eliminate any potential interference from the conditions of the trial set-up, a control condition was also investigated through the use of boxes to which no straw was added.

Infiltration rate was measured once a week for a period of eight weeks using each of three methods with each method replicated in three boxes. The average of the three recorded infiltration rates was used to reduce the effect of soil heterogeneity on the observed infiltration rate (Chowdary et al., 2006).

Method 1 employed an infiltrometer and methodology outlined by the United States Department of Agriculture: this method uses a single ring infiltrometer with a diameter of 152 mm and records the time required for a volume of water equivalent to a 25.4 mm head to infiltrate into the soil (USDA, 1999). Although not included in the USDA methodology, the soil was saturated 48 hours prior to measuring infiltration rate as suggested by Lowery et al. (1996).

Method 2 was based on the falling head method described by Landon (1984) and Gregory et al. (2005) using a double ring infiltrometer of a similar scale to the infiltrometer used in Method 1. Method 2 involves filling a double ring infiltrometer (inner ring diameter: 100 mm; outer ring diameter: 200 mm) with irrigation water and the initial infiltration rate determined by recording the fall in the water level in the inner ring during the initial 15 minutes of the trial. Initial infiltration rate \(i_{15}\) was calculated as

\[
i_{15} = \frac{Q}{AT}
\]

where

- \(Q\) is the total volume of water infiltrated (m\(^3\))
- \(A\) is the area of soil exposed to water in the inner ring (m\(^2\)), and
- \(T\) is the duration of the trial (hr) (Brady and Weil, 2008).

Method 3 employed the same double ring infiltrometer as Method 2 and again was based on the falling head method described by Landon (1984) and Gregory et al. (2005). In this case, however, the rate at which water level fell was monitored such that a cumulative infiltration rate was determined after 120 minutes. Cumulative infiltration rate \(i_{120}\) was calculated as

\[
i_{120} = \frac{Q}{AT}
\]

where

- \(Q\) is the total volume of water infiltrated (m\(^3\))
- \(A\) is the area of soil exposed to water in the inner ring (m\(^2\)), and
- \(T\) is the duration of the trial (hr) (Brady and Weil, 2008).

Methods 2 and 3 were investigated both on boxes which had and had not been saturated prior to infiltration rate determination to investigate the effect of pre-saturation and drying on the recorded infiltration rate. The boxes which were not pre-saturated received irrigation in the form of natural precipitation only. The boxes which were pre-saturated were sheltered such that the pre-saturation water was the only form of irrigation received. Thus there were a total of five method variations investigated: single ring infiltrometer (with pre-saturation); initial infiltration rate (with pre-saturation); initial infiltration rate (without pre-saturation); cumulative infiltration rate (with pre-saturation); and cumulative infiltration rate (without pre-saturation).

Differences in the infiltration rates recorded under each condition were analysed for significance using SPSS 18.0 statistical package (SPSS Inc., 2009). Differences were separated using post-hoc tests with a Bonferroni correction and a significance level of \(p < 0.05\) used to determine significance.
Results and Discussion

Figure 1 shows the average infiltration rate recorded weekly using each method. The infiltration rates recorded under each condition were analysed to determine whether a significant difference existed in the infiltration rates recorded using each method. The significance of the differences observed is shown in Table 1. It was observed that a significant correlation exists between the practice of pre-saturating soil prior to infiltration rate determination and the recorded infiltration rates, and between the moisture content of the soil at the time of measuring infiltration rate and the infiltration rates recorded. Despite these correlations the infiltration rates recorded for soils which had been pre-saturated were not significantly different from those recorded for soils which were exposed to precipitation only (Table 1).

There was no significant difference observed between the infiltration rates recorded using each of the method variations (Table 1). Although the infiltration rates recorded using the single ring infiltrometer were generally higher than those recorded using the double ring infiltrometer (Figure 1) this difference was not significant. This result is in keeping with that of Bouwer (1986) who reported no benefit of using a buffer ring when working at a small scale, and Burgy and Luthin (1956) who reported no significant difference between the infiltration rates recorded using a single ring infiltrometer and a double ring infiltrometer under their moisture conditions.

![Figure 1: Average infiltration rate recorded weekly for eight weeks (June to August 2010) under each of the five assessment conditions](image)

Table 1: Significance of method used on recorded infiltration rate of a medium clay-loam soil

<table>
<thead>
<tr>
<th>Condition investigated</th>
<th>Statistical output</th>
</tr>
</thead>
<tbody>
<tr>
<td>Correlation between pre-saturation of soil and recorded infiltration rate</td>
<td>( r_s = -0.265^{**} )</td>
</tr>
<tr>
<td>Effect of pre-saturation of soil on recorded infiltration rate</td>
<td>( F(1,19) = 2.886, \text{ ns} )</td>
</tr>
<tr>
<td>Correlation between soil moisture content and recorded infiltration rate</td>
<td>( r_s = -0.212^{**} )</td>
</tr>
<tr>
<td>Effect of instrument used on recorded infiltration rate</td>
<td>( F(2,30) = 0.721, \text{ ns} )</td>
</tr>
</tbody>
</table>

\( ^* \text{ns} = \text{non significant}, ^* = \text{significant at } p < 0.05, ^{**} = \text{significant at } p < 0.01 \)
Conclusions

There was no significant effect of pre-saturation of soil prior to measuring infiltration rate. This result suggests that under Irish conditions of rainfall the infiltration rate of a soil can be determined without the need to pre-saturate the soil. This result has the potential to minimise delays and bias introduced by changing weather conditions which may be important where multiple replications are required.

The infiltration rates recorded using a single ring infiltrometer did not vary significantly from those recorded using a double ring infiltrometer; this suggests that either method is suitable when working at this scale. From a land owner’s perspective the ease of handling of a single ring may be the deciding factor in choosing this method without having to sacrifice the accuracy associated with using a double ring infiltrometer. The water savings associated with using a single ring infiltrometer over a double ring infiltrometer in addition to not having to pre-saturate the soil may make the single ring method more favourable both from an environmental and a labour point of view.

Acknowledgements

This research was supported financially by the Department of Agriculture, Fisheries and Food under the FIRM research programme.

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Offshore Wind Energy – A Cost Benefit Analysis for Ireland’s Atlantic Coast

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Abstract

A diverse range of renewable energy sources (RES) are required to meet EU RES directive targets by 2020. Meeting such targets will help insulate economies against imminent peaks in oil prices. The full potential of offshore wind energy in meeting Ireland’s RES obligations has yet to be realised. This study investigates a preliminary environmental and economic analysis of costs and considerations of offshore wind energy on Ireland’s Atlantic coast. This involves scenario modelling using HOMER and RETscreen models. Economically competitive potential is calculated based on the forecasted costs of developing and running offshore wind farms, relative to projected average energy generation costs derived from the European Commission's baseline scenarios.

Introduction

Despite this increasing use of renewable sources of energy, Ireland (like many modern economies) is facing a wide range of challenges in energy policy due to a number of factors, including: rising prices of primary inputs (especially fossil fuels), energy supply security, GHG emissions, non-GHG emissions, rising demand, and the requirement to invest/replace grid and infrastructure (Indecon, 2008). Considering these challenges, renewables policy is an important issue for Ireland. Within the portfolio of possible renewables, offshore wind power presents a possible means for Ireland to increase the amount of electricity that is produced by emission-free power generation capacity (Indecon, 2008).

Several factors must be taken into account when evaluating energy sources, such as remaining reserves, stability of prices, geographical distribution, production shares, commercial status, reliability and environmental effects (Rourke et al., 2009). Renewable energy technologies are a priority and are rapidly being implemented throughout the world. The development of renewable energy technologies in Ireland is influenced by Irish government energy policy. Since renewable energy sources are indigenous and non-polluting, they can deal with concerns on security of supply and environmental issues (Rourke et al., 2009).

There are several reasons why authorities should consider offshore wind power:

- Offshore wind power can be less expensive than its competitors, either at a local or national scale,
- It can have the potential to be less expensive than its competitors, or
- It can have less severe social and environmental impacts than its competitors (Snyder & Kaiser, 2009).

The use of oil and gas fired power has been the dominant source of electricity in Ireland, however, it is both inexpensive and a major source of greenhouse gas emissions.

The objective of this study is to conduct a preliminary examination of the economic feasibility for a large offshore wind power facility in the Atlantic Ocean by means of analytical modelling and assess outcomes with comparable onshore wind power and conventional power generation.

Materials and Methods

Energy production and social benefits
This analysis has two main components: (1) estimation of the energy production potential and financial feasibility of a large hypothetical offshore wind farm, and, (2) quantification of socioeconomic benefits.

To estimate the energy production and financial feasibility of the hypothetical offshore plant, this study will use RETScreen software and HOMER software. RETScreen was created in 1996 by Natural Resources Canada’s Canmet Energy Research Center to provide low-cost preliminary assessments of renewable energy projects. HOMER is a computer model that simplifies the task of evaluating design options for both off-grid and grid-connected power systems for remote, stand-alone and distributed generation (DG) applications. HOMER's optimization and sensitivity analysis algorithms permit evaluation of the economic and technical feasibility for a large number of technology options and account for variation in technology costs/energy resource availability. HOMER determines how to serve the load in each time step by evaluating the economic cost of a unit of energy from each power source, and using the lowest cost source to meet the load. A dispatch strategy input variable determines whether HOMER assigns higher priority to meeting the load (Gilman, 2007; Harder, 2011).

The above models will also be used in conjunction with Microsoft Excel to evaluate the economics of offshore wind, and provide quantitative estimates of:

- Displaced thermal generation
- Additional capital costs
- Additional operation and maintenance costs
- Additional grid and system costs (provide backup to wind which is variable)
- Expenditure on construction
- Possible additional costs either direct (e.g. feed in tariffs) or indirect (e.g. grid connections)

Site selection, Wind energy penetration/Integration and Seascape analysis

Optimal siting of wind-power stations requires proper information on wind speed & profile of the under examination area (Xydis, et al., 2009). Sites along the Atlantic coast of Ireland are to be investigated for suitability. Figure 1 shows the initial potential of wind energy generation in the Atlantic.

![Wind speed map of Ireland at 50 metres (Matthies and Garrad, 1993)](image)

**Figure 1:** Wind speed map of Ireland at 50 metres (Matthies and Garrad, 1993)
Considering large-scale integration of wind energy in the context that wind will meet a substantial share of the European electricity demand in the future, the key issue is how to develop the future power system so that wind power can be integrated efficiently and economically. Since integration efforts such as costs and decision making are related directly to the penetration level of wind power, it is essential to have a commonly defined term. Wind energy penetration can be defined in a number of ways (EWEA, 2010):

Wind energy penetration (WEP)

\[
\text{WEP (per cent)} = \frac{\text{Total amount of wind energy produced (annually) (TWh)}}{\text{Gross annual electricity demand (TWh)}}
\]

Wind power capacity penetration (WPCP)

\[
\text{WPCP (per cent)} = \frac{\text{Installed wind power capacity (MW)}}{\text{Peak Load (MW)}}
\]

Maximum share of wind power (MSWP)

\[
\text{MSWP} = \frac{\text{Maximum wind power generated (MW)}}{\text{Minimum load (MW) + Power exchange capacity (MW)}}
\]

A seascape characterisation and baseline visual analysis should be undertaken to define the area of seascape units, their characteristics, activities, visibility and views. Regional seascape units are the most appropriate scale for Seascape and Visual Impact Assessment (SVIA) of offshore wind energy developments (DTI, 2005).

**Results and Discussion**

Economic exclusive zones have been used to determine the national jurisdictions of different countries over offshore areas. Unsurprisingly, the United Kingdom (114,000 km$^2$) and Norway (88,000 km$^2$) comprise the largest share of available offshore area for wind energy generation in Europe. In Ireland 24,000 km$^2$ is available and is predominantly in the west, with a technical potential for offshore wind energy of over 1,000 TWh. In order to clarify the relationship between wind energy potential and distance to the shore, offshore areas are split into categories according to the distance to the coast: 0–10 km; 10–30 km; 30–50 km; and > 50 km (EEA, 2009).

The existing wind data is not currently split between on-shore and off-shore wind energy. This is because there is currently only one off-shore wind farm in Ireland. This is the Arklow Bank with a capacity of 25.2 MW. A renewable energy feed-in tariff (REFIT) of 14 cents per kWh is available from the Irish government since February 2008. Within the first 8 years of the Gate 3 ITC programme (2010 - 2017) 601.5 MW of offshore wind is due to be connected to the grid. The new connections are on the east coast of Ireland at Carrickmines (364 MW) and Oriel (237.5 MW) (SEAI, 2010). The Atlantic coast has only one project in consideration for wind powered electricity generation in the foreseeable future (The Sceirde wind farm).

**Current analysis of offshore wind power generation in Europe.**

So far in Europe 1,136 turbines between onshore and offshore have been installed and connected to the grid, totalling 2,946 MW in 45 wind farms in nine European countries. The offshore wind capacity installed by the end of 2010 will produce 11.5 TWh of electricity. The average wind turbine size is now 3.2 MW. 65% of substructures are monopiles, 25% are gravity and 8% are jacket based turbines (EWEA, 2010). The average offshore wind farm size in 2010 was 155.3 MW, up from 72.1 MW the previous year. Average water depth in 2010 was 17.4m, a 5.2m increase on 2009, with projects under construction in water depth averaging 25.5m. Average distance to shore increased in 2010 by 12.7 km to 27.1 km, substantially less, however, than the 35.7 km average for projects currently under construction. 2010 saw two major deals come to financial close: Thornton Bank C-Power
(325 MW) and Trianel Wind Farm Borkum West II (200 MW). Both projects use turbines of 5 MW or more, signalling that financing institutions are willing to invest in the large turbines likely to dominate the sector in the coming years (EWEA, 2010). Siting, layout and design offer scope for integrating offshore wind farms into the seascape and to prevent, reduce and mitigate seascape and visual effects. Seascape needs to be considered at the outset of the layout and design process to have the desired effect (DTI, 2005).

Conclusion

Offshore wind energy has experienced fast growth over the past decade. Economic costs of offshore wind power are site specific. These costs can be mitigated with current technology and detailed site selection. In some cases, offshore wind power may be able to cheaply produce electricity with negligible environmental impacts, however, in many more cases; offshore wind power will be more expensive than its competitors, even when the costs of carbon offsets are included. This study lays the foundations for a detailed analytical analysis using HOMER and RETScreen of a large scale wind farm off the west coast of Ireland by determining model simulation design programmes, site selection process and a detailed review of offshore power generation across Europe.

References
WIND ENERGY FEASIBILITY STUDY – SMALL SCALE WIND FARMS

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Abstract
Wind energy is a clean renewable energy source. It is an inexhaustible resource that can be used as a replacement for finite fossil fuels. As the price of fossil fuel continues to rise, wind energy can be seen as a cheaper and sustainable alternative. The use of wind energy to generate electricity will also help Ireland to meet its requirements set out under renewable energy sources (RES) EU directives, to reduce carbon emissions. Failure to meet the agreed targets will result in fines. This makes investment in wind energy more attractive. At the moment Ireland imports the majority of fossil fuel used to generate electricity. This combined with our geographic location at the edge of Europe leave Ireland badly exposed to any future fuel shortages. Wind energy can offer fuel security. Ireland has the second largest wind energy resources in Europe (WCD 2010). For these reason Ireland should implement the use of wind energy to generate electricity.

Introduction
The use of commercial wind farms to generate electricity is a relatively recent development in Ireland. The first commercial wind farm in Ireland was constructed in 1993 in Bellacoric, Co. Mayo. It had installed capacity of 6.45MW (SEAI, 2005). Since then the generation of electricity has grown steadily and the total on shore installed capacity in the Republic of Ireland is 1746.1MW, correct on 03/03/2011. The off-shore installed capacity is 25.2MW, which is generated in one off shore wind farm, Arklow Bank, off the coast of Co. Wicklow. In total there are 146 wind farms in operation in 25 counties in Ireland, including off-shore (IWEA 2010). If a load factor of 31% is assumed this means that a turbine will generate 31% of its maximum capacity, i.e. wind energy currently generates 4,743,339MWh a year. In 2008 the average household in Ireland consumed 5.557MWh of electricity, if we assume growth of 3%, in 2010 this will have risen to 5.895MWh per year (SEAI 2009). This means at current levels wind energy is generating enough electricity to for over 753,000 homes in Ireland.

Wind energy is a renewable carbon neutral fuel with the potential to provide Ireland with fuel security. This coupled with the constantly rising oil prices make wind energy a very attractive alternative to fossil fuels. It is for this reason that this report will examine the potential use of wind energy to meet Irelands’ energy needs.

The main objective of this report is to determine the potential of small scale wind farms meeting Irish energy needs, and their optimum location and size.

Methods & Materials
This paper will examine the feasibility of using wind energy to supply electricity to the Irish market, in particular the use of small scale wind farm developments. To determine the locations, sizes and possible amount of wind energy which can be produced several factors have to be considered. Site location is the first step in developing a wind farm. The locations will be determined by reviewing wind atlas maps for Ireland. These highlight the areas with suitable wind speeds for development. Planning permission also needs to be reviewed, not all areas of the country are zoned for wind farm construction. With the potential sites selected scenario modelling using HOMER and RET screen
models will help to determine viability of possible wind farm construction along with optimal size of development.

Small scale wind farms are being looked at as it is expected that smaller scale developments will encounter less public resistance during the planning process, this will also be investigated. This is done by taking an in-depths look at other European countries and their use of wind energy, including how wind farm sizes and locations are determined. Three countries have been selected for review under the same criteria; current use of wind energy, government support for wind energy and a case study of existing wind farms detailing the reasons for their location and size. Ireland is also compared under the same headings to gain perspective on our current use of wind energy.

The issue of energy storage is very relevant when dealing with wind energy, as energy is only generated when the wind is blowing, for this reason energy storage is examined and reviewed as a possible barrier to the increased use of wind energy. Current storage methods such as, pumped hydro storage, compressed air storage and flywheel energy storage are reviewed along with emerging technologies. Other barriers which affect the use and development of wind farms are also examined, such as grid connections, planning process and power purchase agreements.

A financial review, using Microsoft Excel, is also carried out to determine the commercial viability of small scale wind farms, with a view to determining not only the most commercial viable size of development but also the best route to market; commercial developer, state/semi-state organisation, community based developments etc. This will be done by assessing the total investments required and possible returns for investors. All this will aim to provide a clearer picture of the possible contribution small scale wind farms could make to Irish energy supply.

**Results & Discussion**

The results are expected to show that small scale wind farms are an economically viable way of increasing the use of wind energy in Ireland. This will be done through the financial review, which details constructions costs, set up costs, maintenance costs, required investment, loan repayments and potential returns on investment. It is expected that the results will indicate the further potential of wind energy in Ireland, from small scale developments.

The results will also point to the optimal locations for these developments, this depends largely on planning constraints and wind speeds in the areas being considered. The ideal size of these developments will be determined by potential to generate electricity, wind speeds, planning constraints and the financial review. Both of these parameters will be aided with scenario modelling using HOMER and RET screen models.

The results will also compare and contrast the current use of wind energy in Ireland with other European countries. This will help to identify how other countries have grown their use of wind energy and highlight successful strategies which can be adopted in Ireland. A review will have been carried out on lessons that can be learned from other experiences.

The potential storage solutions will be explored and reported with recommendations being made for the most effective results. Current energy storage systems in use in Ireland and abroad will be reviewed. A look at emerging energy storage solutions will also help to identify possible future solutions to the energy storage solutions.

**Conclusions**

As is already known, Ireland needs to expand its renewable energy sources. This must be done while meeting an ever growing energy demand and reducing greenhouse gas emissions. At present the most
likely way to achieve this is through wind energy. It is expected that is report will conclude that small scale wind farms have the potential to greatly increase the amount of energy generated by renewable means in Ireland. Small scale wind farms have been selected as planning permission and local objections can often be a problem for the development of wind farms.

This report is expected to show that small scale developments are financially viable and offer attractive returns on investment. The optimal size of a wind farm in given locations, number of turbines, height of turbines etc will also be decided.

Recommendations on further work that needs to be done to increase the use of wind energy will be outlined along with the barriers that prevent more widespread use of wind energy in Ireland.

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Pre and Post analysis of feedstocks for optimum pellet production using decision support tools

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Abstract

The successes of making pellets are governed mainly by the parameters of moisture content, and feedstock quality. Various physical aspects were consulted on adjustments for raw materials. Adjusting raw materials composition ratios, with or without binders could be problematic. Pellet manufacture is somewhat of a black art by only those experts working in the field. Hence, a decision support tool is being developed to assist with the "know-how" of quality pellet making - a pellet recipe tool. A program was developed and used to create an interactive graphical user interface in Matlab environment. The program can diagnose the potential quality of the pellets in response to parameters chosen by the operator. Parameters such as the raw materials, their corresponding chemical composition and what mixing parameters may be needed to help inform the user how to make pellets from a range of different materials such as wood, wheat and barley straws, paper etc.

Introduction

Pellet design is the process of choosing suitable raw ingredients for biomass pellets and determining their relative quantities with the objective of producing the most economical pellets while retaining the specified minimum properties according to CEN 14961 Standards such as ash content, durability, and calorific values.

The inaccuracy of pellet design becomes more pronounced with moisture content. The main problem is the availability of water from the raw materials in pre-pelletizing and storage. During pelletizing, the heat from the pelletizer will remove some moisture of the materials. If lignin is present, it will act as a binder property and fuse the pellet and retain its shape.

To enhance the search for limitation of moisture composition, a means of background knowledge to pellets is imperative. Guidance on adjustment the suitable raw materials can be found in literatures, but from very wide sparse sources. The operator may not have the time to referring to literatures before decision making. A compilation of this formulating information would be a useful reference document for process guidance. In doing so, diagnosing and adjusting moisture content for pellets is justifiable. This would be useful to personnel both experienced or novice in the area.

The economics trend will also be looked at along with pellet production. Materials taken from within the locality will have predisposed effects to the prices of production i.e. within the country vs. overseas. Pricing of the raw materials is subjected to the demands of the current market as is seen with crude oil prices.

The objective of this study was to determine the optimum method of pellet production (other than wood) by developing a Decision Support System Tool (DSS) that informs the user in a step by step guide how to make pellets for a range of different feedstocks - The Pellet Recipe Guide.

Materials and Methods

Raw Materials of interest
Paper, wheat straws, miscanthus, willow, rapeseed straws, sawdust and brown bin waste are the raw materials to be used.
Paper with wheat straw can achieve greater density as to wholly homogenous and able to stabilize at such density without binder. Materials such as corrugated/non corrugated cardboard, newsprint and pamphlets, mix paper and grey board can be compacted at a high pressure without binders.

Currently in Ireland approximately 409,000 tonnes of paper and board is produced annually, and 176,000 tonnes are recovered through Repak according to Repak 2004 statics. The waste paper with lowest recoverable value is MRF (material recovery facility) paper grade. This grade of paper occasionally contaminated with many contaminants from the collection facility or during collection process. Utilisation of this paper grade is welcome within the industry since they are deemed to be disposed off at landfills. Table 1 shows higher heating value (HHV), volatile matter and Ash content.

**Figure 1:** Combustion characteristics of different waste paper grades (Li.Y & Liu.H 1999)

<table>
<thead>
<tr>
<th>Material</th>
<th>HHV (MJ/kg)</th>
<th>Volatile matter (%)</th>
<th>Fixed carbon (%)</th>
<th>Ash content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Office paper</td>
<td>14.4</td>
<td>79.9</td>
<td>11.3</td>
<td>8.8</td>
</tr>
<tr>
<td>Newsprint</td>
<td>17.6</td>
<td>80.4</td>
<td>14.2</td>
<td>7.4</td>
</tr>
<tr>
<td>Corrugated board</td>
<td>16.4</td>
<td>79.8</td>
<td>15.4</td>
<td>4.8</td>
</tr>
<tr>
<td>Commercial printing</td>
<td>11.9</td>
<td>70.2</td>
<td>7.0</td>
<td>22.8</td>
</tr>
<tr>
<td>Box board</td>
<td>16.9</td>
<td>79.0</td>
<td>14.7</td>
<td>6.3</td>
</tr>
<tr>
<td>Average for the paper mix</td>
<td>15.4</td>
<td>77.9</td>
<td>12.5</td>
<td>9.6</td>
</tr>
</tbody>
</table>

HHV = higher heating value.

Waste paper with wheat straws shows great proposal for energy conversion approach, since abundant resources are made available in many countries. They are residues where many would only consider openly burn or land filled. These residues could be of use if they were managed in a better way.

**Moisture Content**

The moisture in biomass acts as a facilitator and binding agent (Kaliyan & Morey, 2006). The MC varies for different raw materials. Being able to experiment and document various MC for each material into the DSS is needed here. In 2000 Li and Liu did tests on wood logs and concluded that initial moisture content can be 6-12% (wb), as the optimum was found to be 8% (wb). A similar result suggested by Grover and Mishra in 1996 where high quality pellets are made at 8-10% moisture content. In 2004 Obernberger and Thek claims high quality pellets can be made only moisture content range between 8-12% (wb). If the moisture range falls outside this threshold lower quality pellets are made. Kaliyan & Morey (2006) reviewed differences of briquette density for corn stover with 10 and 15% moisture under 100Mpa and show no significant differences, however under 150Mpa it showed density has decreased. Such increase has done same to switchgrass at 15% moisture and a significant decrease in density, 30-40% as stated. This dominantly justifies the fact as moisture increases density decreases. A review was done by Mani in 2002 and 2006, tests were run on pellets from wheat straw, barley straw, corn stover and switchgrass which also shown a similar affect.

**Method**

In determining whether feedstocks of interest can or cannot be made into a pellet, a number of set testing parameters are developed to justify CEN 14961 parameters such as: Ash Content, Calorific value, Durability, Moisture content, Ultimate and TGA analysis.

In the course of this research two suggestions were examined. In the first approach only pellet size of 6mm is looked at. The feedstocks are miscanthus, willow, rapeseed straws and wheat.
straws. Finding the threshold for moisture both maximum and minimum limits allowance for making into pellet. The actual calorific value of each raw material and energy input/output ratio will be looked at by analysing the throughput of the pellet press and operating temperature. The data is been recorded and compiled in a form of database where a decisions support model analysis the results.

The second approach would be looking into making 6, 8 and 10 mm pellets. The feedstocks are paper, miscanthus, willow, rapeseed straws, wheat straws and brown bin waste. They are comparable to sawdust which is served as the basic references. The calorific value, energy I/Output, temperature and throughput of the pellets press and how well it stands in combustion situation will also be looked, similar to approach one.

The results from the above tests are recorded in a form of excel spread sheet. The thresholds of each parameter i.e. maximum and minimum points are pre set into the diagnostic program in a form of a plotted graph. The user can import new data in excel form to the program. An updated graph is generated with new data and the threshold in real time recommendations, explanatory comments and conclusion decision in accordance to the graph.

Conclusion

A diagnosis program is created in MatLab. This will give a clear indication of materials that are suited to make into pellets. The objective of the program is to allow the operator to make decisions in accordance to the input parameters followed by a given pre set explanations and recommendations so that optimum conditions can be followed to produce pellets to CEN specifications in a hassle free approach to mono and co-pellet production.

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THE PREDICTION OF BIOMASS PELLET QUALITY INDICES USING HYPERSPECTRAL IMAGING

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Abstract
The development of rapid, non-destructive biomass pellet characterisation techniques will facilitate the production of optimised feedstocks for use in biomass to energy systems. Biomass pellet quality indices were predicted using hyperspectral imaging. The results obtained demonstrated that ash content, carbon content and calorific value could be predicted with R² values of 0.86, 0.95 and 0.90 respectively. The range error ratio’s (8.4-12.4) for the developed models indicated they had good to excellent practical utility values. The development of prediction models for the rapid determination of quality indices will facilitate the optimal use of feedstocks in the biomass to energy chain.

Introduction
The Kyoto Protocol has placed strict limits on the amount of greenhouse gases (GHG’s) that can be emitted by nations, (UNFCCC, 2010). The majority of GHG released is due to the combustion of fossil fuels (Sami, Annamalai, & Wooldridge, 2001). Co-firing energy crops, such as Miscanthus and Short Rotation Coppice Willow (SRCW) with fossil fuels in power stations has the potential to reduce GHG emissions such as CO₂ (Broek, et al., 1997; Styles & Jones, 2008). Both of these energy crops are ideally suited to Ireland’s climate with yields of 12 t ha⁻¹ yr⁻¹ and 13 t ha⁻¹ yr⁻¹ for Miscanthus and SRCW respectively (Caslin, Finnan, & McCracken, 2010a, 2010b). Hyperspectral Imaging (HSI) is an emerging platform technology that integrates conventional imaging and spectroscopy to attain both spatial and spectral information from an object. It can be used to determine both qualitative and quantitative properties of a substance. It has been employed in both the food (ElMasry, Iqbal, Sun, Allen, & Ward, 2011) and pharmaceutical industries (Maurer & Leuenberger, 2009). There is increased interest in the use of non-destructive sensing technologies, such as HSI, for the prediction of quality indices in the bioenergy sector (Allison, et al., 2009; Fagan, Everard, & McDonnell, 2011; Huang, Han, Yang, & Liu, 2009). This would enable the rapid and non-destructive prediction of a number of critical biomass parameters, facilitating optimisation of biomass conversion.

The objective of this study was to determine the potential of HSI to predict quality indices of biomass pellets.

Materials and Methods

Biomass pellet production
Pellets were produced from biomass (wood, Miscanthus, SRCW, rape straw) obtained from the Teagasc Crops Research Centre (Oakpark, Co. Carlow). The pellets were produced using a Farm Feed Systems biomass pellet mill, (Cinderford, England). The raw materials were firstly chopped using a Teagle Tomahawk straw chopper, (Teagle Machinery Ltd., Truro, England) with a 24 mm sieve. The biomass was blended to produce seven varieties of pellet (Table 1). The pelleting process involved movement through a 5 kW hammer mill with a 4 mm screen. The material was then forced through a 6 mm die to form the cylindrical pellets. A portion of the pellet samples were ground to a particle size of 1 mm for use in the laboratory analysis. The samples were stored in sealed containers prior to analysis.

Determination of quality indices
Ash content (AC), carbon content (CC) and calorific value (CV) of the ground pellets were determined in duplicate according to International standards (British Standards, 2009a, 2009b, 2010). AC was determined by completely combusting the samples at 550°C in a furnace (Carbolite, Hope, England). CC was determined in duplicate using a carbon analyser (Skalar, Breda, Holland). CV was determined using a bomb calorimeter (Parr Instrument, Moline, IL, USA).

<table>
<thead>
<tr>
<th>Biomass</th>
<th>W100</th>
<th>W80M20</th>
<th>W60M40</th>
<th>R100</th>
<th>R100</th>
<th>S100</th>
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<th>S25M75</th>
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</table>

¹Short Rotation Coppice Willow

**Hyperspectral Imaging**

The hyperspectral image of the pellet samples were obtained using a hyperspectral imaging system (DV Optics, Italy) consisting of a high performance CCD camera (580 x 580 pixels), a spectrograph (Specim V10E) attached to the camera covering the spectral range between 880 and 1720 nm, a zoom lens, a light source transmitted through fibre optics, a moving table and a computer system equipped with DV Optics Spectral Scanner software (V1.4.5). Samples were presented in a tray approximately 55 mm in diameter.

**Data Processing and Analysis**

The mean spectra of the samples were obtained using the interactive region of interest tool in Spectral Scanner and the resulting spectra were transferred into The Unscrambler software (V8, Camo Software AS, Norway). In order to eliminate wavelengths that had a low signal to noise ratio the spectra were cropped from 950 to 1650 nm. The spectra were smoothed using a moving average smoothing function with a 5 points segment size. The smoothed spectra were subjected to a number of pre-treatment’s including multiplicative scatter correction (MSC), first and second derivative steps. Partial Least Squares Regression (PLSR) was applied to each spectral database using the Unscrambler software to develop prediction models for the determination of AC, CC and CV. Full cross validation was employed and the root mean square error of cross validation (RMSECV) was obtained. The ‘best’ model was that which had the lowest RMSECV, and number of latent variables (LV), and the highest $R^2$ and range error ratio (RER). The RER for each model was calculated by dividing the range in the reference data by the RMSECV. A model with an RER value of less than 3 is considered very poor and should not be considered for any application, models with an RER of between 3 and 10 indicates limited to good practical utility and could be used in a screening application and values above 10 show that the model has an excellent utility value and could be used in any application (Fagan, et al., 2011).

**Results & Discussion**

**Prediction of Ash Content**

AC was successfully predicted from the first derivative MSC spectra with an $R^2$ of 0.86 and an RMSECV of 0.82% (Figure 1a). The RER value determined for this model (8.4) also suggests that the model has a good practical utility and could be used in a screening application. The AC prediction model employed 2 LV which account for 97% and 2% of the spectral variance and 95% and 2% of the variance in the reference data respectively. Figure 1b indicated that the spectral regions of interest include 1135 nm which has been assigned to the second overtone of C-H bond stretching and 1420 nm which is assigned to O-H bond stretching. While simple inorganic compounds do not absorb in the NIR region, inorganic complexes can. Previously developed models (Fagan, et al., 2011) for the prediction of SRCW and Miscanthus were weaker (RER = 7.7, $R^2 = 0.58$) than those in the current study.
This is most likely due to the narrow wavelength selection studied (750 - 1100 nm). Figure 1b suggests that the spectral region located at 1420 nm is of importance in the prediction of ash content, which was not incorporated in the study by Fagan et al. (2011).

**Prediction of Carbon Content**

The CC of the samples was best predicted using the smoothed data that had been treated with MSC and a first derivation step. This model (Figure 1c) gave an $R^2$ value of 0.98 and an RMSECV value of 1.3%. The RER value of this model (12.36) suggests it has excellent practical utility and could be used in any application. The model developed employed 2 latent variables which accounted for 97% and 2% of the variance in the spectral data and 94% and 6% variance in the reference data respectively. The spectral regions of interest are 1153 nm and 1380 nm (Figure 1d) which are related to the stretching and bending of the CH$_3$ bonds (2$^{nd}$ overtone) and the stretching and deformation of the C-H combination bonds of CH$_2$ respectively. These results are in line with results that were reported by Fagan et al. (2011) who reported a $R^2$ value of 0.88 and a RER value of 10.4.

**Prediction of Calorific Value**

The CV of the samples was also accurately predicted with an $R^2$ value of 0.90 (Figure 1e) and an RMSECV of 0.27%. The RER of this model, similar to the carbon model, suggested it has excellent practical utility in a wide range of applications, from screening to quality control. The model uses 3 LV which account for 97%, 2% and 1% of the spectral variance and 90%, 6% and 2% of the reference data respectively. The spectral regions of interest in Figure 1f are 1140 nm which is related to the stretching and deformation of the CH$_2$ bonds present in the sample and at 1390 nm which is responsible for the stretching and deformation of both the 1$^{st}$ overtone of C-H combination bonds and of the O-H bonds of H$_2$O respectively. Calorific value is negatively correlated to the presence of O-H bonds. The results from the
calorific value model agree with results obtained by Fagan et al., (2011) and also Lestander and Rhen, (2005) for ground spruce, SRCW, and Miscanthus samples. Further validation of all the models developed is needed before they can be successfully applied to a practical application.

Conclusions
The models developed using hyperspectral imaging for the prediction of AC, CC and CV presented satisfactory accuracy with R² values ranging from 0.86 to 0.95. The high RER values for both CV and CC (10.02 and 12.36 respectively) indicate they could be employed for qualitative analysis of biomass in a practical situation. However the models were developed using a relatively small sample set therefore further samples need to be evaluated before the models can be accepted as an accurate method for determination of quality indices of biomass pellets. The deployment of such models would facilitate the optimised handling of biomass feedstocks.

Acknowledgements
This research has been undertaken with the financial support of Science Foundation Ireland under Grant Number 06/CP/E001 and IRCSET under the Empower fellowship scheme. The authors also acknowledge the assistance of John Finnan and John Carroll at Teagasc Crops Research Centre, Carlow and Will Hayes, Renewable and Electrical Energy Systems, Limerick IT.

References
ENVIRONMENTAL LIFE CYCLE COMPARISON: THE IMPLICATION OF COFIRING A BIOENERGY CROP WITH PEAT AT EDENDERRY POWER STATION

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Abstract
The Government plan to implement co-firing of biomass with fossil fuels in the three state-owned power generation plants in Ireland aims to decrease reliance on fossil fuels while reducing emissions of greenhouse gases. This paper outlines the details of a LCA study which examines the benefits obtainable from co-firing short rotation coppice willow with peat. The objective of this study is to compare the environmental effects of co-firing short rotation coppice willow with peat, versus purely peat-fired electricity generation at Edenderry power station.

Introduction
In Ireland, there is an increasing awareness of the need to reduce greenhouse gas (GHG) emissions and to develop alternative energy sources to reduce dependence on finite fossil fuel resources. Edenderry is a Bord na Mona owned, peat-fired electricity generation plant, which by the nature of its feedstock, is a major emitter of GHGs. Not only is peat a carbon intensive fuel, but peat extraction from Irish bogs is set to decline over the coming years as the bogs reach the end of their useful lives, meaning that an alternative source of fuel will be required for the peat-fired power plants. Furthermore, the Government has committed to a target of 30% co-firing with biomass at the three State owned peat power generation stations to be achieved progressively by 2015 (DCENR, 2007). Co-firing of short rotation coppice willow (SCRW) willow with peat at Edenderry offers a way to reduce the carbon intensity of the electricity produced while concurrently reducing the reliance on peat.

Life cycle assessment (LCA) is a tool which can be used to assess the performance of energy systems in terms of energy balance and environmental impacts. A wide range of LCA literature exists evaluating the benefits of biomass to energy systems in comparison to traditional fossil energy systems. The literature pertinent to this study focuses on the combustion of biomass alone or when co-fired with fossil fuels (coal and peat), to produce electricity. A number of LCA studies deal with combustion of biomass (SRCW, Miscanthus, hardwood coppice, poplar, Ethiopian mustard) alone (Lettens, Muys et al., 2003; Goglio and Owende, 2009; Butnar, Rodrigo et al., 2010). Several studies evaluated the co-firing of different sources of biomass (SRCW, Miscanthus, wheat straw and Brassica. carinata) with coal (Heller, Keoleian et al., 2004; Sebastián, Royo et al., 2010). Styles and Jones (2008) consider co-firing of SRCW and Miscanthus with coal and peat respectively.

The majority of studies limit the life cycle assessment to GHG and energy balance analysis as mitigation of climate change and reduction of fossil fuel consumption are thought to be the main driving factors for worldwide bioenergy development (Cherubini and Strømman, 2011). However, full LCA studies also take into account other environmental impacts, for example human and ecosystem toxicity, and acidification and eutrophication potential (Heller, Keoleian et al., 2004). Cherubini, Bird et al. (2009) have also recommended that the energy and GHG balances of biomass to energy systems should always be contrasted against fossil fuel systems. This allows comparison of the potential benefits/drawbacks of the bioenergy system in question.

The objective of this study is to determine the environmental benefits that could be achieved by co-firing SRCW at different ratios with peat when compared to peat-fired electricity production in Edenderry power plant.
Materials and Methods

The four stages in LCA methodology are followed in this study.

Goal and scope

The aim of this study is to compare the environmental effects of co-firing SRCW with peat, versus purely peat-fired electricity generation at Edenderry power station. The system under investigation involves the co-firing of SRCW with peat in an existing bubbling fluidised bed boiler at the Edenderry facility in County Offaly. The Edenderry facility is a 120 MW capacity power plant which generates electricity by the combustion of peat for export to the national grid. The functional unit used in this study is 1MWh of power produced at the power plant. The reference flow is the quantity of feedstock required to produce 1 MWh of power at the power plant.

Figure 1 outlines the system boundary of the model. The LCA will encompass all aspects of the power generation system; raw material acquisition (crop production, peat harvesting), feedstock transport and processing (drying etc.), combustion at the plant, and disposal of ash. Plant infrastructure is not taken into account as it is the same for both the co-firing and the peat-fired scenario. The LCA will not consider electricity transmission and use of power by end users and will not take land use change into account.

Life cycle inventory

The LCA will be conducted in GaBi 4 (PE International, Leinfelden-Echterdingen, Germany) using available secondary data from various sources. Data on SRCW production will be obtained from Teagasc (2010) and published literature. Edenderry power plant data will be acquired from Bord na Mona. The gathered data will be supplemented with data from the GaBi inventory database.

Life cycle impact assessment

GHG emissions will be the primary impact category assessed (this may also be termed global warming potential, GWP). However, other environmental impacts such as acidification and eutrophication potential will also be considered.

Interpretation

Comparison between the co-firing and peat-fired systems will be made by the emissions and environmental impact per functional unit. As there is only one functional output to the system, value choices are minimised. In this LCA, the most ‘environmentally friendly’ system will be the one with the lowest GHG emissions. No loads allocation is required in the feedstock option, all the yield will be considered as fuel so that all the inputs have to be taken into account. Power is the only valuable output from the system (for the current analysis ash is considered a waste product which goes to landfill) so allocation between products, in this
case, can be ignored. Future analysis will include scenarios in which the remediation of ash is included.

**Results and Discussion**

*Expected results*

It is expected that the results of this LCA study will support the findings from previous studies which examined similar systems. The analysis of the existing literature indicates that GHG emissions are generally reduced when comparing bioenergy systems to fossil energy reference systems. Cofiring of biomass can result in net global warming potential decreases of between 5.4% and 18.2% depending on biomass source and cofiring rate (5 and 10%) when compared to coal-fired scenarios (Mann and Spath, 2001; Heller, Keoleian et al., 2004). Similarly, net SO$_2$ emissions are reduced by 9.5% and a significant reduction in NOX emissions is expected (Heller, Keoleian et al., 2004). Emissions of non-methane hydrocarbons, particulates, and carbon monoxide are also reduced with cofiring (Mann and Spath, 2001). *Miscanthus* and willow fuel chains emitted 0.131 and 0.132 kg CO$_2$ eq/kWh electricity exported when co-fired at 30% and 10% respectively. When this is compared with 1.150 and 0.990 kg CO$_2$ eq/kWh electricity exported for peat and coal fuel chains, it results in a GHG reduction of approximately 89% and 87%, respectively (Styles and Jones, 2008).

Of the bioenergy studies which examine life cycle consequences on human and ecosystem toxicity as well as on other impact categories, generally all systems lead to increased impacts when compared to fossil reference systems. In the case of energy crop production, intensive agricultural practices added to use of fertilisers can cause environmental concerns in soils, water bodies and the atmosphere (Cherubini and Ulgiati, 2009). When compared to a natural gas reference system, the environmental categories of human toxicity, terrestrial ecotoxicity, acidification and eutrophication present greater impact in bioenergy systems when compared to fossil fuel systems (Gasol, Gabarrell et al., 2007).

*Sensitivity analysis*

LCA results are dependent on input data and value choices throughout the process chain studied, and as such results could vary depending on these parameters. It is therefore important to account for the assumptions and variables inherent in an LCA study. Sensitivity analyses allow the integration of these factors into the LCA results. Parameters which may have a significant effect on LCA results for bioenergy systems include; fertiliser application, crop yield, harvesting and drying techniques, biomass transport, and power plant efficiency. GHG emissions have been shown to be sensitive to changes in cultivation emissions (related to fertiliser use); emissions more than doubled in response to a change in cultivation emissions from 50% below to 50% above the standard value (i.e. a tripling in cultivation emissions) calculated in the LCA by Styles and Jones (2008). Similarly, lower yields resulted in lower area based GHG emission reductions (Styles and Jones 2008).

Transportation of the biomass also has a significant effect on results as reported by Goglio and Owende (2009). They found that willow chips transportation up to distances of 38 km did not have significant impact on the net energy production and CO$_2$ emission, however, chip transportation over distances in excess of 38 km generated significant drop in energy efficiency (25.9% reduction in energy output–input ratio). Conversely, other studies report that transport distances have a minor effect on overall GHG emissions (Styles and Jones, 2008; Sebastián, Royo et al., 2010). Further significant parameters which may influence LCA results include; the cofiring power station net efficiency, the degree of pretreatment required in order to obtain satisfactory biomass cofiring results, and the influence of biomass particles cofiring on the boiler efficiency. Plant infrastructure and ash disposal may be neglected as they have insignificant contributions to global warming potential (Sebastián, Royo et al., 2010).
Conclusion
This study will facilitate evaluation of the environmental benefits which can be obtained by co-firing SCRW in different ratios with peat at Edenderry power station. It will allow identification of ‘hot spots’ in the biomass to energy system which contribute most to GHG emissions from the system. It is envisaged that this comparative assessment will highlight the benefits of co-firing with biomass.

Acknowledgements
This publication has emanated from research conducted with the financial support of Science Foundation Ireland under Grant Number 06/CP/E001. (www.sfi.ie)

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FLUIDISED BED PYROLYSIS OF IRISH BIOMASSES FOR FUEL AND CHEMICAL PRODUCTION

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Abstract
Pyrolysis is a thermochemical conversion process capable of generating renewable chemicals and fuels from biomass. While commercial deployment of the technology has commenced, not all technical issues have been resolved and considerable scope remains optimising the process for various applications. This project aims to evaluate the yield structure (relative portions of bio-oil, char and gas) from pyrolysis of diverse Irish-grown biomasses such as willow chip, wheat straw, miscanthus, and sawdust. The pyrolysis products are chemically and physically characterised to discern their nature and to consider further possible applications.

Introduction
Pyrolysis can be defined as thermochemical decomposition of carbonaceous feedstocks under high temperature inert atmosphere (i.e. oxygen free) conditions, yielding solids, liquids and gases (Bridgwater, 2007). Under so called ‘Fast Pyrolysis’ conditions which employ high heating rates and low vapour residence times, liquid yields from biomass can be maximised at 60-70 wt%. While Fast Pyrolysis has existed since the 1980s, commercial pyrolysis applications have generally remained limited to several facilities producing liquid smoke for food flavouring applications. In recent years however there has been a renewed interest in the use of fast pyrolysis for the production of chemicals and transport fuels. The main barrier to the production of high quality fuels via pyrolysis of biomass are the undesirable physical and chemical properties of the pyrolysis liquids, termed ‘bio-oils’, which are more chemically more similar to the biomasses from which they are derived rather than crude oil-derived products. This has led to significant efforts to improve the quality of bio-oil, with approaches including the use of catalysts in the pyrolysis process, acid washing of biomass feedstocks prior to pyrolysis to remove undesired catalytic agents, hydrotreating bio-oil, hot gas filtering of pyrolysis vapours, the use of hydrogen in the pyrolysis process (hydropyrolysis), addition of additives, removal of problematic bio-oil components etc. While technical and economic challenges associated with pyrolysis have not been yet resolved, it is plausible that pyrolysis-associated processes may form a component of future fuel and chemical production infrastructure.

Although several types of reactors have been developed or adapted for fast pyrolysis of biomass, no one reactor has emerged as being vastly superior to the others. Bubbling fluidised bed reactors are commonly applied since their design is relatively simple and they achieve good heat transfer to biomass in the bubbling sand bed and low vapour residence times.

In Ireland there is significant interest in the cultivation of biomass crops like willow and Miscanthus for biofuel applications, while other biomass sources like agricultural straws and forestry harvesting residues are readily available (Hayes and Hayes, 2009). Irish government policy emphasises the development of a ‘Green Economy’ based on clean technologies (Forfas, 2009). Furthermore, it is bound by European Regulations to meet Renewable Energy targets, which require a 3% biofuel share of total transport fuel consumption by 2010, and 10% by 2020 (Dennehy et al., 2010). Consequently, it is important to investigate the
applicability and suitability of conversion technologies for Irish feedstocks and the value and possible applications of the products as transport fuel or chemical precursors.

The objective of this study is to determine the yield structure of fast pyrolysis products from selected Irish biomasses on a laboratory bubbling fluidised bed and to physically and chemically characterise the liquid and solid products.

Materials and Methods

Biomass Feedstock Pretreatment and Analysis

Miscanthus, willow, wheat straw, and wood shavings, were dried at 40°C for 12 hours, ground and sieved. The 300-500µm fraction is collected for fluidised bed pyrolysis experiments. Feedstock analysis includes moisture and ash analysis, ICP analysis, elemental analysis and analysis of relative lignocellulosic components.

Fast Pyrolysis on a Laboratory Bubbling Fluidised Bed Reactor

The Fast Pyrolysis reactor located at vTI, Hamburg was designed by the University of Waterloo, Canada, and has a design throughput of 300-400g/h. The cylindrical steel reactor has an internal diameter of 41mm. A thermocouple is located in the centre of the reactor and the reactor is surrounded by a heating mantle. Before the experiment, the reactor is loaded with 120g of sand (300-500µm) which rests on a perforated plenum. During the experiment, pre-heated Nitrogen enters the reactor from the bottom and fluidises the sand bed so that it behaves like a bubbling liquid. Hot pyrolysis vapours containing char exit the reactor and pass through a cyclone for separation of solids and vapours/gases. The condenser train consists of an ethanol-cooled condenser coil (0°C), and electrostatic precipitator (-6kV), and an intensive ethylene-glycol cooler (-10°C) in series. The experimental configuration allows for the collection of a char and bio-oil fraction. The biomass feeding system consists of a vertical plexiglass cylinder which tapers to a small circular opening at the bottom of the hopper. An agitator shaft with an auger at the opening rotates periodically dispensing a plug of biomass into a vibrating tube orientated in a horizontal position. Following equilibrium of the feed flow in the vibrator tube, a constant stream of biomass is injected by a high speed screw into the hot bubbling fluidised bed.

![Figure 1: Schematic of the Laboratory Fluidised Bed Reactor (Azeez et al., 2010)](image)

Experimental Procedure

Approximately 250g of biomass is loaded into the feed hopper. The whole system (feeder, reactor and condenser line) is air tight and is purged with nitrogen (to remove oxygen) for 5
minutes while the reactor is heated up. Once the reactor temperature reaches 470°C, the optimal temperature for maximum bio-oil yield, feeding begins. Feeding is maintained at a constant rate throughout the experiment (~250g/h). Following the experiment a partial mass balance is conducted to determine the bio-oil and char yield. Secondary char which accumulates in the condenser line is washed out with ethanol, dried, weighed.

**Analysis of Products**
Bio-oil analysis comprises elemental analysis, pH analysis, Karl-Fischer water content (according to ASTM D 1744), viscosity (DIN 51562), solids content (by filtration) and pyrolytic lignin quantification. Chemical analysis of bio-oil is performed on an Aligent HP 6890 GC (with a DB 1701 Column) fitted with both FID and HP5972 MS systems using fluoroanthene as an internal standard. Char is analysed elementally and calorifically (ASTM D 2015).

**Results and Discussion**
Preliminary experimental data for willow pyrolysis is presented here. Bio-oil yields of 60 wt% and char yields (including secondary char) of 16 wt% can be achieved. The Karl-Fischer water content of the bio-oil was determined to be 35 wt% of the bio-oil, according to. In terms of elemental composition, the carbon and hydrogen content of the oils is 35 wt% and 8% respectively. The kinematic viscosity of the oil was 128 cSt and 41 cSt at 20°C and 40°C respectively, according to. Since bio-oil can contain several hundred chemical compounds, complete characterisation of the bio-oil can be difficult. Here, the portion quantified by GC-MS represents 40.11 wt% (wet basis) of the whole bio-oil.

<table>
<thead>
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<th>Compound Group</th>
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<tr>
<td>Nonaromatic Ketones</td>
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<td>Acids</td>
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<tr>
<td>Furans</td>
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<tr>
<td>Syringols (Dimethoxy phenols)</td>
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<tr>
<td>Sugars</td>
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<tr>
<td>Guaiacols (Methoxy phenols)</td>
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</table>

The residual fraction consists of water and oligomeric fractions from decomposed carbohydrates and pyrolytic lignin that can not be quantified on the GC/MS (Azeez et al., 2010). Some of the main classes of chemical species in the oil are presented in Table 1. In terms of individual chemical compounds, acetic acid was present in the largest quantity, 8.131 wt% (wet basis), followed by hydroxy-acetaldehyde (6.092 wt% (wet basis)), and acetol (3.669 wt % (wet basis)). Slight differences in chemical composition of the bio-oils are expected to be observed for the different due to different chemical compositions.

**Conclusions**
Bio-oil and char yields of 60 and 15 wt% from willow were achieved. Chemical analysis has shown that the bio-oil product slate is quite complex. Slight differences between yield structures and chemical composition of bio-oils are expected for the other biomass feedstocks being investigated as part of this study. Since bio-oil contains 35 wt% water and has poor Carbon and Hydrogen contents (35 wt% and 8 wt %), direct fuel or petrochemical applications from thermal pyrolysis alone are not promising. However, recent upgrading experiments presented in literature seem to have significant potential for the generation of chemical feedstocks e.g. hydrotreating followed by catalytic cracking achieves high
selectivities for fuels and chemicals. Possible routes to producing better quality bio-oil that may be investigated in this project include acid washing of biomass to reduce the metal content, fractional condensation of bio-oil, the use of catalysts in the pyrolysis process, or hydrotreatment of the produced bio-oil.

![Figure 2: GC Chromatogram for bio-oil from willow: a. hydroxy-acetaldehyde, b. acetic acid, c. acetol, d. levoglucosan.](image)

**Acknowledgements**

This research has emanated from research conducted with the financial support of Science Foundation Ireland under Grant Number 6C/CP/E001 (www.sfi.ie).

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RAPID ASSESSMENT OF GROWTH PERFORMANCE OF BIOFUEL-
DIRECTED MICROALGAE USING MULTI-PARAMETER FLOW
CYTOMETRY

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Abstract
Multi-parameter flow cytometry was used to monitor cell growth (density and diameter) and intrinsic fluorescence of *Nannochloropsis oculata* and *Isochrysis galbana* algae species as a means for rapid assessment of viability of biofuel-directed microalgae production. The maximum cell densities recorded in the stationary phase were 74,700 and 21,400 cells/µl for *N. oculata* and *I. galbana*, respectively. The maximum specific growth rates in the exponential phase for *N. oculata* and *I. Galbana* were 0.58 and 0.43 day⁻¹. It was found that the cultures for the two experimental species could be distinguished by comparing their respective median fluorescent single intensity ratio. *N. oculata* and *I. galbana* registered median fluorescent FL4 to FL1 ratios of 93.5 and 31.7, respectively. On these bases it could be argued that the multi-parameter flow cytometry technique is capable of measuring physiological information at an individual cell level, which would be difficult to obtain otherwise. When combined with fluorescence calibration aimed at the determination of quantity and quality of algal lipids, flow cytometry can be used for rapid assessment of optimal production conditions for biofuel-directed microalgae.

Introduction
It is widely accepted that the use of fossil fuels as a primary energy resource is unsustainable with respect to depleting resources and progressive environmental degradation arising from the accumulation of associated greenhouse gases in the atmosphere (Schenk et al., 2008). Deployment of renewable and sustainable fuels is therefore necessary to meet energy demands, while contributing to the amelioration of climate change (Kruse and Hankamer, 2010). On the basis of extensive literature review (Brennan and Owende, 2010; Mata et al., 2010), optimal cultivation of biofuel-directed microalgae is deemed to have potential as a source of renewable fuels which does not conflict with food production (Chisti, 2010).

For biofuel extraction, microalgae offer numerous advantages over conventional energy crops, however due to the large number of unknown species and strains, the current efforts are focused on screening wild microalgae for desirable characteristics for biofuel production. As such, commercial production of biofuel-directed microalgae is still at a very early developmental stage (Singh and Gu, 2010). It is increasingly obvious that basic techniques used for quantified viability assessment are too time-consuming and, in most part, labour intensive to adequately support the necessary species screening towards economic production. Rapid assessment tools for the screening of microalgal strains towards optimisation of biofuels production processes are therefore invaluable. Multi-parameter flow cytometry (FC) is a method for the qualitative and quantitative measurement of biological and physical characteristics of cells (Vives-Regó et al., 2000). It can be used to monitor cells *in situ* at near-real time and with a high degree of statistical resolution during microalgae growth (da Silva et al., 2009). Principal applications of FC are in the monitoring of cell growth by cell-counting; cell diameter measurement; and quantified characterisation of intrinsic fluorescence, which can be used to check for homogeneity of cell cultures; monitoring of cell lipid content to optimise harvesting; and monitoring lipid type to determine the optimum co-product, hence, the right processing pathway.

The objective of this paper was to use flow cytometry to monitor selected growth parameters of two microalgae species - *Nannochloropsis oculata* and *Isochrysis galbana* - as a precursor for determination of projected biofuel quality.
Materials and Methods

Organisms: *Nannochloropsis oculata* (CCAP No: 849/1) and *Isochrysis galbana* (CCAP No: 927/1) starter cultures were obtained from the Culture Collection of Algae and Protozoa (CCAP), Dunstaffnage, Scotland and were maintained axenically in F/2 medium. *N. oculata* (class Eustigmatophyceae) is a small, coccoid, unicellular, and non-motile microalga (cell diameter of 2 – 4 µm) and contains chlorophyll *a* and violaxanthin as its major photosynthetic pigments. *I. galbana* (class Prymnesiophyceae) is a small, unicellular, green-brown flagellate (cell diameter of 4 – 7 µm) and contains chlorophyll *a*, *c*₂, and fucoxanthin as its major photosynthetic pigments. The stock cultures were maintained by weekly sub-culturing in F/2 medium and autotrophic conditions at 25 °C, 16:8 light:dark ratio and 150 µmol s⁻¹ m⁻².

Photobioreactor description and operation: Each experimental photobioreactor unit (PBR) consisted of an individual vertical glass tube column (height 500 mm, diameter 60 mm), with a working volume of 1000 ml. Fig. 1 shows a schematic of the experimental set-up. Up to four units were operated in a culture growth cabinet (Binder ATP.line™ KBWF) which allowed for the control of both temperature and illumination intensity. Air was supplied using a pneumatic compressor via a rotameter to control flow rate, and a humidifier was used to control evaporation in each of the PBR units. No external CO₂ was injected and the system maintained its own pH equilibrium.

Growth conditions: Stationary phase stock solutions (300 ml) for each microalgal species were used to inoculate the respective PBR units and mixed with standard F/2 medium to obtain a final working volume of 1000 ml. Two PBR units each were inoculated with *N. oculata* and *I. galbana* in the configuration illustrated in Fig. 1. The culture growth chamber was maintained at 20 °C, 24:0 light:dark ratio and 175 µmol s⁻¹ m⁻². The PBR was injected with air at 500 ml min⁻¹ flow rate in each of the columns, and the air bubbles provided continuous mixing. The cultures were grown over a 160 hour period with 10 ml samples collected at regular intervals for analysis in the FC.

Cell growth and intrinsic fluorescence: Cell growth, cell diameter, and intrinsic fluorescence were measured daily in the Accuri C6 flow cytometer (Accuri, Michigan, USA). Measurements were taken in triplicate with sample sizes of 50,000 to 300,000 cells each. Cell growth was determined as the cell density per unit volume of sample (µl) and directly calculated using the volume measurement function of the flow cytometry system. Specific growth rates were determined from the gradients of exponential phase of respective growth curves (Wood et al., 2005). Microalgae can be detected from the image background on the
basis of their intrinsic fluorescence properties in the forward angle light scatter (FALS, FSC or FS) and the right angle light scatter (RALS), also known as side scatter (SSC or SS) (da Silva et al., 2009). Cell fluorescence was determined from SSC which is measured at 90° to the projected laser beam and provides information on cell granularity and the internal cell structure.

Results and Discussion

Cell growth monitoring: Cell growth during the observation period was monitored by cell counting. The cell densities for N. oculata and I. galbana cultures started at 10,000 cells µl⁻¹ and 5,000 cells µl⁻¹, respectively, and their growth followed similar paths (Fig. 2). It was observed that both N. oculata and I. galbana displayed an approximately 24 hour delay before achieving exponential growth, and subsequently entered their stationary phase after 96 hours. The maximum cell densities attained were 74,700 and 21,400 cells µl⁻¹ for N. oculata and I. galbana, respectively. The corresponding maximum specific growth rates (µ) recorded were 0.58 and 0.43 day⁻¹, respectively.

![Fig. 2: Multi-parameter flow cytometry cell counts for N. oculata and I. galbana.](image)

Cell intrinsic light scatter measurements: The two experimental cultures were distinguished by comparison of the median fluorescent ratios in FL4 to FL1. Fig. 3 illustrates the comparison for experimental samples at the beginning of the stationary phase after a 96 hour growth period. N. oculata is dominated by chlorophyll a and violaxanthin, both of which are excited in the range of FL4 (675 ±12.5 nm). The major pigments present in I. galbana are chlorophyll a and fucoxanthin (Graham et al., 2009). Again, chlorophyll a will be excited by FL4 but importantly, fucoxanthin excites at 510 to 525 nm, which is in the range for FL1 (530 ±15 nm). N. oculata and I. galbana recorded ratios of 93.5 and 31.7, respectively.

Conclusion

The multi-parameter flow cytometry approach was successfully used for rapid characterisation of two microalgae species: N. oculata and I. galbana. It facilitated the monitoring of growth rates through cell counting, and allowed the two cultures to be separated based on the ratio of their respective fluorescent intensities. A similar approach could be used for quantitative assessment of algal lipids content for a complete assessment of growth performance and production of biofuel-directed microalgae.

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Acknowledgements

This publication has emanated from research conducted with the financial support of Science Foundation Ireland under Grant Number 6C/CP/E001.

References


Preliminary study of the potential of *Nannochloropsis oculata* to sequester carbon under varying temperatures and carbon dioxide concentrations

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**Abstract**

Biological carbon mitigation is a technique used to reduce emissions from point sources. This approach utilises carbon dioxide (CO₂) from the flue gases of, for example, a power plant to cultivate photosynthetic autotrophic organisms. Microalgae, with high photosynthetic efficiency and rapid growth rates, have shown great potential for this process. This study assessed the feasibility of cultivating micro-algae using CO₂ enhanced air streams at varying temperatures and determined the rate of carbon mitigation. *Nannochloropsis oculata*, a unicellular microalgal species, was selected and assessed for its potential to sequester carbon from a high concentration CO₂ source. Flue gases may contain up to 15% CO₂ and a direct relationship between CO₂ concentration and growth rate can be seen for many microalgal strains. Temperature can also have a significant effect on biomass production. Therefore the optimum temperature and CO₂ concentration at which individual strains of microalgae can sequester carbon should be determined.

**Introduction**

Concerns over global warming and carbon emissions have sparked interest in methods of sequestering carbon which has been released through the anthropogenic production of CO₂. If the terrestrial biological carbon cycle were properly managed, it could make a major contribution to mitigation of this greenhouse gas (Hughes and Benemann, 1997). Carbon capture and sequestration is a process of removing CO₂ from flue gases of point sources emitters and storing it for extended periods. Biological sequestration is a temporary storage of CO₂ whereby the biomass produced can be used as an energy source by converting it to biofuels (Mata et al., 2010). Essentially the CO₂ 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 (Olaizola et al., 2004). Using this process, captured flue gases containing high concentrations of CO₂ 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 (Stephan et al., 2001). Selection of the best media for carbon sequestration is crucial in achieving a high level of CO₂ removal while also ensuring an economic benefit from the process (Olaizola et al., 2004).

In this study *Nannochloropsis oculata*, a small microalgal species, is assessed for its potential to sequester carbon from a high concentration CO₂ source. Flue gases may contain anything up to 15% CO₂ and a direct relationship between CO₂ 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 CO₂ concentration at which individual strains of microalgae can sequester carbon should be determined.

The objective of this study was to assess the feasibility of cultivating *Nannochloropsis oculata* at laboratory scale using CO₂ enhanced air streams at varying temperatures to assess the rate of carbon mitigation which could be achieved.
Materials and Methods

Selection of the 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 ideally produce valuable by-products to offset the cost of 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 (BERR, 2008; Chiu et al., 2009; Hsueh et al., 2009).

Experimental design
A two-factor, fully randomised factorial design was employed. The two factors selected as independent variables were flue gas temperature and CO₂ concentration. Cultivation was carried out on an 18/6 hr, light/dark photo period. Light for the experiment light was provided by red/blue LED grow lights to achieve a light intensity of 200µmol.m⁻².s⁻¹ at the surface of the culture flask. The algae were cultivated in three, 3 L batch reactors for a period of 7 days. The culture medium was seawater enriched with f/2medium. Air enhanced with CO₂ was bubbled through the 3 L of media in the reactors at a rate of 1 L/min/L (media) at varying temperatures according to the experimental design. The pre-reactor CO₂/air mixture was achieved using a set of flow meters and pressurised gas sources. A two-factor, fully randomized factorial design was employed. The two factors selected as independent variables were flue gas temperature and CO₂ concentration. 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.

Data Collection
Exit gases were analysed using a gas analyser (Applus+ Auto Logic, Sussex, UK) in order to calculate CO₂ removal rates. Growth rates were also monitored to calculate the biomass productivity. Growth was assessed using a Sedgwick counting chamber and microscope. A sample of broth was taken periodically and analysed under the microscope to calculate the microbial cell count per ml of medium. This information was used to calculate the total carbon sequestered and therefore the sequestration rate was quantified.

Results and Discussion
Initial results showed that a cell density of 60 x 10⁶ cells ml⁻¹ was achieved in the air (0% added CO₂) bubbled media for *Nannochloropsis oculata* at a temperature of 20°C. This resulted in a growth curve (Fig 1) where the log phase of growth could be identified. Keeping the algae in this phase in a continuous process maximises carbon mitigation so this is an important element to be determined. 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 that research showed 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 1**: Typical growth curve of *Nannochloropsis oculata* in a batch reactor at 0% added CO₂ and 20°C

**Conclusions**

The potential of *Nannochloropsis oculata* to mitigate carbon at laboratory scale was demonstrated. The process is to be further optimised to increase the growth rates at higher CO₂ concentrations following the identification of the challenges associated with using this strain to sequester carbon. The results of this experiment support the use of microalgae as media for biological carbon mitigation of CO₂ in which they have shown great potential due to their rapid growth rates, high carbon mitigation rates and the creation of valuable by-products from algal biomass. The result of varying light intensity and lighting period on carbon sequestration rate, growth rates and yield will also be determined. The results from these experiments will allow the optimum conditions for growth to be established while sequestering the maximum amount of CO₂.

**Acknowledgements**

This publication has emanated from research conducted with the financial support of Science Foundation Ireland under Grant Number 6C/CP/E001.

**References**


AN EVALUATION OF OZONE APPLICATION AS A DISINFECTANT IN IRISH FOOD PROCESSING PLANTS

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Abstract
It is of high importance that Irish food processing plants assure customers about the safety of their products. A number of disinfection methods and agents are currently used to inhibit the growth of pathogenic micro-flora, restricting food decay and prolonging its storage time. However, it is also vitally important that such methods do not leave any harmful residues, a condition which is a priority for food quality. It has therefore become timely to examine emerging disinfectants as alternatives to conventional methods. Ozone application is an increasingly utilized disinfection method for the food processing industry. This study aims to establish a best technical approach to disinfection in food processing facilities with an emphasis on environmental impact.

Introduction
There is an increasing interest in ozone as an alternative to chlorine and other chemical disinfectants in cleaning and disinfection operations. Ozone has a high biocidal efficiency, wide antimicrobial spectrum, absence of by-products that are detrimental to health and the ability to instantaneous generation on demand, ‘in situ’, without needing to store it for later use. As a result, the interest in additional or alternative disinfectants has been observed to increase (Moore et al., 2000). With growing environmental concerns, ozone as an environmentally friendly technology has the potential to reduce environmental costs, thus facilitating compliance with statutory obligations. New environmental legislation, in particular the IPPC Directive 96/61/EC, will help drive a policy and attitude change in the food industry. Cleaning and disinfection operations are responsible for the greatest environmental impacts (water and energy consumption, wastewater, etc.) in most food processing plants. In processing plants, areas that are in contact with food should be microbiologically pure. Therefore, surfaces that appear visually clean may still be contaminated with a large number of microorganisms that can further contaminate food (Moore et al., 2000). Adopting ozone application can help to address concerns about these potential issues.
Ozone has high reactivity leaving no harmful residues and has been documented as an effective disinfectant in assuring the quality and microbiological safety of food (Kim et al., 1999). Its chemical structure is the tri-atomic form of oxygen and has highly effective disinfection and oxidizing properties. Ozone as a disinfectant has proven to be more powerful than chlorine and 3000 times more reactive. Ozone also causes the coagulation of proteins and fats. As a result, fat “catchers” work more effectively and the degree of waste contamination is lower. Being the strongest oxidiser and disinfectant, Ozone is able to oxidise remnants of fat and protein and remove them from the surface of containers. The reaction between Ozone and the contaminated surfaces lasts several seconds when the concentration of contaminations is about 10%. Compared to traditional chemicals, this time is considerably shorter. Detailed microbiological tests have proven that at all stages of washing Ozone caused the total inactivation of bacteria (Wysok et al., 2006).

The objective of this study was to directly compare ozone to traditional disinfectants for use in food processing plants considering efficiency and environmental/economic benefits.

Methodology
The work involves collaboration with dairy and brewery sectors as representative of Irish industries where large amounts of water and potential cleaning chemicals are consumed and discharged as a consequence of cleaning and disinfection. In order to achieve the objectives of this investigation a prototype model was simulated in conjunction with Irish food industry members, to replicate facilities surfaces which are treated with different disinfectants and to investigate the needs and demands of the industry partners. Several surfaces, reproducing different contact areas within food processing...
facilities were tested for assaying disinfection processes simulating different industrial CIP processes currently carried out in breweries, and dairies in order to evaluate equivalent disinfection processes being treated with ozone. The experimental results are to provide environmental indicators and representative values according to “European Best Available Technologies Reference Documents” (BREFs). Also models of technical and economical viability are to be generated to facilitate possible practical large scale implementation in Irish food processing.

The methodology plan consists of the following tasks:

- With preliminary activities based around an investigation of several different food processing plants focusing on establishing current practices and disinfection techniques, and assessing food contact surface types in order to replicate and simulate multiple food processing facilities to determining optimal disinfection practices considering on Best Available Technologies (BATs) Documents, Clean in Place (CIP) technology and Ozonation Technology.

- Field work performed collaboration with several companies in order to obtain a better knowledge of current practices at industrial scale and get environmental impact data on its operations.

- Ozone prototype designs would be created to replace current disinfection practices, considering all the important input data from the previous actions, laboratory experiments would then be possible testing effectiveness and efficiency.

- Evaluation of results in terms of water, energy and chemical consumption, and hygienic efficiency are key to determining indicators.

Table 1. General ratios on water consumption in dairy industries:

<table>
<thead>
<tr>
<th>Disinfection</th>
<th>Ozonation</th>
<th>Electrolyzed Water</th>
<th>Chlorine Dioxide</th>
<th>Liquid Chlorine</th>
<th>Hydrogen Peroxide</th>
<th>Steam</th>
</tr>
</thead>
<tbody>
<tr>
<td>Contact time</td>
<td>Strongest</td>
<td>Weak</td>
<td>Ok</td>
<td>Ok</td>
<td>Strong</td>
<td>Strong</td>
</tr>
<tr>
<td>Eliminates Odors</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
<td>No</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>Eliminates Pesticides</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
<td>No</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>Eliminates Chemicals</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
<td>No</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>Affects Food Quality</td>
<td>No</td>
<td>Yes (Taste)</td>
<td>Yes (Taste)</td>
<td>Yes (Taste)</td>
<td>Forms harmful substances from starch</td>
<td>Not suitable for produce</td>
</tr>
<tr>
<td>Poses Health Hazard</td>
<td>No</td>
<td>No</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>Removes Chlorine</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
<td>No</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>Leaves harmful by-products</td>
<td>No</td>
<td>No</td>
<td>Yes</td>
<td>Yes</td>
<td>May contain</td>
<td>No</td>
</tr>
<tr>
<td>Safety</td>
<td>Very Safe</td>
<td>Safe only at low pH levels, residual chlorine is harmful</td>
<td>Harmful</td>
<td>Harmful</td>
<td>Harmful</td>
<td>Harmful</td>
</tr>
</tbody>
</table>

The project is projected to fulfill the expectations detailed in the project proposal: to contribute to the reduction of the environmental impact of sanitation operations in the food industry through use of an innovative sanitation technique, based on the use of ozone. The experimental activities would focus on Irish food processing practices, and the results look to be very favourable when examining existing data (OzoneCIP Project), with the ozone as a disinfectant leading to the following results:
• Up to 50 percent water savings per cleaning cycle compared to conventional cycles;
• Up to 50 percent reduction in organic load in wastewater, in terms of weight per cleaning cycle, compared to traditional cycles. This was due to the fact that ozone is quite unstable and quickly breaks back down into oxygen. This meant that effluents could be treated in the same way as urban wastewater;
• Achievement of better environmental results than current CIP practice while maintaining, if not increasing the level of efficiency in terms of cleanliness and disinfection;
• Reduced energy costs, and reduced use of disinfectants, in particular chlorine, one of the most commonly used disinfectants for water.

Table 2. Comparison of Ozone to Chemical Treatment

<table>
<thead>
<tr>
<th>Items</th>
<th>Ozonation</th>
<th>Liquid Chlorine</th>
<th>Chlorine Dioxide</th>
<th>UV</th>
</tr>
</thead>
<tbody>
<tr>
<td>No harmful chemical residues or by-products</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
<td>Yes</td>
</tr>
<tr>
<td>Kills bacteria</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>Also effective on viruses</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>Short term cost</td>
<td>Medium</td>
<td>Lowest</td>
<td>Low</td>
<td>Highest</td>
</tr>
<tr>
<td>Treatment time under 10mins</td>
<td>Yes</td>
<td>No</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>Effective deodorizer</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>Residual disinfection</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>Does not require regular purchase of inputs</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
<td>Yes</td>
</tr>
</tbody>
</table>

Results and Discussion

Recently the potential of ozone as a replacement for chlorine for treatment of industrial water and removal of biological growth from surfaces has been recognised. Ozone in solution, because of its instability, unlike chlorine does not persist in the system to which it is added. Laboratory tests in a flowing system have demonstrated the effectiveness of ozone dissolved in water at very low concentration (of the order of 0.1 ppm), in removing microbiological accumulations on surfaces. Intermittent application over a period of time results in substantial biofilm removal.

To summarise results of the food processing plant model proved:
1. Water saving possibilities
2. Faster disinfection times
3. Water re-use possibilities, the water used for disinfection could be applied for initial cleaning steps
4. No storage of hazardous chemicals
5. Energy saving, as it is used at low temperatures

European environmental legislation has established that there is a need for polluting industries to utilise clean technologies with the most important regulation. The Integrated Pollution Prevention and Control (IPPC) Directive 96/61/EC, has considerable relevance and far-reaching effects for all European food manufacturers. The IPPC directive attempts to encourage the Best Available Techniques (BATs). BATs are defined as techniques that enable competitive levels of quality and productivity to be achieved and are noted for their greater environmental efficacy. This has placed ozone to the forefront as an alternative disinfection technique. This study has preliminarily established considerable environmental benefits such as a reduction of water and energy consumption within a food processing plant. In terms of food safety increased disinfection efficiency with little or no by-
products as a result of ozone use are predicted. Finally the economic feasibility of adapting a new ozonation disinfection system in place of current practices will need to be viable.

Conclusion
Ozone is an effective disinfectant that is increasingly being used for a wide variety of applications. Its ability to eliminate harmful residues in food or on contaminated surfaces highlights its potential for the food processing industry. Compared to chlorine and other disinfectants, ozone has also proven effective against resistant viruses and spores. Exposing some products (e.g. fruit or vegetables) to ozone during their storage period extends their shelf life without affecting their sensory value. The use of ozone does not require high temperature, hence it offers the possibility of energy saving. Ozone must be produced on the spot, which leads to savings on transport and storage costs of disinfectants. The cost of an ozone generator may raise concerns in small businesses; however, such fears are unfounded because the purchase of such a generator may prove economical in the long run. Despite such reservations, it must be said that when used under controlled conditions, it is an effective and totally safe disinfectant.

Acknowledgement
The authors would like to thank Dr Frank Lynch, technology and development director at the Diageo Global Beer Technical Centre for providing extensive technical information of facilities, its components and technical details. They are also grateful to Dr Adam Anderson, R&D Director EME Region, Kerry Ingredients & Flavours for providing access to dairy facilities of the dairy group, and also Bulmers Ireland for information provided.

References
A LIFE CYCLE ASSESSMENT APPROACH TO URBAN WATER INFRASTRUCTURE

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Abstract
The efficiency of an integrated urban water system is assessed using a Life Cycle Assessment (LCA) approach in this study. A systematic review of the current infrastructure in Ireland together with LCA methodology will provide the platform upon which a weighting system will score efficiencies in terms of increased water supply to satisfy growing demand.

Introduction
A number of supply issues relating to Ireland in recent years have highlighted the importance of a safe and secure water infrastructure for everyday life. For example the outbreak of cryptosporidiosis in Galway during 2007, which resulted in restrictions by way of boil water notices, affecting a population of approximately 90,000 and the Galway water supply for a period of 5 months (Page et al., 2007). Another area affected is Dublin which has the imposition of bi-annual water shortage announcements due to warm spells in summer and cold snaps in winter. This is mainly due to increases in population and gross domestic product (GDP) which has outpaced the capacity of the aging water infrastructure which will have a predicted 25% leakage rate (RPS and Veolia, 2008) upon completion of a network rehabilitation programme costing €118m this year. The average demand for drinking water in Dublin is between 530 and 540 million litres a day and the combined maximum output of Dublin’s four main water treatment plants is between 540 and 550 million litres a day (RPS and Veolia, 2010). Such supply and demand figures hold little room for manoeuvre in times of growing requirements and uncertain climate conditions.

The population in Ireland increased by 18.2% to 4.42 million persons in the period 1999-2008 which was the highest rate of increase in the EU 27. Although there has been a decline over the last 2 years, the combined effect of a strong natural increase and negative net migration resulted in an overall small increase in the population of 11,400 bringing the population estimate to 4.47 million in April 2010 (CSO, 2010). Such continued population increase with industrial development will induce further competition for allocating freshwater among different end-uses raising sustainability challenges (Koehler, 2008). A report by Forfas, Ireland’s national advisory board on enterprise and science, focuses on the ability of infrastructure to meet enterprise development needs in Ireland during 2013 to 2018. This report indicates a similar situation to Dublin arising in urban centres namely Athlone, Galway and Letterkenny with deficits in water supply of 30%, 13% and 37% respectively predicted by 2013 (Forfas, 2008). Therefore, effective urban water planning and policy are required to resolve water issues emerging from population growth and urbanization (Lim et al., 2010).

The objective of this project is to determine efficiency measures based on a life cycle assessment of the urban water system in Ireland.
Materials and Methods

Current water infrastructure

In Ireland the majority of drinking water (83%) originates from surface water (i.e. rivers and lakes) with the remainder originating from groundwater (11%) and springs (6%) (Page et al., 2007). The majority of the population (85.1%) receive their water from public water supplies. Under the provisions of the Water Services Act 2007, it is the duty of the Minister for the Environment, Heritage and Local Government to facilitate the delivery of water services infrastructure. In turn the responsibility for the management and strategic planning of water services is relayed to the local authorities within their area. For the purpose of the Water Framework Directive, Ireland’s water network is divided into seven river basin districts where good status and sustainable management are the primary objectives to be established by 2015. The Overall quality of the water services rests with the Environmental Protection Agency (EPA).

The World Health Organisation has put forward a strategy in the Water Safety Plan (WSP) which provides guidelines aimed at a risk management based assessment of organised water supplies. The current infrastructure will be examined based on the System Assessment criteria developed in the WSP manual (Bartram et al., 2009) which is shown in figure 1. The data collected here will allow an inventory assessment of the existing system.

![System Assessment](image)

**Figure 1:** System Assessment (Bartram et al., 2009)

Integrated urban water systems

Integrated urban water systems have been suggested to incorporate all the water infrastructures related to water supply, storm drainage, and wastewater systems into a system for efficient and effective water management (Anderson and Iyaduri, 2003). To investigate the metrics of an efficient infrastructure it is necessary to develop a superstructure model for urban water systems which integrates all water resources, water demand systems and water treatments plants as proposed by Lim et al. (2010) and Fagan et al. (2010). This is achieved by examining LCA’s of urban water systems and defining parameters to build a model which will enable an investigation into the sub-systems identified in the water cycle.

While many advanced tools and analytical methods for integrated water resource management exist, scientific efforts in LCA should be directed towards methodologies that allow, at an appropriate level of detail, effort, and sophistication, for comparing product alternatives based on different production systems and inducing multiple consumption patterns (Koehler, 2008).
Examing the integrated urban water system based on the model shown in figure 2 allows for such comparisons and will identify efficient production systems which can complement the urban water infrastructure in Ireland to meet increasing water demands.

![Figure 2: An example of a large-scale process flowsheet of the water cycle, showing a system with central treatment of sewage and stormwater, a central recycled water treatment plant, and recycling links to all consumers (Fagan et al., 2010)](image)

**Life cycle assessment**

Life Cycle Assessment (LCA) by definition is the compilation and evaluation of the inputs, outputs and the potential environmental impacts of a product system throughout its life cycle (ISO14040, 1997). The importance of LCA’s in determining environmental impacts led to the production of the ISO14040-49 series of standards to lay down a methodology for conducting and reporting on LCA projects. Its main advantage over other, site-specific, methods for environmental analysis, such as Environmental Impact Assessment (EIA) or Environmental Audit (EA), lies in broadening the system boundaries (Azapagic, 1999) and therefore the application of a LCA in this research allows an evaluation of the bigger picture of an integrated urban water system. In general, impact categories are chosen to examine the issues which are considered relevant to the current business impacts of the service provider and the changes in environmental performance which new scenarios may cause (Lundie et al., 2004). In this case the impact category will relate to supply issues. This LCA will identify the critical processes and compartments of the water system that will affect the impact categories of water volume, energy and eco-efficiency which is defined as the economic cost of environmental improvement.
Results and Discussion
The results of this model will allow the comparison of current water supply data associated with the present water system against that of an integrated water system incorporating efficiency gains achieved through improved catchment management, advances in treatment technologies and improvements in water consumption patterns.

Conclusion
In Ireland water services are in a state of transition as the implementation of the EU Water Framework Directive continues to a target date in 2015. The present infrastructure is finding it difficult to meet the demands associated with rising population and industrial growth. This project will develop potential improvements associated with an integrated urban water system to ease short term and long term capacity issues.

Acknowledgements
The authors would like to thank Mingjia Yan for an introduction to Simapro and ongoing LCA advice.

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Analysis of Alternative Landfill Gas Utilisation Technologies in Ireland

Kevin O’ Neill and Tony Woodcock
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Abstract

Energy recovery from waste represents an important way to reduce the amount of energy used from fossil fuels and can also present interesting economic revenues. Since a large amount of waste in Ireland is still disposed of in landfills the recovery and utilization of Landfill Gas (LFG) is an interesting prospect. In this study the different LFG utilization technologies are compared using a cost benefit analysis to determine which option is most suitable both economically and environmentally. A monetary value is calculated for one tonne of CO₂ equivalent (€/tCO₂e) so that the environmental aspects can be represented economically in the cost benefit analysis. Finally a government tax credit scheme is proposed to provide an incentive for operators of Landfill Gas to Energy (LFGE) facilities to use a more environmentally friendly option which may not be as economical as the consolidated internal combustion engine (ICE) technology.

Introduction

The integrated waste prevention and treatment management is commonly recognised as the only way for reducing the environmental load related to waste disposal. According to the waste hierarchy the least preferred option is disposal to landfill as it represents a loss of resources. In 2000 Ireland landfilled approximately 90% of municipal waste arisings and while this was reduced to 62.5% in 2008, Ireland remains predominantly reliant on landfill in managing waste (EPA 2010). Waste going to landfill will be further reduced in the coming years as Ireland aims to achieve the standards set by the EU landfill directive 1999/31/EC. Ideally we could move away from the use of landfill totally in the future if waste management practices higher on the waste hierarchy continue to be adopted and if emerging technologies such as pyrolysis, plasma arc gasification etc become economically viable and environmentally acceptable. However with almost 1.2 million tonnes of Biodegradable Municipal Waste (BMW) landfilled in 2008 it is clear that energy recovery from landfill should be regarded as an important area for Irish waste management in the foreseeable future.

One of the environmental problems directly related to landfill disposal of Municipal Solid Wastes (MSW) is the emission of LFG which consists mostly of the greenhouse gases (GHGs) methane (CH₄) and carbon dioxide (CO₂). EU legislation requires that the Member States collect the LFG from all landfills receiving biodegradable waste and this LFG must be treated and used (Lombardi et al., 2006). The simplest way to treat the LFG is to flare it, however LFG has a rather high energy content of around 18-22 MJ/m³ since it typically consists of 50-60% methane (Spokas et al., 2006). Therefore flaring LFG is a waste of a potentially valuable resource and so the recovery of LFG and its utilization as an energy source have become an increasingly attractive option in recent times. In Ireland, there are 29 open landfills of which 11 have LFGE facilities in place. The main ways for LFG utilization include direct heating, electricity generation, purification for pipeline quality gas or use as a vehicle fuel. In Ireland, direct heating and electricity generation using an ICE are the only adopted options in LFG utilization projects since they are perceived to be the most economical and are a low risk consolidated technology.

The objective of this study was to complete an economic analysis for each of the available LFG utilisation options while incorporating a monetary value for
environmental aspects to determine which technology would be best employed on Irish landfills in the future.

Materials and Methods

The overall purpose of this project is to show how life cycle for environmental impact and costs can be combined to compare the alternative options for the utilization of landfill gas in Ireland. One of the unique aspects of this study will be to place a monetary value on emissions associated with LFG and its utilization i.e. the author will calculate a monetary value on emissions of CO₂ equivalent (CO₂e). This value will represent the amount of money in Euros that the Irish government would be willing to pay in order to prevent the release of 1 tonne of CO₂ equivalent, €/tCO₂. By doing this a cost benefit analysis can be conducted which incorporates the environmental aspects associated with LFGE projects. This study will use the Economic Input-Output Life Cycle Assessment (EIO-LCA) method. This method will allow the economic activity and environmental effects associated with the production of energy from LFG to be assessed throughout the entire life cycle of the process which is assumed in this study to be 20 years.

Previous studies have conducted economical evaluations or environmental assessments of LFG utilization technologies but the application of a cost benefit analysis which incorporates environmental impacts for supporting decisions of LFGE projects has not yet been documented in Ireland and this study presents a framework for such evaluations.

This study will examine a number of methods for utilizing LFG:

Electricity generation technologies
- Internal Combustion Engine
- Gas turbine
- Fuel cells
- Organic Rankine cycle
- Stirling cycle engine

Upgrading the LFG for
- Injection into natural gas grid
- Use as vehicle fuel

LFG upgrading technologies:
- Water scrubber
- Membrane separation
- Pressure swing adsorption
- Adsorption by activated carbon
- CO₂ wash process

For each option the calculated monetary value for the environmental aspects will be used to determine the feasibility of the technology. This feasibility study will also involve gathering data for each technology relating to capital costs, operating and maintenance costs, efficiency, emissions, and revenue. Data for the ICE will be obtained from the operation of the Arthursown LFGE facility which is run by Bioverda Power Systems Ltd. However since none of the other technologies are currently employed in Ireland the data for these will largely be obtained from their application in other countries and various studies which have been conducted on the individual technologies. Once all the necessary data has been compiled for each alternative the report will present key results such as the return on investment and the payback period for each option to assist in decision making.
A government tax credit will be calculated based on the calculated monetary value for emissions and the emission factor of GHG emissions from producing 1 MWh of electricity in Ireland by conventional fuel. The purpose of this tax credit scheme will be to provide a financial incentive for LFGE operators to choose a more efficient environmentally friendly alternative for the utilization of LFG.

A sensitivity analysis will be conducted to represent the factors relating to LFG that are site specific due to variations in composition of waste, waste depth, waste density, date landfilling commenced etc. The analysis will illustrate the effect that changes in the methane generation rate, oxidation rate and efficiency of the LFG collection system will have on the overall efficiency of the proposed technologies and the resulting GHG emissions. The methane generation rate, oxidation rate and the efficiency of the LFG collection system at Arthurstown landfill will be used for this analysis. These figures will be obtained by using The Landfill Gas Emissions Model (LandGEM) which provides an automated estimation tool for quantifying air emissions from MSW landfills.

Results and Discussion

As experimental work is on-going, only expected results are shown here. The results of the cost benefit analysis should show which LFG utilization alternative is the most attractive from both an economical and environmental point of view over the entire life cycle of each option. Ultimately the monetary value that is calculated for the environmental impacts of these technologies is going to be crucial in determining which is the most suitable alternative and so it is important that this value is as accurate as possible. Placing a monetary value on one tonne of CO2e is a unique proposal as it has never been undertaken for the Irish economy but from an examination of literature the author estimates that a value of €25/tCO2e will be expected as this is the average market price of long term carbon (Parry & Small, 2005).

The LFGE operators will always choose the most economical option available. Therefore, in order for the findings of this study to be practical the author proposes a government tax credit scheme which will act as an incentive to utilize more efficient environmentally friendly alternatives. Under this scheme the LFGE operators will be awarded tax credits if their facilities reach a certain level of performance in terms of efficiency and emissions. This provides LFGE operators with a financial incentive to utilize more environmentally friendly LFG utilization technologies thereby reducing GHG’s which is beneficial for the Irish government to reach its Kyoto Protocol targets. An estimate on the cost of the proposed tax credit cannot yet be made as it is based on the calculation of the monetary value on emissions and the average GHG emission from conventional electricity generation in Ireland, which is expected to be around 740kgCO2e/MWh.

The author expects to find that the most economical LFGE technology currently available is the ICE but that this has the worst environmental performance. The use of fuel cell technology will be the worst option economically but have the best environmental performance. With the implementation of the proposed tax credit scheme, upgrading the LFG for use in the natural gas grid will be the best option, achieving best results both economically and environmentally.

The sensitivity analysis will show that decreasing the gas collection efficiency from the existing 75% by 5% results in a decreased electricity production by 6% and increased net Global warming potential (GWP) by 40%. On the other hand, increasing the gas collection efficiency by 5% results in an increased electricity production by 9% and decreased net GWP by 40%. The assumed methane oxidation rate is 10%, the IPCC default. Increasing the
methane oxidation rate by 5% and 10% decreases the net GWP from landfill by 8% and 19% respectively.

Conclusions

The authors will predict which alternative technology is the most viable option for future use in Ireland taking into consideration the economical and environmental aspects from the cost benefit analysis. Whatever the final conclusion regarding the best practice for the utilization of LFG the author intends to highlight the conflicting priorities of the government and the LFGE operators and to illustrate that the environmental aspects are considered somewhat irrelevant to the LFGE operators. It is expected that without financial incentive such as the proposed tax credit scheme there will be no economic reason for LFGE operators to depart from their current practices which are not as efficient or environmentally friendly as the alternatives. The author will also state whether the proposed government tax credit scheme will be feasible and if it would be beneficial for both the government and LFGE operators. The results of the sensitivity analysis will show that all of the LFG utilisation technologies are sensitive to the methane oxidation rate and particularly to the gas collection efficiency.

Acknowledgements

This publication has emanated from research conducted with the assistance of Bioverda Power Systems Ltd.

References

Abstract
In this project, the performance of a biofilter performance on a small scale residential composter was measured. The information developed will be of use in the provision of successful adoption of composting to meet national regulations.

Introduction
Benefits of composting include assisting diversion from landfill, utilising potential fertiliser and reducing green house gas emissions (Benton and Foster, 2008). For municipal solid waste in landfill the organic fraction decomposes anaerobically producing landfill gas and leachate. Upwards to 90% of all converted organic carbon is released as CO₂ and CH₄ (Methane) and a fraction of this as leachate (Binns, 2005). Food waste regulations require segregation of food waste from main waste streams through the food supply chain and to be dealt with in a sustainable manner such as aerobic composting and anaerobic digestion. This study focuses on small scale composting (DEHLG, 2009).

The objective of this study is to relate the performance of a woodchip biofilter to performance of an in-vessel composter within a residential area.

Materials and Methods

Plant description: The composter and biofilter were utilised previously in a 2008 study of small scale residential composting. In-vessel composting is not necessarily an odour free process and the Big Hanna composter system was able to offer an integrated odour management solution in addition to a comprehensive maintenance support programme (Miller et al., 2009) which is essential in proximity to residences. A study of a similar composter Neter using a gas analyser found that a maximum of 2ppm hydrogen sulphide, with carbon monoxide levels varying from 4 to 99.5 ppm within the compost vessel (Stokes, 2008).

The “Big Hanna T120” in-vessel composter was designed for composting organic wastes, primarily catering waste with added sources of carbon and the optional addition of horticultural waste. It was designed as a single-stage, fully contained, continuous flow-through system, with waste fed via an in-auger into one end and compost automatically removed through an outlet at the other end. The composter consists of a horizontal insulated stainless steel cylinder approximately 3.5m long, 1.0 m diameter (volume = 2 m³, of this a maximum of 60% is occupied, with remaining head space assisting aeration).

The vessel rotates against fixed end walls and supports, which are housed within a stainless steel outer casing 3.9 m long, 1.08 m wide and 1.55 m high. This outer casing acts as a safety barrier for the moving parts and provides some buffering from external temperature fluctuations. The rotation of the cylinder tumbles the material being composted, mixing and aerating it, whilst moving it along the vessel. The fan operation creates a negative pressure within the vessel drawing air through the compost chamber pile; the airflow rate is approximately 0.085 m³/sec, which is routed through a Ø0.11m I.D wavin pipe to an adapted biofilter. The empty bed contact time (EBCT) expected=

Packed volume/ Flow rate

Pathogen and nutrient analysis
A pathogen and nutrient analysis of fresh compost samples was carried out, to assess the waste composition of the compost residue, to find out whether they comply with provisions of the Animal By Products Regulations on Bio Wastes and to compare this with the pathogen and nutrient analysis of similar in-vessel composter studies. Measurements are to be taken at an sealed port, bored on the exhaust line between the operating fan and the biofilter, to assess the air flow exiting the composter vessel both when the vessel was rotating and static. Additionally, air was sampled from inside the
composting mass itself, using a stainless steel, 20 mm diameter, air sampling tube of approximately 1 m length. Air was also sampled inside the biofilter when the vessel was static. All results were expressed as % volume except for hydrogen sulphide and carbon monoxide concentrations which were expressed in parts per million (ppm) (Stokes, 2008).

**Biofilter structure**
The biofilter used in this study was an adapted Wheelie bin size 120 Litre, material was HDPE, dimension 580(W) x 710(L) x 1070(H). A stainless steel sieve plate was placed 0.25 m from the base of the bin. This is to support the packing material and ensure even distribution of the inlet air stream. Two sample ports are located at 0.2 m and 0.7 m- (above and below the suspended filter layer). Excess water that percolated from the system was removed via a port at the bottom of the bin. The biofilter was packed to a height of 0.3 m with 10kg of generic untreated wood chip. The approximate final packed volume was 0.1218 m³. The pH of average 4.7 - 4.9 for sawdust pellets and wood-shavings was found in another study (Stokes, 2008). High flow rates result in shorter EBCT with air steams following least resistance path through the biofilter reducing efficiency (Chitwood et al., 1999).

![Biofilter Exhaust Air](image)

**Figure 1**: Schematic of Composter and biofilter

A total of two samples – were taken from the composter exhaust airstream before and after the biofilter. Air samples were collected using a vacuum sampler from the exhaust air stream from the in-vessel compost pile, a stable period of composter operation in the thermophilic temperature range, 50-65°C with optimum microbial digestion of the food waste. This produces the maximum level of volatile organic compounds (VOCs) discharged into the exhaust airstream. The odour samples were collected in 10 litre Nalphan bags using a battery powered vacuum pump and a rigid container. The odour measurements were carried out according to the European standard EN13725 (CEN, 2003) in the olfactometry laboratory in University College Dublin. The composter studied operates under negative pressure.

**Measurement of odour threshold concentration**
The Ecoma T07 dynamic olfactometer (Ecoma, Honigsee, Germany) is used to measure the odour threshold concentration of the vented exhaust air from the in-vessel composter. The odour threshold concentration is defined as the dilution factor at which 50% of the panellist’s can just detect an odour. The panellists are pre-screened using the certified gas n-butonal (CAS 71-36-3). Only panellist’s that have a average response threshold to n-butonal are selected. The odour threshold concentration will be calculated according to the responses of the panel members, will be carried out and will be displayed in Otu m⁻³. This refers to the physiological response from the panel equivalent to that elicited by 40 ppb. v-1 n-butanol in 1 m³ of neutral gas (CEN, 2003)

**Measurement of hydrogen sulphide concentration**
Hydrogen sulphide (H2S) was analysed in situ by a portable multi-gas monitor fitted with a 4-cell electro-chemical sensor. The sensor has a measurement range of 0-200 ppm, in 1 ppm increments. The sensor was set to take reading every five minutes. The mechanical ventilation of exhaust stream, requires a sampling pump to draw air from exhaust vent before and after the biofilter. The measurement assumes that ambient concentrations of hydrogen sulphide, outside the composter are zero.

The odour sample is diluted by the olfactometer and assessed by screened panellists (CEN, 2003). Screening of panellists using a certified reference gas (n-butanol) is to eliminate any panellist who may have anosmia low sensitivity or super noses high sensitivity. Some factors can influence the performance to the odour panellists therefore the panellist should follow the strict rules for odour test (Bliss et al., 1996), (Stuetz et al., 1999). This pre-screening ensures olfactometry test repeatability. The test was carried out in an odour free laboratory environment while strictly adhering to the European standard for olfactometry, EN13725 (CEN, 2003).

Collection of odour samples.
Odorous air samples are collected in Nalophan bags using a battery powered vacuum pump and a rigid container. The samples are collected using the lung principle whereby the air is removed, creating a vacuum around the bag. This draws odorous air extracted from the exhaust vents. The air samples are immediately sealed, labelled and stored securely. These must be analysed within 24 hours, preferably on the day of sampling.

Determination of odour threshold concentration
The odour threshold concentration is defined as the dilution factor at which 50% of the panellists can just detect the odour. The odour threshold concentration is calculated according to the response of the panel members, in OuE m⁻³. Threshold refers to the physiological response from the panel equivalent to that elicited by 40 ppb v⁻¹ n butanol evaporated in 1 m⁻³ of neutral gas (CEN, 2003). Individual threshold estimates (ITE’s) are calculated from a statistical analysis of the panellist’s responses. A mean of the panellists results give a valid response which is used to calculate the odour concentration from sample. Odour units are considered a dimensionless unit (McGinley et al., 2000).

Determination of odour intensity
The determination of an odour threshold alone is not an adequate criterion for assessing an odorant. Odour intensity is a subjective measurement of the strength and unpleasantness of an odour (Misselbrook et al., 1993; Wolkoff et al., 2006). VDI 3882 guidelines 1992 are followed for this test.

Results and Discussion
As identified in another study (Murray, 2001) the biofilter can be expected to achieve high removal efficiencies of odorous gases from the inlet air stream routed from the in vessel composter. Microbial breakdown maybe impeded by changes in variables air flow rates, pH and relative humidity. However a well designed biofilter can deal with short term shock loads. The temperature profiles in the composter influence both temperature and aerosols levels in airflow through the biofilter. In the present study, as can be seen in Figure 1. The focus of this study is processing food waste from a hotel kitchen as a reliable source to maintain critical compost temperatures. The biofilter was operated at ambient temperature in a freely ventilated shed. The temperature during the study ranged from -10 to +18°C. For measurement of biofilter performance, the temperature and the relative humidity (R.H.) of the airflow, will be measured at regular intervals. As per a previous study (Murray, 2001) study, the R.H. of the air passing through the filter bed was between 60-95%. The biofilter as a result requires no addition of moisture to the media.

Conclusion
The biofilter has high removal efficiencies of malodorous compounds including ammonia and hydrogen sulphide from the exhaust air stream during operation. Various experiments will be carried out to quantify this potential reduction in odours.
Figure 2: Graphs of food waste throughput and temperature profile, respectively.

Acknowledgements
The authors would like to thank Dr. Patrick Solan, and Anthony Fitzpatrick, UCD and the staff of Ballymun Regeneration, Dublin City Council. The participation of the Metro hotel management and staff in this study was greatly appreciated.

References
SIMULATION OF HYDROGEN PRODUCTION IN ANAEROBIC DIGESTION OF ORGANIC WASTE

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Abstract

The demand for hydrogen has been increasing over the decades and the current methods used to produce hydrogen such as steam reforming and water electrolysis, though efficient, are expensive and energy intensive. Therefore, more economical methods, like anaerobic digestion (AD) are of significant value. The major setback of this process is the immediate conversion of hydrogen to methane by anaerobic microorganisms (methanogens like Methanosarcina and Methanothrix). Therefore a previously developed AD system of inhibiting these organisms and the model dynamics that describe it are considered in this study. The model includes four stages involved in the digestion process: the hydrolysis of waste, growth of hydrogen-producing bacteria, production of volatile acids, and growth/inhibition of methanogenic bacteria. The developed equations and reactions were used in order to assess different scenarios, i.e., the effect of temperature and pH conditions that contribute to the increase of hydrogen production.

Introduction

Hydrogen has gained the attention of most countries as the best alternative to fossil fuels (Crabtree et al., 2004). Hydrogen is considered to be the energy carrier of the future. It is a clean fuel that can be used in the generation of electricity and produces no carbon emissions (Kapdan and Kargi, 2006). Unlike fossil fuels, its combustion releases no greenhouse gases, and no chemicals that cause ozone depletion (Veziroglu, 2008). It also has a higher energy yield than that of hydrocarbon fuels (Kapdan and Kargi, 2006) and can be obtained from renewable sources instead of fossils (Ghosh and Prelas, 2009). Hydrogen can be produced from renewable sources of energy such as solar, wind, hydropower and biomass (Ghosh and Prelas, 2009; Turner, 2004). An example of the latter is AD which is a source of biomass energy and can be used to produce hydrogen from organic waste (Hansen and Cheong, 2009). Certain bacteria such as Clostridium butyricum and Clostridium butylicum found in organic waste are necessary for hydrogen production (Hansen and Cheong, 2009). These bacteria are able to produce acetate and hydrogen from hexose (Kim et al., 2004). However, during the natural process, they are overpowered by methanogenic bacteria and produce methane using the hydrogen and acetate. Examples of these are methanogens like Methanothrix thermophila (Hansen and Cheong, 2009). If the activities of these microorganisms can somehow be inhibited, there will be a greater potential for biohydrogen production under anaerobic conditions (Lay et al., 1999). Some inhibition methods involve chemical treatment which is added to waste containing hydrogen-producing bacteria and hydrogen-consuming bacteria. The hydrogen-consuming bacteria are inhibited, while hydrogen-producing bacteria survive by creating spores which dominate the created environment. When pH, Hydraulic Retention Time (HRT), and Temperature (T) of the digester are regulated and the enriched biomass is mixed with untreated (not enriched) substrate hydrogen is produced (Hansen and Cheong, 2009). In order to assess quantitatively the products of anaerobic digestion, models in the form of differential equations can be applied.

The objective of this study is to assess through simulations the impact of production of hydrogen and methane during anaerobic digestion treatment of livestock manure for varying pH, HRT and temperature conditions.
Materials and Methods

A model that can describe the dynamics of the anaerobic digestion of livestock manure through a set of differential equations has been selected (Garcia-Ochoa et al., 1999). The model is built on the following reactions: (i) hydrolysis of the waste to obtain an accessible substrate for biomass; (ii) growth of acetogenic bacteria; (iii) production of organic acids by acetogenic bacteria from the accessible substrate; (iv) consumption of the accessible substrate for acetogenic bacteria maintenance; (v) growth of methanogenic bacteria and production of methane from organic acids; and (vi) organic acids or accessible substrate consumption for methanogenic bacteria maintenance. The use of Matlab software will enable the technical variation of parameters and plotting of graphs by incorporating the equations that describe the reactions into the model.

\[ S \rightarrow S_{\text{acc}} \]

\[ Y_{2} \cdot S_{\text{acc}} + X_{\text{agb}} \rightarrow 2X_{\text{agb}} \]

\[ S_{\text{acc}} \rightarrow Y_{3} \cdot VA \]

\[ S_{\text{acc}} \rightarrow Y_{4} \cdot CO_{2} \]

\[ Y_{4} \cdot VA + X_{\text{met}} \rightarrow 2X_{\text{met}} + Y_{4} \cdot P \]

\[ VA \rightarrow Y_{6} \cdot CO_{2} \]

Where \( S = \) substrate, \( S_{\text{acc}} = \) accessible substrate, \( X_{\text{agb}} = \) biomass with acetogenic bacteria, \( Y = \) stoichiometric coefficient, \( VA = \) volatile acids, \( CO_{2} = \) carbon dioxide, \( X_{\text{met}} = \) methanogenic bacteria biomass, \( P = \) leftover product.

The corresponding equations are:

\[ \frac{dS}{dt} = -r_{1} = -[Y_{2} \cdot r_{2} + Y_{5} + r_{4}] \quad (1) \]

\[ \frac{dX_{\text{agb}}}{dt} = r_{2} \quad (2) \]

\[ \frac{dVA}{dt} = Y_{3} \cdot r_{3} - Y_{5} \cdot r_{5} - r_{b} \quad (3) \]

\[ \frac{dX_{\text{met}}}{dt} = r_{b} \quad (4) \]

\[ \frac{dP}{dt} = Y_{5} \cdot r_{5} \quad (5) \]

\[ \frac{dX}{dt} = \frac{dX_{\text{agb}}}{dt} + \frac{dX_{\text{met}}}{dt} \quad (6) \]

where \( t = \) time (days), and \( r_{1}, r_{2}, r_{3}, r_{4}, r_{5}, r_{6} \) are the reaction rates.
Results and Discussion

A model based on anaerobic digestion was selected to perform simulation studies for hydrogen production under specific scenarios. The parameters of pH, T and HRT were identified as the independent variables of the model and the biomass containing the acetogenic and methanogenic bacteria was the dependent variable. By varying sets of processing conditions as expressed through the independent variables of this model, the biomass and biogas yield is evaluated for proposing design criteria for hydrogen production from anaerobic digestion of organic waste. Similar experiments have also been performed in literature, in which hydrogen is produced without significant formation of methane. Maximum volumes of hydrogen were generated at HRT of about a day and slightly acidic pH at ambient temperature (Lay et al., 1999; Hansen and Cheong, 2009).

Conclusions

Anaerobic digestion is a good alternative to producing hydrogen from petroleum and natural gas. This process utilises food waste or/and animal waste to produce hydrogen and is therefore a cheaper method of hydrogen production which has a lot of potential in the energy sector. The simulation of the dynamics of the anaerobic digestion process requires the choice of validated model structures that take into account all the parameters affecting the production of the required output. Simulation studies could enable the generation of scenarios that can enhance hydrogen production in anaerobic digestion.

References

Application of hyperspectral imaging to assess soil salinity

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Abstract

Soil salinization is a common soil degradation processes in many countries. It has a huge influence on soil productivity. Recently advances in techniques for measuring soil properties have included optical spectroscopy techniques such a hyperspectral imagining (HSI), which makes it possible to define models for quantitative prediction of soil salinity. A review of the case studies that have used spectroscopy for soil salinity applications was conducted. Identifying a method that has potential for determining soil salinity was the primary focus of the research. Laboratory spectroscopy combined with multivariate analysis has the potential to be a useful tool for salinity management. The potential benefits of HSI technology for quantifying of salts in soil is worth pursuing because there is evidence that salinized soils have distinctive spectral features in the visible and near-infrared spectrum.

Introduction

With rapid global population growth, demand and stress on agricultural regions has increased. An important environmental hazard that emerged in many countries is soil salinity, which is now one of the most common soil degradation processes (Dehaan and Taylor, 2003; Metternicht and Zinck, 2003) that impacts on soil fertility and thus soil productivity (Taghizadeh et al., 2008). In regions where soil profiles have a naturally high concentration of salts; rising water tables transport these natural salts in the soil to the surface where they accumulate. Evaporation of surface and near surface water with high EC result in precipitation of salt on soil particles (Howari et al., 2002). In general soil salinity can be classified as dryland salinity, which occur on land without irrigation and irrigated land salinity, which arises due to the irrigation process (Juan et al., 2010). Salinity has detrimental effects on soil chemical and physical properties by reducing infiltration rate, hydraulic conductivity, and increasing erosivity and accumulation of dispersive cations such as Na⁺. Furthermore, soil salinity has effects on soil organisms, plant growth and overall biological productivity (Leone et al., 2007). Electrical conductivity (EC) is the conventional measure used to describe soil salinity but it only provides an indirect measurement of soil salt content. (Brady and Weil, 2002). Monitoring of soil salinity is required to enhance soil management approaches since salinization problems are localised and may change during the year. In this regard conventional techniques for identifying and predicting soil salinity are time-consuming, expensive, and difficult for broad-scale quantitative evaluation. For this reason more effective methods for rapid quantification of soil salinity are needed. In recent years, many soil properties, such as salinity, organic matter and moisture content have been measured using optical sensing techniques and the emerging technology of hyperspectral imaging (HSI) holds great promise (Nanni et al., 2006). Studies have revealed the VIS, NIR, and SWIR spectral regions offer the potential to develop powerful tools for assessing soil properties (Ben-Dor et al., 2009). The relationship between soil spectral data and soil properties were perhaps first studied by Condit (1970) and since then spectroscopy has became an effective method for predicting soil properties (Farifteh et al., 2006). Visual observation of the soil spectra cannot discriminate all the information in the spectrum, and statistical techniques have been developed to extract the maximum possible information from spectral data. Although HSI is capable of being used to create quantitative indicators of soil characteristics, it remains undeveloped for soil applications. This is because of a limited
availability of laboratory and field spectroscopy instruments in many countries and therefore few soil scientists are exposed the potentials of spectroscopy (Ben-Dor et al., 2009). HSI makes it possible to define models for quantitative prediction of soil salinity (Howari et al., 2002; Farifteh et al., 2006)

The present work will test the possibility of predicting salt concentrations in soils using reflectance spectroscopy for a wide range of applications for predicting soil salinity. This relatively new method has great promise for multi-temporal mapping of salt affected soils. The initial focus will be visible and near infrared reflectance (VIS-NIR) spectroscopy to demonstrate the potential of hyperspectral data for predicting and detecting soil salinity. to the technology should enable work that can help to recognise and explain areas where progressive salinization occurs rapidly and thus it could be developed as a practical management tool.

The objectives of this paper are: (1) to develop a theoretical understanding of salinazation and its relationship to reflectance data; and (2) to assess the potential efficiency of laboratory based HSI to detect soil salinity.

Materials and Methods

Laboratory experiments under controlled conditions will be carried out in order to recognize the presence and amount of salt in soils by use of laboratory spectroscopy.

Soil sampling and laboratory analyses

The soil samples will be collected from around Ireland. Soil will be air-dried, crushed and passed through a 2 mm sieve. Soil properties that are known to be influenced by accumulation of salts or affecting soil optical properties will be determined by standard laboratory methods, these include: organic matter, pH, electrical conductivity (EC), moisture content, texture, and soluble salt content (SO4, CO3, HCO3, Cl, Ca Mg, K, Na).

Each soil type will be subject to laboratory simulation of salinisation by forced surface evaporation (Farifteh et al., 2006). Saline solutions in various densities of MgCl2, NaCl, KCl, K2SO4, MgSO4, Na2SO4 and their mixtures will be prepared. The soil samples will be sub-irrigated with saline water and left to dry at room temperature. Once samples are dried, soil spectra and soil salinity will be measured for each sample. Any change in soil reflectance spectra should be due to variation in salt type and content because there will be no change in the other soil properties.

Spectral measurements and predicting soil salinity

All soil samples will be analyzed and scanned by a HSI system. All spectral replicates per sample will be averaged and subjected to multivariate analyses by, in the first instance, partial least square (PLS) regression. Samples will be allocated into calibration and validation datasets by a random split selection of the reference samples. Half of the samples will be used for calibration, while the other half will be left for validation. The best models will be defined according root mean square error in cross validation (RMSECV), coefficient of determination (R2) and RPD (define). Further multivariate statistical models will be developed as the project progresses

Discussion

There are many factors that cause soil salinization. Capillary rise, driven by evaporation is the most significant cause of precipitation of salts. Topography, farming practices, land use, drainage and rainfall also influence the salinization process. The accumulation of salts in top soil or sub soil is called salinization (Ghassemi et al, 1995). In general saline soils and Sodic soils are the two major salt-affected soil groups. There are many differences between the two groups in terms of biological, chemical and physical properties. The electrical conductivity is the most conventional indicator of salinity which is a rapid measure of soil salinity. Richards
(1954), defined soil salinity classes in terms of EC. In this classification system, non-saline soils have EC less than 2 dS/m, slightly saline; 2-4 dS/m, moderately saline; 4-8 dS/m, very saline; 8-16 dS/m and extremely saline soils were reported with EC more than 16 dS/m. The most important cations and anions that are responsible for salinity of soil are sodium, calcium, magnesium, potassium, chloride, sulphate, carbonate and bicarbonate. (Farifteh et al., 2006). They often refer to the salt minerals which are rarely pure in nature (Richards, 1954). According the research which has done by Farifteh (2008), molecules such as water and anion groups mainly result in VIS-NIR-SWIR absorption bands in the spectra of saline minerals. Furthermore, the fundamental vibration of minerals occurs in the mid infrared region and far infrared region (Nakamoto, 2009).

Varieties of analytical techniques have been developed to recognize spectral soil properties such as monovariate regressions to multivariate analyses. Recently, partial least squares regression has been extensively used for quantitative analysis of reflectance spectra. According Farifteh et al (2006), Taylor (1994) was the first researcher to show that it was possible to use spectral data to map salinity in soils. Farifteh et al (2006) showed that VIS-NIR-SWIR reflectance can be use to distinguish salt minerals from each other and others Metternicht and Zinck (2003) and Ben-Dor et al (2009), found that spectral data have potential for predicting soil salinity. Field and laboratory spectral data have been used to map soil salinization (BenDor et al, 2002). Relatively little research on the relationship between amount of salts in soils and their influence on soil spectral characteristics has been conducted. In addition the examination of spectral characteristics of salt-affected soils can help in discrimination of saline areas in order to prevent increase in soil salinity and to find approaches to sustainable soil resource management. In this regard, more attention should be given to the analysis of reflectance spectra obtained from salt affected soils. The results of this study will be used to establish a link between spectroscopy and soil salinity prediction in order to define soil salinity change over time. The approach offers more than EC because it should allow estimation of salt type rather than merely presence.

Conclusions

This paper summarizes a plan for research on the reflectance properties of soil salts to assess soil salinity using the laboratory spectroscopy. It will develop HSI as a means to predict soil salinity and cause. The short discussion presented confirms that there is a potential benefit in developing HSI technology for recognizing amount and type of salt in soil. Although there is no doubt that HSI has high potentiality for soil applications, it is not widely used in soil sciences and there is much scope for development. Spectroscopy can be a sensitive laboratory and field method to define soil salinity and assess the correlation between soil salinity and other soil properties.

References

characteristics of salt-affected soils. Geoderma 145, 196–206
Leone, A., Menenti, P. M., Buondonno, B. Letizia, A. Maffei, C. and Sorrentino, G. (2007) A field experiment on spectrometry of crop response to soil salinity, agricultural water management 89 3 9 – 4 8
IMPACT OF BIOSOLID AMENDMENTS TO SRC WILLOW PLANTATIONS ON GROUNDWATER CONCENTRATION-TRENDS

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Abstract
The impact over time on groundwater underlying short rotation coppiced willow plantations, following biosolid amendments, was assessed. Biosolid was spread using rates of 0%, 50% and 100%, where 100% represented the maximum permissible P-load. Groundwater was sampled on a monthly basis. Samples were analyzed for pH, electrical conductivity, N, P, K, Cu, Cd, Cr, Pb, Ni, and Zn. Results were analyzed for significant treatment-effects and concentration-rate trends over a 14-month period. Assessment of groundwater quality was limited to within-plot using a well-bottom approach. Movement of groundwater plumes and the direction of soil-water percolation through profile were not studied. Results showed significant treatment-effects for groundwater K and groundwater Cu arising from biosolid amendments. There were also significant downward concentration-rate trends observed over time for NO₃, Cu, and Cr but these did not appear linked to biosolid amendments. No significant upward groundwater concentration-rate trend was observed for any nutrient or heavy metal studied. Risks to groundwater quality from biosolid amendments to short rotation coppiced willow appear to be low at the spreading rates and time-scales used in this study.

Introduction
Land-spreading to energy-crop plantations is a disposal route for biosolid (BS). However, the impact of constituents such as nutrients and heavy metals (HM) on groundwater (GW) quality has still to be fully examined. This includes determining the risk of percolation of BS constituents through soil-profile, the consequent impact of these constituents on GW quality and the evolution of GW quality over time following repeated BS amendments. This paper examines the evolution of GW concentration rates following the spreading of BS on plots of short rotation coppiced (SRC) willow.

The objective is to determine whether application of BS to SRC willow plots leads to significant and sustained increases in concentration-rates of nutrients and HM in GW underlying the treatment plots.

Materials and Methods:
A plantation of SRC willow (*Salix viminalis*) was established in 2007 in Oak Park, Carlow (52°51’55” N 6°54’43” W). In Early 2008, six plots of 0.059 ha (14 m x 42 m) were laid out in the plantation, with three of the plots being used for BS application. Groundwater wells were inserted into each plot and samples taken between September 2008 and October 2009. Biosolid was applied at 3 treatment rates: 100% (BS₁₀₀), 50% (BS₅₀) and 0% (BS₀) (control) where 100% was based on the maximum rate allowable; based on the soil P-load (Teagasc 2008a). Biosolid was spread using a conventional slurry-spreader. All spreading was conducted as per regulation (DEHLG 1998; 2001; 2009). Groundwater samples were collected in accordance with USEPA guidelines (USEPA, 1996). Samples were analyzed at Teagasc’s Water Laboratory (Johnstown Castle, Co. Wexford) for N, P, K, Ni, Cd, Pb, Zn, Cu, and Cr using atomic absorption spectroscopy. Electrical conductivity (eC) and pH analysis were also conducted on all samples. Laboratory results were analysed using the SAS statistics package (SAS, 2004) and MS Excel (Microsoft Corporation, 2003). An effect was deemed to be significant at p < 0.1 due to the limitation in the number of replications.
Results and Discussion

Tables 1 to 3 show the mean, minimum and peak groundwater concentrations for BS\textsubscript{100} (Table 1) BS\textsubscript{50} (Table 2) and BS\textsubscript{0} (Table 3). The dates on which peak values were recorded is also given. The \(p\)-values outlining treatment-effects arising from BS-amendments are provided with a statement of significance. The general direction of each concentration trend is provided with significance indicated. The \(R^2\) values for GW trend-lines are provided. Table 4 shows the total quantity of each BS-amendment (per plot) applied during the experimental period, as well as a constituent breakdown by weight.

Table 1: BS\textsubscript{100} trend-rates and groundwater data

<table>
<thead>
<tr>
<th>BS\textsubscript{100}</th>
<th>units</th>
<th>(C) Mean</th>
<th>(C) Min</th>
<th>(C) Peak</th>
<th>Date of (C) Peak</th>
<th>(\text{Plot}_{TE}) ((p)-val)\textsuperscript{a}</th>
<th>Concentration trend\textsuperscript{b}</th>
<th>Trend-line (R^2)\textsuperscript{c}</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>pH Units</td>
<td>7.61</td>
<td>7.10</td>
<td>7.90</td>
<td>Sep-09</td>
<td>0.58\textsuperscript{NS}</td>
<td>Downward\textsuperscript{ns}</td>
<td>0.137</td>
</tr>
<tr>
<td>eC</td>
<td>mS/gm\textsuperscript{3}</td>
<td>0.601</td>
<td>0.350</td>
<td>0.730</td>
<td>Oct-08</td>
<td>0.17\textsuperscript{NS}</td>
<td>Upward\textsuperscript{ns}</td>
<td>0.03</td>
</tr>
<tr>
<td>NO\textsubscript{3}\textsuperscript{-}</td>
<td>mg l\textsuperscript{-1}</td>
<td>6.26</td>
<td>0.00</td>
<td>20.1</td>
<td>Feb-09</td>
<td>0.61\textsuperscript{NS}</td>
<td>Downward\textsuperscript{*}</td>
<td>0.26</td>
</tr>
<tr>
<td>PO\textsubscript{4}\textsuperscript{3-}</td>
<td>mg l\textsuperscript{-1}</td>
<td>0.016</td>
<td>0.0</td>
<td>0.196</td>
<td>Oct-08</td>
<td>0.38\textsuperscript{NS}</td>
<td>Upward\textsuperscript{ns}</td>
<td>0.14</td>
</tr>
<tr>
<td>K</td>
<td>mg l\textsuperscript{-1}</td>
<td>10.8</td>
<td>0.0</td>
<td>21.0</td>
<td>Feb-09</td>
<td>0.07\textsuperscript{*}</td>
<td>Downward\textsuperscript{ns}</td>
<td>0.00</td>
</tr>
<tr>
<td>Cd</td>
<td>ug l\textsuperscript{-1}</td>
<td>0.3</td>
<td>0.00</td>
<td>1.7</td>
<td>Mar-09</td>
<td>0.22\textsuperscript{NS}</td>
<td>No Trend\textsuperscript{ns}</td>
<td>0.00</td>
</tr>
<tr>
<td>Cr</td>
<td>ug l\textsuperscript{-1}</td>
<td>0.8</td>
<td>0.0</td>
<td>2.9</td>
<td>Feb-09</td>
<td>0.50\textsuperscript{NS}</td>
<td>Downward\textsuperscript{ns}</td>
<td>0.01</td>
</tr>
<tr>
<td>Cu</td>
<td>ug l\textsuperscript{-1}</td>
<td>12.3</td>
<td>0.00</td>
<td>29.8</td>
<td>Nov-08</td>
<td>0.01\textsuperscript{*}</td>
<td>Downward\textsuperscript{*}</td>
<td>0.61</td>
</tr>
<tr>
<td>Pb</td>
<td>ug l\textsuperscript{-1}</td>
<td>5.5</td>
<td>0.00</td>
<td>25.4</td>
<td>Feb-09</td>
<td>0.67\textsuperscript{NS}</td>
<td>Downward\textsuperscript{ns}</td>
<td>0.035</td>
</tr>
<tr>
<td>Zn</td>
<td>ug l\textsuperscript{-1}</td>
<td>4.9</td>
<td>0.00</td>
<td>33.5</td>
<td>Dec-08</td>
<td>0.64\textsuperscript{NS}</td>
<td>Downward\textsuperscript{ns}</td>
<td>0.24</td>
</tr>
<tr>
<td>Ni</td>
<td>ug l\textsuperscript{-1}</td>
<td>1.8</td>
<td>0.00</td>
<td>9.8</td>
<td>May-09</td>
<td>0.16\textsuperscript{NS}</td>
<td>Downward\textsuperscript{ns}</td>
<td>0.02</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Plot\textsubscript{TE} = \(p\) value from SAS significance testing for plot treatment-effect on mean groundwater concentrations.

\textsuperscript{b}Directional trend of groundwater concentration from Sept 08 to Oct 09;

\textsuperscript{c}Trend-line \(R^2\) square values obtained from MS Excel analysis of coefficient of determination for groundwater concentration trend-lines (2008-2009).

\* = \(P < 0.1\); ** = \(P < 0.05\); ns = Not significant.

Table 2: BS\textsubscript{50} trend-rates and groundwater data

<table>
<thead>
<tr>
<th>BS\textsubscript{50}</th>
<th>Units</th>
<th>(C) Mean</th>
<th>(C) Min</th>
<th>(C) Peak</th>
<th>Date of (C) Peak</th>
<th>(\text{Plot}_{TE}) ((p)-val)\textsuperscript{a}</th>
<th>Concentration trend\textsuperscript{b}</th>
<th>Trend-line (R^2)\textsuperscript{c}</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>pH Units</td>
<td>7.65</td>
<td>7.40</td>
<td>7.90</td>
<td>Sep-09</td>
<td>0.58\textsuperscript{NS}</td>
<td>Downward\textsuperscript{ns}</td>
<td>0.005</td>
</tr>
<tr>
<td>eC*</td>
<td>mS/gm\textsuperscript{3}</td>
<td>0.639</td>
<td>0.540</td>
<td>0.810</td>
<td>Aug-09</td>
<td>0.17\textsuperscript{NS}</td>
<td>Upward\textsuperscript{ns}</td>
<td>0.03</td>
</tr>
<tr>
<td>NO\textsubscript{3}\textsuperscript{-}</td>
<td>mg l\textsuperscript{-1}</td>
<td>5.21</td>
<td>0.00</td>
<td>20.9</td>
<td>Jan-09</td>
<td>0.61\textsuperscript{NS}</td>
<td>Downward\textsuperscript{*}</td>
<td>0.27</td>
</tr>
<tr>
<td>PO\textsubscript{4}\textsuperscript{3-}</td>
<td>mg l\textsuperscript{-1}</td>
<td>0.011</td>
<td>0.0</td>
<td>0.055</td>
<td>Aug-09</td>
<td>0.38\textsuperscript{NS}</td>
<td>Upward\textsuperscript{ns}</td>
<td>0.02</td>
</tr>
<tr>
<td>K</td>
<td>mg l\textsuperscript{-1}</td>
<td>9.6</td>
<td>3.4</td>
<td>20.8</td>
<td>Sep-08</td>
<td>0.07\textsuperscript{S}</td>
<td>Downward\textsuperscript{ns}</td>
<td>0.01</td>
</tr>
<tr>
<td>Cd</td>
<td>ug l\textsuperscript{-1}</td>
<td>0.4</td>
<td>0.00</td>
<td>1.5</td>
<td>Mar-09</td>
<td>0.22\textsuperscript{NS}</td>
<td>No Trend\textsuperscript{ns}</td>
<td>0.02</td>
</tr>
<tr>
<td>Cr</td>
<td>ug l\textsuperscript{-1}</td>
<td>3.8</td>
<td>0.00</td>
<td>43.2</td>
<td>Sep-08</td>
<td>0.50\textsuperscript{NS}</td>
<td>Downward\textsuperscript{*}</td>
<td>0.21</td>
</tr>
<tr>
<td>Cu</td>
<td>ug l\textsuperscript{-1}</td>
<td>9.4</td>
<td>0.00</td>
<td>25.1</td>
<td>Dec-08</td>
<td>0.01\textsuperscript{S}</td>
<td>Downward\textsuperscript{*}</td>
<td>0.25</td>
</tr>
<tr>
<td>Pb</td>
<td>ug l\textsuperscript{-1}</td>
<td>4.1</td>
<td>0.00</td>
<td>20.3</td>
<td>Jan-09</td>
<td>0.67\textsuperscript{NS}</td>
<td>Downward\textsuperscript{ns}</td>
<td>0.004</td>
</tr>
<tr>
<td>Zn</td>
<td>ug l\textsuperscript{-1}</td>
<td>4.1</td>
<td>0.00</td>
<td>18.2</td>
<td>Dec-08</td>
<td>0.64\textsuperscript{NS}</td>
<td>Downward\textsuperscript{ns}</td>
<td>0.04</td>
</tr>
<tr>
<td>Ni</td>
<td>ug l\textsuperscript{-1}</td>
<td>2.3</td>
<td>0.00</td>
<td>15.7</td>
<td>Apr-09</td>
<td>0.16\textsuperscript{NS}</td>
<td>Downward\textsuperscript{ns}</td>
<td>0.05</td>
</tr>
</tbody>
</table>

BS\textsubscript{50} = The plot with a 50% (intermediate) spreading rate of biosolid; all else as per Table 1
### Table 3: BS₀ trend-rates and groundwater data

<table>
<thead>
<tr>
<th>BS₀</th>
<th>Units</th>
<th>C_Mean</th>
<th>C_Min</th>
<th>C_Peak</th>
<th>Date</th>
<th>Plot (P Val)</th>
<th>Concentration Trend</th>
<th>Trend R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH*</td>
<td>pH Units</td>
<td>7.64</td>
<td>7.20</td>
<td>8.00</td>
<td>Aug-09</td>
<td>0.58NS</td>
<td>Downward***</td>
<td>0.003</td>
</tr>
<tr>
<td>eC*</td>
<td>mS/gm⁻³</td>
<td>0.606</td>
<td>0.540</td>
<td>0.660</td>
<td>Nov-08</td>
<td>0.17NS</td>
<td>Upward**</td>
<td>0.04</td>
</tr>
<tr>
<td>NO₃⁻</td>
<td>mg l⁻¹</td>
<td>3.78</td>
<td>0.00</td>
<td>12.2</td>
<td>Mar-09</td>
<td>0.61NS</td>
<td>Downward***</td>
<td>0.31</td>
</tr>
<tr>
<td>PO₄³⁻</td>
<td>mg l⁻¹</td>
<td>0.008</td>
<td>0.0</td>
<td>0.046</td>
<td>Jun-09</td>
<td>0.38NS</td>
<td>Upward**</td>
<td>0.00</td>
</tr>
<tr>
<td>K</td>
<td>mg l⁻¹</td>
<td>7.8</td>
<td>0.9</td>
<td>17.7</td>
<td>Jan-09</td>
<td>0.07S</td>
<td>Downward NS</td>
<td>0.01</td>
</tr>
<tr>
<td>Cd</td>
<td>ug l⁻¹</td>
<td>1.1</td>
<td>0.00</td>
<td>5.0</td>
<td>Dec-08</td>
<td>0.22NS</td>
<td>No Trend NS</td>
<td>0.05</td>
</tr>
<tr>
<td>Cr</td>
<td>ug l⁻¹</td>
<td>1.1</td>
<td>0.00</td>
<td>5.0</td>
<td>Feb-09</td>
<td>0.50NS</td>
<td>Downward NS</td>
<td>0.06</td>
</tr>
<tr>
<td>Cu</td>
<td>ug l⁻¹</td>
<td>8.5</td>
<td>0.00</td>
<td>20.4</td>
<td>Sep-08</td>
<td>0.01S</td>
<td>Downward **</td>
<td>0.54</td>
</tr>
<tr>
<td>Pb</td>
<td>ug l⁻¹</td>
<td>3.1</td>
<td>0.00</td>
<td>17.3</td>
<td>Feb-09</td>
<td>0.67NS</td>
<td>Downward NS</td>
<td>0.019</td>
</tr>
<tr>
<td>Zn</td>
<td>ug l⁻¹</td>
<td>3.4</td>
<td>0.00</td>
<td>16.9</td>
<td>Jun-09</td>
<td>0.64NS</td>
<td>Downward NS</td>
<td>0.02</td>
</tr>
<tr>
<td>Ni</td>
<td>ug l⁻¹</td>
<td>4.3</td>
<td>0.00</td>
<td>9.1</td>
<td>Feb-09</td>
<td>0.16NS</td>
<td>Downward NS</td>
<td>0.05</td>
</tr>
</tbody>
</table>

BS₀= The plot with a 0% (control) spreading rate of biosolid; all else as per Table 1

The only species that demonstrated a treatment-effect and a significant trend in GW over time was GW-Cu (Tables 1, 2 and 3). However this GW-Cu concentration trend was *downward* during the 14 months of sampling (Tables 1, 2 and 3). Biosolid treatment-effects on GW-concentrations seem limited to short-term peaks in concentration; longer-term trends did not appear linked to BS-amendment. There were GW concentration-rate trends for NO₃⁻, Cr. For NO₃⁻ all observed trends were downward and independent of BS-amendment rates. This general downward trend was also observed for all HMs (including Cr). Only GW eC and PO₄³⁻ exhibited any upward-trend, though the increases could not be linked to amendment or percolation to GW through plot soil-profiles. It is important to note that mean GW-K exceeded Interim Guideline Values (EPA, 1993) on all plots, which appears due to site-specific background soil-K problems. Amendment rates were limited by the high soil-P index of Oak Park soils. All soils were rated at soil-P Index 4 and spreading was limited to the P-uptake of SRC willow (Teagasc 2008b). The use of higher BS-amendment rates, or the use of BS products with higher concentrations of nutrients (or HMs) may present a greater risk to GW over time. Longer term risks to GW-quality from soil-profile percolation of BS-borne N, P, Zn, Ni, Pb, Cr or Cd or Cu following BS-amendment appears low. Given the high variance in GW concentrations, it would be useful to study GW concentration trends over longer...
periods of time and at higher rates of BS-application to determine whether the risks to GW quality from profile percolation increase at higher BS-amendment levels.

**Conclusions**

These results indicate there are risks to GW-quality from short-term pollution events involving K, linked to soil K-rates and soil- and site-specific conditions that promote K-percolation through profile. No significant upward GW-concentration trend was observed for any other nutrient or HM studied. Direct risks to GW-quality from BS-amendments to SRC willow with low background soil-K levels therefore appear low at the spreading rates and time-scales used in this study.

**References**


Adsorption isotherms of chlorothalonil in selected Irish soils

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2 Teagasc, Johnstown Castle, Wexford

Abstract

Batch adsorption experiments were performed using four tillage and one grassland soil for the non-polar fungicide chlorothalonil. The distribution coefficients ranged from 12 to 42 L kg⁻¹, indicating different behaviour of chlorothalonil in the various soils tested. The adsorption of chlorothalonil was approximately linear and the regression constant ranged from 0.71 to 0.96. The Freundlich adsorption isotherms ranged from 9 to 39 (mg⁻¹ L⁻¹) (L g⁻¹)⁻¹/n. Results showed that the adsorption of chlorothalonil was correlated to cation exchange capacity and soil organic carbon.

Introduction

Adsorption is one of the most important processes for controlling the fate of chemicals in soil. Generally, sorption of non-polar pesticides is mainly due to hydrophobic interactions with organic substances whereas sorption of polar chemicals is influenced by pH because it determines the degree of dissociation (Richter, 1996). 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 2 kg ha⁻¹ active substance and between 3 and 12 kg ha⁻¹ to vegetables and fruits. 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 to 80 µg L⁻¹ (Caux et al., 1996). Selected properties and characteristics of chlorothalonil are presented in Table 1.

Since the amount of adsorbed solute is difficult to measure directly, the extent of adsorption is usually determined indirectly by measuring the change in solution concentration after an adequate equilibration period (Green and Yamane, 1970). In equilibrium, the parameter called the distribution coefficient (Kd) is obtained and this is used in pesticide models to predict the solution concentration and the pesticide movement in the soil. However, the empirical relationship between the amount adsorbed at constant temperature and the concentration of the solute in solution determined at equilibrium is the adsorption isotherm (Hance, 1988) indicating a near-linear relationship between amounts adsorbed and concentrations in residual solution (Hartley, 1976). For many pesticides, the isotherm is nonlinear (Richter, 1996). The earliest empirical equation used to describe equilibrium data is the Freundlich isotherm (1932).

Table 1: Physical properties of chlorothalonil

<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>2.5 x 10⁻²</td>
</tr>
<tr>
<td>Water solubility (mg L⁻¹ at 25 °C)</td>
<td>0.61</td>
</tr>
</tbody>
</table>

The objective of this work was to determine the adsorption isotherms of chlorothalonil in selected Irish soils.
Materials and Methods

Chemicals
Chlorothalonil as an analytical grade (97.5% purity) was obtained from Dr. Ehrenstorfer GmbH, Germany. The stock solution of 1 mg L\(^{-1}\) was prepared in ethyl acetate from which the dilutions were made. Aqueous solutions of chlorothalonil were prepared in 0.01 M CaCl\(_2\) at final concentrations of 0.1, 0.21, 0.31, 0.42 and 0.52 mg L\(^{-1}\). All aqueous samples were made in MQ water (Purelab Ultra). All chemicals, solvents and salts were of the highest available purity.

Soils
The experiment was carried out with four major Irish soils types: Oakpark, (Co. Carlow); Rathangan (Co. Wexford), Clonroche (Co. Wexford) and Elton (Co. Limerick). The soil samples were taken from tillage sites for all the soils and from one grassland site (Elton). Five sub-samples per site were removed from 0-15 cm depth with a Dutch auger. Each subsample was air dried, sieved to <2 mm and then composited for each site. The composite samples were also analysed for parameters thought to be largely responsible for adsorptive capacity: pH, soil texture, soil organic carbon and CEC.

Extraction and chromatography
From all aqueous samples chlorothalonil was extracted using an SPE manual vacuum manifold (Phenomenex) and Strata X (Phenomenex) extraction cartridges. Briefly, ethyl acetate (2 mL) was applied for conditioning followed by the same volume of MQ water at a flow rate of 6 mL min\(^{-1}\). Samples were loaded at a flow rate of about 2 mL min\(^{-1}\) and washed at the same rate with MQ water (2 mL). Drying time was approximately 10 min after which, the chlorothalonil residue was eluted with 4 mL of ethyl acetate at a flow rate of 1 mL min\(^{-1}\). Extracted samples were analysed by GC/MS (Agilent Technologies). The column used was the HP-5, 30 m x 0.250mm x 0.25 µm (Agilent J&W) that was the equivalent to the DB-5 capillary column. All standards were made in ethyl acetate and were injected together with the samples in every run to build the calibration curve.

Determination of adsorption equilibrium during kinetic study
The preliminary equilibrium experiment started with 1:5 soil to solution ratio at a single chlorothalonil concentration of 0.31 mg L\(^{-1}\) at 20 ± 2 °C. Control and blank samples were also prepared. All the soil samples were pre-equilibrated overnight on a mechanical shaker in 25 ml glass tubes with Teflon-lined screwed caps and then spiked with chlorothalonil. At different time intervals (~0, 1, 3 and 5 hours) the soil suspensions were centrifuged and supernatants extracted. The preliminary test showed fast adsorption of chlorothalonil in the soils and thus 1:10 soil to solution ratio was adopted. The experiment continued at time intervals of ~0, 1, 3, 5, 7, and 10 hours. A 3 hours contact time was sufficient to reach the adsorption equilibrium. At equilibrium, the distribution coefficient (Kd) and the carbon normalised adsorption coefficient (Koc) were calculated (Table 2).

Determination of adsorption isotherms
The adsorption isotherm experiment was similar to the equilibrium study with one difference: the adsorption was studied at five different initial concentrations and the samples were shaken until adsorption equilibrium was reached as determined in the kinetic experiment. The equilibrium adsorption was described by the Freundlich sorption isotherm:

\[
x/m = Kf Ce^{1/n}
\]

where x/m is the amount adsorbed (mg kg\(^{-1}\)), Ce is the equilibrium concentration (mg/L), Kf is the adsorption constant, which represents the degree or strength of adsorption. The exponent 1/n takes into account non-linearity in the adsorption isotherm. When n is close to 1,
adsorption is linearly proportional to the equilibrium solution concentration. Hamaker & Thompson (1972), who summarized available data for the Freundlich isotherm of chemicals in soil, have shown that the exponent 1/n varies from about 0.7 to 1.0.

**Results and Discussion**
The adsorption isotherms of chlorothalonil in selected Irish soils are presented in Figure 1. It can be seen that the greatest rate of adsorption occurred in ET and EG soil. The statistical analysis showed that the parameter Kd was also significantly different for these soils (p=0.000).

![Figure 1: Adsorption of chlorothalonil on selected Irish soils (Error bars represent standard deviation of duplicates). □ Oakpark tillage; ◊ Clonroche tillage; Δ Rathangan tillage; × Elton tillage; and * Elton grassland](image)

The calculated values of Koc, Kd, Kf and n are given in Table 2. The Kf values were different for each soil and they were correlated to CEC (0.896) and OC (0.845) for the soils tested. The slopes (n<1) of the isotherms indicated that as the initial concentrations of chlorothalonil increased, the percentage adsorbed by the soil decreased.

<table>
<thead>
<tr>
<th>soil</th>
<th>texture</th>
<th>OC (%)</th>
<th>pH (water)</th>
<th>CEC (cmol kg⁻¹)</th>
<th>Clay (%)</th>
<th>Koc (L kg⁻¹)</th>
<th>Kd (L kg⁻¹)</th>
<th>Kf (mg 1⁻¹ kg⁻¹)</th>
<th>1/n</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oakpark T</td>
<td>sandy loam</td>
<td>2.7</td>
<td>6.64</td>
<td>15.6</td>
<td>5</td>
<td>557</td>
<td>15</td>
<td>9</td>
<td>0.71</td>
<td>0.996</td>
</tr>
<tr>
<td>Clonroche T</td>
<td>silt loam</td>
<td>3.9</td>
<td>6.33</td>
<td>19.9</td>
<td>2</td>
<td>306</td>
<td>12</td>
<td>11</td>
<td>0.89</td>
<td>0.989</td>
</tr>
<tr>
<td>Rathangan T</td>
<td>loam</td>
<td>2.9</td>
<td>6.31</td>
<td>14.9</td>
<td>21</td>
<td>582</td>
<td>17</td>
<td>12</td>
<td>0.87</td>
<td>0.997</td>
</tr>
<tr>
<td>Elton T</td>
<td>silt loam</td>
<td>4.0</td>
<td>6.57</td>
<td>23.4</td>
<td>6</td>
<td>774</td>
<td>31</td>
<td>24</td>
<td>0.86</td>
<td>0.991</td>
</tr>
<tr>
<td>Elton G</td>
<td>silt loam</td>
<td>4.7</td>
<td>6.33</td>
<td>26.1</td>
<td>10</td>
<td>888</td>
<td>42</td>
<td>39</td>
<td>0.96</td>
<td>0.994</td>
</tr>
</tbody>
</table>

R²: the correlation coefficient of the linear Freundlich adsorption equation

Elton grassland and tillage soil accounted for the highest value of CEC and OC content among all the soils tested and this was reflected in the highest sorptivity potential.
Conclusions

By using the batch technique it was possible to calculate the adsorption isotherms of chlorothalonil in Irish soils. The linearization using the Freundlich model showed that for all soils used in the study the adsorption is approximately linear. It can also be concluded that Clonroche tillage soil has a higher leaching potential for chlorothalonil into the groundwater than the Elton grassland and tillage soil based on the results of Kd parameter. The results also showed the dependency of chlorothalonil mobility on cation exchange capacity and soil organic carbon.

Acknowledgements

The author would like to thank to Pesticide Control Laboratory, Department of Agriculture, Food and Forestry, Backweston Campus, Celbridge, Co. Kildare for providing access to their facilities. This project is funded by Department of Agriculture, Fisheries and Food, Research Stimulus Fund 2008, Assessment of the vulnerability of groundwater to pesticides inputs from Irish agriculture. RSF 07-554.

References


Appendix 1
(Research projects in progress which have not been included in the Research Review)


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)

Doyle P and F Butler. Utility of HACCP to minimise risk of pathogenic bacteria in farm milk (PhD)

Donnelly-Swift R, J Connolly and N Holden. Remote sensing as a tool to monitor slurry spreading in line with the nitrates directive (PhD). Environmental Protection Agency (EPA), STRIVE programme under the National Development Plan (2010 -2013).

Herbin T and N Holden. Effects of dairy technology management on soil structure and nitrogen content (PhD) Irish Environmental Protection Agency

Keenan D, R Gormley and F Butler. Quality, antioxidant and storage properties of fruit smoothies (PhD). ISAFRUIT project was part-funded by the European Commission [Thematic Priority 5 (Food Quality & Safety), 6th Framework Programme of RTD (Contract No. FP6-FOOD 016279)].

Luijckx NL and F. Butler. Vulnerabilities in the food chain: Risk ranking of contaminants in relation to vulnerability. (PhD) European Commission (EC) ΣChain (FP6) research project.


Mussida A and F Butler. Implementation of sampling plan and application of microbiological criteria for Cronobacter Sakazakii in Ireland. (PhD) Food Institutional Research Measure (FIRM) administered by the Irish Department of Agriculture, Fisheries and Food

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: Drs Gonzales Barron, Corkery, Devlin, Drummond, ElMasry, Everard, Fagan, Francisco García Martin, Gowan, Li, Morsy, O’Rourke, Pöschl, Redmond, Shanahan, Talens-Oliag, Valdramidis, Zhang).

Ursula Andrea Gonzales-Barron, BSc, Eng, PhD

Project Title: Microbial Risk Assessment Network of Ireland

Project Leader: Prof. Francis Butler

Abstract

The overall objective of the Network is the application of microbial quantitative risk assessment to underpin national risk management actions. Currently, the researchers of the Network are generating novel modeling tools in this emerging area of risk analysis and are addressing how microbial quantitative risk assessment can be used as a risk management tool to develop appropriate food safety objectives, related industry performance objectives and performance criteria for microbial pathogens of major public health concern.

Background, Skills & Qualifications

Dr. Gonzales-Barron, an honours graduate from the Faculty of Food Industries at the National Agricultural University La Molina in Peru (1999), obtained her PhD degree at the Biosystems Engineering Department of University College Dublin, Ireland (2006). She has considerable expertise in the use of a series of classical and Bayesian predictive statistical tools for food safety applications including modelling and simulation for the conduction of risk assessments, particularly those of food pathogens. She is experienced also in predictive microbiology modelling, statistical process control and acceptance sampling, meta-analysis, zero-modified count data models for microbial load. Her current goal is to integrate all this knowledge into the development of food safety objectives and performance objectives. Dr. Gonzales-Barron has also worked on other quality aspects of food, food traceability and biometrics.

Recent publications

Gerard Corkery, BAgrSc, N.DipEng., PhD

Project Title: An Investigation of Facial Recognition of Sheep and Comb Recognition of Poultry as a method of Biometric Identification and Verification

Project Leaders: Dr Kevin McDonnell & Prof Shane Ward

Abstract
The emergence of critical disease outbreaks and escalating consumer demand for secure and traceable food has initiated global interest into novel methods of tracking and tracing animals. Food scares coupled with modern technology enhancement has helped to investigate and develop a new direction in current day electronic identification. The studies undertaken in this research investigates biometric methods as a form of identification for sheep and poultry. Facial recognition using the independent component analysis technique and retina recognition of sheep demonstrated matching rates of 96% and 99% respectively. A novel study of avian comb recognition using Fourier shape matching technique was also performed producing matching rates of ~84%. Other matching algorithms are currently being assessed and the comb matching rate is predicted to increase. An additional study considered the potential application of a novel method of e-tracking in the poultry food chain with the aim to deliver tamper-proof traceability to the consumer.

Background, Skills & Qualifications
My PhD thesis was completed in 2009 under the supervision of Dr Kevin McDonnell. I am currently employed under the Charles Parsons Energy Research Programme and the SAFSVM, School Innovation Programme as a research manager.

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**


Project Title: COOL-MEAT: A novel method for improving the vacuum cooling of cooked meats

Project Leader: Prof. Da-Wen Sun

Abstract
Strict EU guidelines demand that cooked meat joints including ham, turkey, chicken, pork and beef be cooled within rigid time limits after cooking. Conventional cooling methods depend on heat conduction to cool the inside of the joints, but the relatively low thermal conductivity of meat, coupled with restrictions on the minimum temperature of the cooling medium (to avoid surface freezing) makes it difficult to increase the rate of cooling significantly. Vacuum cooling is a rapid evaporative cooling technique for moist and porous products that offers many advantages over conventional cooling methods. However it leads to substantial weight loss and as a consequence, vacuum cooked meats are slightly less tender, drier and darker. A novel combined cook–cool technique known as immersion vacuum cooling (IVC), whereby the vacuum cooling of cooked meat is performed together with some of its cooking solution, was explored for its potential use for rapid cooling of water-cooked meat joints. Reduced yield losses and improved quality for cooked pork ham and large cooked beef joints have been reported. This project will build on this past research in order to apply and validate the technique in industry and to plan for the post-project commercial scale up of the IVC system and its subsequent market entry, whereby its uptake will improve the competitiveness of European Small and Medium Enterprises (SMEs) from the cooked meats sector.

Background, Skills & Qualifications
Graduated in 1991 at the University of Rio de Janeiro, Brazil with a BSc. in Chemical Engineering and in 1997 from the South Bank University, London, UK, with a MSc. in Food Safety and Control. Worked as a Research Assistant in Delft University of Technology: TU Delft, in The Netherlands, as part of a research team responsible for developing and testing new applications for a novel separation process (eutectic freeze crystallization). Awarded a PhD from the Biosystems Engineering Department in UCD, in 2008. The research work conducted was on an innovative combined cooking/cooling technology for cooked meat products – Immersion Vacuum Cooling. The research advanced the understanding and application of vacuum cooling allowing its application to large cooked beef products, providing rapid cooling within established quality and safety parameters. Recently appointed for a postdoctoral position in Biosystems Engineering, working on the development of IVC for the cooked meat industry, particularly aimed at European SMEs, with the objective of a potential scale-up and commercial application of this technology.

Peer-reviewed Publications


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 Publications
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**


Juan Francisco García Martín, BSc, MSc, PhD

Project Title: Novel method for assisting and accelerating the aging process of wine (ULTRAFINEWINE).

Project Leader: Professor Da-Wen Sun

Abstract
Wine producers are constantly striving to achieve a stable product with an extended period of peak taste and bouquet. Naturally aged wine tends to be milder tasting and smoother to drink than non-aged wine. Research to date has revealed that the aging process can be enhanced with the application of high pressures and temperatures over time. This project will build on past research that has demonstrated promising results for the application of temperature and pressure by ultrasonic radiation which can alter the interaction of wine ingredients to obtain chemical changes in the wine resembling many years of natural ageing. A prototype ultrasound device will be designed, built and integrated into existing wine fermentation vats in order to validate its usefulness at industrial scale for the production of homogenous wines with an extended shelf-life in very short periods of time compared to natural ageing.

Background, Skills & Qualifications
I have completed a BSc degree in Chemistry in 2001 and an MSc degree in Biotechnology and Agri-Food Engineering in 2003, both at the University of Jaén (Spain). I obtained in 2007 a PhD summa cum laude from the same University, focused on the production of xylitol and ethanol by fermentation with yeast. My PhD Thesis was awarded two Spanish National Research Environment Prizes. In 2008, I worked as a Postdoctoral researcher in the Department of Chemical Engineering at the University of Granada (Spain) for 2 years. I am currently working in Biosystem Engineering Department as postdoctoral researcher under the guidance of Prof. Da-Wen Sun.

Recent publications


Aoife Gowen, BA M.Sc., PhD

Project Title: Hyperspectral imaging system for the non-destructive assessment of mushroom quality and shelf-life prediction

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. Xinning 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:**
Noha ElSayed Morsy, BSc, MSc, PhD

**Project title:** Spectroscopic Technique for Food Authentication by Detecting Adulteration and Microbial Spoilage

**Supervisor:** Professor Da-Wen Sun

**Abstract**

The determination of food authenticity and the detection of adulteration are major issues in the food industry, and are attracting an increasing amount of attention. The intensification of agriculture and urbanisation over the last decades has created a major concern of many consumers about the authenticity and the safe of their food. Proper product description is of crucial importance in ensuring fair trading practices and enabling consumers to make liable choices. Among other motives, the high commercial value of food products of high consumer popularity leads to an expressed need for fast and reliable methods to recognise essential information about food products and to ensure the authenticity of these products. Food authenticity issues in the form of adulteration and improper description have been around for a long time and probably for as long as food has been offered for sale. Adulteration of food can be in the form of complete or partial omission or abstraction of valuable constituents; whole or partial substitution of food component with an undeclared alternative (usually cheaper); concealment of damage or inferior foodstuffs and/or adulteration by adding undeclared substances or material to increase product bulk or weight or make the product appear better value than it is. With food products major authenticity issues concern the substitution of high value raw materials with cheaper materials. On the other hand, with increased expectations for agricultural products of high quality and safety standards, the need for accurate, fast and objective quality determination of food characteristics continues to grow. Although there are some traditional methods for discovering and detecting wide range and low levels of food adulteration, spectroscopic methods are attractive options due to the speed of analysis and minimal sample preparation. Therefore, this project aims to investigate the feasibility of NIR spectroscopy for quality monitoring and authentication in minced meat to discover adulteration by offal, liver, kidney, tongue and pork as well as predicting the microbial load in minced meat due to abuse storage.

**Background and skills**

I have completed BSc and MSc degrees in Department of Food Science and Technology, Faculty of Agriculture, Suez Canal University, Egypt. My PhD study was focused on using some postharvest treatments and minimal processing techniques for enhancing the shelf life of some agricultural products. Currently, I am a visiting researcher in Biosystems Engineering Department, UCD under the guidance of Prof. Da-Wen Sun.

**Selected Peer reviewed articles**


Sharon O’Rourke, BAgrSc, PhD.

Project Title: Optical sensing and chemometric analysis of soil properties

Project Leader: Prof. Nick Holden

Abstract
Analytical costs associated with high resolution soil sampling, such as that required for precision agriculture, assessment of carbon stocks and remediation of contaminated sites, are prohibitively expensive using conventional wet chemistry techniques. Cost-effective methodology is required to validate sequestered carbon in National Greenhouse Gas accounting and to assist in soil monitoring under the pending Soil Framework Directive. The broad aim of the application of optical sensing in soil analysis is to build large scale global/national prediction models in order to overcome the heterogeneity of soil composition. National scale calibrations are being developed on Irish soils to examine the feasibility of accurate predictions for soil organic carbon, pH, available nutrients and geochemical properties. Emphasis on the influence of soil type, land use and parent rock material on prediction accuracy is being assessed. Methodology for soil image analysis is being developed to characterise soil organic carbon at the micro scale for to assess carbon security.

Background, Skills & Qualifications
I graduated in 2004 from the Faculty of Agriculture, UCD with a BAgrSc in Agriculture and Environmental Science. My PhD was completed in the Agri-Food and Biosciences Institute, Belfast and awarded from Queen’s University Belfast in December 2009. It examined a number of mitigation strategies to reduce phosphorus loss in intensive dairy farming systems; manipulation of dairy cow diets, amendment of manure with waste water treatment residual, timing and seasonality of manure applications and rainfall-runoff interactions to reduce the availability of phosphorus to overland flow pathways. In July 2009, I started my current postdoc position (Level 1) in the Bioresources Research Centre on the assessment of near infrared technology as a tool for soil analysis in Irish soils.

Peer-reviewed Publications


Martina Ringeisen (nee Pöschl), Dipl. Wirtsch.-Ing. (FH).

Project Title: Integrated Assessment of Sustainable Biogas Technology Options

Project Leaders: Prof. Shane Ward and Dr. Philip Owende

Abstract
Biogas is arguably a more versatile renewable energy source (cf. wind and solar energy), due to its determinate energy value and ease of storage, hence, potential utilization is significantly independent of factors such as geographical location and season. It can be used directly for heating and electricity generation, and as substitute for natural gas and fossil fuel applications, e.g., transportation fuel after appropriate upgrading. The potential utilization of the digestate as fertilizer can also reduce dependence on energy intensive mineral fertilizers, to further mitigate GHG emissions. Therefore, the aim of this study was to carry out an Integrated Assessment of Sustainable Biogas Technology Options for the full life cycle, from feedstock supply logistics to the derivation of useful by-products, the disposal of the spent digestate. The specific objectives were: (i) To assess the prospects for expanded utilization of biogas in Germany; (ii) To evaluate the energy efficiency of various biogas production and utilization pathways, and; (iii) To determine the environmental impacts of biogas deployment by Life Cycle Assessment of multiple production and utilization pathways. The analyses were conducted for defined case scenarios for single feedstock digestion and multiple feedstock co-digestion in small-scale (<500 kW_e) and large-scale (≥500kW_e) biogas plants, coupled with selected biogas utilization pathways, and digestate management strategies.

Background, Skills & Qualifications
I graduated in 2004 from the University of Applied Science, Munich in Germany with a Diploma in Industrial Engineering and Management (Diplom Wirtsch.-Ing. (FH)). In addition I have worked for Dr. Johannes Heidenhain GmbH (Measurement and Control Technology) and as a project engineer for Brückner Group with the main focus on biogas plants. Since 2007 I am a lecturer at the University of Applied Science, Munich for the Master courses R&D, Total Quality Management (TQM) and Innovation Management. Following my PhD, in April 2011 I took up an employment at Swiss Re Europe S.A., division in Munich, Germany as an Engineering Underwriter. Insurance underwriters evaluate the risk and exposures of potential client/ engineering projects. They decide how much coverage the client/ project should receive, how much they should pay for it, or whether even to accept the risk and insure them. I am responsible for writing treaty and facultative business for technical risks and portfolios for renewable energy projects in markets like Germany, Eastern Europe and Russia.

Peer-reviewed 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:**

Project title: Quality classification and high-speed assessment of fat, moisture and protein content distribution in Spanish cooked ham using NIR hyperspectral imaging system.

Supervisor: Professor Da-Wen Sun

Abstract

The objective of this study is to investigate the potential of hyperspectral imaging in the NIR spectral region of 900–1700 nm for the classification and characterization of Spanish cooked hams. Three different qualities of Spanish cooked ham named according to the Spanish legislation as: Category I (extra quality), Category II (normal quality) and cold cut ham (low quality), are being employed in these studies. Total protein content, sarcoplasmic and myofibrillar protein amounts, and moisture and fat content, are being measured in all hams. Hyperspectral images are being acquired for ham slices originated from each quality grade, and a subsampling approach for relating spectral and chemical features will be applied.

Background, Skills & Qualifications

Associate professor Pau Talens-Oliag received the M.Sc. in Food Science and Technology (1998) and Ph.D. in Food Science and Technology (2002) at Universitat Politecnica de Valencia (UPV). In 2003 he received a special award for his doctoral thesis “Osmotic Treatments on the cryoprotection of strawberry and kiwi fruit”. Since 2000 he has worked as a Research Professor at the UPV. He is affiliated to the School of Agricultural Engineering and Environment and practises his profession as a Tenured Associate Professor in the field of Food Science and Technology at the Department of Food Technology (DTA). He conducts his research activity in the area of Physical Chemistry of Foods at the Research Group and Food Innovation (CUINA). His research interests are focused on prediction and measurement of food physical properties in relation to food processes and the development and application of edible films. Currently, he is a Visiting Lecturer assigned to the UCD School of Agriculture, Food Science and Veterinary Medicine.

Recent Publications

Vasilis P. Valdramidis, BSc, PhD.

Project Title: Identification and simulation of microbial kinetics

Abstract
Novel accurate modelling methodologies combining knowledge of predictive modelling and engineering in order to assess the performance of bioprocesses are developed. Construction of experimental designs and integration of technological aspects in studying microbial, enzymatic and chemical inactivation phenomena under thermal and non-thermal processing conditions are the key steps of the research activities. Identification and simulation of microbial kinetics under dynamic processes by the use of deterministic and probabilistic modelling approaches are suggested. Other research activities include simulation of the dynamics of conversion of agriculture biomass and food waste energy.

Background, Skills & Qualifications
I obtained my BSc in Food Science and Technology at Aristotle University of Thessaloniki (Greece). Part of the degree was held at the University of Nottingham, UK and ATO-DLO, Wageningen, The Netherlands. I was awarded my PhD at Catholic University of Leuven, Belgium (Department of Chemical Engineering) for research on Predictive Modelling in Foods. I undertook research at the Agricultural University of Athens (Greece) in Predictive Modelling, the Agri-Food and Bioscience Institute (Northern Ireland) in non-thermal technologies, the French National Institute for Agricultural Research (France) in food equipment Hygiene and the Dublin Institute of Technology (Ireland) in non-thermal technologies before joining UCD as a research and teaching fellow.

Peer-reviewed Publications


Zhihang Zhang, BEng., PhD.

Project Title: A novel method for improving the vacuum cooling of cooked meats

Project Leaders: Prof. Da-Wen Sun

Abstract
In order to minimise the growth of pathogens in the cooked meat industry, strict EU guidelines demand that cooked meat joints must be cooled within tight time limits after cooking. Conventional cooling methods depend on heat conduction to cool the inside of the joints, but the relatively low thermal conductivity of meat coupled with the necessity to maintain a temperature of the cooling medium above 2°C (to avoid surface freezing) makes it difficult to increase the rate of cooling significantly. Vacuum cooling is a rapid evaporative cooling technique for moist and porous products that offers many advantages over conventional cooling methods, such as short processing time, extension of product shelf life and improvement of product quality, safety and nutritional content. However it leads to considerable weight loss and, due to high moisture loss, vacuum cooked meats are slightly less tender, drier and darker. There is a need to provide cooked meat producers with an effective rapid cooling method. A novel technique known as immersion vacuum cooling (IVC) has recently been researched, whereby the vacuum cooling of cooked meat together with some of its cooking solution was explored for its potential use for rapid cooling of water-cooked meat joints. Reduced yield losses and improved quality for cooked pork ham have been reported. This project will build on this past research in order to apply and validate the technique in industry and to plan for the post-project commercial scale up of the IVC system and its subsequent market entry, whereby its uptake will improve the competitiveness of European SMEs from the cooked meats industry.

Background, Skills & Qualifications
I got my Bachelor degree in Food Engineering in Shanghai fisheries University. My thesis was about ice cream manufacture. After graduation, I did research in School of Light Chemistry and Food Science in South China University of Technology, as a PhD student, for about 4 years. During the period, I was involved in many projects, like date exploitation, sugar manufacture, crystallization of an antibiotic, beer brewing, vinegar soft drink exploitation, and solution of sedimentation in soy sauce. Thereafter, I pursue a doctoral study in UCD. During the study, I carried out an EU project, about vacuum cooling of cooked ready-meal components, like meat (beef, pork and lamb), carbohydrate (rice, pasta and potato), vegetables (broccoli, carrot) and sauces. Between 2005 and 2008, I presented food safety training to food companies in Ireland, on behalf of FSAI. In 2008, I completed the PhD degree in Biosystems Engineering Department, UCD, with the thesis “Experimental and numerical study of vacuum cooling of cooked diced beef and rice”. Between 2008 and 2010, I worked as a postdoctoral researcher in UCD, on a project named MINICRYSTAL, which used power ultrasound to reduce freezing time of meat and improve quality of frozen meat. I am currently working for the above mentioned project.

Peer-reviewed Publications
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