



**FORUM FOR  
SCIENTISTS, ENVIRONMENTAL CONSULTANTS,  
REGULATORS AND ATTORNEYS**



**St John's College, Cambridge, UK  
July 24<sup>th</sup> to July 27<sup>th</sup>, 2011**

[www.rsc.org/inef](http://www.rsc.org/inef)

# FORUM FOR SCIENTISTS, ENVIRONMENTAL CONSULTANTS, REGULATORS AND ATTORNEYS

Welcome to the Cambridge 2011 edition of the International Network of Environmental Forensics (INEF) conference. The theme of the conference is the presentation of environmental topics that are uniquely focused on the use of scientific techniques to identify the source, age and timing of contaminant release to the environment (air, surface water, soil, groundwater, and marine). INEF was founded in 2008 for the express purpose of providing a forum for scientists, environmental consultants, regulators and attorneys to share state of the art information regarding the use of environmental forensics.

We hope this 3-day conference provides you with a cordial opportunity to meet and interact with your environmental forensic colleagues and to learn about the latest scientific findings and achievements of experts in the field of environmental forensics. The conference is designed to provide formal and informal setting for you to engage with other scientists, working in this field, all to allow opportunities for in-depth discussion and questioning regarding emerging environmental forensic techniques as applied in actual situations.

The organizing committee thanks the sponsors for generously supporting this event and to all of the speakers and presenters for volunteering their time and effort to make this a successful conference.

Kind Regards,

Gwen O'Sullivan,  
Conference Committee Chair

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## PROGRAM COMMITTEE

Raul J. Cano ..... California Polytechnic State University  
Lorna Dawson ..... McCauley Institute  
Frank Dorman ..... The Pennsylvania State University  
Angus Evers ..... SJ Berwin  
Jeff Focant ..... University of Liège  
Mike Fowler ..... University of Portsmouth  
Alan Jeffrey ..... Zymax Forensics  
Robert Morrison ..... DPRA, Inc.  
Steve Mudge ..... Exponent UK  
Brian Murphy ..... Exponent  
Gwen O'Sullivan ..... University of Plymouth  
Gil Oudijk ..... Triassic Technology Inc.  
Donald Patterson ..... Exponent  
Paul Philp ..... University of Oklahoma  
Leo Rebele ..... Gannett Fleming  
Ileana Rhodes ..... Shell Global Solutions  
Court Sandau ..... TRIUM Inc.  
Peiyan Sun ..... North China Sea Monitoring Center  
Zhendi Wang ..... Environment Canada



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## PROGRAM AT A GLANCE

### Sunday, July 24, 2011

4:00-8:00 Early Registration (St John's College)  
8:00-9:30 Evening Meal

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### Monday, July 25, 2011

7:30-9:00 Breakfast and Registration  
9:00-9:05 Welcome and Opening Address,  
Steve Mudge, Exponent UK  
9:05-9:10 Keynote Speakers Introduction,  
Gwen O'Sullivan  
9:10-10:00 Forensic Techniques from Exxon Valdez to Deepwater  
Horizon  
10:00-10:30 Coffee/Refreshment Break  
10:30-12:00 Petroleum Hydrocarbons (PALMERSTON ROOM)  
Environmental Litigation (BOYS SMITH ROOM)  
12:00-1:00 Lunch  
1:00-3:00 Petroleum Hydrocarbons (PALMERSTON ROOM)  
Persistent Organic Pollutants and Emerging  
Contaminants (BOYS SMITH ROOM)  
3:00-3:30 Coffee/Refreshment Break  
3:30-5:30 Petroleum Hydrocarbons (PALMERSTON ROOM)  
Air Quality (BOYS SMITH ROOM)  
5:30 Adjourn  
6:00-8:00 Lawn Games  
8:00-9:30 Banquet Dinner

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### Tuesday, July 26, 2011

7:30-9:00 Breakfast and Registration  
9:00-10:30 Petroleum Hydrocarbons (PALMERSTON ROOM)  
Air Quality (BOYS SMITH ROOM)  
10:30-11:00 Coffee/Refreshment Break  
11:00-1:00 Refined Products (PALMERSTON ROOM)  
Stable Isotopes (BOYS SMITH ROOM)  
1:00-2:00 Lunch  
2:00-3:30 Contaminated Land (PALMERSTON ROOM)  
Mine Sites (BOYS SMITH ROOM)  
3:30-4:00 Coffee/Refreshment Break  
4:00-5:30 Workshops (PALMERSTON ROOM and BOYS  
SMITH ROOM)  
5:30 Adjourn

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### Wednesday, July 27, 2011

7:30-9:00 Breakfast and Registration  
9:00-10:30 Workshops (PALMERSTON ROOM and BOYS  
SMITH ROOM)  
10:30-11:00 Coffee/Refreshment Break  
11:00-12:30 Workshops (PALMERSTON ROOM and BOYS  
SMITH ROOM)  
12:30 Adjourn followed by Punting and Lawn Picnic

## KEYNOTE SPEAKER

### Paul D Boehm



Dr. Paul D. Boehm is a Principal Scientist at Exponent and has overall responsibility for Exponent's Environmental business. He has devoted his 34 years of consulting experience to advising industrial, legal, and government clients on scientific aspects of contaminated sediments, terrestrial sites, and oil spills.

Dr. Boehm has studied and published extensively on subjects associated with the fate and effects of oil spills in the North America, Europe, and the Middle East. He has pioneered the development of chemical fingerprinting methods for petroleum hydrocarbons and PAHs and regularly contributes to the scientific literature on these matters as well as PCB fingerprinting methods. His body of work also involves investigations on historical reconstruction of chemical pollution; petroleum chemistry and methods development; water and shoreline fate and transport studies; exposure assessments; and bioavailability.

Dr. Boehm has served on several national panels on environmental/marine pollution matters; has served on several National Research Council panels; and has published over 120 papers in peer-reviewed journals.

## GENERAL INFORMATION

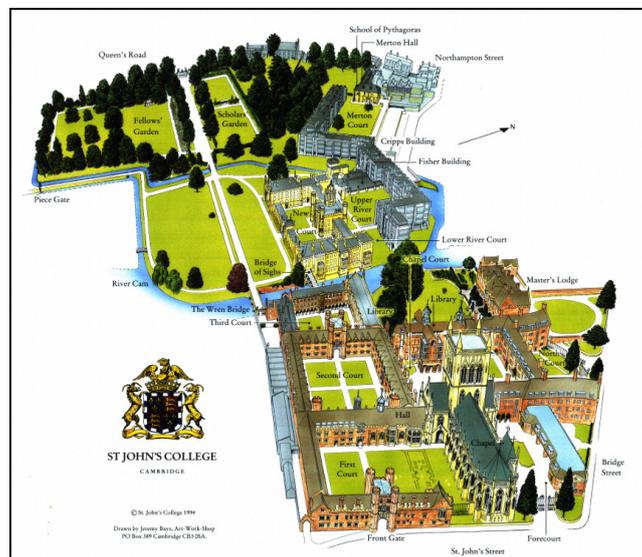
### Location and Schedule

St John's College was founded in 1511 by the last will and testament of Lady Margaret Beaufort, mother of Henry VII, on the original medieval site of the hospital of St John. The buildings have been added to steadily over the years. Outstanding features include the Dining Hall with its 16<sup>th</sup> century hammer beam roof and fine old linen-fold paneling and the Chapel built by Sir George Gilbert Scott in the Victorian Gothic style. St John's College is one of the largest of the University's residential colleges. The serene atmosphere of the ancient courts is complemented by the comfort, spaciousness and convenience of its modern accommodation

All technical sessions will be held within the Fischer Building within St John's College in either the Palmerston Room (main floor), Boys Smith Room, or Castlereagh Room. Social functions will be held in a number of locations within St John's College including the Dining Hall, Breakfast Room and Pub, further details may be obtained at the registration desk.

Early registration is available on Sunday 24<sup>th</sup> July between 16:00 and 20:00 followed by an evening meal at 20:00.

Registration is again available on Monday 25<sup>th</sup> July from 07:30. The conference will open at 09:00 and keynote presentation will follow. Technical sessions will begin mid-morning Monday and continue until lunchtime on Wednesday 27<sup>th</sup> July. For more information on the program please see program (Pages 7 - 8).



St John' College was found by Lady Margaret Beaufort, mother of King Henry VII

## Registration Desk Hours

The registration desk is located in the Fischer Building within St John's College and will be open during the following hours:

Sunday .....	16:00 to 20:00
Monday.....	07:30 to 17:30
Tuesday.....	07:30 to 17:30
Wednesday .....	07:00 to 09:00

## Speaker Information

Oral presenters are asked to provide their presentation in Microsoft PowerPoint format on disc or flash drive to the Audio Visual assistants within the session room at least 30 minutes prior to the beginning of their presentation session. Presentation should be approximately 25 minutes with 5 minutes for questions. Each speaker will be provided with a laptop, projector and microphone for their presentation.

Poster presenters are asked to hang their posters at the commencement of the conference and removed them on the final day. Poster board allocation will be provided upon check in at the conference registration desk. Material for hanging poster will be made available at each poster stand. Poster dimensions will be 4 feet (122 cm) tall by 6 feet (183 cm) wide. Authors of posters should be available to discuss content during the morning coffee breaks.

## Publication of Proceedings

Contributions made by researchers at the conference will be made available in two formats; a collection of abstracts and as a published proceedings.

Abstracts for all platform, plenary, workshop and poster presentation may be found with this technical program. Abstracts are arranged according to the individual day, time period and session according to program schedule.

All platform, plenary and poster presenters are asked to submit a manuscript for consideration within a Published Proceeding. The Royal Society of Chemistry (RSC) will publish manuscripts submitted to the conference in a book available in January 2012. Guidelines for authors may be found at the following link:

<http://rsc.org/Publishing/Books/CRCAuthors.asp>.

Presenters are asked to send manuscripts to Gwen O'Sullivan ([gwen.osullivan@plymouth.ac.uk](mailto:gwen.osullivan@plymouth.ac.uk)) before 15<sup>th</sup> July 2011 so that we can commence the peer-review process.

## Student Competition

INEF has an active student outreach program with the express purpose of encouraging students to pursue studies in environmental forensics. INEF would like to thank DPRA who have kindly sponsored the student competition at the inaugural conference in Calgary and have again agreed to sponsor the prize at the Cambridge conference.

INEF committee would also like to congratulate Caroline Gauchotte (University of Strathclyde), So-Young Moon (The University of Seoul) and John Guanhua Xie (University of Calgary) for winning the DPRA student prizes at the inaugural 2009 INEF conference in Calgary, Alberta Canada.

Caroline won 1<sup>st</sup> prize (\$500) for her oral presentation entitled "Unveiling intramolecular carbon isotopic variations in contaminants: development of on-line position specific isotope analysis". So-Young won 2<sup>nd</sup> Prize (\$250) for her poster presentation entitled "Chemical oxidative degradation of MTBE in groundwater by waste steel scrap" and John Xie won 3<sup>rd</sup> prize (\$100) for his poster presentation entitled "S and B isotope variations to track air pollutant deposition in the Castle river of Southern AB, Canada".



**Dr. Alan Jeffrey (DPRA/Zymax) presenting Caroline Gauchotte the prize for first place at the 2009 INEF**



**Dr. Court Sandau (Trium Inc.) presenting So-Young Moon prize for second place at the 2009 INEF Calgary Conference**



**Dr. Alan Jeffrey (DPRA/Zymax) presenting John Guanhua Xie prize for third place at the 2009 INEF Calgary Conference**

Building from the success and high quality of student presentations at the Calgary conference student abstracts submitted at the Cambridge conference, as posters or for technical session presentations, will be evaluated by a conference committee. Awards of \$1000 (1<sup>st</sup> prize), \$500 (2<sup>nd</sup> prize) and \$250 (3<sup>rd</sup> prize) will be presented to the three best student presentations.

## Meals and Receptions

The following meals and reception will be hosted within St John's College:

### SUNDAY, JULY 24, 2011

8:00-9:30 Dinner

### MONDAY, JULY 25, 2011

7:30-9:00 BREAKFAST AND REGISTRATION

10:00-10:30 COFFEE/REFRESHMENT BREAK

12:00-1:00 LUNCH

3:00-3:30 COFFEE/REFRESHMENT BREAK

5:30 ADJOURN

6:00-8:00 SOCIAL MIXER

8:00-9:30 DINNER

### TUESDAY, JULY 26, 2011

7:30-9:00 BREAKFAST

10:30-11:00 COFFEE/REFRESHMENT BREAK

13:00-2:00 LUNCH PRESENTATION

3:30-4:00 COFFEE/REFRESHMENT BREAK

5:30 ADJOURN

8:00-9:30 DINNER

### WEDNESDAY, JULY 27, 2011

7:30-9:00 BREAKFAST

10:30-11:00 COFFEE/REFRESHMENT BREAK

12:30 ADJOURN

1:00-5:30 PICNIC AND PUNTING

Should delegates require additional meals there are a number of cafes and restaurants within and surrounding the St John's College.

## Accommodation

St John's College is one of the largest of the University's residential colleges. The serene atmosphere of the ancient courts is complemented by the comfort, spaciousness and convenience of its modern accommodation.

Delegates who have registered at the required level (full, student and daily residential) will be provided with accommodation on campus. Check in begins on Sunday 24<sup>th</sup> July at 16:00 and may be completed at the Fischer Building within St John's College. Final check out is at 09:00 Wednesday 27<sup>th</sup> July. Facilities will be available to store luggage at the conference centre following check out. Keys and directions to rooms will be provided by staff. Each room has internet access.

## Social Activities

The committee has arranged a number of social activities to provide delegates with an opportunity to interact in an

informal setting on a professional and personal level. The following activities have been planned (weather permitting):

### MONDAY, JULY 25, 2011: Lawn Games and Social Mixer

Following the technical session on the Monday afternoon lawn games will commence in the green space in front of the Fischer Building.

A brief introduction to the etiquette and rules of croquet will be provided and the games will commence. The Royal Society of Chemistry (RSC) has kindly sponsored this event.

Following the lawn games the conference banquet will take place in the main dining hall at 8:00 pm.

### WEDNESDAY, JULY 27, 2011: Picnic and Punting

Following the workshops on Wednesday morning a lunch picnic will be provided on the banks of the River Cam. There will also be an opportunity to test your punting skills on the River Cam.

A punt is a narrow flat-bottomed boat that somewhat resembles a Venetian gondola with the curve removed. Punts generally seat up to four adults while a fifth person stands at the rear and propels the boat with a long pole.

The design was developed in the medieval period to allow for easy navigation in areas with shallow water. Until recently punts were used by commercial fishermen working the fens of East Anglia, but today they are almost exclusively used for recreation.



Punting in flat-bottomed boat, resembles a Venetian gondola

SUNDAY, July 24, 2011							
16:00-18:30	Conference Registration						
19:30-21:00	Dinner and Social Mixer						
MONDAY, July 25, 2011							
7:30-9:00	<b>BREAKFAST AND REGISTRATION</b>						
9:00-9:05	Welcome and Introduction – Steve Mudge, Exponent, UK						
9:05-9:10	Keynote Speakers-Introduction – Gwen O’Sullivan, University of Plymouth, UK						
9:10-10:00	Forensic Challenges from Exxon Valdez to Deepwater Horizon Paul Boehm, Exponent, USA.						
10:00-10:30	<b>COFFEE/REFRESHMENT BREAK</b>						
BREAK OUT PLENARY SESSIONS							
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5:30-7:00	<b>LAWN GAMES (Bowling and Croquet) and SOCIAL MIXER</b>						
7:30-9:00	<b>DINNER</b>						

TUESDAY, July 26, 2011			
7:30-9:00	<b>BREAKFAST</b>		
	<table border="0" style="width: 100%;"> <tr> <td style="width: 50%; text-align: center;"> <b>ROOM A</b>            Petroleum Hydrocarbons            Moderator – Chun Yang         </td> <td style="width: 50%; text-align: center;"> <b>ROOM B</b>            Air Quality            Moderator – Ileana Rhodes         </td> </tr> </table>	<b>ROOM A</b> Petroleum Hydrocarbons Moderator – Chun Yang	<b>ROOM B</b> Air Quality Moderator – Ileana Rhodes
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13:00-2:00	<b>LUNCH</b>		
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3:30-4:00	<b>COFFEE/REFRESHMENT BREAK</b>		
	<b>WORKSHOPS</b>		
4:00-5:30	<table border="0" style="width: 100%;"> <tr> <td style="width: 50%;"> <b>ROOM A</b>            Source Apportionment of Industrial Fugitive Dusts: Developments in Passive Dust Monitoring            Hugh Datson (DustScan Ltd), Mike Fowler (University of Portsmouth), and Ben Williams (DustScan Ltd)         </td> <td style="width: 50%;"> <b>ROOM B</b>            Utilization of Stable Isotopes in Environmental and Forensic Geochemistry Studies.            Paul Philip (University of Oklahoma)         </td> </tr> </table>	<b>ROOM A</b> Source Apportionment of Industrial Fugitive Dusts: Developments in Passive Dust Monitoring Hugh Datson (DustScan Ltd), Mike Fowler (University of Portsmouth), and Ben Williams (DustScan Ltd)	<b>ROOM B</b> Utilization of Stable Isotopes in Environmental and Forensic Geochemistry Studies. Paul Philip (University of Oklahoma)
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5:30	<b>ADJOURN</b>		

WEDNESDAY, July 27, 2011			
7:30-9:00	<b>BREAKFAST</b>		
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12:30	<b>CONFERENCE ADJOURNS FOLLOWED BY PUNTING AND LAWN PICNIC</b>		



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## KEYNOTE SPEAKER

MONDAY, JULY 25, 2011  
 9:00 – 10:00

### PALMERSTON ROOM:

#### FORENSIC CHALLENGES FROM EXXON VALDEZ TO DEEPWATER HORIZON

Paul D. Boehm, Ph.D.

Exponent, 3 Clock Tower Place, Suite 205, Maynard, MA 01754

Presenting Author: Telephone: 978-461-4601, Fax: 978-461-1223,  
 E-mail: [pboehm@exponent.com](mailto:pboehm@exponent.com)

The chemical fingerprinting of petroleum for purposes of supporting environmental investigations has evolved from the 1970s reliance on packed column gas chromatograms and infrared spectroscopy to today's reliance on molecular and isotopic methods. Major events such as the Exxon Valdez and Deepwater Horizon oil spills have given impetus to the evolution of forensic methods by presenting new and complex questions to environmental forensic chemists. Challenging questions have ranged from source differentiation in mixed petrogenic source inputs characteristic of the background in Alaska and the Gulf of Mexico to apportionment of PAHs in sediments. In this evolution, the Exxon Valdez and Deepwater Horizon oil spills have accelerated the merging of petroleum geochemical methods used for exploration of petroleum resources and those environmental chemical methods used for environmental fate, transport, and damage assessment studies. This history, the developments over the last 20+ years, and recent advances in the last 18 months will be discussed.

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## PLENARY ABSTRACTS

MONDAY, JULY 25, 2011

10:30 – 12:00

### PALMERSTON ROOM: PETROLEUM HYDROCARBONS

#### FINGERPRINTING CRUDE OIL SPILLS, FROM LOS ANGELES TO DEEPWATER HORIZON

##### PLATFORM PRESENTATION

Alan JEFFREY<sup>1</sup>, and Robert BARRICK<sup>2</sup>

<sup>1</sup>DPRA/Zymax Forensics 600 S. Andreasen Drive, Suite B,  
Escondido, CA 92029

<sup>2</sup> Cardno Entrix

\*Presenting Author: Telephone: 760.781.3338  
E-mail: alanj@Zymaxusa.com

Just when memories of the Exxon Valdez crude oil spill were fading, the Deepwater Horizon blowout in the Gulf of Mexico reminded us how catastrophic crude oil releases to the environment can be. A crucial aspect in investigating oil releases is definitively identifying the source. Where a source has been identified, as in the Deepwater Horizon blowout, the issue then becomes distinguishing the oil from that source from oil from other potential sources.

Chemical fingerprinting provides the most direct way of correlating released oil with potential sources. Fingerprinting crude oils utilizes the distributions of hydrocarbons like alkanes, polyaromatics, and biological markers, and stable isotope ratios, which can be unique to a particular crude oil. What can confuse the correlation of spilled oil with potential sources are the effects on the spilled oil of biodegradation and other weathering processes, which can eliminate some chemical fingerprints and alter others. In some cases, however, weathering can be a useful correlation indicator itself, eliminating as a suspected source a crude oil that is more degraded than the released oil.

There have been a number of well publicized incidents recently of crude oil spills. In October 2010, crude oil entered a water supply pipeline in Long Beach, CA and workers had to shut off water supplies to the Port of Long Beach. Because of the difficulty in removing the oil residues, the city has had to divert water supplies around the affected pipeline. A few months later, oil surfaced along the Dominguez Channel in Los Angeles, sparking a search by divers to determine the source. In an earlier incident twenty years ago, an oil tanker off Huntington Beach ruptured its hull and spilled crude oil that washed up as tar balls along the beach, mixing with the omnipresent population of southern California tar balls from natural offshore seeps. In these cases, identification of the source is complicated by the fact that Los Angeles sits on top of a large oil province, where crude oil is pumped from many producing fields, natural oil seeps are common, eg La Brea tar pits, and old, improperly sealed oil wells leak crude oil. In the Deepwater Horizon incident, crude oil from the blowout was released into the Gulf of Mexico, which has its own population of oil from natural seeps, other oil production, and tanker traffic.



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For further information & registration please contact SepSci@leco.de or visit Alec Kettle at the LECO stand.

**Fingerprinting**

- Age Dating
- Fuel Identification
- Source Identification



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**D/H <sup>13</sup>C/<sup>12</sup>C <sup>15</sup>N/<sup>14</sup>N <sup>18</sup>O/<sup>16</sup>O <sup>34</sup>S/<sup>32</sup>S Isotope Analysis**

- <sup>13</sup>C/<sup>12</sup>C of MTBE, BTEX, & Chlorinated Solvents in Water & Soil
- D/H & <sup>13</sup>C/<sup>12</sup>C of Crude, Petroleum Fuels & Gases
- <sup>34</sup>S/<sup>32</sup>S & <sup>18</sup>O/<sup>16</sup>O of Sulfate in Water
- <sup>15</sup>N/<sup>14</sup>N & <sup>18</sup>O/<sup>16</sup>O of NO<sub>3</sub>
- D/H & <sup>18</sup>O/<sup>16</sup>O in Water
- <sup>15</sup>N/<sup>14</sup>N of NH<sub>3</sub>

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The various fingerprinting techniques that were used to shed light on the sources of the crude oil releases in these incidents will be presented. In particular, chemical fingerprints of Deepwater Horizon crude oil will be compared with other Gulf of Mexico crude oils, and ways to distinguish Deepwater Horizon crude oil from chemically similar South Louisiana crude oils will be discussed.

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## NEW METHODS AND CONCEPTS IN ENVIRONMENTAL FORENSICS

Gil OUDIJK<sup>1\*</sup>

Triassic Technology, Inc., 57 Hamilton Avenue, Hopewell,  
New Jersey 08525 USA

\*Presenting Author: Telephone: +1.609.466.9628  
Fax: +1.609.466.4437, E-mail:  
goudijk@triassictechnology.com

Four case studies are provided where new methods are used to fingerprint and age date petroleum releases impacting ground water.

Leaded gasoline: To assess the age of leaded gasoline releases, chemical analyses can now be performed for tetraethyllead (TEL) and tetramethylead (TML) degradation byproducts. Previously, investigators could only analyze separate-phase samples for TEL and TML, because of the low aqueous solubility of these compounds. However, the degradation byproducts of TEL and TML are water soluble and can be identified in ground-water samples. Their presence confirms that a leaded gasoline release occurred.

Diesel fuel: Releases of diesel fuel to the environment have been dated through the use of weathering rates, in particular, the ratios of n-alkanes to isoprenoids. However, the n-alkanes are quite susceptible to environmental weathering and they are often depleted within 20 years. The isoprenoid, pristane, exists as three different stereoisomers and their degradation rates can differ. By comparing the ratios of these stereoisomers, the magnitude of weathering and, potentially, the age of the releases can be assessed.

Anaerobic versus aerobic conditions. The presence of oxygen in the subsurface environment will have significant impacts on the weathering of diesel-fuel components. Knowledge of the subsurface geochemical and microbiological environment (oxic v. anoxic or aerobic v. anaerobic) will provide valuable information on the weathering and transformation of diesel-fuel releases and help to fingerprint and/or age date these releases.

Biomarkers. The use of biomarkers, such as bicyclic sesquiterpanes can provide information on the mode of petroleum releases, such as a catastrophic versus a chronic (long-term) discharge. Changing biomarker signatures commonly represent a long-term release. The biomarker signature will vary as the crude-oil source to refineries changes. Therefore, a long-term discharge should exhibit different signatures. However, a catastrophic release is often evidenced by similar biomarker signatures.

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## FORENSIC FINGERPRINTING AND SOURCE IDENTIFICATION OF THE 2009 SITE X (ONTARIO) OIL SPILL

Zhendi WANG<sup>1\*</sup>, C. Yang, Z. YANG, J. Sun, B. HOLLEBONE

C.E. Brown, and M. Landriault

1 Emergencies Science and Technology Section, EOALRSD,  
Science & Technology Branch, Environment Canada, 335  
River Road, Ottawa, Ontario, Canada K1A 0H3

Presenting Author: Telephone: 613-990-1597  
Fax: 613-991-9485, E-mail: zhendi.wang@ec.gc.ca

This paper presents a case study in which integrated forensic oil fingerprinting and data interpretation techniques were used to characterize the chemical compositions and determine the source of the 2009 Site X (Ontario) oil spill incident. The diagnostic fingerprinting techniques include determination of hydrocarbon groups and semi-quantitative product-type screening via GC, analysis of oil-characteristic biomarkers and the extended suite of parent and alkylated PAH (polycyclic aromatic hydrocarbon) homologous series via GC-MS, determination and comparison of a variety of diagnostic ratios of "source-specific marker" compounds, and determination of the weathering degree of the spilled oil, and whether the spilled oil hydrocarbons have been mixed with any other "background" chemicals (biogenic and/or pyrogenic hydrocarbons). The detailed chemical fingerprinting data and results reveal the following: (1) All four samples are mixtures of diesel and lubricating oil with varying percentages of diesel to lube oil. Both samples 1460 and 1462 are majority diesel-range oil mixed with smaller portion of lube oil. Sample 1461 contains slightly less diesel-range oil. Sample 1463 is majority lubricating-range oil. (2) The diesel in the four diesel/lube oil mixture samples was most likely the same diesel and from the same source. (3) The spill sample 1460 and the suspected-source sample 1462 have nearly identical concentrations and distribution patterns of target analytes including TPHs, n-alkane, PAHs and biomarker compounds; and have nearly identical diagnostic ratios of target compounds as well. Furthermore, a perfect "positive match" correlation line (with all normalized ratio data points falling into the straight correlation line) is clearly demonstrated. It is concluded that the spill oil water sample 1460 (#1, from the water around the Vessel enclosed by a boom) matches with the suspected source sample 1462 (#3, from the Vessel engine room bilge pump). (4) From the n-alkane and PAHs analysis, it appears that the oil in the spill sample 1460 is slightly more weathered in comparison with sample 1462. The minor differences in fingerprints of two samples were most likely caused by weathering effects. (5) The sample 1461 (#2, from the Vessel engine room bilge) and the sample 1463 (#4, from the Vessel bilge waste collection tank) demonstrated significantly different fingerprints and diagnostic ratios of target compounds from that of the spill sample 1460. This was caused most likely by percentages of diesel to lube oil in these two samples different from that in the spill sample 1460.

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## BOYS SMITH ROOM: ENVIRONMENTAL LITIGATION

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### ENVIRONMENTAL LIABILITY- THE EU AND UK LEGAL FRAMEWORK

Angus EVERS<sup>1\*</sup>

<sup>1\*</sup> SJ Berwin LLP, 10 Queen Street Place, London EC4R 1BE,  
United Kingdom

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Fax: +44 (0)20 7111 2000,  
E-mail: angus.evers@sjberwin.com

In 2004 the European Union (EU) adopted Directive 2004/35/EC on environmental liability with regard to the prevention and remediation of environmental damage, more commonly known as the "Environmental Liability Directive". The Directive creates an EU-wide framework for preventing and remediating environmental damage which Member States were required to implement by 30 April 2007. The Directive covers damage to, or the imminent threat of damage to, land, water and protected species or habitats. Where environmental damage or an imminent threat of environmental damage occurs, the Directive adopts a "polluter pays" approach to liability.

This presentation will review the main provisions of the Environmental Liability Directive, including the rationale behind it, its scope, and the defences and exemptions to liability. The case law on the interpretation of the Directive will also be analysed.

The presentation will use the UK as an example of how an EU Member State has implemented the Directive, with a review of the Environmental Damage (Prevention and Remediation) Regulations 2009, which apply in England and Wales. Particular emphasis will be placed on enforcement procedures and case studies of how the Regulations have been used to deal with pollution incidents will be used. The presentation will also address briefly how the Regulations interact with pre-existing regulatory regimes in England and Wales, in particular the Environmental Protection Act 1990, the Water Resources Act 1991 and the Wildlife and Countryside Act 1981.

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### ENVIRONMENTAL FORENSIC APPROACH IN MALAYSIA: AN ANALYSIS OF ENVIRONMENTAL LEGISLATION

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Environmental management in Malaysia has shown remarkable achievements with little approach in early years and gradually ascending to advocate better and more focus control with the introduction of Environmental Quality Act, 1974. Over the years the law concurrently supports the environmental policy regarding the pollution control, prevention approach and also enhancement of the environment. One of the key elements of pollution control is the environmental enforcement and inspections related to functions of the environmental organisation; the Department of Environment and the provision of the environmental legislation. In many instances the environmental enforcement and inspection are led to the investigation and identification of the environmental predicaments, sources of the contaminants and identifying who are the responsible parties involved. This situation fits the new approach called environmental forensic. The paper discussed the integration of the environmental management in Malaysia with environmental pollution approach. Focus is on the discussion of the Environmental Quality Act, 1974 and its provision that fits the environmental forensic approach with a complementary reference to the United Kingdom and European Directives.

**Keywords:** environmental management, environmental legislation, pollution control, environmental forensics

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### NATURAL RESOURCE DAMAGES

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The overriding public interest in the preservation and reclamation of natural resources is one of the most important factor driving the rapid development of natural resource damages (NRD) programs in the United States. As the nature of the public interest in natural resources has evolved, so has environmental legislation. The idea of having polluters pay to resolve restorable resources is taking hold on both the state and federal level. Historically, this development marks another step in the evolution of environmental laws. The focus of the first significant environmental laws in the 1950s and 1960s was significantly different than the present day focus of environmental legislation. Initially, environmental efforts were prompted by preservationist ideals -- the desire to maintain the "great" natural resources and save such sites from exploitation. For example, in the 1960s, the proposed construction of a dam in the Grand Canyon raised awareness about environmental protectionism -- the need to preserve the legacy of a nation's natural resources. Legislation was directed primarily at the behavior of government agencies, as opposed to private individuals. Congress enacted environmental legislation to "ensure that government agencies respected social and cultural values when pursuing development projects," rather than to address the illegal conduct of polluters and the consequences of their actions.

In effect, we have begun to move from a “great places” approach to natural resources to a “reclaiming” or “restoring” approach. While a few “great place” battles still continue, such as the effort to preserve the Arctic Wilderness, today environmental activism and legislation is inspired by the need to restore and prevent further exploitation of injured and diminishing natural resources such as the nation’s coastal areas. Environmentalism is motivated less by the need for preservation and more by the desire for reclamation. People now understand two things about natural resources. First, natural resources can be salvaged, even in seemingly impossible industrial and urban locales. The technology and the capacity to reclaim and recreate natural resources have improved exponentially and will continue to improve. The Meadowlands in New Jersey is a classic example of this type of transformation potential. At one time the world’s largest dump, “[t]he Hackensack Meadowlands is perhaps the largest urban wetland complex in the northeastern United States. It lies along the Hackensack River and is located within the New York-Newark metropolitan area. Given this location, the Meadowlands has been greatly impacted by urban and port development . . . . The New Jersey Meadowlands Commission (“NJMC”) is acquiring wetlands and management rights and making zoning changes . . . in an effort to protect the remaining wetlands. Plans are underway to restore the Hackensack Meadowlands ecosystem . . . . Wetland restoration and enhancement efforts include restoring tidal flow, removing contaminated soils, creating open water areas, controlling invasive species . . . and regulating water levels . . . . The main hope for the future of Meadowlands wetlands as well as for other urban wetlands is that as many as possible will be set aside as open space for our benefit and for future generations and that wetland restoration efforts will be accelerated to revitalize significantly impacted wetlands and to rebuild lost wetlands wherever practicable. Wetlands are natural resources that, among other things, increase the quality of life for urban residents across America.” Second, people take property rights more seriously and also understand that the public’s right to its property or “commons” is important for both monetary and nonmonetary reasons. Natural resources that were formerly viewed with little interest or real understanding, such as groundwater, have generated a special need for attention in light of the crucial role they will play in the future of this country’s survival.

The enactment of the Comprehensive Environmental Compensation, Response and Liability Act of 1980 (“CERCLA” or “Superfund”) was an attempt by Congress to respond to the massive pollution and contamination of the environment in the United States. However, as the past twenty-five years has demonstrated, CERCLA has not been effective in enabling the recovery of damages for pollution and restoring injured natural resources. In fact, CERCLA has actually enabled polluters to prolong any meaningful cleanup of natural resources by permitting them to engage in years of ineffective and mostly useless remediation and feasibility studies. Moreover, the response time of CERCLA is poor, thus prolonging what is already a tediously slow road to restoration.

The pursuit of NRD is the last chance to accomplish what the United States originally wanted to do with Superfund - - to cleanup the nation’s natural resources and make the polluters compensate both the government and the public for the injuries that they have suffered and will continue to

endure. Because our natural resources are being destroyed and disappearing at an alarming rate, NRD litigation has become increasingly important to preserve these natural assets for the public and for future generations.

<sup>1</sup> Richard L. Berkman & W. Kip Viscusi, DAMMING THE WEST: RALPH NADER’S STUDY GROUP REPORT ON THE BUREAU OF RECLAMATION 75 (1973).

<sup>2</sup> Robert V. Percival, Environmental Federalism: Historical Roots and Contemporary Models, 54 MD. L. REV. 1141, 1158 (1995).

<sup>3</sup> Id.

<sup>4</sup> RALPH W. TINER, JOHN Q. SWORDS, & BOBBI JO MCLAIN, U.S. FISH & WILDLIFE SERVICE, WETLAND STATUS AND TRENDS FOR THE HACKENSACK MEADOWLANDS 1, 27 (Dec. 2002), available at <http://library.fws.gov/Wetlands/Hackensack.pdf>.

<sup>5</sup> See Allan Kanner, The Public Trust Doctrine, Parens Patriae and the Attorney General as the Guardian of the State’s Natural Resources, 16 DUKE ENVTL. L. & POL’Y F. 57, 94-96 (Fall 2005). Historically, the public “common” was a public area used by villagers for livestock grazing. Additionally, the villagers had the right to “cut wood, to fish, and to cut peat or turf for fuel.” Id. at 64. The common area was used and regulated by the villagers for purposes of mutual sustainability and benefit.

<sup>6</sup> See id. at 83.

<sup>7</sup> 42 U.S.C. §§ 9601-9675 (2000).

<sup>8</sup> See generally Allan Kanner, Rethinking Superfund, 20 NAT’L ASS’N ENVTL. PROFS News 19 (May-June 1995).

**MONDAY, JULY 25, 2011**  
**1:00 – 3:00**

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**PALMERSTON ROOM:**  
**PETROLEUM HYDROCARBONS**

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**SOURCES OF PETROLEUM POLLUTION: NEW  
DIMENSION OF HOPANE**

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Source identification of petroleum pollution in the marine environment is one of the most challenging tasks faced by environmental organic geochemists. Molecular markers such as hopane and polycyclic aromatic hydrocarbons are frequently employed to determine the petroleum pollution origins. Although PAHs represent both non-petroleum and petroleum sources of pollution, hopane provides a unique chemical structure for the identification of lubricating and crude oil sources. Eight sediment cores were collected from selected locations in Peninsular Malaysia from 2005 to 2008 to identify the source of petroleum pollution.

The results revealed significant heterogeneity in PAHs and hopane source identifiers. Alongside petrogenic PAHs, hopanes exist as dominant peaks in total ion chromatograms. However, hopane peaks were comprehensively depleted alongside pyrogenic PAHs. Pyrogenic PAHs originate from petroleum combustion and/or burning process of organic materials. Hence, the absence of hopanes indicates negligible contribution of petroleum pollution as observed in most samples dated in the beginning of 20th century and before. Depletion of hopanes alongside of pyrogenic PAHs showed existence of R and S peaks from C31 to C35 homologues. The hopane compounds with single peak from C27 to C30 either showed dramatic decline or total absence. The stereochemistry, symmetry and polarity of R and S peaks for hopanes remained stable in pyrogenic PAHs fractions.

It can be postulated that high temperature combustion process may have altered the molecular structure of single peaks to an unknown triterpanes, hopenes or even terpenes. However, hopanes does not exist in some petroleum products such as gasoline, studying the effect of high temperature combustion of organic molecules resulting in the formation of new hopane or hopene compounds is the subject of interesting future research and deserves special attention in the organic geochemists community.

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#### **APPLICATION OF SOLID PHASE EXTRACTION CATRIDGES (SPE) AND PROGRAMMABLE TEMPERATURE VAPORIZATION LARGE VOLUME INJECTION (PTV-LVI) COUPLED TO GAS CHROMATOGRAPHY-MASS SPECTROMETRY (GC-MS) IN OIL FINGERPRINTING ANALYSIS**

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Forensic oil spill identification relies largely upon the analysis of the chemical fingerprints of a series of petroleum hydrocarbons of the spilled oil and the suspected source. The established oil analysis methods are usually time-consuming and tedious in the sample preparation and instrumental analysis. This work aims to develop a rapid analytical method, which meanwhile does not compromise the function and reliability. Commercial solid phase extraction (SPE) cartridges were applied for the cleanup and fractionation of oil samples into aliphatic and aromatic fractions, and the fractions were subsequently subjected to direct analysis using a programmable temperature vaporization-large volume injection (PTV-LVI) system coupled to gas chromatography-mass spectrometry (GC-MS) without further concentration procedure.

Operational parameters for SPE fractionation and PTV-LVI-GC-MS analysis were investigated. Commercial silica gel/cyanopropyl (SiO<sub>2</sub>/C<sub>3</sub>-CN) SPE cartridges were able to successfully separate oil samples into aliphatic and aromatic fractions with a small volume of hexane and dichloromethane (DCM)/hexane mixture, respectively. PTV-LVI-GC-MS analysis demonstrated high repeatability

and sensitivity particularly for relatively higher boiling points compounds. The detection limits of chromatographic analysis were improved between 1 and 2 orders of magnitude for n-alkanes and PAHs by increasing conventional injection volume of 1.0 µL to a large injection volume of 20 µL through an Agilent Multimode inlet in solvent vent mode. Tedious sample pretreatment procedures were simplified by eliminating the preparation of chromatographic column and the solvent evaporation step. In addition, a less amount of sample is needed for sample preparation since the detection limits are enhanced greatly for target compounds.

This method was tested for the fingerprinting analysis of various crude oils, refined petroleum products, and environmental contaminated sediment samples. Characterized target hydrocarbons include n-alkanes, unsubstituted priority PAHs and their alkylated homologues, and biomarker terpanes and steranes. The concentration profiles and diagnostic ratios of target compounds are both comparable to those obtained by the conventional silica gel column-hot split/splitless GC-MS method.

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#### **AN OBJECTIVE METHOD FOR COMPARING UNRESOLVED COMPLEX MIXTURE (UCM) 'HUMPS' IN GAS CHROMATOGRAMS OF HYDROCARBON EXTRACTS FROM SOILS POLLUTED WITH PETROLEUM PRODUCTS**

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Petroleum and many of its products contain complex mixtures of hydrocarbons, which are only partially resolved when analysed by gas chromatography (GC), producing chromatograms with distinctive 'humps', usually referred to as 'unresolved complex mixtures' (UCM). In such chromatograms, resolved compounds, such as n-alkanes, appear as rider peaks on the UCM. The shape of a UCM on the horizontal (time) axis is determined by the relative proportions of the individual compounds which contribute to the UCM. Although sophisticated methods, such as two-dimensional GC and GCMS, have been used to identify the components of UCMs, a simpler approach of using UCMs to compare different petroleum sources is to consider UCM shape (after smoothing). Such a method has been used to make visual comparisons of different brands of motor oils (Reardon et al., 2007). In many environmental matrices, including soils, some of the resolved rider peaks may originate from non-petroleum sources, such as plant waxes. Under such conditions, comparison of UCM humps of petroleum origin would require the rider peaks to be removed, so as not to influence the smoothed UCM shape. An objective method of comparing UCM shapes was developed for soils potentially contaminated with petroleum products.

Using raw chromatographic data imported into Microsoft Excel, the UCM comparison method involved the following stages:

- (i) Reducing the number of data points comprising the chromatogram, typically using every 50th original data point, for original data points collected at a rate of 600/min.
- (ii) Removal of rider peaks and smoothing to produce a smoothed UCM by obtaining the 40% percentile value from a 'moving average' of 20 data points.
- (iii) Subtraction of a 'background' sample (reagent blank) run under identical conditions to those of the samples, and smoothed in the same way.
- (iv) Producing a scatter plot to compare two samples (plotting the points from one sample against the other).
- (v) Obtain correlation coefficients from the scatter plots of all pairwise comparisons. These values give an indication of the degree of similarity, with a perfect 'match' yielding a value of unity.

Reference: Reardon, M.R., Allen, L., Bender, E.C. and Boyle, K.M. (2007) Comparison of motor oils using high-temperature gas chromatography-mass spectrometry. *J. Forensic Sci.* 52,656-663.

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### NEXT GENERATION CHEMICAL FINGERPRINTING: CASE STUDY OF COAL TAR FROM FORMER MANUFACTURED GAS PLANTS

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Traditional chemical fingerprinting methods generally follow a tiered approach using gas chromatography (GC) in combination with either flame ionisation detection (GC-FID) or mass spectrometry (GC-MS). We propose an updated version of this approach by incorporation of advanced analytical techniques such as comprehensive two-dimensional gas chromatography (GCxGC TOFMS) and compound specific isotope analysis (CSIA).

Firstly, a one-step sample extraction and cleanup is performed by accelerated solvent extraction (ASE), to provide a single extract for analysis by reversed phase GCxGC TOFMS. This approach avoids time-consuming chemical fractionation and allows all chemical classes to be monitored in a single analytical step. Statistical data processing methods, including principal component

analysis (PCA) and artificial neural networks (ANN), are then employed to uncover relationships within the large datasets, and thus assist with source differentiation. Finally, CSIA is employed as an ancillary method to resolve any ambiguous data. Accelerated solvent extractions were modified to provide fractionated extracts suitable for carbon and hydrogen isotope analysis, once again avoiding conventional chemical fractionation processes.

We present this novel approach through the example of coal tar; a common subsurface contaminant found at former manufactured gas plants (FMGPs). Coal tar is generally found as a dense non-aqueous phase liquid (DNAPL), a liquid which is both heavier than water and immiscible in water. The complex chemical composition of coal tar, and the worldwide abundance of FMGP sites, poses an interesting challenge for environmental forensic investigations.

We offer an insight into the chemical composition of coal tar by the assessment of nineteen tars, from FMGP sites across the United Kingdom, using our advanced chemical fingerprinting method. Correlations were discovered between coal tar composition and historic gas manufacturing processes allowing a classification model to be developed to aid source identification and to help identify liability at FMGP sites.

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### BOYS SMITH ROOM: POPS AND EMERGING CONTAMINANTS

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#### CHANGES IN SIGNATURE DURING MATERIAL TRANSFER OF PCBs IN EUROPEAN PLAICE

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Polychlorinated biphenyls (PCBs) are an important class of ubiquitous, environmental contaminants. Commercial mixtures are often complex containing a number of congeners each with its own physical and chemical properties; they are stable and environmentally persistent, potentially over geological time scales. The congener profile may be used as a signature of the original PCB source and used in apportioning contribution in multi-source environments. However, the variation in the three-dimensional structure of PCBs in terms of both the degree of chlorination and chlorination pattern, influences physical properties such as the n-octanol/water partition coefficient (Kow) leading to differential partitioning. This study exposed female European plaice (*Pleuronectes platessa*) to Aroclor 1254 (A1254) during the spawning season and assessed the degree and nature of maternal PCB transfer to the eggs by subsequent tissue analysis. Following quarantine, plaice were given either low, medium or high doses of A1254. Fish in the control tank received placebo doses. Fish were fed every two days. When females were

judged ripe, they were removed from the holding tanks, anaesthetised lightly, measured and weighed. Eggs were hand-stripped, collected in a clean, glass beaker and weighed. A sub-sample of eggs (ca. 20 g) was retained for GC-MS analysis along with liver samples. The methods used for extraction and analysis of the samples were based on contemporary methods described by de Boer et al. (2001) with minor modifications. Twenty one PCB congeners were identified and quantified in each sample using the internal OCN standard and the A1254 samples as the standard PCB mixture. The female plaice broodstock accumulated A1254 readily in their body tissues during the dosing period while PCBs were not detected in the eggs and livers from undosed female fish. Multivariate analysis revealed differences in the congener profiles of the PCBs extracted from liver and egg samples and the A1254 mixture used to dose the fish. As a general pattern, there was an increase in the proportions of lower chlorinated congeners in the egg samples when compared with livers or A1254 while in the liver samples there is a trend toward higher proportions of the more highly chlorinated congeners. Significant differences in congener proportions existed between all three sets of samples. Signature analysis (PLS) using A1254 as the source indicated mean similarities of 97% for the livers and 89% for the eggs although the lowest value was 60%. Of the ICES 6 congeners, the proportions of the more highly chlorinated congeners in the liver samples were often greater than those in either the egg samples or the original A1254 used to dose the fish. Likewise, the proportions of the lower chlorinated congeners in the egg samples were often greater than those in either the liver samples or the original A1254. PCB profiles differed between samples from individual fish resulting in larger confidence intervals for each congener proportion in comparison with those from the A1254 standard.

If the relative contributions for each congener within a single fish are plotted against their  $K_{ow}$  as a proxy for lipophilicity, a distinct pattern can be seen (Figure 1).

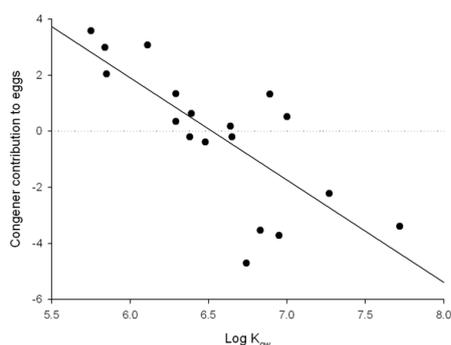


Figure 1. Scatter plot of the relative contribution from Figure 1 versus the log  $K_{ow}$  values for each congener for a single, representative, female plaice dosed orally with Aroclor 1254. Points above the dotted line denote greater PCB congener proportions in the eggs whilst those below denote greater proportions in the liver. The relationship was significant ( $r = -0.759$ ,  $p < 0.001$ ,  $n = 18$ ) and described by the equation  $y = -3.64x + 23.80$ .

PCBs are transferred from adult plaice to their offspring. This study has shown that the PCB congener profile of the A1254 used to dose female plaice was significantly different to those of both the eggs spawned by the female

fish and the female livers. In turn the congener profiles of liver and egg samples from individual fish were also dissimilar. The PCB concentrations in the eggs were equal to or higher than those in the livers. Although the study did not provide a detailed analysis of the transfer mechanisms, the results suggest that congener transfer is related to the physico-chemical properties of individual congeners and that lower-chlorinated, less hydrophobic congeners are transferred to the ovaries more easily than more hydrophobic congeners. Of the four most toxic congeners transferred to the eggs (CBs-52, 105, 118 and 138) CB-52 consistently increased in proportion whilst CBs-118 and 138 were always greater in proportion in the liver samples.

## A PCDD/F STORY IN SOUTHERN ITALY: THE TARANTO CASE

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This presentation deals with the story of an industrial site located in the deep southern part of Italy. The site has been industrialized in the sixties by the Italian government by settling there some heavy industries including an iron and steel plant, a refinery and a cement kiln factory. After these companies have been established, the site has been enriched by other smaller plants including an urban waste incinerator and a clinic waste incinerator. In the nineties the Italian government has proceeded in the privatization of the three major factories. The iron and steel company started to act, at that time, an important plan to implement new environmental technologies to ameliorate the environmental performances.

This is the story of how the improvements have affected the emissions of PCDD/F from the nineties to today, and how we are working to reconstruct and to evaluate their effects on the environment and to detect who is responsible for what.

## ASSESSING CHANGES TO THE CONGENER PROFILE OF PCDD AND PCDF DURING BIOACCUMULATION IN CHICKEN AND DUCK EGGS

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Many allotments in use in the UK today are situated on urban brownfield areas which creates potential human health risks from soil borne contamination. Poultry such as chickens and ducks are commonly reared on these sites by allotment owners who then eat the eggs that are produced. At sites close to waste incinerators there is the potential for soil to be contaminated with dioxins (PCDD) and furans (PCDF). PCDD and PCDF are almost insoluble in water however they can be fairly soluble in organic solvents and fats. Due to this increased solubility in lipids, PCDD and PCDF have been found to bioaccumulate in fatty foods

such as milk products, and in meat fat, offals, eggs and fish compared to other foodstuffs. There are some natural background sources of PCDD and PCDF including forest fires and volcanic eruptions however these are not normally a significant source of PCDD and PCDF in the UK. The main sources tend to be anthropogenically produced through the production and use of organochlorine chemicals contaminated with dioxins and furans and the combustion of materials that contain trace amounts of chlorine such as wood, plant matter, fossil fuels and municipal and industrial waste. These can either be transferred through areal deposition or through the spreading of combustion residues such as fly ash.

There are 75 possible congeners of chlorinated dibenzo-p-dioxins and 135 possible congeners of chlorinated dibenzofurans. By analysing the different proportions of the congeners that are present it is possible to establish the source of a contamination event. It is also important to understand which congeners are present as the different congeners have markedly different toxicities. The congener profile from samples taken from the soil can be different from the congener profile in eggs taken from poultry which have been raised on that soil. These differences can complicate the source identification process and can also lead to bioaccumulation of higher proportions of the more toxic PCDD/F.

This presentation shows a worked example of techniques used successfully to establish the most likely source of PCDD/F contamination at an allotments site near a former waste incinerator. It takes a detailed look at the specific congener profile of soil samples from the site and how these are altered by the poultry which resulted in a different profile being recorded in the egg samples. Although there were clear differences between the congener pattern in the soil and egg samples, by focusing on just the hexachlorinated congeners we were able to match the profile in the eggs to the profile of soil samples from the individual plots that the poultry was raised on.

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### **PREDICTION OF THE ENVIRONMENTAL FATE OF METHYLAMPHETAMINE WASTE**

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The clandestine manufacture of methylamphetamine has been detected in over 60 countries worldwide. Methylamphetamine can be manufactured easily using a variety of common household chemicals and several different methods, or routes. Information on how to synthesise methylamphetamine is readily available on the Internet, publically accessible scientific journals, chemical patents and published books.

The environmental impact of clandestine methylamphetamine laboratories is a growing concern. The

illicit manufacture of methylamphetamine produces a huge amount of waste: one kilogram of methylamphetamine produces five to seven kilograms of toxic waste. Methylamphetamine waste contains many volatile, flammable, and corrosive chemicals, as well as heavy metals. This waste is most often illegally disposed of in a number of different ways. Such routes of disposal include: poured down indoor plumbing, dumped directly into ditches, rivers, canals, etc., dumped into burn pits and/or dumped into burial pits. With the public's growing interest and awareness in preserving the environment, it is increasingly desirable to prosecute polluters – clandestine lab cooks being no exception. Scientific advances make this process more feasible than ever. The aim of this project is to provide the appropriate tools and information to forensic chemists and law enforcement personnel to allow clandestine chemists to be prosecuted to the fullest extent of the law.

While much work has been completed investigating the reaction impurities of clandestine methylamphetamine manufacture, little research has been conducted into profiling the waste. In this work, we present data on the environmental fate and distribution of methylamphetamine waste. Environmental partition coefficients were measured and subsequently compared against the default values from the US EPA's EPISuite computer modelling programme. Total organic carbon content is an important parameter in fate prediction; therefore sediment samples from different locations were used to experimentally determine partition coefficients in a wide range of sediment types. This will aid in the understanding of the behaviour of methylamphetamine waste in the environment and will provide information for the investigation of a suspected dumpsite.

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**MONDAY, JULY 25, 2011**  
**3:30 – 5:30**

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### **PALMERSTON ROOM: PETROLUUM HYDROCARBONS**

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#### **HIGH RESOLUTION SITE CHARACTERIZATION AND INTEGRATION WITH ENVIRONMENTAL FORENSICS**

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This presentation provides a brief description of hydrocarbon fuel chemistry and some of the techniques used to identify different types of petroleum materials in environmental media. A case study involving a large NAPL plume extending offsite multiple distribution terminals will be discussed to illustrate the integration of various conventional and innovative investigation and forensics tools to develop and verify the site conceptual model with independent multiple lines of evidence including:

- Hydrogeologic Conditions

- Vapor, Soil, and Groundwater Analyses
- Laser Induced Fluorescence
- Forensic Analyses
- Data visualization tools

### COMPREHENSIVE CHEMICAL FINGERPRINTING OF THE EFFECTS OF WEATHERING ON COAL TAR DNAPLS AND COAL TAR CONTAMINATED SOIL SAMPLES

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Coal tars are the waste products in the manufacture of gas from coal or oil. Between the 1810s and the mid 20th century, tens of thousands of manufactured gas plants (MGP) across Europe and North America produced gas for cooking, heating and lighting. Coal tars were stored and moved around on site before being sold as a feedstock for the chemical industry. Minor leaks and spillages occurred frequently and coal tar contamination is therefore a common occurrence at former MGP sites. Coal tars are thought to be composed of between 300 and 5000 inorganic and organic compounds, many of them toxic to the environment and human health; the exact composition of a given tar being dependent on the manufacturing conditions. The need for accurate forensic chemical fingerprinting of coal tar contamination has thus grown in the past decade in Europe as legislations based on the "polluters pay principle" have been implemented.

Using a new state-of-the-art 2-step method for the forensic analysis of coal tar that provided us with a unique chemical fingerprint containing up to more than a thousand resolved compounds, we studied the evolution of the chemical fingerprints of coal tar dense non-aqueous phase liquids (DNAPLs) and coal tar contaminated soils in order to identify the family of compounds that remain unchanged during weathering and the composition changes that are specific to given natural attenuation processes such as chemical reactions, water-washing, evaporation but also biodegradation.

The analytical method we used for coal tar DNAPLs and soil samples consists of a unique clean-up/ extraction stage by Accelerated Solvent Extraction (ASE) and a single analysis of its organic chemical composition using comprehensive two-dimensional gas chromatography couple to time of flight mass spectrometry (GCxGCTOFMS). Moreover, the uniqueness of the fingerprinting was further improved using a derivatisation method for the tar compounds containing a labile hydrogen atom (such as those present in -OH, -NH and -SH groups). The addition of polar compounds to the fingerprint provides

more information about the source and the fate of the compounds since they can originate from either the manufacturing stage or the degrading processes in the subsurface.

### INVESTIGATION OF POLYCYCLIC AROMATIC HYDROCARBONS AND SELECTED NITRATED DERIVATIVES CONCENTRATIONS IN GREATER CAIRO, EGYPT

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Polycyclic aromatic hydrocarbons (PAHs) and their nitrated derivatives are often by products of petroleum processing or incomplete combustion of fuel. These products are common contaminants that are difficult to be biodegraded in the environment. Many of these compounds are highly carcinogenic and/or endocrine disrupting at relatively low levels. This report presents the profile of PAHs and selected nitrated derivatives (NPAHs) such as 1-nitropyrene (1-NP) and 6-nitrocrysene (6-NC) in air and water environment. Atmospheric concentration variations of fifteen PAHs and two selected NPAHs (1-NP and 6-NC) were measured at two sites, El Dokki (a traffic site) and El Teppen (an industrial site) in Greater Cairo, Egypt. Both the PAH and NPAH concentrations in El Teppen were higher than those in El Dokki. PAHs having four to six rings were the predominant compounds in particulate matters. These concentrations were compared with those of several cities in Asia that have been undergoing rapid economic and industrial development. The [NPAH]/[PAH] and [PAH]/SPM ratios, were used to estimate the major sources and secondary reactions of PAHs and NPAHs. Grape water samples were collected from six different sites along the River Nile from North to south and Esmailia canal. These sites were selected to represent the different parts with the different activities and the distribution levels of PAH and their nitrated derivatives in the fresh water stream in Egypt.

### DISTRIBUTION OF PAHS ACROSS THE SOILS OF SCOTLAND

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Recently there has been concern about effects of environmental levels of exposure to endocrine disrupting compounds (EDCs) on human and animal health. Polycyclic aromatic hydrocarbons (PAH) comprise one such environmentally-persistent group which has the potential to adversely affect health and reproductive function. Low molecular weight (LMW; three carbon rings

or less) PAHs are produced, primarily, by combustion at low to moderate temperature (coal and wood burning), while those with a greater number of rings (four or more) (HMW) are produced at high temperatures, such as through vehicle emissions from combustion of fossil fuels. Other contributions to the environmental PAH burden include contamination with petroleum products, such as tar and heavy oil residues and biogenic sources.

Once PAHs are released into the atmosphere, they can be deposited on soil by both dry and wet deposition and can adsorb strongly to the soil organic matter, and are retained for a long time. Thus soil can potentially be one of the main reservoirs for PAHs in the environment. Since PAHs are variably volatile, environmental profiles are likely to vary with proximity to sites of production and use, and it was hypothesised that there will be spatial distribution patterns in relation to the likely source.

As part of a national soil sampling scheme, approximately 180 surface soil samples (0-5cm depth) were collected at 10km grid intersect points throughout Scotland and analysed for selected PAHs using GC-MS. Using a recursive regression and classification tree, relationships between PAH concentration and soil, land cover and position were investigated. Concentrations of LMW PAHs were influenced significantly by soil type and altitude, while the HMW PAHs were influenced, in addition, by vegetation. Geographic position was an important factor for all PAHs. Such spatial patterns are important for consideration of the impact on human health and in the context of the interpretation of data used for forensic case investigations.

Acknowledgements: Thanks to surveyors Allan Lilly, Andrew Nolan, Gordon Hudson, Willie Towers and John Bell for sampling the soils, and to RERAD for funding to support this research.

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## BOYS SMITH ROOM: AIR QUALITY

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### VOLCANIC ASH IN THE UK: EVIDENCE FROM ENVIRONMENTAL CHANGE NETWORK SITES

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The eruption of Eyjafjallajökull, Iceland, in April 2010 released large plumes of volcanic ash raising concerns about air quality and the fear of long term detrimental effects to the environment. The prevailing winds directed the volcanic plume towards the UK where it was anticipated that ash would be deposited. A prolonged period of activity, increase in intensity or the eruption of a larger volcano in the future could increase the potential for negative impacts on UK air, water, soils and vegetation. Immediate and effective monitoring was required in order that any potential impacts from an eruption of this magnitude could be detected as soon as possible.

The UK Environmental Change Network (ECN) was founded in 1992 and now has twelve terrestrial field sites where common variables are measured using agreed protocols. Pre and post eruption rain and snow samples from UK ECN sites were compared. Standard chemical analysis revealed no significant difference between the sample sets. Detailed Scanning Electron Microscopy (SEM) of the filtered solids from the same samples confirmed, however, that volcanic ash was present at many of the sites in post eruption samples.

SEM imaging coupled with Energy Dispersive Spectroscopy (EDS) enabled the identification of volcanic glass through morphology and elemental composition. The elemental composition of identified glass particles was compared to a reference ash sample from Eyjafjallajökull provided by the Icelandic Institute of Earth Sciences to ascertain their origin. The temporal resolution and spatial distribution of sampling sites enabled the pattern of deposition across the UK to be clearly identified.

The origin, temporal and spatial distribution of air borne contaminants can be difficult to assess. In this case study a number of factors such as sample collection methods, effective processing, reliable baseline data, temporal and spatial representation, acquisition of reference material and application of innovative forensic analytical techniques facilitated a positive outcome.

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### SOURCE ALLOCATION OF PAHS AND HYDROCARBONS IN PARTICULATED MATERIAL (PM10) IN THE CITY OF VALDIVIA, CHILE

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Is typical for Environmental Authorities to evaluate and assess the air quality through the amount of particles that is in the atmosphere according to values of PM10 or PM2.5. Nevertheless, the chemical composition may be poorly known and characterised. It is well known that some toxic and carcinogenic chemicals such as Polycyclic Aromatic Hydrocarbons (PAHs) may be present and consequently determination of these chemicals has become important. The aim of this research was to assess the concentrations and signatures of n-alkanes, and PAHs and to determine the possible sources.

Concentrations of n-alkanes (n-C10 to n-C33) and PAHs (18 compounds including the EPA priority substances) were determined in air filters during a year period in an urban area of the city of Valdivia, Chile. The extraction was

done using Soxhlet apparatus. The analysis was done by GC-MS techniques and quantification was done using internal standard calibration.

Concentrations of total hydrocarbons varied from 45 to 352 ng.m<sup>-3</sup> and Total PAHs varied from 2.93 to 78.01 µg.m<sup>-3</sup>. Hydrocarbons from both anthropogenic and biogenic sources were present with high concentrations during summer which then decreased during autumn to then increase linearly to the summer again. Interpretation of the Polytopic Vector Analysis (PVA) suggests the main sources of hydrocarbons to the atmosphere in Valdivia were both from biomass and oil combustion with an unknown source which is also suspected to come from organic matter combustion.

Concentration of PAHs showed a good correlation with total particulated material (PM<sub>10</sub>) R<sup>2</sup>=0.97. Levels of PAHs in the atmosphere were higher during the winter period and low during summer. Polytopic vector analysis detected three possible sources; where one derived from oil combustion rich in compounds such as naphthalene, 2-methylnaphthalene and 1-methylnaphthalene among others. The other sources detected derived from wood combustion, especially during the cold period as this is the main way of warming houses. Principal component Analysis (PCA) and PAH ratios were also employed to determine the sources and the results were similar to those using PVA analysis.

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### **SOURCE APPORTIONMENT OF INDUSTRIAL FUGITIVE DUSTS: DEVELOPMENTS IN PASSIVE DUST MONITORING**

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DustScan is a passive (i.e. unpowered) dust sampling method. It uses a transparent adhesive 'sticky pad' to sample dust in flux and in deposition for subsequent image-based quantification and, as appropriate, geochemical analysis. Samples are obtained over typically 7 – 14 day intervals in the vicinity of industrial sites such as quarries, surface coal mines, landfill sites and construction and demolition sites. DustScan was developed at the University of Leeds (Farnfield and Birch, 1997) and refined at DustScan Ltd and the University of Leeds (Datson and Birch, 2006). Dedicated geochemical analysis methods of DustScan samples using ICP-AES and ICP-MS have been developed (Datson and Fowler, 2007) and their use in environmental forensics has been demonstrated by quantifying dust propagation at a hazardous waste landfill site (Fowler et al. 2010).

However, wider environmental forensic applications of the method have been constrained largely by the impracticality of detaching the sampled dust from the collection media. Until recently, the sticky pads have been die-cut from sheets of a proprietary transparent PVC film with a permanent, cross-linked polymer-acrylic adhesive. Whilst

this type of adhesive has excellent environmental dust sampling characteristics, its formulation renders it essentially insoluble (except in solvents that also dissolve much of the dust, e.g. HF). Furthermore, on retrieval after field sampling the sticky pads are sealed with a transparent film to facilitate handling and minimise contamination, thus making physical removal of dust at a later date difficult. Since the most effective means of dust 'extraction' from the sticky pads has been in solution and the image-based quantification method does not assess dust mass, geochemical data have been reported in terms of concentration in the extraction (e.g. ppm in solution) rather than in the dust (e.g. mg g<sup>-1</sup>). Confidence in adequately low detection limits has also been compromised by variable concentrations of some metals (e.g. Zn, Ba) in the sampling media.

Funding was obtained from the Finance South East Ltd (FSE) proof of concept (PoCKeT) fund to investigate alternative dust sampling media and, initially, to improve the elemental coverage and method detection limits. The project was carried out in conjunction between DustScan Ltd and the School of Earth and Environmental Sciences (SEES) at the University of Portsmouth. The new adhesive has similar transparency, tack and UV-resistance to the original but can be dissolved in an appropriate solvent. The new design has been tested in the field at a range of UK industrial sites as well as in a comprehensive bench testing programme.

In the field trials, the new sampling media performed well in relation to the original sticky pads. Dust capture and retention were apparently similar and sample handling and processing for image analysis were satisfactory, although transparency was marginally less uniform. In the bench tests, both types of sticky pad were exposed to a known dust at different concentrations and wind speeds in an environmental wind tunnel. Correspondence between the sample media types was good to excellent in relation to the different image quantification methods applied. In addition, an array of elemental analysis tests was performed. NIST standard reference materials were applied to the new sticky pads, then extracted by dissolution of the adhesive and filtration onto 25 mm PTFE filter circles for ICP-MS analysis. Bulk dusts from a number of industrial sources were similarly applied, and analysed before and after application.

An unanticipated benefit of the investigation has been the development of a practicable method to determine sampled dust mass in passive directional and deposited environmental dust samples, which has enabled reporting of mass/mass element concentrations in the dust samples after ICP-MS analysis.

## PREDICTION OF TURBULENT TRANSPORT USING VARIABLE EFFECTIVE DIFFUSIVITIES OF VOC VAPOUR IN INDOOR AIR.

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Mechanical and natural ventilation in a workplace will encourage the dispersion of volatile organic carbon (VOC) vapours from a source into the surrounding air. Exposure is estimated using time weighted averages of vapour concentrations and ventilation efficiency is defined using mixing factors. Both methods are stipulated in legislation and industry standards yet have been criticised as seriously underestimating risk as variation over space and time is not considered. In the large scale atmospheric environment variable effective diffusivities are used to describe net transport driven by molecular diffusion, turbulent mixing and convection. The purpose of the present investigation is to empirically estimate effective diffusivity values for types of VOC vapour in ventilated workroom air, assess their variability over time and space and their application in dispersion prediction models. Bayesian Monte Carlo (BMC) updating of prior distributions of effective diffusivity were used to improve prediction accuracy and reduce uncertainty in prediction at Eulerian grid points over time and one dimensional space.

Continuous sources of VOC vapours (n-butyl ethanoate, methylbenzene and a mixture of the two) were placed in the centre of a full sized workroom with a range of typical ventilation conditions. The airborne vapour concentrations were measured using an array of mixed metal oxide semiconductor sensors. Air velocities and accompanying velocity fluctuations were measured across the same grid using an omni directional hot sphere anemometer. It can be concluded from the study results that dispersion of VOC vapours at the low air flow rates typical to ventilated workspaces was anisotropic and effective diffusivity varied over space and time. Where the vapour concentration was high the effective diffusivity value was small indicating a barrier to transport whereas higher effective diffusivity values corresponded with stronger mixing. A correlation between air velocity and vapour concentration was not found, this suggests that air velocity may not be representative of mass transport. As a consequence an analytical one dimensional convection – diffusion model was modified by replacing the Peclet number with a Sherwood number.

Application of effective diffusivity distribution parameters to analytical predictive modelling will be reviewed in this presentation. Effective diffusivity values had the greatest influence on both the accuracy and the uncertainty of the prediction outcome yet predictions at each of the grid nodes were accurate to within the vapour concentration measurement error of  $\pm 13\%$ . This novel method for predicting VOC dispersion over real time and space could support ventilation design and improve risk assessment.

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**TUESDAY, JULY 26, 2011**  
**9:00 – 10:30**

**PALMERSTON ROOM:**  
**PETROLUUM HYDROCARBONS**

**ENVIRONMENTAL FORENSIC INVESTIGATION  
 OF HYDRAULIC FRACTURING FLUIDS USED IN  
 SHALE GAS WELLS IN THE EASTERN UNITED  
 STATES**

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Recently there has been considerable interest in gas well drilling into the Marcellus shale in the Eastern United States. In states such as Pennsylvania, Ohio and New York, there has been a dramatic increase in the development of such wells, but this has not been without controversy. While the gas-drilling industry claims that their processes are completely safe and undamaging to the environment, several environmental groups strongly claim otherwise. Adding to the controversy, the process of hydraulic fracturing of these wells may use various chemicals that are not without concern. The industrial companies claim to self-disclose their formulations, but this is an overstatement, as the exact compositions are not revealed. If a hydraulic fracturing caused some environmental contamination, it would not be easy to determine the source of the contamination due to the lack of disclosure and oversight of the operators. This results in potentially complex environmental forensics analytical method development and sample analysis to determine if a contamination event has occurred, and who the principle polluter may be.

This presentation will address the sampling, sample preparation and analysis of these materials. Various sample preparation strategies will be discussed. GC-TOFMS will be used as the determinative technique due to its inherent advantages over other possible techniques. Finally data will be presented that may allow for the development of protocols to determine both composition of these fluids, and possible point source of pollution should an event occur.

**FINGERPRINTING OF GAS CONTAMINATING  
 GROUNDWATER AND SOIL IN A  
 PETROLIFEROUS REGION, ALBERTA, CANADA**

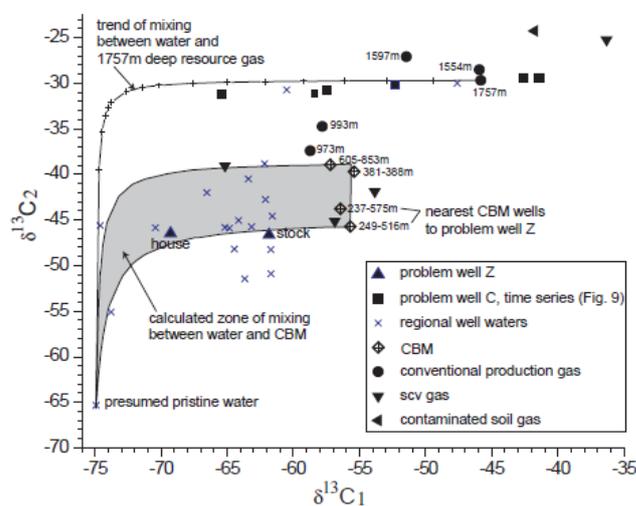
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Sixty years of petroleum development has resulted in over 500,000 petroleum wells drilled in the Western Canada Sedimentary Basin, many in agricultural areas that rely on groundwater. The impact on groundwater quality by

petroleum development is increasingly becoming a societal and regulatory concern triggered by intensive, recent CBM and shale gas development. To protect groundwater, the production tubing of a resource well is encased by a larger diameter surface casing (SCV) that is set deeper than the depth of potable water. Because of poor cementing, the SCVs and soils near the wells often contain gas, heightening concern for the integrity of groundwater. Carbon isotope analyses of thousands of SCV gases show them only rarely to be sourced from the target zone of the resource well, but rather from an intermediate depth. It has long been known that many water wells produce methane and traces of ethane and it needs to be determined if the water wells have been impacted. Alberta now requires all water wells to be tested prior to drilling of nearby resource wells. Carbon isotope analyses are mandated on a proportion of all gases produced by water wells and many hundreds of gas analyses will be placed in a public data base.



*Methane versus ethane carbon isotope plot for gases from problem water wells Z and C, compared to gases from water wells, CBM, resource wells, and SCV flows in the surrounding area. Mixing curves were calculated using the mass balance approach of Jenden et al.*

Carbon isotope values of gases vary within the basin and can be used to quantify natural gas contamination of groundwater. Three case studies will be presented where landowners have filed complaints about gas contamination of their water wells. There is evidence in one case of 1700m deep gas impacting the groundwater. Carbon isotope analyses of water wells in another area suggest a few per cent of shallow CBM contamination in water. Attributing specific contaminant sources to a given resource well has proven to be difficult in areas where there is ongoing CBM development. Gases from multiple water wells in one region of CBM development illustrate the complexity of attributing the source of contamination to a specific resource well. Four wells appear to be impacted by shallow CBM, whereas three are impacted by conventional petroleum development. One of these wells had a history of gas loading prior to CBM development.

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## **GASOLINE DIFFERENTIATION IN WATER TABLE FREE PRODUCT IN A NEIGHBORHOOD OF MEXICO CITY**

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As a result of an apartment building construction activity, free product was detected in the subsoil area. The whole urban area is located at Mexico City, where a gasoline station, small factories with solvents, fuel and oil storage tanks are located near by the leak area. On December 1, 2005, Instituto Mexicano del Petróleo (IMP) was hired to characterize the contamination as well as suggest remediation alternatives. Because of the urban area, IMP used a number of indirect methods that described the contamination plume.

Electromagnetic Profiling (EMP) was used, considering the interference of the underground pipe lines and sanitary sewer. IMP performed a Vertical Electrical Sounding (VES) that was used obtaining geoelectrical anomalies profile, a geoelectrical vertical section and isovalues maps. In order to discern if these anomalies were associated with the presence of hydrocarbons, a Volatile Organic Compounds (VOC) study was also performed. Soil gas samples were collected to measure BTEX, CH<sub>4</sub> and, CO<sub>2</sub> concentrations, to discern between recent free product and biodegradable product. It was conducted a soil and groundwater sampling activities based on results obtained from EMP, VES and VOC integrated map. In agreement with the integrated map of indirect methods, the profiles of VES and stratigraphy registered during the drilling, the results from geochemical analysis were extrapolated. A profile map of actual concentrations, with the area and the volume of the contaminated soil, was developed.

Results showed a study area of 41,000 m<sup>2</sup>, within which 2,592 m<sup>2</sup> were affected (about 6,676 m<sup>3</sup>). In order to assess the source and time frame of product released chemical characterization and chemical ratios method to age-date and fingerprint fuel released to the environment was used. Several samples of soil, water and free product were collected from monitoring wells. The samples of free product included PIANO analyses through gas chromatography-FID. Comparing the relation B+T/E+X (Kaplan et al., 1996), three different types of hydrocarbons (of the gasoline range) were detected with different levels of weathering. Based on results, the gas station was responsible for the recent contamination. The water did not show any VOCs. Aerosparing and Soil Vapor Extraction were the best remediation technology proposed.

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## **BOYS SMITH ROOM: AIR QUALITY**

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### **DIFFERENTIATION OF VOCS SOURCES IN RESIDENTIAL AIR BY CSIA FOR VAPOR INTRUSION MANAGEMENT**

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At corrective action sites with vapor intrusion (VI) concerns, the presence of indoor sources of volatile organic compounds (VOCs) complicates the exposure pathway investigation. The detection of a target VOCs in a potentially affected building does not necessarily indicate a VI impact due to ubiquitous presence of the same compounds in domestic consumer products. Unfortunately, the current methods for identification of indoor sources are expensive and have limited effectiveness. A novel approach presented herein relies on determination of stable isotope ratios of the target VOCs (<sup>13</sup>C/<sup>12</sup>C and <sup>37</sup>Cl/<sup>35</sup>Cl for PCE and TCE) by compound-specific isotope analysis (CSIA). The isotope ratios can be used to differentiate between VOCs sourced from subsurface (the true VI) and those sourced from miscellaneous household products. The premise for such discrimination is that the isotope compositions of a given chemical compound manufactured at different facilities and/or at different times tend to vary, reflecting the isotope ratios inherited from the manufacturing precursors and processes. Moreover, subsurface biodegradation often results with an enrichment of the heavier isotope species in the remaining VOCs residue, while no such enrichments are feasible for household product VOCs. The similarity/dissimilarity of the isotope ratios between VOCs in indoor air, in soil gas and in household products (if identified on site) permits identification of those sources with best match to the indoor air VOCs isotope composition. Key challenge of applying CSIA to indoor VOCs is the low concentration of the analytes. In the present study, an application of thermal desorption sorbent tubes was proven to be successful for TCE and PCE at low ug/m<sup>3</sup> concentrations.

Samples of TCE and/or PCE were collected and analyzed by CSIA, to determine their C and Cl isotope ratios in residential indoor air, soil gas and in the ground water in the proximity of a chlorinated solvent plume at Hill AFB (Utah, USA). At one of the residences, a household product containing PCE was found and sampled for direct comparison with the isotope ratios of indoor air PCE. The residences were selected for the study based on previous work – sites with and without likely VI impact were chosen to allow independent validation of the CSIA results. The results of the survey of the four residences demonstrated that the isotope ratios of VOCs present in indoor air may be similar to those of the same VOCs in soil gas or in household products. In the former case, VI scenario is suggested; in the latter case, domestic product impact is suggested. Combined carbon and chlorine data were more

informative than single isotope data, permitting 2D-correlation of the sources and indoor air samples. In one residence, the isotope ratios of TCE were clearly indicative of extensive degradation of the compound. In such case, even if soil gas samples were not available, the TCE could be inferred to originate from the subsurface, as degradation of household product VOCs is not feasible. The conclusions from CSIA matched the conclusions from traditional assessment of VI impact, with a benefit of simplified implementation.

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### SUB-SOIL TO15 VOLATILE ORGANIC COMPOUND (VOC) VAPOUR INTRUSION ANALYSIS

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A renewed interest in vapour phase transport of volatile organic compounds (VOCs) through soil has emphasised the need for Jones Environmental Laboratory to provide an accredited (ISO 17025) analytical solution for sub-soil vapour monitoring analysis of the USEPA method TO15 VOCs. Vapour intrusion is a potential concern at sites with soil or groundwater impacted by volatile chemicals. Soil gas measurements have become one of the primary tools in assessing vapour intrusion pathways. Soil vapour transport to indoor air is an important potential exposure pathway at many sites impacted by subsurface VOCs contaminants. The analytical results obtained from the analysis of soil gas samples can be used to determine whether a potential indoor inhalation risk is present. The USEPA method TO15, detailed in the second edition of the Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air (1999), lists many volatile compounds typically encountered in routine ambient air analysis. They can be sampled in specialised silonised canisters or bottle vacs which are then easily transported to the laboratory for analysis. This method applies to ambient concentrations of these targeted VOC down to 2 ppbv using gas chromatography (GC) to achieve separation and a selective ion monitoring mass spectrometry (MS) for identification and quantitation. The presentation goes to demonstrate the on-site sampling requirements and the typical laboratory analysis results which can be obtained from this analysis.

**Keywords:** Sub slab, TO15, VOCs, Indoor air, GCMS

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### APPLICATION CHANGE OF ATMOSPHERIC POLYCYCLIC AROMATIC HYDROCARBONS AND NITROPOLYCYCLIC AROMATIC HYDROCARBONS IN LAST 12 YEARS OF KANAZAWA,

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Polycyclic aromatic hydrocarbons (PAHs) such as benzo[a]pyrene and nitropolycyclic aromatic hydrocarbons (NPAHs) such as 1-nitropyrene and 1,3-dinitropyrene are ubiquitous environmental pollutants, and many of them have carcinogenicity and/or mutagenicity. Several PAHs also have estrogenic/antiestrogenic or antiandrogenic activities. Both PAHs and NPAHs mainly originate from imperfect combustion of organic matters such as fuel oil and coal and major sources to the atmosphere include automobiles, industrial processes and domestic/city coal heating. Furthermore, several NPAHs are formed in the atmosphere via reactions of PAHs with OH or NO<sub>3</sub> radicals.

Kanazawa, capital city of Ishikawa Prefecture, Japan, is a typical commercial city whose population is about 463,000. We collected airborne particulates by the side of a busy traffic road in Kanazawa for two weeks in both summer and winter for the last 12 years. Airborne particulates were collected by a high-volume air sampler with quartz fiber filters. Filters were changed newly every day. Both PAHs and NPAHs were extracted from the filter with benzene-ethanol and cleaned up with acid, alkaline and water, successively. PAHs and NPAHs were determined by HPLC with fluorescence detection and HPLC with chemiluminescence detection, respectively.

Both atmospheric concentrations of PAHs and NPAHs decreased significantly in the last 12 years, although the concentration of total suspended particulate matter showed a slight decrease. During this period, the concentrations of PAHs in summer and winter decreased to 1/4.4 and 1/2.8, respectively, while the concentrations of NPAHs in summer and winter decreased to 1/8.2 and 1/7.9, respectively. The [NPAH] to [PAH] concentration ratio, which is an indicator of the contributor, decreased significantly. As a major reason for the decrease of atmospheric PAHs and NPAHs, the improvement in the quality of automobile exhausts was considered.

**TUESDAY, JULY 26, 2011**  
**11:00 – 1:00**

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### PALMERSTON ROOM: REFINED PRODUCTS

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#### MASS BALANCE METHODS FOR RETAIL GASOLINE OUTLETS

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Mass balance methods can be used to determine if there have been leaks or pilferage from retail gasoline outlets, and if so when this occurred. In order to apply these methods, however, vapor capture at the pump and

temperature changes after gasoline is delivered must be included. This presentation illustrates these concepts using a simple model applied to retail gasoline outlets in central and northern Florida.

We estimate vapor capture to be about 0.7%-0.9% of the product sold. The seasonal effect is consistent with volume expansion and contraction due to a temperature difference between above-ground storage tanks at a depot and the temperature of buried tanks at the outlet, with the latter being at approximately the average annual temperature. The coefficient of expansion estimated using these assumptions is consistent with literature values for both diesel and regular gasoline.

One of the conclusions is that a dip in apparent volume for a tank is not necessarily related to an environmental release. An alternative possibility is that volumetric shrinkage occurring in the summer is larger than vapor capture during the same time period. Our data set also exhibits several cases in which a faulty blending valve may have product apparently lost by one tank and gained by another. The data set also includes at least one outlet where there appears to be a real loss over the period analyzed.

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## RESOLUTION OF A COMINGLED LNAPL PLUME TO ADDRESS CONCERN ON POTENTIAL MTBE RELEASE

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At an active refinery located in the US West Coast, neat Methyl Tert-Butyl Ether (MtBE) was released and dispersed into an existing comingled light, non-aqueous phase liquids (LNAPL) plume. Periodic sampling of LNAPL indicates that the concentration of MtBE in the LNAPL plume has in general decreased over time; however, fluctuations of MTBE concentration in the LNAPL are observed in one of the monitoring wells. Plausible causes for the MTBE fluctuation include 1) the change of relative proportion of the "end member" product in the comingled LNAPL plume due to hydrodynamics resulting from operation of the recovery system (e.g., on and off, and change in pumping rates, etc.); and 2) release of potential residual MTBE from abandoned MTBE-carrying pipelines. In order to rule out the release scenario, which is a concern for both the site owner and the regulator, it is critical to understand if the makeup of the LNAPL (i.e., relative proportion of the "end member" product in the comingled LNAPL plume) changes over time.

A substantial amount of LNAPL forensic data is available owing to the site's Product Release Detection Program. Review of the chromatograms revealed that MTBE-containing LNAPL is a mixture of primarily three types of intermediate refining streams or "end members". Based on characteristics of three types of products, the chromatograms were optimally sectioned into a number of areas to differentiate between products. Peak areas of selected sections were estimated with the aid of a chromatogram processing software. For the areas that

represent more than one type of product, an equation was developed to apportion areas to two different products. After assigning areas to each "end member" product, correlation was made between the relative proportions of each "end member" product with MTBE concentration in LNAPL over time.

This paper presents the forensic study that details the methodology developed to resolve the comingled MTBE-containing LNAPL plume. The finding was that the fluctuation of MTBE correlates well with the change of relative proportion of one "end member" product that ranged from 20% to 70%. This correlation is consistent with the current understanding of the release history and historical recovery data. The finding addressed the site owner's and regulator's concern on release of potential residual MTBE in abandoned pipelines.

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## APPLICATIONS OF COMPOUND-SPECIFIC ISOTOPE ANALYSIS IN STUDIES OF MTBE REMEDIATION

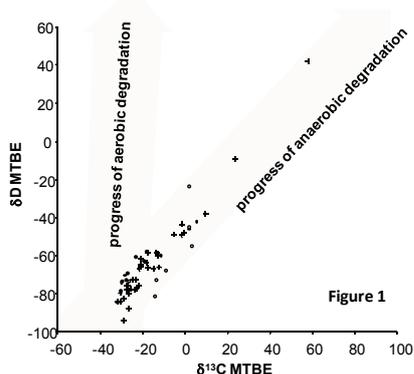
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MtBE (methyl tert-butyl ether) is a common groundwater contaminant in the USA and worldwide. MtBE contamination is typically associated with gasoline spills. Biodegradation of gasoline hydrocarbons co-occurring with MtBE tends to deplete oxygen at the release sites, and MtBE plumes are frequently anaerobic. Historically, the occurrence of anaerobic biodegradation of MtBE was considered as problematic. Developments in contaminated site assessment, including the results from compound-specific isotope analysis (CSIA) resulted with mainstream acceptance of biodegradation of MtBE as valid remediation pathway. This presentation will summarize the role of CSIA in the studies of the environmental fate of MtBE, based on work performed at OU and elsewhere. One unique aspect of stable isotope characterization of MtBE is that this compound is particularly well-suited to so-called two-dimensional (2D-) CSIA, involving both C and H CSIA of splits of the same sample (Figure 1). The real practical benefit of 2D-CSIA is in discrimination between the most common types of aerobic and anaerobic pathways of biodegradation. Moreover, several alternative degradation pathways and physical attenuation processes can be discriminated from each other and from the more common types of biodegradation by their 2D-CSIA characteristics. Such identification of attenuation mechanism is of great value in validation of conceptual models for contaminant attenuation for a specific field site.

This presentation provides a brief overview of the isotope effects in various degradative and non-degradative attenuation pathways of MtBE, with a focus on 2D-CSIA applications. While most attention has been devoted to characterize isotope effects in MtBE biodegradation, the principles of CSIA can be extended to scenarios where remediation of MtBE proceeds through vapor removal. A number of case studies are discussed to illustrate the potential of applications of CSIA in this area.



## PHYTO-SCREENING AND DENDROCHEMISTRY OR THE USE OF TREES IN ENVIRONMENTAL FORENSICS

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As trees uptake water and chemical elements that are physiologically vital to them, through their rhizosphere, other chemicals present in soils and groundwater are also uptaken by sap, including pollutants. As such, trees can be used as bio-indicators, or passive recorders of their current and past chemical exposures. Both approaches will be presented along with case studies.

For phyto-screening, small samples of 0,2 g of outermost rings are enough to document current exposure by HVOCs or fossil fuels, using respectively GC/ECD and GC/FID, by the ppt in transpiration stream. Studied at dozens of sites, this method has shown its capacity to delineate plume, at a reconnaissance, phase I site assessment level. Pollutant or tracers found in trees can be viewed as an integral of contaminants present in groundwater and soils, whilst bioconcentration factors depend on tree species and soil parameters. Case studies show an amazing match between maps arranged for groundwater and soil data with phytoscreening evidence. Phytoscreening can be detailed enough to highlight presence of multiple sources, or fill material, which are important to know of when characterizing plumes and establishing liabilities.

Because tree rings keep building at time of contamination, and they, or their tracers, are fixed in annual wood, dendrochemistry allows to age-date plumes' impacts to trees. Main analysis is by EDXRF line scanning, and elemental tracers include Cl for HVOCs, Sand Cl for gasoline, eventually coupled with Pb for leaded gasoline or other metals present in oils or tanks, such as V or Ni ; when also can document past metal releases, including As, Cd, Cr, Cu, Hg, Ni, Pb, Zn, and many others, and dozens of cases already published.

Whilst both methods are being more and more used worldwide, phyto-forensics experts have checked on their legal acceptability under Daubert criteria, and such considerations proved useful to anticipate judges or experts acceptance, which is now the case in 5 countries. Both methods are cheap, non invasive, fast.

Balouet, Jean Christophe, Smith, Kevin T., Vroblesky, Don and Oudijk, Gil (2009) 'Use of Dendrochronology and Dendrochemistry in Environmental Forensics: Does It Meet the Daubert Criteria?', *Environmental Forensics*, 10: 4, 268 – 276, First published on: 16 December 2009 (iFirst)

## BOYS SMITH ROOM: STABLE ISOTOPES

### STABLE ISOTOPES IN ENVIRONMENTAL FORENSICS-PAST PRESENT AND FUTURE

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With the commercial availability of gas chromatograph-isotope ratio mass spectrometer systems, the number of environmental forensic applications has increased exponentially. There are many well documented EPA methods used in environmental studies but these methods are of little use in environmental forensic studies, where the major goal is to find responsible parties rather than simply obtaining concentration data. In general environmental forensic studies utilize a tiered approach, with gas chromatography (GC), providing an initial indication of the contaminant type; gas chromatography-mass spectrometry (GCMS) identifying specific compounds and undertaking correlation or discrimination studies. However in many cases the results at this point may still be ambiguous and not clearly pointing to any specific source(s) for the contaminant. This is particularly true in the case of contaminated ground water where there might be a single component such as MTBE or PCE etc., where GC and GCMS, whilst telling us it is one compound, will certainly not differentiate sources of the contaminant.

There are two major applications of stable isotopes in environmental forensics, the first being a tool to differentiate sources and the second to monitor the onset and extent of natural attenuation. This paper will provide examples from both of these areas. First though it is important to mention that early applications of stable isotopes only considered utilization of carbon isotopes, but in recent years utilization of H and, even more recently, Cl isotopes has become more widespread. A number of isotope specific challenges have become apparent along the way to developing these as routine tools for these applications. For example whilst H isotopes can be readily determined in the case of hydrocarbons, in a compound such as TCE (trichloroethylene) with only one H and 3 Cl, this requires higher contaminant concentrations for the H but at the same time may provide valuable information as to whether the TCE was an original synthetic product or formed from degradation of PCE. Determination of Cl isotopes of chlorinated groundwater contaminants is now becoming a routine tool and can be obtained through the use of GCMS and does not require GCIRMS.

The outcome is that it is now possible to use 2D or 3D stable isotope fingerprinting to study both sources of groundwater contaminants as well as the onset and extent of natural attenuation. In this paper case histories will be described where stable isotopes, C, H and Cl, have been

used to discriminate sources of MTBE, chlorinated solvents and hydrocarbons at contaminated groundwater sites. Whilst this approach may not provide the silver bullet every attorney or regulator is looking for, it will certainly provide additional evidence not available from the traditional techniques of GC and GCMS. Ranges of isotope values for non-degraded samples of many of the common groundwater samples are now well established and samples with isotope values heavier than these values are typically considered to have undergone natural attenuation. Incorporation of isotope data and concentration data into fate and transport models permit quantitative estimates of the rates of degradation of chlorinated contaminants in groundwater plumes to be determined.

In brief stable isotopes are playing an invaluable role in environmental investigations related to groundwater contamination but a huge potential for additional applications remains.

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### ADVANCE SITE INVESTIGATION WITH 3D-CSIA APPROACH REVEALS MULTIPLE SOURCES

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The U.S. EPA's Newsletter "Technology News and Trends" (March issue 2011) briefly reported an advanced site investigation conducted by Florida Department of Environmental Protection (FL DEP) and ZymaX Forensics Isotope Laboratory, by using "Three Dimensional Compound Specific Stable Isotope Analysis (3D-CSIA)", at the Florida Agricultural and Mechanical University (FAMU) site in downtown Orlando. Previous FAMU sponsored groundwater investigations identified chlorinated hydrocarbons at levels that exceed Florida Primary Drinking Water Standards, but failed to determine the sources due to the lack of vadose zone contamination and the absence of groundwater contaminants in shallow portions of the surficial aquifer.

The same compounds of different sources are chemically identical (e.g., on GC-MS), but may have isotopic differences. Determining up to three isotope ratios for carbon (<sup>13</sup>C/<sup>12</sup>C), chlorine (<sup>37</sup>Cl/<sup>35</sup>Cl), and hydrogen (<sup>2</sup>H/<sup>1</sup>H) of each chlorinated hydrocarbon in groundwater samples helped distinguish multiple release sources and assess biodegradation. Gas chromatography - isotope ratio mass spectrometry (GC-IRMS) and sample preparation techniques that could detect chlorinated hydrocarbons at concentrations as low as 10 ppb were used.

Besides the commonly used "1D-CSIA, i.e., carbon only", more than one isotopic signature for different elements within the same compound are useful, esp. additional discriminates for the same contaminant is required. In the industrial manufacture of chemicals the multiple isotopic signatures of the final product depend on the isotope ratios of the feedstock and the manufacturing processes used to

convert the feedstock into the final product. Several investigations have documented that, for example, differences exist in the carbon, chlorine, and hydrogen isotope ratios of TCE and PCE produced by various manufacturers in the United States. PCE from different manufactures presenting similar carbon isotopic signatures may be further differentiated using their chlorine isotopic signatures. High hydrogen isotope ratios for manufactured TCE are due to the dehydrochlorination reactions used in the industrial production of TCE, whereas TCE generated as a dechlorination product of PCE could be significantly depleted in hydrogen isotope ratios, a result of H atom incorporation from the environmental water. Thus 3D-CSIA provide an advanced site diagnostic tool for potentially discriminating between chlorinated hydrocarbons, such as PCE (2D-CSIA) and TCE (3D-CSIA), from different sources, and conversely, identifying solvents potentially from the same source, and distinguishing between degradation products and manufactured solvents at complex sites.

The FAMU site is approximately 8 city blocks with various business and residential complexes scattered throughout. Over the course of the study, 74 monitor wells and over a hundred screen points have been installed and sampled with nearly all of the deep samples reporting a detect or an excess over ground water cleanup target levels set forth by the state of Florida. Primary contaminants of concern include PCE, TCE, and cDCE due to their detection frequency and concentrations in the surficial aquifer. Potential contaminant sources could be from a variety of historic industrial activities including dry cleaners, print shops, automobile repair shops, etc. Given the numerous concentration and hydrogeologic data, no definitive conclusions could be made regarding the release sources and biodegradation at the site.

Groundwater samples were taken for both VOCs and 3D-CSIA tests. Techniques for collecting and preserving groundwater samples for 3D-CSIA are identical to those used in collecting samples for VOCs using EPA Method 8260B. All samples were collected in the same manner and shipped to the offsite ZymaX Forensics Isotope laboratory. Results of the analysis are reported as  $\delta^{13}\text{C}$  for carbon (‰, VDPB),  $\delta^{37}\text{Cl}$  for chlorine (‰, SMOC), and  $\delta^2\text{H}$  for hydrogen (‰, SMOW). The precision of 3D-CSIA was demonstrated to be better than  $\pm 0.5\text{‰}$  for both carbon and chlorine, and  $\pm 5\text{‰}$  for hydrogen.

Considering the new lines of evidence obtained by using the advanced site diagnostic tool 3D-CSIA, Florida DEP was finally able to identify multiple chlorinated hydrocarbon releases from several sources at the FAMU Law School site. Remediation of the site is being planned as efforts to delineate other contaminant sources continues, and anticipate using results of this study as background information for future FL DEP investigations.

During this presentation, a brief introduction on the technique is given firstly, followed by site information and 3D-CSIA forensics performed to all samples, with new lines of evidence and data interpretation into details step by step. The effectiveness and limitation of 3D-CSIA forensics will be discussed.

## TRACING PLANT INPUTS TO SEDIMENTS: A COMBINED ISOTOPIC AND MOLECULAR FORENSIC APPROACH

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The relationship between surface vegetation and organic material contained within soils and sediments can represent an important source of information when attempting to link a questioned soil sample, taken as part of a forensic investigation to a location of interest. Previous research has shown that molecular parameters of well-preserved, long-chain n-alkanes from epicuticular waxes of higher plants are well preserved in soils and represent an opportunity to reconstruct a surface vegetation profile which may assist in sourcing sample origin. However, molecular distribution data alone often fails to provide species-specific information, as patterns of n-alkanes can overlap among different plant types.

Compound-specific stable isotopic analysis of plant and soil long-chain n-alkanes has been shown to provide greater resolution when seeking to discriminate between plant species, although studies seeking to characterise the molecular and isotopic n-alkane profile of vegetation and sediments in a particular location to ascertain the power of this multi-method approach are limited. Here we present n-alkane molecular,  $\delta^{13}\text{C}$  and  $\delta\text{D}$  data from plant and sediment samples taken from four locations ranging from sand flat to high marsh, at a salt marsh near Stiffkey on the north Norfolk coast. This site contains both C3 and C4 grasses (*Spartina anglica* and *Elytrigia atherica*), along with succulent species (*Suaeda vera*), and angiosperms (such as *Limonium vulgare* and *Atriplex portulacoides*). We observed differences of  $>10\text{‰}$  among species with respect to n-alkane  $\delta^{13}\text{C}$ , and up to  $20\text{‰}$  when considering n-alkane  $\delta\text{D}$ .

Statistical analysis of sediment samples taken from different locations within Stiffkey salt marsh demonstrates that they reflect the isotopic and molecular distributions of the dominant higher plant species in that location. These characteristics could potentially be mapped to create a predictive model for plant biomarkers in marsh sediments at the site. Our study shows that a combined analytical approach to n-alkane analysis in a forensic context could enhance the resolution of surface vegetation reconstruction and thus improve the ability to provenance soils. Because the dominant species identified at Stiffkey are common at coastal sites around the UK and in Europe, a thorough understanding of their molecular and stable isotopic composition would prove valuable on a national and international scale.

## ISOSCAPING SOIL CARBONATE ACROSS NORTHERN IRELAND

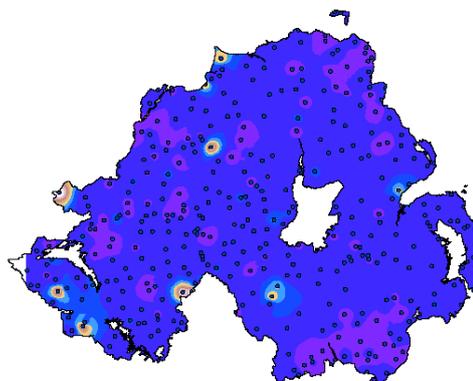
Neil OGLE\*, Declan CREAMER, Luc ROCK

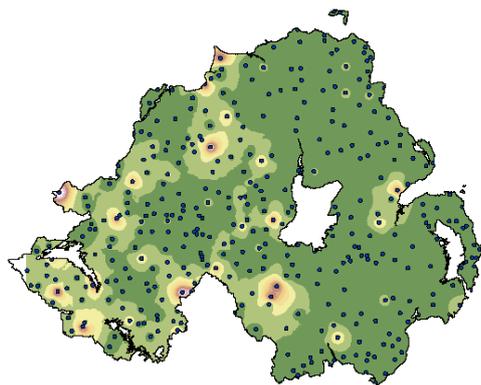
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Isoscapes depict the variation in isotopic ratios across a known geographic area. They can be applied to any media from which isotopic numbers can be derived, applicable to a number of fields of study and range from local to global in scale. This study depicts an isoscape of carbon ( $\delta^{13}\text{C}$ ) and oxygen ( $\delta^{18}\text{O}$ ) stable isotopes from approximately 300 soil carbonate samples across Northern Ireland (Figure 1). Isotopic soil carbonate values are useful within a number of fields. For example, they can be applied to studies of global climate dynamics, as carbon isotope values can reflect historical vegetational shifts while oxygen values reflect past hydrological change. Such inferences, however, can usually only be derived from studying ancient soils. Modern soil carbonate isotope analysis can readily be applied within an ecosystem by acting as a baseline for food chain dynamics and geoforensics. In this study,  $\delta^{13}\text{C}$  values for soil carbonate ranged from  $-10.5\text{‰}$  to  $-32.4\text{‰}$  and  $\delta^{18}\text{O}$  values ranged from  $-10.9\text{‰}$  to  $-21.2\text{‰}$ . The most enriched values of both carbon and oxygen were concentrated in pockets around the country (Figure 1, A and B) and while prevailing environmental conditions will undoubtedly have some influence these pockets coincide with specific types of underlying parent material such as limestone and peat. Potential exists to refine this data set further by increasing the scale of analysis, but currently a baseline of soil carbonate isotope values has been achieved. If combined with other data sets, such as the  $\delta^{15}\text{N}$  content of soil, there exists the potential to identify dynamic factors such as environmental change, pollution sources and biological traceability.

A





B

**Figure 1.** Isoscape of soil carbonate carbon (A) and oxygen (B) isotope values across Northern Ireland. Lighter shades denote enriched values. Blue dots are sampling locations

**TUESDAY, JULY 26, 2011**  
**2:00 – 3:30**

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**PALMERSTON ROOM:  
 CONTAMINATED LAND**

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**APPLICATION OF ENVIRONMENTAL FORENSIC  
 TECHNIQUES**

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Gasworks otherwise known as Manufactured Gas Plants (MGP) in America were a common feature across the UK, present in every city, town and many villages. There were at least 3500 MGPs in the UK and many more worldwide being constructed in every continent with the exception of Antarctica.

With the development of isotopic and state of the art GCxGC ToF MS methods to compliment traditional approaches to site investigation, former MGP sites are now a suitable subject for the application of environmental forensics. Whilst the importance of these analytical methods cannot be underestimated an understanding of the complex 200 year development the coal carbonisation industry is just as important.

The ability to utilise inflammable gases goes back to ancient times through the presence of eternal flames at sacred sites and willow the wisps. The first industrial application of gas dates back to ancient china when gas was piped through bamboo to heat salt pans for salt production. It is however, not until much later that the great potential of gas was realised and a practical process to manufacture it developed. Many people from across Europe experimented with the distillation of coal, splitting it into its constituent parts of inflammable gas, ammonia rich water, tar and coke. Most credit for the discovery of gas goes to William Murdoch a genius Scottish engineer. Murdoch developed a scientific curiosity into a practical

reality for commercial exploitation. From the first demonstration of gas lighting of Murdoch's house and office in Redruth in 1792 to the eventual demise of the manufactured gas industry in the 1970's, continuous development was undertaken to improve the manufacture of gas. When this is combined with the changing demands the UK gas industry faced, from its original purpose primarily for street lighting to its eventual use for domestic and commercial heating purposes, this has led to a very wide diversity of gas manufacturing processes being used across the UK.

These former MGPs have left an environmental legacy, for which the application of highly accurate environmental forensic methods may help provide a greater degree of understanding than that currently provided by standard analytical methods. Within this presentation we review the development of this industry and the technologies used and try to demonstrate how this industry's evolution may impact on how environmental forensics techniques are used in the UK and abroad.

The land ownership issues posed by the former MGPs in the UK are complex and this greatly effects how forensics may be used in the UK. When this is combined with the range of different processes used, the different by-products formed, how these were handled, used and disposed of and the potential impacts other nearby historic industries, it creates a very complex picture. Supported by case studies this presentation will attempt to highlight some of the complex issues which exist and how they may effect the application of environmental forensics.

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**A FORENSIC APPROACH TO EVALUATING  
 SOURCES AND RELATIVE AGES OF FREE  
 PRODUCT AND CHLORINATED SOLVENTS AT A  
 COMMINGLED PLUME SITE IN SUPPORT OF  
 CLEANUP COST RECOVERY LITIGATION**

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The proper planning of a forensic investigation is paramount to being able to develop a strong case against potentially responsible parties. Planning includes proactively collecting media samples before evidence is inadvertently destroyed, collecting ample samples and archiving for possible future analysis, identifying the most critical sample locations, and then developing a sound, scientifically-based analytical suite designed to answer specific questions relating to the age and origins of a release, or the potential sources of commingled contaminants.

This paper will examine a case study of a site in the greater Los Angeles Area where a commingled plume of free product gasoline and chlorinated solvents has impacted an approximately 6-acre area. The area of interest includes multiple former gasoline service stations, a dry cleaner, and automobile repair operations whose relative contributions have not been clearly established, but

require detailed forensic evaluation as part of discovery in a litigation.

Due to the multiple potential sources of petroleum and chlorinated solvent impacts dating back to the 1950s, and the complicated geologic conditions beneath the Site controlling the lateral and vertical distribution of dissolved-phase and free product petroleum and chlorinated solvents, it was critical to develop an advanced forensic sampling and analysis plan that would allow identification of the potential sources, and ultimately assist with the allocation of cleanup responsibility. The forensic plan had the primary objectives of: 1) Evaluating whether releases of non-oxygenated fuel had occurred that could potentially implicate larger oil companies that operated at the Site; 2) Discerning whether there was a significant release of petroleum hydrocarbons by the hydraulically downgradient operator who had alleged that the upgradient property was the location of the release; 3) Establishing whether high concentrations of chlorinated compounds detected in a monitoring well adjacent to a commercial moving and storage facility are associated with the dry cleaner or historical automobile repair operations; and 4) Evaluating whether the most recent gasoline service station operators are potentially liable as a result of the detection of ethanol in soil in the immediate vicinity of the fuel dispenser island.

This paper will also explore the historical context for the current forensic investigation, including how prior forensic work was used in litigation by an adjacent property owner. The prior forensic data were evaluated to determine what supplemental data are needed to address the objectives. Additionally, understanding how environmental forensics and other supporting environmental data were generally viewed by the court helped develop a more sound overall strategy.

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### **CARBON DISULPHIDE - CONTAMINANT OR BIOGENIC COMPOUND?**

Marcus TRETT<sup>1\*</sup>, Richard MOSS<sup>2</sup>, Beatriz CALVO<sup>1</sup> and George WILKINSON<sup>2</sup>

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A survey undertaken in July 2009 of a former landfill associated with the disposal of carbon disulphide (CS<sub>2</sub>) indicated a linkage between the site and adjacent, intertidal estuarine habitats. Although concentrations of up to 0.15 ppm CS<sub>2</sub> were identified in the foreshore sediments, the transfer pathways from the site to the foreshore were far from clear. This prompted a forensic review of the conceptual and exposure models that had been advanced by the site investigation team. The review comprised a combination of meiofaunal studies and multivariate correlation (ARESC) analyses which were used to examine the natural and contaminant factors that shaped intertidal assemblages of species. The analyses, which capitalise on the high diversity and high densities of meiofaunal nematodes, as well as their spectra of sensitivities to

different environmental stressors, confirmed a linkage between CS<sub>2</sub> concentrations and community structures.

To describe and delineate the distribution of CS<sub>2</sub> concentrations in the tidal habitats above and below the site within the estuary, further analyses were undertaken during the autumn months. In this instance, the analyses of core samples collected from different depths within the intertidal zone identified the highest CS<sub>2</sub> concentrations at sites 3 km seaward of landfill. In all cases the elevated concentrations were recorded in deeper sediments situated below the redox potential discontinuity layer. As potential waste disposal sources were absent from this location, a scientific literature review was carried out to evaluate the potential for biogenic production of CS<sub>2</sub>.

The review provided evidence that supported the existence of natural, microbially-mediated biogenesis of CS<sub>2</sub> in sulphate-rich, marine sediments. The authors will describe the forensic studies and the evidence that these yielded and, based on recently published work, will present a model in which electron donation by intertidal, algae (epipellic diatoms) may fuel the reduction of SO<sub>4</sub><sup>2-</sup> to CS<sub>2</sub> under anoxic conditions.

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### **BOYS SMITH ROOM: MINE SITES**

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#### **DISCRIMINATING BETWEEN BACKGROUND AND MINE-IMPACTED GROUNDWATER AT THE PHOENIX MINE, NEVADA USA**

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Differentiating between mineralized and non-mineralized background groundwater chemistry at a mine site can be challenging if there is an overprint of past and/or current mining on naturally mineralized conditions. At the Phoenix mine in the Copper Canyon mining district of Nevada, quantile-quantile H<sup>+</sup>/SO<sub>4</sub><sup>2-</sup> plots were initially used to segregate four wells clearly impacted by historical mining activity, then mineralogy from bore logs across the well screen elevation used to partition the 53 remaining wells into mineralized and non-mineralized populations. For each class, groundwater chemistry was examined to identify if SO<sub>4</sub><sup>2-</sup> and H<sup>+</sup> trends were stable (unimpacted) or increasing (impacted), then each well mapped as one of four resulting groundwater types across the mine site, defining the spatial extent of the different groups.

Several groundwater regions were identified. A group of mineralized, mine-impacted wells (Type II) are located in Philadelphia Canyon adjacent to the copper leach facility, with the anthropogenically impacted area bounded by several hydrologically downgradient, mineralized, unimpacted wells (Type I) to the south and east. There is a set of non-mineralized, impacted wells (Type III) downgradient from the tailings pond facility, where a historical release of sulfate is apparent in the well record.

However, in some downgradient wells the tailings pond pump-back mitigation system has resulted in recovery of the groundwater quality to a non-mineralized background condition. Finally, in the vicinity of the Reona heap leach pad, there is a group of non-mineralized, unimpacted wells (Type IV). Not surprisingly, most mineralized wells (Type I and II) are located in or near mined areas, while non-mineralized wells (Types III and IV) tend to be in the southern portion of the facility in the alluvia of Buffalo and Reese River valleys.

Once the well population was categorized, outliers, e.g., Phx-F were identified. This groundwater represents an extreme example of mineralized background (pH = 3.8; SO<sub>4</sub> = 4,600mg/L; As = 0.056 mg/L; Cu = 72 mg/L; Zn = 61 mg/L), which required further analysis. The elevation of the Phx-F screen interval had up to 5% jarosite, with mineralized fracture zones mapping directly to cavities in the adjacent Iron Canyon mine that originally contained a saturated ferrous sulfate solution, explaining the anomalous chemistry in this well. PHREEQC modeling confirmed that Phx-F groundwater could be derived from non-mineralized groundwater reactions with the host rock mineral assemblage.

This study demonstrates that an empirical approach using mining history, deposit geology, hydrogeology, well screen elevation mineralogy, groundwater chemistry trends, statistical analysis, and geochemical modeling provides a technique to distinguish among different classes of groundwater at the operating Phoenix mine site. Such an approach (or a derivative) may prove useful at other mines with different mineralogies and hydrogeologic settings.

### QUANTITATIVE MAPPING OF THE ENVIRONMENTAL IMPACT OF HAZARDOUS WASTE DERIVED FROM MINE SITES USING AN AIRBORNE HYPERSPECTRAL AND LIDAR REMOTE SENSING

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The release of hazardous mine waste from both active and abandoned gold mining areas is a major global environmental problem. The complexity of the processes, the scale of the mine sites, problems with accessibility and the lack of site information means that field-based survey methods are often too costly and provide incomplete coverage. The results of a study of an abandoned gold mine at Rodalquilar in southern Spain have demonstrated the potential of an integrated airborne remote sensing approach to the quantitative mapping of the distributions of mine waste on the mine site and in adjacent rivers. The advantages of using higher spatial resolution hyperspectral data integrated with airborne LiDAR and thermal datasets, in identifying secondary iron and clay species and resolving geomorphological settings of mine waste accumulations have been demonstrated. Integration of laboratory derived correlations of secondary iron species, cyanide and heavy metals concentrations with the results of the remote sensing study enabled the identification of locations of hazardous materials over the study area and a

more accurate understanding of the environmental status of the Rodalquilar area.

### INTEGRATED METHODS FOR SOURCE APPORTIONMENT: A CASE STUDY AT A CONTAMINATED LAND SITE IN MALAYSIA

Stephen MUDGE<sup>1\*</sup> and K F WONG<sup>2</sup>

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Many contaminated land sites contain materials from multiple sources including the natural background. A study was undertaken two years after remediation had taken place at an illegal landfill that had received aluminium dross; the original issue was "had the remediation been successful?" but the project identified other potential sources of metals. Soil samples were collected, acid extracted and analysed by ICP-OES and ICP-MS: the former method provided a multiple metal signature and the later technique was used to determine signatures from the stable isotopes of lead. Multivariate statistical methods were employed to define the signatures and apportion the three sources across the site.

Three separate sources were identified by PCA. Each signature was defined by PLS and the amount of variance explained by this signature was quantified in each sample. The background lead made a mean contribution of 0.09 g.kg<sup>-1</sup> across the site. The source related to the largely removed aluminium dross signature contributed a mean of 0.19 g.kg<sup>-1</sup> while a previously unidentified contamination source had a mean lead concentration of 0.96 g.kg<sup>-1</sup> at the impacted locations. Inspection of the full metal signature indicates that this waste may be indicative of a galvanic sludge with elements consistent with electroplating wastes (Fe, Cu and Zn).

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## WORKSHOPS

TUESDAY, JULY 26, 2011

4:00 – 5:30

### PALMERSTON ROOM:

#### SOURCE APPORTIONMENT OF INDUSTRIAL FUGITIVE DUSTS: DEVELOPMENTS IN PASSIVE DUST MONITORING

Hugh DATSON<sup>1</sup>, Mike FOWLER<sup>2</sup>, and Ben WILLIAMS<sup>1,2</sup>

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The workshop will open with an introduction to the context for passive (i.e. unpowered) dust monitoring at industrial sites. Typically, passive methods are used to assess non-specific fractions of fugitive dust (commonly, but potentially misleadingly, referred to as 'nuisance dust'). Given that 'dust' is defined in BS6069 Part 2 (BSI, 1994) as particulate matter < 75 µm diameter, specific fractions (e.g. PM10, the fraction having median aerodynamic diameter 10 µm) have been identified as having particular significance, especially in terms of potential harm to human health through inhalation. Whilst monitoring methods and limit values for PM10 dust are generally agreed (e.g. in relation to National Air Quality Standards, NAQS) there are no such standards for 'nuisance dust'. Consequently, a range of methods for monitoring 'nuisance dust' has been developed and there is a variety of 'custom and practice' criteria for its assessment, generally specific to a particular monitoring method.

Passive dust sampling can be considered in terms of 2 distinct approaches, each having 2 categories. Fugitive dust can be quantified in terms of its mass or visibility (i.e. soiling) (QUARG, 1996) and for either approach, samples may be taken in deposition (the vertical passage of dust to a surface, or the ground, driven by its deposition velocity) or flux (the horizontal passage of dust past a point, usually driven by the wind). Guidance on usage of various common methods and relevant criteria is freely available, if somewhat dated (e.g. Environment Agency, 2004) and misconceptions about appropriate utilisation of equipment occur (e.g. Hanby, 2011). Therefore, in the workshop, the passive dust monitoring methods in use in the UK and beyond will be considered and delegates will be invited to discuss the relative strengths and weaknesses of the methods; both in terms of their dust sampling characteristics and their suitability for sampling for environmental forensics.

The workshop will then consider the DustScan sampling method in detail. DustScan is a passive dust sampling system that uses a transparent adhesive 'sticky pad' to sample dust in flux and in deposition for subsequent image-based quantification and, as appropriate,



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geochemical analysis. DustScan samples are obtained over typically 7 – 14 day intervals in the vicinity of industrial sites such as quarries, surface coal mines, landfill sites and construction and demolition sites and as part of the workshop, delegates will be able to examine DustScan samples from a range of industrial sites. DustScan was developed at the University of Leeds (Farnfield and Birch, 1997) and refined at DustScan Ltd and the University of Leeds (Datson and Birch, 2006). Dedicated geochemical analysis methods of DustScan samples using ICP-AES and ICP-MS have been developed (Datson and Fowler, 2007) and their use in environmental forensics has been demonstrated by quantifying dust propagation at a hazardous waste landfill site (Fowler et al. 2010).

The sub-sample selection criteria, methodology and analytical processes involved for ICP-MS analysis (in particular) will be examined in detail in the workshop. Likewise, limitations in the pre-existing DustScan sampling methodology that have constrained its wider environmental forensic applications will be discussed. In particular, it has been impractical to detach the sampled dust from the collection media. Until recently, the sticky pads have been die-cut from sheets of a proprietary transparent PVC film with a permanent, cross-linked polymer-acrylic adhesive. Whilst this type of adhesive has excellent environmental dust sampling characteristics, its formulation renders it essentially insoluble (except in solvents that also dissolve much of the dust, e.g. HF). Furthermore, on retrieval after field sampling the sticky pads are sealed with a transparent film to facilitate handling and minimise contamination, thus making physical removal of dust at a later date difficult. Since the most effective means of dust 'extraction' from the sticky pads has been in solution and the image-based quantification method does not assess dust mass, geochemical data have been reported in terms of concentration in the extraction (e.g. ppm in solution) rather than in the dust (e.g.  $\text{mg g}^{-1}$ ). Confidence in adequately low detection limits has also been compromised by variable concentrations of some metals (e.g. Zn, Ba) in the sampling media.

The presentation to the workshop will set out the process by which a research project was successfully designed to investigate alternative dust sampling media and, initially, to improve the elemental coverage and method detection limits. Funding for the project was obtained from the Finance South East Ltd (FSE) proof of concept (PoCKeT) fund and the project was carried out in conjunction between DustScan Ltd and the School of Earth and Environmental Sciences (SEES) at the University of Portsmouth. As a consequence, new sticky pads have been specifically manufactured, with the new adhesive having similar transparency, tack and UV-resistance to the original but which can be dissolved in an appropriate solvent. The new design has been tested in the field at a range of UK industrial sites as well as in a comprehensive bench testing programme.

The workshop will be presented with results of field trials, in which the new sampling media performed well in relation to the original sticky pads. Dust capture and retention were apparently similar and sample handling and processing for image analysis were satisfactory, although transparency was marginally less uniform. In the bench tests, both types of sticky pad were exposed to a known dust at different concentrations and wind speeds in an environmental wind

tunnel. Correspondence between the sample media types was good to excellent in relation to the different image quantification methods applied. In addition, an array of elemental analysis tests was performed. NIST standard reference materials were applied to the new sticky pads, then extracted by dissolution of the adhesive and filtration onto 25 mm PTFE filter circles for ICP-MS analysis. Bulk dusts from a number of industrial sources were similarly applied, and analysed before and after application. An unanticipated benefit of the investigation has been the development of a practicable method to determine sampled dust mass in passive directional and deposited environmental dust samples, which has enabled reporting of mass/mass element concentrations in the dust samples after ICP-MS analysis.

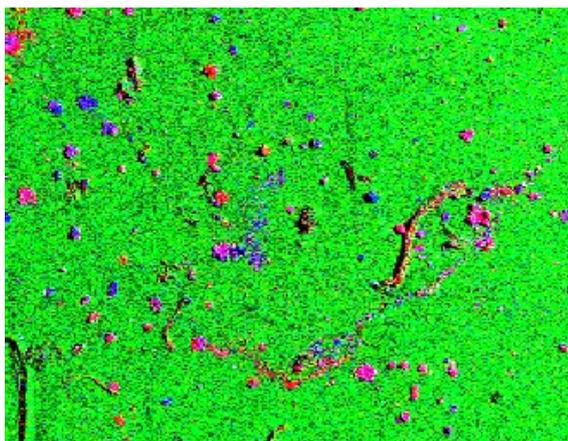
Consequently, delegates attending this workshop will participate in a review of passive dust sampling methods, consider the DustScan methodology in detail and learn how it has been investigated and developed to have many potential applications for environmental forensics.



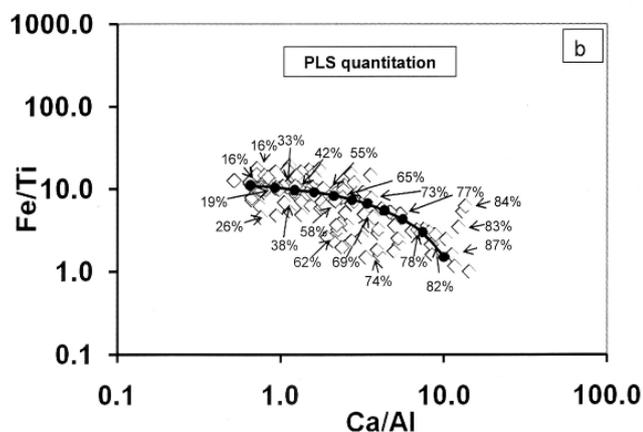
**Figure 1:** Fugitive dust generated by road traffic at a minerals site



**Figure 2:** DustScan directional and deposited dust gauge at a minerals site



**Figure 3:** False-colour SEM-EDX image of directional dust sampled at a waste transfer station, showing Ca (red), Si (blue) and C (green).



**Figure 4:** Binary mixing estimation showing data distribution annotated with target % estimate, derived by PLS from ICP-AES analyses of directional dust samples

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## BOYS SMITH ROOM:

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### UTILIZATION OF STABLE ISOTOPES IN ENVIRONMENTAL AND FORENSIC GEOCHEMISTRY STUDIES

Paul PHILP\*<sup>1</sup>

<sup>1</sup>School of Geology and Geochemistry, University of Oklahoma, Norman, OK, USA 73019

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Stable carbon and hydrogen isotopes have been used for decades in the petroleum industry and the development of gas chromatography-isotope ratio mass spectrometry (GCIRMS) has led to an explosion in applications of this technique in petroleum exploration and environmental and forensic geochemical fields. This workshop will present an introduction to stable isotope geochemistry and discuss applications of stable isotopes to various environmental problems, including their potential for monitoring attenuation of compounds such as PCE, MTBE, BTEX, etc. Topics will include an introduction to the concept of stable isotopes, with particular attention to carbon, hydrogen, and

chlorine. Techniques for determination of bulk isotope values will be described along with the advantages and disadvantages of the GCIRMS approach.

Examples of using bulk isotopic data combined with GC or GCMS data for the purpose of determining whether or not contaminants are related to each other or not will be given. This is particularly important where there might be multiple sources potentially responsible for a particular spill and it is necessary to see whether any of them were actually responsible for the spill. In cases where the contaminant has multiple components, and the GC and GCMS data are ambiguous, relationships between source and product might only be determined through the stable isotopes of individual compounds. GCIRMS is also extremely valuable for single component contaminants, such as MTBE or PCE, where GC and GCMS will be of no use for correlation. In this workshop, particular emphasis will be placed on the chlorinated compounds. There are a number of examples that have already been published where GCIRMS has been used to both differentiate sources of PCE/TCE as well as studying natural attenuation at the contaminated sites.

Most early applications of stable isotopes to environmental problems were limited to carbon and hydrogen isotopes. Efforts are being made to introduce the use of chlorine isotopes as an additional tool for monitoring chlorinated compounds. The approach is not as mature as with carbon and hydrogen isotopes but the methodology involved will be discussed along with problems associated with the use of chlorine isotopes. One particular area where chlorine isotopes are being successfully utilized is that of vapor intrusion and examples from this area will be discussed.

Finally the use of the various fingerprinting techniques described above in monitoring attenuation at sites undergoing remediation will be discussed. The combined use of the stable isotopes, GC and GCMS can be extremely valuable tools monitoring remediation as well as determination of the onset of natural attenuation.

**WEDNESDAY, JULY 27, 2011**  
**9:00 – 10:30**

## **PALMERSTON ROOM:**

### **MULTIDIMENSIONAL GC\*GC FINGERPRINTING FOR ENVIRONMENTAL AND BIOLOGICAL FORENSICS**

Donald PATTERSON\*<sup>1</sup>, Alec KETTLE<sup>2</sup> and Frank DORMAN<sup>3</sup>

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<sup>2</sup> LECO Separation Sciences, LECO UK

<sup>3</sup> The Pennsylvania State University, Forensic Science, 107 Whitmore Lab, University Park, PA 16802, USA

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**Objective:** To introduce the technology and development of GCxGC, within environmental and human forensics, supported with examples of applications and case studies

**Overview:** The number of chemicals measured by routine laboratories has limited uses in environmental forensic investigations involving chemical fingerprinting. A technology is currently available that allows the separation of thousands of chemicals using comprehensive two-dimensional gas chromatography (GCxGC). In addition to the large increase in resolving power of the GCxGC system, it also allows a three-dimensional visualization of the data in support of the environmental forensics investigation. The comprehensive GCxGC approach utilizes two columns with different separation characteristics such as a polar and a non-polar column. This approach generates three-dimensional structured chromatograms that constitute a fingerprint which is characteristic of the source matrix. The GCxGC system can be coupled with many different detection systems. The most powerful system involves the use of time of flight mass spectrometry (TOFMS) which collects full scan spectra at the sensitivity of conventional mass selective detectors set in selected ion monitoring mode. This increase in sensitivity using the GCxGC system (a factor of ~10) is due to the focusing effect of the modulation device located between the first and second GC column. Through the collection of full scan spectra, any of the thousands of chemicals can be identified by comparing to known spectral libraries. This Workshop will have speakers covering a wide range of topics including: The history and analytical advances leading to this new technology; the use of GCxGC in environmental (soils, oils, gasoline, dust) and human (blood and urine) forensics; the use of GCxGC in various matrices of SRMs; Chemometric approaches to forensic GCxGC data.

## **BOYS SMITH ROOM:**

### **CHLORINATED SOLVENTS: A FORENSIC HISTORY OF DEGREASING AND DRY CLEANING**

Brian MURPHY<sup>1\*</sup> and Robert MORRISON<sup>2</sup>

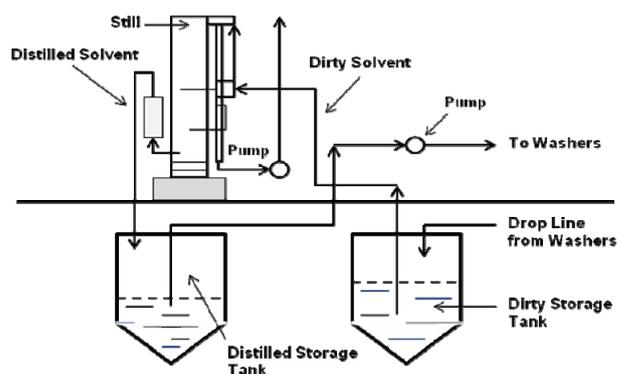
<sup>1</sup> Exponent Inc. 1255 Gulfstream Avenue, 202, Sarasota, Florida, 03235, USA

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This workshop focuses on selected topics relevant to forensic investigation of chlorinated solvent releases into the environment from dry cleaning equipment and vapour degreasers. The premise of this workshop is that a historical knowledge of this equipment is necessary prior to initiating an environmental forensic investigation.

A knowledge of the chemicals used in all facets of a vapour degreasing and drycleaning operation and their periods of commercial availability and composition are frequently key in identifying the age of a chlorinated solvent release from these operations. In addition to the actual vapour degreasing or drycleaning solvents, other operational categories include chemicals used in the vapor/drycleaning machines exclusive of the degreasing solvents which are often useful as forensic surrogates when detected with a chlorinated solvent used for drycleaning/vapour degreasing to date the release. While vapour and drycleaning solvents are the focus of this workshop, it is prudent to forensically identify other potential surrogate chemicals as to whether they represent a potential age dating marker.



Schematic of dry cleaning clarifier and still system used in the United States in the 1940s.

Once an understanding of the equipment is known, an investigation that optimizes the probability of detecting chemical diagnostic indicators of the age or source of a release can proceed. The diagnostic indicators include using stabilizers and feedstock impurities to bracket when a chemical used in dry cleaning or for degreasing can be identified through proper analytical testing. The primary chlorinated solvents emphasized in this workshop are trichloroethylene and perchloroethylene along with the stabilizers specifically used in this equipment at different points in time.

**WEDNESDAY, JULY 27, 2011**  
**11:00 – 12:30**

**PALMERSTON ROOM:**

**HISTORICAL AND FORENSIC ASPECTS OF  
LEADED GASOLINE**

Gil OUDIJK<sup>1\*</sup>

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goudijk@triassictechnology.com

Tetraethyl lead (TEL) was first introduced as a gasoline additive in 1923. After many years of research, TEL was discovered by researchers at General Motors in Dayton, Ohio. Credit for its discovery is normally given to Thomas Midgley, Jr., who later went on to discover chlorofluorocarbons (CFCs). However, the research work was headed by Charles F. Kettering, who was the discoverer of many automotive inventions, such as the electric starter.

In the late 1800s and the early part of the 20th Century, automobiles were run on many different types of fuel, such as steam, alcohol, diesel fuel and natural gas. Gasoline was also used, but it was limited by a drawback known as "knock". As the motor engines became more powerful and the compression ratios increased, a knocking or pinging would occur in the cylinders. This was caused by detonation of the fuel. TEL was introduced as a way of reducing that knock and it allowed engines to be produced of greater power. Many may claim that TEL paved the way for the great industrial expansion of the early 20th Century.

At the time, many believed that TEL would only be used for a few years. Petroleum reserves were believed to be small and it was anticipated that alternative fuels would need to be found. At the time, Henry Ford believed that ethanol would be the fuel of the future. However, ethanol was not a fuel that could be patented (unlike lead gasoline) and, therefore, it was in the interest of industry that leaded gasoline be used.

In 1924, workers at Jersey Standard's (today's ExxonMobil), DuPont's and GM's TEL manufacturing facilities began to develop lead poisoning and about 15 died. A large outcry developed from the public and leaded gasoline was subsequently banned. GM and Jersey Standard petitioned the government, the Surgeon General reviewed the situation and eventually leaded gasoline went back on the market. However, research into the adverse health impacts of leaded exhausts was not investigated at that time in much detail. It was not until the 1960s that researchers began to realize the full impact of leaded gasoline on the environment. Despite the impact to the environment and the known ill effects on children, it took another 30 years before leaded gasoline was fully banned in the United States.

The history of leaded gasoline is an important subject because it allows us to see where this country has been as

far as our past energy choices and possibly through these mistakes, it will help to better guide us in the future.

**BOYS SMITH ROOM:**

**CHLORINATED SOLVENT RELEASES: CSIA  
CASE STUDIES**

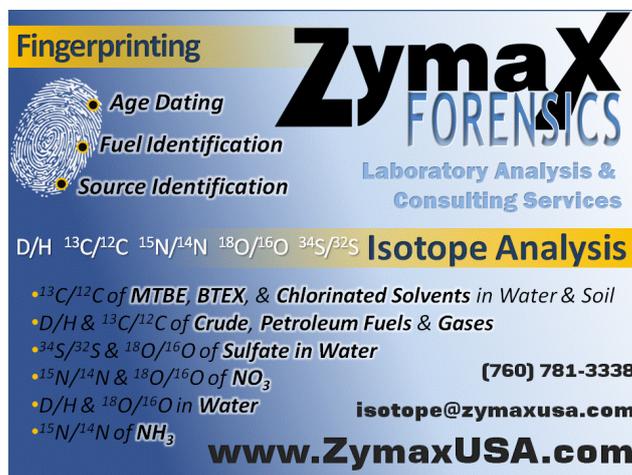
Yi WANG<sup>\*1</sup> and Alan JEFFREY<sup>1</sup>

<sup>1</sup>DPRA/ZymaX Forensics, 600 S. Andreasen Drive, suite B,  
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This workshop will show how CSIA techniques have been used to investigate chlorinated solvent plumes and determine whether releases from multiple sources have occurred. The case studies progress from simple studies using a single isotope ratio to more complex studies, using three isotope ratios. In some cases where there was little evidence of biodegradation of PCE or TCE, source identification was relatively straightforward. Where biodegradation was suspected, fractionation (alteration) of the isotope ratios complicated the source identification. However, the case studies will show how the direction of the isotopic fractionation (positive or negative), isotope mass balance, and hydrogen isotope ratio of TCE were used to clarify the source identifications. The case studies will illustrate how CSIA was used in the following situations:

- Carbon isotope ratio of PCE with little evidence of biodegradation
- Carbon isotope ratio of TCE with little evidence of biodegradation
- Carbon isotope ratio of PCE and TCE with evidence of biodegradation of PCE
- Carbon and Chlorine isotope ratios of PCE in multiple aquifers
- Carbon, Chlorine, and Hydrogen isotope ratios of PCE and TCE.



**Fingerprinting**

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- Fuel Identification
- Source Identification

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- <sup>13</sup>C/<sup>12</sup>C of MTBE, BTEX, & Chlorinated Solvents in Water & Soil
- D/H & <sup>13</sup>C/<sup>12</sup>C of Crude, Petroleum Fuels & Gases
- <sup>34</sup>S/<sup>32</sup>S & <sup>18</sup>O/<sup>16</sup>O of Sulfate in Water
- <sup>15</sup>N/<sup>14</sup>N & <sup>18</sup>O/<sup>16</sup>O of NO<sub>3</sub>
- D/H & <sup>18</sup>O/<sup>16</sup>O in Water
- <sup>15</sup>N/<sup>14</sup>N of NH<sub>3</sub>

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## POSTERS

### CASTLEREAGH ROOM:

#### SOURCE IDENTIFICATION OF METHAMIDOPHOS BY USING STABLE CARBON ISOTOPE RATIO

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In December to January, 2007, some people have suffered food poisoning in Chiba and Hyogo prefectures, Japan after eating Chinese-made frozen dumplings (gyoza). Very high concentration of methamidophos (O,S-dimethyl phosphoramidothioate), 410ppm to 19,290ppm, was found in dumplings (gyoza) on January 30th 2008 by the health ministry and police in Japan. Methamidophos is organophosphorus insecticide, marketed only reagent for research. The police science in Japan made a point, methamidophos was mixed in China, since some impurities in methamidophos in gyoza were existed (impurities identification). However, the government in China claimed that the impurities were mixed later, and in Japan. The biggest problem of this incident was whether methamidophos mixed in Japan or China. Thus, the impurity existence or nonexistence seemed to be not enough evidence.

In this study, stable carbon isotope ratio of methamidophos using GC/C/IRMS was measured for source identification. Moreover, the system was fused with cryofocus system for methamidophos analysis. Analysis of methamidophos was carried out with a GC (Agilent Technologies, 7890A) coupled via combustion-interface to IRMS (Isoprime corp., Isoprime). The cryofocus system (Brech Buhler, Cold Trap 9000) was set up between combustion-interface and IRMS. In addition, the some combustion tubes, CuO stick (ready-made products by Isoprime); CuO stick with 1% Pt and 1% Ni (Elemental Microanalysis (abbr., EM), B1149); CuO grainy with 1% Pt and 1% Ni (EM, B1158); nickel oxide grainy (EM B1130); tungsten powder (EM, B4000), were tested for high accuracy and precision. Seven methamidophos reagents (Wako Pure Chemical Industries, Supelco, GL Science, Sigma-Aldrich) one Chinese agricultural chemicals (MTD600: Silverstre Peru S.A.C) were analyzed. For analytical method, the GC was equipped with a fused silica capillary column (30 m × 0.25 mm i.d.). The GC oven was programmed from 30°C for 25 min to 175°C for 10 min at 20°C/min and 320°C for 10 min at 20°C/min. The ultra high purity helium (<99.9999%) was used as the carrier gas. Cryofocus of liquid nitrogen was done for 220 seconds at detection time of methamidophos peak.

As a result of the comparison of 7 oxidizer tubes, grainy CuO with 1% Pt and 1% Ni (EM, B1158) was indicated highest precision, 0.05‰ (SD) as fifth analyses. As a result,  $\delta^{13}C$  of methamidophos was ranged from -46.26‰ to -32.60‰ with the average S.D., 0.21‰. Methamidophos of Chinese agricultural chemicals (MTD600) was -45.02‰. Although we can not collect and analyze the methamidophos in gyoza itself, if the methamidophos in gyoza is approximately -45‰ near MTD600, the methamidophos in gyoza might be mixed in China by using Chinese methamidophos like MTD600. Moreover, methamidophos of MTD600 was very close to GL



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science (-44.99 ‰). However, even if the methamidophos in gyoza might be mixed in Japan by using methamidophos reagent of GL science, pesticide and chemical reagent must be recorded in Japan. Thus, we can judge by investigating distribution channel of GL science. The terrorist can obtain easily the pesticide like methamidophos. Therefore, it is very important to identify the pesticide source and channel quickly using stable isotopic science in the future.

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### ONE-STEP ACCELERATED SOLVENT EXTRACTION OF SOIL AND COAL TAR SAMPLES FOR COMPOUND SPECIFIC ISOTOPE ANALYSIS OF PAHS

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We present a one-step extraction of soil and coal tar samples for carbon and hydrogen compound specific isotope analysis (CSIA) of polycyclic aromatic hydrocarbons (PAHs) using accelerated solvent extraction (ASE).

CSIA has been used in Environmental Forensics for source identification by comparison with putative sources. It has proven efficient in cases where the classical tiered approach for chemical fingerprinting failed to positively identify a match, for example, in cases where weathering had critically altered the fingerprints. CSIA is employable only when the isotopic signatures of the target compounds remains constant over time and space. Biodegradation is the most likely culprit when the isotopic signatures of a contaminant or a group of contaminants vary over time; CSIA can therefore be used for source matching only when the biodegradation has not affected the signatures. The most evident instance where biodegradation does not affect the isotopic values is when biodegradation does not take place. This can be the case in free phase samples and non aqueous phase liquids (NAPLs) such as dense tar NAPLs (DNAPLs) but also when contaminants are protected from biodegradation because of their sorptive interactions with the soil; PAHs in soil being a good example of this phenomenon.

PAHs are the most abundant compounds in coal tar DNAPLs found in former manufactured gas plants sites; their stable isotopic values therefore represent a very good fingerprint of the source while in soils, the carbon isotopic signatures of PAHs permit to distinguish between possible origins (creosote, urban background, natural occurrence...).

Traditionally, after extraction of a complex hydrocarbon sample, the aromatic fraction is separated from the rest of the sample using a silica/alumina column. We propose here a one-step extraction-clean up stage: soil samples are placed in the ASE cell above a mix of silica gel and drying agent (sodium sulfate) and two fractions are eluted, one with hexane (F1) and one with a mixture of hexane and toluene (9:1) (v:v) (F2). The PAHs with lower molecular weights come out in F1 while the heavier PAHs come out in F2. We also developed a similar procedure for coal tar

DNAPLs during which DNAPL is first combined with diatomaceous earth and sodium sulfate (1:1:1) and then extracted in the same two fractions.

The possible carbon and hydrogen isotopic fractionations of the PAHs associated with the extraction process were investigated and the results are presented here.

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### SIMULTANEOUS CHEMICAL AND MICROBIOLOGICAL STUDY OF BIODEGRADATION OF COAL TAR RESIDUES FROM FORMER MANUFACTURED GAS WORKS

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Poly Aromatic Hydrocarbons (PAHs) are found in complex mixtures e.g. Coal Tar. Perhaps the most common source of industrial PAH contamination is from Gas Work sites, where tanks of Coal Tar are stored underground. Although this industry is now declining, many of the storage tanks have eroded, leaching Coal Tar and PAHs into the surrounding soil.

Previous studies have consistently recognized only a few bacterial groups are associated with PAH degradation in soils, mainly *Sphingomonas*, *Burkholderia*, *Pseudomonas* and *Mycobacterium*.

These bacterial groups are naturally occurring in many different environments. Using soil and water samples from a former Gas Works site, indigenous bacteria are supplied with Coal Tar as a carbon source. The effects of coal tar degradation on the microbial community metabolic rates will be tracked using molecular biology tools PCR and DGGE. These techniques analyse 16S rRNA nucleotides produced by the bacterial community. The assembly and storage of RNA molecules is a sign of increased metabolic activity and the first stage of bacterial reproduction and so it is hypothesised that a link can be made between the consumption of PAHs in Coal Tar and bacterial metabolic activity. These techniques also provide background information on the different species of bacteria present and how species hierarchy change as PAHs breakdown.

In order to establish a pattern between the stage of bacterial activity and the point of breakdown of coal tar, following DNA/RNA extraction, the coal tar organic compounds remaining in the samples are removed using Accelerated Solvent Extraction (ASE) and examined using comprehensive two-dimensional gas chromatography coupled to time of flight mass spectrometry (GCxGCTOFMS). This allows correlation of marked changes in chemical structure of coal tar/PAHs with molecular fluctuations in microbial populations.

It is important to explore these links to further understand natural attenuation of contaminants and aid in developing management strategies. Determining the stage of

degradation of coal tar can be linked to the metabolic activity of indigenous bacterial community and therefore suspected rates of degradation, allowing a more reliable estimation of time scales and cost associated with natural attenuation of PAHs to be achieved. Also, the presence of specific bacteria could reveal past contaminants of the site, which would benefit early site investigations.

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## VISUALIZATION AND ANALYSIS OF ENVIRONMENTAL FORENSIC DATA

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Environmental forensics is an additive discipline to traditional observational science in that one must consider not only the what, but also the when and the how. The complexity of an environmental forensic investigation – often a function of the relationships between the manifest what and the theorized when and how – presents unique challenges for data analysis and presentation. While the data and information encountered during a forensic investigation can be overwhelming, tools are available to take advantage of these relationships and transform a chaotic web of complexity into linear, easy-to-understand, defensible positions. Technologies such as geographic information systems (GIS) can be coupled with other tools to allow access and interactive visualization of all aspects of the data. Geographic data can pose challenges to visualization and analysis when moving from two to three dimensions or when a temporal component is introduced. Effective data management practices can overcome these challenges. Any type of information can be effectively analyzed and presented in a litigation setting if it has been organized to utilize spatial, temporal and evidentiary relationships. Using forensic case studies for chlorinated solvents, polychlorinated biphenyls (PCBs), and hydrocarbons, the authors will introduce readers to the types of data typically encountered in an environmental forensic project. More importantly, instances where traditional data analysis or visualization will likely fail are presented side-by-side with alternate techniques proven to be effective.

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## EFFECTS OF COMBUSTION EMISSIONS FROM THE EURASIAN CONTINENT IN WINTER ON SEASONAL $\Delta^{13}\text{C}$ OF ELEMENTAL CARBON IN AEROSOL IN JAPAN

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Particulate matter (PM) can have adverse effects on human health. Moreover, because the mechanisms of PM formation and behavior in the atmosphere are very complicated, it is difficult to determine relationships between potential source and receptor. We investigated suspended particulate matter (SPM, particles with a 100%

cut-off aerodynamic diameter of 10  $\mu\text{m}$ ) and PM<sub>2.5</sub> (particles with a 50% cut-off aerodynamic diameter of 2.5  $\mu\text{m}$ ) concentrations in aerosols sampled in Akita Prefecture, Japan, from April 2008 to January 2010, and the carbon isotope ratios ( $\delta^{13}\text{C}$ ) of elemental carbon (EC) in both SPM and PM<sub>2.5</sub> and in samples from possible sources for source apportionment. In this study, we can measure  $\delta^{13}\text{C}$  of EC of PM with high accuracy and precision, after separating EC and organic carbon (OC). In addition, we also determined the ion contents of SPM and estimated the back trajectories of air masses arriving at Akita Prefecture during the study period.

The SPM concentration was very low (annual average, 15.2  $\mu\text{g}/\text{m}^3$ ), and it tended to be higher in spring and lower in winter. We attributed the higher SPM in spring to dust storms brought from the Asian continent. The average annual PM<sub>2.5</sub> concentration was 8.6  $\mu\text{g}/\text{m}^3$ .  $\delta^{13}\text{C}$  of source samples (gasoline and diesel vehicle exhaust, fireplace soot, open biomass burning emissions, street dust, soil, charcoal, and coal) ranged from  $-34.7\%$  to  $-1.8\%$ .  $\delta^{13}\text{C}$  values of soot from gasoline light-duty ( $-24.4 \pm 0.7\%$ ) and passenger vehicles ( $-24.1 \pm 0.6\%$ ) were very similar to that of soot from all diesel vehicles ( $-24.3 \pm 0.3\%$ ).  $\delta^{13}\text{C}$  was enriched in SPM in winter compared with summer values, moreover, only a slight seasonal trend was detected in  $\delta^{13}\text{C}$  in PM<sub>2.5</sub>.

From these data and the source results, we hypothesized that the enrichment of  $\delta^{13}\text{C}$  of SPM and PM<sub>2.5</sub> in winter was a long-range effect of overseas combustion processes such as coal combustion. In addition,  $\delta^{13}\text{C}$  of SPM was correlated with Cl<sup>-</sup> and Mg<sup>2+</sup> contents in SPM, suggesting the influence of sea salt. We verified this hypothesis by back trajectory analyses. The results indicated a continental influence effects on EC of SPM and PM<sub>2.5</sub> in winter.

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## USING GCXGC TO IDENTIFY PRODUCTS OF CHEMICAL OXIDATION REMEDIATION FOR POLYCYCLIC AROMATIC HYDROCARBONS

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Polycyclic aromatic hydrocarbons (PAHs) are common organic contaminants of soil, originating from industrial activities such as gas production from coal, posing a threat to both human health and the environment. The low polarity and high hydrophobicity means that PAHs are often resistant to remediation by biodegradation. It is possible to use in situ chemical oxidation (ISCO) in order to enhance and increase biodegradation, possibly due to the increased polarity and solubility of the oxidised products. Using chemical fingerprinting to monitor remediation allows for better understanding and identification of products and intermediates of these processes than other techniques such as monitoring stable isotope composition.

Chemical oxidation treatment, using oxidising agents such as potassium permanganate and sodium persulphate, was used to treat soil contaminated with PAHs. Analysis of soils was carried out using Accelerated Solvent Extraction (ASE) for a combined clean-up/extraction stage, and chemical analysis by comprehensive two-dimensional gas chromatography couple to time of flight mass spectrometry (GCxGC/TOFMS). The technique of GCxGC/TOFMS offers the capability of identifying and characterising a much wider range of compounds and obtaining a chemical fingerprint of the reaction. Identifying changes in the chemical fingerprint as remediation proceeds allows for identification of oxidised products that may be more susceptible to degradation by microorganisms. A better understanding of these processes will be important for future monitoring of remediation.

### SOURCE IDENTIFICATION OF VOCs IN ROADSIDE USING H/D ISOTOPE

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Volatile Organic Compounds (VOCs) are important precursors of ozone and secondary organic aerosols, some of these compounds have carcinogenic, teratogenic or mutagenic character. Sources of VOCs in ambient air exist very complexly, e.g. vehicle exhausts, gasoline evaporation, solvent use, natural gas emissions, and industrial processes etc. In order to develop efficient air pollution abatement strategies, it is important to identify the emission sources clearly. In recent years, compound specific isotope analysis (CSIA) is development, and stable carbon isotope ratio of VOCs in air has been measured as a novel method of source identification. However, studies of CSIA of atmospheric VOCs were very few, especially hydrogen of atmospheric VOCs as source apportionment have not been existed. Stable hydrogen isotopes have bigger mass differences than carbon isotopes. Therefore, bigger isotopic distribution might be indicated and caused the differences between sources. If CSIA of hydrogen isotope of atmospheric VOCs can be measured with high accuracy and precision, it might be powerful tool for source identification. In addition, the results might be expanded various fields, forensics field.

In this study, we try to analysis hydrogen stable isotope ratios ( $\delta D$ ) of VOCs for air pollution using a coupling system of thermal desorption instrument and GC/TC/IRMS (TD+GC/TC/IRMS). Firstly, the precision of  $\delta D$  of VOCs-mix standard gas using TD+GC/TC/IRMS was measured. Secondly, we applied to analysis of sources and roadside samples. Source analyses were conducted about vehicle emission (hot and cold mode) and gas station. Roadside samples collected from three points in Akita prefecture, Japan. Thirdly, experiments of VOC photochemical reaction by UV irradiation were performed to estimate effect of photochemical reaction for atmospheric VOCs. Finally, the influence of sources in the roadside was discussed with a focus on benzene and toluene.

As a result, the precision (standard deviation; SD) of TD-GC/TC/IRMS was 1.1–5.1‰ for  $\delta D$  of 30 VOCs of VOCs-

mix standard gas. The results seemed to be reasonable in comparison with other few studies. The difference between hot mode and cold mode in the vehicle emission analyses was clearly shown about benzene (approximately 46‰), and not shown so much about toluene (approximately 4‰). Thus, it seemed that hot mode and cold mode could be identified for benzene. From the result of sources and roadside, it found that the benzene of the roadside in this study might be influenced by hot mode of the vehicle emission.

### PUBLIC PERCEPTION OF CRIMINAL LEGAL SANCTIONS AND ITS ROLE IN WILDLIFE PROTECTION

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The definition of Environmental Crime in the UK is both problematic and uncertain, distinguishing whether the crime is a technical regulatory breach, or whether its offenders should be considered truly criminal and thus liable. Definitions reflect different perspectives from moral, philosophical, and legal to local amenity-led perspectives (Bell and McGillivray (2008)).

Consistency and uniformity is completely fragmented within the British legal system. UK Environmental Law is driven by estranged enforcement bodies enforcing for example, the Environmental Act 1995, Environmental Protection Act 1990, Town and Planning Act 1990, Water Resources Act 1991 and the Wildlife and Countryside Act 1981, Countryside and Rights of Way Act 2000, Natural Environment and Rural Communities Act 2006. It is a system where liability is strict but not absolute with the added complication of a flexibility of enforcement which includes persuasion, a warning letter, enforcement notice, criminal penalty, suspension or revocation of a licence, as illustrated in the enforcement pyramid by Ayres and Braithwaite (1992). Options vary across the country, reflective of budgets and areas of depravity or crime where the environment is not seen as imminent priority. Natural England has few enforcement options available, for example damage of SSSI sites, however an Environment Agency officer has many. It is suggested by some academics that there is a distributional deficit in current policy and impact appraisal tools (Walker (2007)).

The situation with regard to wildlife crime is complicated by the fact that distinctions are made between those wildlife crimes committed as a result of ignorance, those resulting from neglect and those which occur as the result of a deliberate act. Furthermore the situation is exacerbated by the fact that distinctions are made between those actions which are unlawful and thus criminal, and those which may cause damage and destruction to both species and habitat, but which are not, under current legislation, unlawful. Thus we are in situation where our environmental policies and

legislation do not provide a clear and coherent definition of what constitutes wildlife crime. It is suggested that these policies and regulations do little to promote society's understanding of the wider implications that our commercial and leisure activities have on our flora and fauna.

This research will discuss the effectiveness of the criminal laws regarding environmental crime focusing on harm to wildlife and the impact of the societal perception.

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### SEASONAL VARIATION OF TRIHALOMETHANES CONCENTRATION IN DRINKING WATER OF CONCEPCION-TALCAHUANO, CHILE

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Chlorination is widely used as disinfection processes to reduce microbiology load in drinking water. During this process chlorine reacts with organic matter generating a family of disinfection by-products such as trihalomethanes (THMs). This family includes chloroform (CHCl<sub>3</sub>), bromoform (CHBr<sub>3</sub>), dichlorobromomethane (CHBrCl<sub>2</sub>) and dibromochloromethane (CHBr<sub>2</sub>Cl). The presence of these compounds in drinking water can pose a severe health threat due to a potential carcinogenicity effect. It has been reported that THMs in waters increase the cancer risk of bladders and cause reproductive defects.

The main objective of this research was study the seasonal variation of THMs in the distribution network of drinking water in the city of Concepción and Talcahuano, Region of Bio Bio, Chile. The samples were taken in two campaigns, summer of 2007 and winter 2008. For each period one litre of drinking water was taken in triplicate for each sampling point and carried to laboratory for their analysis. THMs were extracted using solid phase microextraction (SPMe) and analysed by Gas chromatography and mass spectrometry (GC-MS). Simultaneously, several parameters were measured such as temperature, pH, conductivity, turbidity, free chlorine, chloramines, total chlorine, residence time, distance from de source, UV-245nm and total organic carbon (TOC).

The concentration ranges of THMs during summer were 9.7-111.6, 0.1-1.0 and 0.9-25.5 mg/L for CHCl<sub>3</sub>, CHClBr<sub>2</sub> and CHCl<sub>2</sub>Br respectively. For winter the concentrations were 5.6-132.4, 0.1-0.9 and 0.9 -35.2 mg/L for CHCl<sub>3</sub>, CHClBr<sub>2</sub> and CHCl<sub>2</sub>Br respectively. Bromoform was not detected within samples.

Principal component analysis (PCA) was performed for THMs concentrations and physicochemicals parameters for both campaigns. It showed that THMs are well correlated to residence time. For both campaigns TOC, UV-254, free chlorine behaved similarly. However pH and temperature behaved differently. The higher concentrations of THMs were detected during the winter campaign. The concentration of each THM showed a well correlation with residence time for this period, being with the temperature the main variables during the formation of these compounds in the network of drinking water of Concepcion-Talcahuano.

The authors would like to dedicate this research to the cities of Concepción and Talcahuano, Region of Bio Bio, Chile that were devastated after the earthquake 8.8 Richter and posterior tsunami the last 27th of February of 2010.

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### ENVIRONMENTAL FORENSIC IN BRAZIL

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The emerging economy of Brazil also leads to many environmental crimes. Criminal prosecution counts on thousands of laws and regulations in Federal, State and local levels. The Brazilian Federal Police has 200 forensic scientists working with environmental forensic, only on federal cases. Geologists, biologists, forest engineers, agronomists, veterinarians, mining engineers, cartographers, chemists, distributed in the 27 states of Brazil, compose a multi-disciplinary team that produced about 2200 environmental forensic reports in 2010, in the whole country. The Chart 01 shows distribution of environmental forensic reports by type, in 2010. Chart 02 shows the growing of environmental reports in the past 5 years compared with other kinds of forensic reports as engineering and crime scene (only federal jurisdiction).

The major works of environmental forensic team are done in field surveying, such as interpreting, measuring and collecting evidences of crimes. The diversity of biomes and ecosystems' components, besides a wide range of regulations of each kind of areas and/or species protected, require multidisciplinary field investigation to identify and profiling environmental crimes. Global Navigation Satellite Systems (GNSS) receivers, multi parameter probes, soil sampler, forest inventory instruments, geophysical equipment (GPR), are examples of apparatus used in the field surveys.

The National Criminalist Institute facilities support Environmental Forensic Section in laboratory analysis of evidences. Specialized labs include remote sensing and geointelligence, gemstone analysis, DNA, magnifying and multispectral lenses systems, scanning electronic microscopes, micro tomography, and chemical analysis such as infrared/Raman, ion chromatography, atomic absorption spectroscopy, stable isotopes (IRMS), Inductively Coupled Plasma Mass Spectrometry – ICP-MS, and others.

Great efforts and large police operations, such as “Arc of Fire Operation” in course over the hotspots of Brazilian Amazon deforestation, are increasing the demand of environmental forensic reports. International cooperation with reference institutions is seen as an opportunity to develop methods and exchange experiences to cooperate with law enforcement an environment protection. Data basis developments, reference material exchange, partnership in research and development projects are now the major interest of Environmental Forensic Section of Brazilian Federal Police.

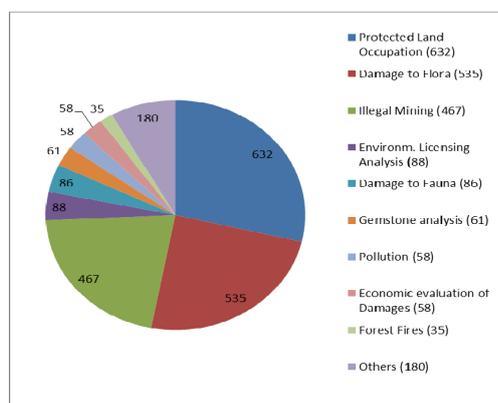


Chart 01: Distribution of environmental forensic reports in Brazilian Federal Police – 2010

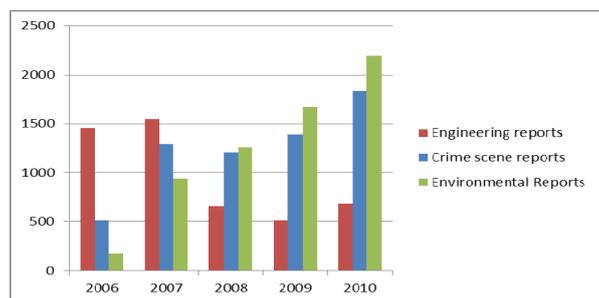


Chart 02: Growing of number environmental forensic reports of Brazilian Federal Police compared with other crime scene.

## ORGANIC MARKERS TO FINGERPRINT SEWAGE SLUDGE TO ASSIST IN FORENSIC TRACKING IN THE ENVIRONMENT

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In recent years, the application of sewage sludge to agricultural and forestry land has increased due to the removal of the marine environment as a disposal route. With concurrent tightening of the regulations relating to spreading sewage sludge on to land, there is an increasing need for fingerprinting tools to track sewage sludge from individual sources. Potential hazards arising from the application of sewage sludge on to land have long been recognised. These include harmful faecal bacteria (mainly coliforms), a range of heavy metals, and organic pollutants that may be endocrine disruptor compounds (EDCs) such

as phthalates, polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs). However, some of these components may have limited value as fingerprinting markers. Appropriate heat treatment of sludges, in accordance with current regulation would reduce coliforms to very low levels. The behaviour of EDCs from sewage sludge applied to land can be very variable, depending not only on the particular compounds but also on soil, vegetation and climatic factors. The purpose of this work was to examine the potential of other organic compounds, known to be relatively long-lived, as markers to fingerprint individual sewage sludges.

Coprostanol has been widely recognised as the predominant stanol and has been used as a marker for contamination by sewage. However, sewage sludge also contains a range of other stanols, including isomers of coprostanol (epicoprostanol and cholestanol), 24-ethyl coprostanol and its equivalent isomers (24-ethyl epicoprostanol and stigmastanol), together with the parent sterols, cholesterol and  $\beta$ -sitosterol, all being present in sewage sludge in relatively high concentrations. Sewage sludges also contain a range of hydrocarbons in addition to the 16 'priority' PAHs listed by the United States Environmental Protection Agency; these include n-alkanes and, when analysed by gas chromatography (GC), a complex mixture constituting an 'unresolved complex mixture' (UCM), producing characteristic 'hump' on the gas chromatogram. The relative concentrations of sterols and stanols, and the shape of the hydrocarbon UCM were considered as potential markers to characterise individual sewage sludges.

A range of dried sewage sludges from different treatment plants throughout the UK were solvent-extracted and heated with ethanolic KOH solution to hydrolyse esters. Heptane extracts were separated into crude hydrocarbon and alcohol fractions which were respectively analysed by GC and (after derivatisation with BSTFA) GCMS.

Differences were observed between the sludges, in both concentration and patterns of the sterols and stanols. Furthermore, some of the sludges contained archaeol (a component of archaeal cell membranes) in relatively high concentrations, while archaeol was absent in other sludges. In addition, every sludge analysed appeared to have a different UCM hydrocarbon shape. These results suggest that sterols, stanols, archaeol and the shape of the UCM hydrocarbons have the potential to be used as combined markers to fingerprint individual sewage sludges.

## DERIVATISATION AND EXTRACTION FOR COMPREHENSIVE ANALYSIS OF COAL TAR.

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Sites of former Manufactured Gas Plants (MGPs) are found throughout the towns and cities of industrialized countries around the world. MGPs produced gas for heating, cooking and lighting prior to the spread of natural gas during the mid 20th century. The process of generating gas involved heating coal anaerobically, and the purification of the gas left a complex mixture of residual heavy organic substances, known as coal tar. Coal tar consists of a large number of different organic compounds, many of which are toxic and some are known to be carcinogenic, the exact composition depends on the details of the process used and the source of coal.

In this study, we present the optimisation and application of a three-step process for the analysis of coal tar dense non aqueous phase liquids (DNAPL) and coal tar-saturated soil samples; derivatisation, extraction and analysis, to enable identification of components of coal tars that have labile hydrogen atoms, i.e. OH, NH and SH groups. Derivatisation by trimethylsilylation prior to extraction with hexane enables extraction of the otherwise insoluble polar components in the same solvent as PAHs. Accelerated Solvent Extraction (ASE) and GCxGC TOFMS enable fast and highly resolved separation and analysis.

This three-step method has been used to generate comprehensive fingerprints of 19 coal tars samples and three coal tar-saturated soil samples with various origins within the UK. Possible correlations between the fingerprint and the properties and history of the coal tar, including the nature of the parent MGP process, post-formation fractionation and weathering were also investigated.

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**A NEW TOOL FOR ENVIRONMENTAL  
FORENSICS: A LIGHTWEIGHT, BATTERY-  
OPERABLE PROTON TRANSFER REACTION  
MASS SPECTROMETER USING UP TO FIVE  
SWITCHABLE CHEMICAL IONIZATION REAGENT  
GASES**

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Conducting environmental forensic investigations in situ with minimal needs for sample preparation without using pre-concentration and with the ability to speciate trace gases, VOCs and SVOCs without using chromatographic separation technologies has been a desirable goal for many environmental forensic scientists.

This poster presentation provides a technical overview of the capabilities and some illustrative environmental forensic applications of a new type of Proton Transfer Reaction Mass Spectrometer (the ASI PTR600), jointly developed by Tracer Measurement Systems Ltd and ASI, funded by Tracer Measurement Systems Ltd and partially supported by a Technology Transfer Fund grant awarded to Tracer Measurement Systems Ltd. by the UK Regional Development Agency Advantage West Midlands, which is gratefully acknowledged.

Proton Transfer Reaction Mass Spectrometry (PTR MS) was developed by Lindinger et al (Int. J. Mass Spectrometry & Ion Processes (1995) 149/150 605) as a new type of soft chemical ionization mass spectrometry in an attempt to drastically improve on the Selected Ion Flow Drift Tube (SIFDT, see e.g. W. Dobler et al: J. Chem. Phys. (1983) 79 1543) as a versatile instrument that had been evaluated for its possible application in trace gas analysis by Lindinger et al (Int. J. Mass Spectrometry & Ion Processes (1994) 134 55). In PTR MS, the chemical ionization reagent gas is water vapour which is fed into a plasma discharge in a hollow cathode "reagent ion source". The major reagent produced is  $H_3O^+$  which can donate (transfer) a proton to an analyte molecule (M) relatively softly to produce  $MH^+$  ions for subsequent analysis. The  $H_3O^+$  reagent ions are drawn out the ion source and injected into a drift tube into the start of which flows sample gas containing trace analytes to be analysed and were the Proton Transfer Reaction takes place with any molecules whose proton affinity is greater than that of the water molecule. This is so for a very large number of VOCs but not for the major gases in air, so Lindinger et al (Int. J. Mass Spectrometry & Ion Processes (1998) 173 191) promoted PTR MS for use in various applications for on-line monitoring of trace VOCs. They subsequently spun out a company (Ionicon Analytik GmbH) from the Institute of Ion Physics at Innsbruck University to commercialise their work. The smallest of Ionicon's PTR MS instruments, the PTR-QMS 300, is only moderately portable at 80kg and 56x61x53cm but very power hungry (max 1200W at 100-230V) and uses  $H_3O^+$  as the reagent ion with options to include use of  $NO^+$  and  $O_2^+$  as charge transfer reagent ions.

We have developed the PTR600 specifically to address the need to improve reduce the weight (32 to 48kg, depending on options, such as single or triple quadrupole analyser) and volume (70x37x40cm), so improving the portability and the desirability for a versatile trace VOC analysis instrument with a very much low power requirement (60 to 80W) suitable for field use. To improve the speciation capability, rather than relying on using higher resolution mass spectrometry with Time of Flight (TOF) as Ionicon and Kore have done with PTR TOF MS, we have chosen to offer the capability of built-in, switchable, easily refillable high-pressure cylinders of up to 5 reagent gases, making it now possible to have speciation and selectivity based on analyte proton affinity as well as other chemical ionization mechanisms as was commonly done in conventional chemical ionisation mass spectrometry (e.g., Harrison "Chemical Ionization Mass Spectrometry" 1983, CRC Press). To this end, use of methane, propane and isobutane as reagent gases will be presented in examples of environmental forensic applications. These will include air from the environs of various waste treatment facilities and of landfill, as well as headspace analysis of contaminated soils, polluted river water, landfill leachate and of groundwater sampled from areas surrounding landfill.

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## TRACE VOCs IN LANDFILL GAS AND LEACHATE: ENVIRONMENTAL FORENSIC INVESTIGATIONS USING PROTON TRANSFER REACTION MASS SPECTROMETRY

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The impact of landfill on the surrounding environment is monitored in many different ways, including analysis of landfill gas and leachate. If landfill gas contains sufficient methane, it may be flared periodically or continuously to reduce its impact on global warming and stratospheric Photochemical Ozone Creation Potential (POCP) or even used for combustion in gas turbines for electrical power generation. The Environment Agency in its "Guidance on the Management of Landfill Gas" has listed more than 550 trace components (both inorganic and organic) that have been identified in landfill gas.

If landfill gas is only flared periodically, the trace VOCs will be emitted directly into the surrounding environment and may present environmental health risks as well as having their own individual global warming potentials. Currently, these trace VOCs are not routinely monitored to enable evaluation of such associated risks and how they might be spread geographically.

For the feasibility investigation presented in this poster paper, specimens of landfill gas from the sites evaluated was collected in tedlar bags from which it was sampled directly into our Proton Transfer Reaction Mass Spectrometer (PTR MS) to investigate the trace Volatile Organic Compounds (VOCs), no sample preparation was needed. Three different types of landfill were investigated for the trace VOCs in landfill gas: (A) a closed "inert" landfill, that had been licensed to take nonhazardous waste and whose operator was seeking approval for surrender of the licence, (B) a landfill taking domestic waste, engineered to produce sufficient methane to fuel a 25 MW electric power generator, and (C) from a landfill taking mixed commercial/municipal and industrial wastes producing only enough methane for periodic flaring. Landfill leachate specimens were also sampled from landfills B and C and headspace analysis for trace VOCs was done directly using PTR MS.

It was clear from these investigations that the three different types of landfill at different stages in their histories had very different trace VOC patterns. In landfills taking domestic waste such as B, the cells within such landfills are filled according to pre-defined plans and the wastes ferment and are known to evolve through acetogenic and methanogenic phases of decomposition but, in the past, it has been difficult to regulate what householders put in such waste and to understand how it may actually decompose. In landfill C, which takes mixed municipal and

non-hazardous industrial wastes, similar problems occur in predicting decomposition behaviour. Landfill A, classed as "inert" should only receive waste that is unlikely to decompose or present environmental risks but, to our surprise, had a pattern of trace VOCs in its landfill gas suggesting hazardous substances had been deposited as significant components of the so-called "inert" waste consignments. Thus rapid analyses with PTR MS for trace VOC patterns in landfill gas and leachate headspace may provide valuable data for forensic investigations of such landfills to check compliance with waste management regulations.

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## VOC EMISSIONS FROM A CARDBOARD REPROCESSING PLANT: AN ENVIRONMENTAL FORENSIC INVESTIGATION USING PROTON TRANSFER REACTION MASS SPECTROMETRY

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The environmental forensic investigations reported in this poster paper were done to comply with a Variation Notice issued by the Environment Agency of England and Wales to Smurfit Kappa, in connection with their Pollution Prevention and Control Permit, for their Waste Cardboard Reprocessing plant in Birmingham (UK) which required them to speciate the trace VOC emissions to air from process vent stacks on the factory roof.

There were significant problems associated with the physical sampling and subsequent analysis of emissions from such vents. These included high bulk flow-rates (31-38 m<sup>3</sup>s<sup>-1</sup>), temperatures (>65°C) and water content (supersaturated) of such emissions. The high temperatures and water content made trapping of trace VOCs on NIOSH sorbent tubes unreliable. Attempts to collect condensates of emissions from the top of vent stack A1 although moderately successful were difficult to undertake. Emissions from each stack initially pass through heat exchangers on the factory roof and condensates from each of these collect in open shallow concrete-walled tanks beneath these heat-exchangers.

It was considered that most trace VOCs in these emissions would be hydrophilic and, as a result, would be very likely to co-condense with the water as emissions passed through the heat exchangers. So, as surrogates for direct samples of the emissions, specimens were collected of such bottom condensates from under the heat exchangers of two of the stacks, A1 and A3. Stack A1 is above the process at the beginning of the continuously moving belt on which process liquor is deposited to produce new paper sheet. At this point, the liquor is very hot (80°C) and contains about 1% solids in suspension from the macerated mixed cardboard and paper waste. A process liquor specimen, as a precursor of the emissions from the

vents, was taken to analyse for trace VOCs. Vent A3 is further along above the moving belt where deposited suspension is still drying.

Analysing such aqueous specimens for the trace hydrophilic VOCs using conventional GC/MS techniques presents difficulties. Proton Transfer Reaction Mass Spectrometry (PTR MS) is a soft chemical ionisation MS technique using water vapour as the chemical ionisation reagent gas producing  $H_3O^+$  reagent ions that react with large numbers of VOCs that have greater proton affinities greater than water molecules. Thus direct sampling headspace analysis using PTR MS for the trace hydrophilic VOCs in the condensates and process liquor with no sample preparation was very appropriate for this forensic investigation. We were able to predict possible volatile metabolites resulting from the likely microbial decomposition of the cellulose in waste bales stored in the factory yard and this successfully correlated with major and some minor VOCs found in both condensates and process liquor. It was also known that there were thermophilic microbes growing profusely in the hot process liquor, because of the need for large amounts of biocides to control this growth and to prevent it from completely blocking the continuous process operation. So we were also able to successfully predict and subsequently measure, using the PTR MS technique, the occurrence of these thermophile volatile metabolites in the emission condensates. We were very concerned that conventional FID measurements of the Total Organic Carbon (TOC) content of the stack emissions were gross underestimates compared with direct analysis of the TOC contents of the stack condensates, so our PTR MS analyses were much more realistic even though they were only semi-quantitative.

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