出國報告（出國類別：國際會議）

參加第 32 屆土壤、底泥、水和能源國際研討會報告

服務機關：行政院環境保護署環境檢驗所

姓名職稱：羅仕麟助理研究員

派赴國家：美國

出國期間：105 年 10 月 16 日至 10 月 22 日

報告日期：105 年 12 月 6 日

摘要

檢測儀器發展逐年進步，越來越多污染物因為儀器的靈敏度提昇逐漸被檢測出，這些污染物近年來被稱為新興污染物，不僅存在微量，環境風險也比傳統知道的污染物相對較高；另一方面，在眾多相同產品工廠的廠區與週遭複雜的環境介質下，如何知道是哪一家工廠偷排這類的問題，讓環境鑑識技術的建立成為目前環境領域的新課題。

筆者本次參與第 32 屆 (2016) 土壤、底泥、水和能源國際研討會，其以專題研習 (Workshops)、分類議題演講 (Platforms Sessions)、壁報論文報告 (Posters)、廠商儀器展示 (Exhibits) 等方式進行技術分享，整體而言研討會以污染物的整治為核心，基於對污染物的整治首先必須要發展客觀與足以說服眾人的監測方法，除了已知道污染物濃度的檢測技術，建立一套評估污染物來龍去脈的流程對於污染物整治的決策是重要的。污染整治如果能以自然降解的方式處理，可以減少額外添加藥劑或為了將污染物控制在標準值以下而進行的耗大工程成本的負擔，也對環境較為友善，在本研討會上介紹以同位素比值的技術來辨別污染來源以及污染物降解途徑的監測。此外，1,4-二氧環已烷 (1,4-Dioxane) 這類新興污染物一直在本次研討會中的鑑識與分析技術的簡報議題多次論述，很顯然在美國多數污染場址 (尤其是含氯) 是較為重視的新興污染物。

本次研討會上收穫良多，尤其在同位素比值技術上看到比國內更進步的分析模式，對於本所環境鑑識的分析未來又多一個選擇方法可以運用；另一方面也瞭解國外對於環境議題重視的方向，藉由他山之石提供本所業務一個新的思維方向。

目　　次

壹、目的

隨著環境檢測技術發展逐漸成熟，越來越多高感度的儀器陸續被發展出來，因此原本未檢出的潛在高度風險污染物因而陸續被檢出，新興污染物 (Emerging Contaminants, ECs)即是這樣被定義出，如水中全氟化物 (Perfluorinated Chemicals, PFCs)、亞硝基二甲基甲醯胺類消毒副產物 (Nitrosodimethylamine, NDMA)。大部分新興污染物有幾項特徵，包括致癌風險相對高、環境管制濃度相對低以及常見於生活物品添加物等，基於以上特徵越來越多研究進一步探討新興污染物的來源、風險評估以及後續整治。

另一方面，對於污染場址以及週遭位置檢出的數據是否具有代表性?是否能代表場址真實污染情形?甚至是否可進一步推估污染來源與責任釐清?環境鑑識即是在各項儀器漸趨成熟穩定下發展出回答前述問題的一項學門。環境鑑識不單只是儀器檢測，更包含了前期規畫，後續數據統計處理以及結果邏輯性描述，每一層的技術都具有其專業性，並且是一環扣著一環有層次的解析。相對於傳統單一或多個環境污染物濃度分析，環境鑑識是跨領域技術的結合，其解讀結果容易受到挑戰也容易被質疑客觀性，然而公信力極高的環境鑑識流程被建立後，有助於遏止不良廠商的恣意排放。

新興污染物的分析檢測與環境鑑識技術的精進一直是本所積極發展的方向，兩者在環境議題的重要性也受到全世界各個環境相關領域人士關注，基於瞭解國外技術現況發展並蒐集資訊以提昇專業能力，105 年本所派筆者參加第 32 屆 (2016) 土壤、底泥、水和能源國際研討會 (32rd Annual International Conference on Soils, Sediments, Water, and Energy)於麻薩諸塞州阿默斯特多市麻州大學阿默斯特多分校舉辦的研討會，藉由會議演講中各個學者發表個人研究之突破技術獲取技術精進資訊，並利用參與此研討會之機會，蒐集相關議題技術，希冀能將此次國外取經所得資訊有助於本所前瞻性檢測技術與環境鑑識技術之提升。

貳、過程

一、行程紀要

2016 年第 32 屆土壤、底泥、水和能源國際研討會（32rd Annual International Conference on Soils, Sediments, Water, and Energy）於美國麻薩諸塞州阿默斯特多市麻州大學阿默斯特多分校（University of Massachusetts Amherst, Amherst, MA)舉行，會議舉行時間為我國時間 10 月 18 日至 10 月 21 日共計 4 日（如表一所示)。

表一　筆者行程紀要表

日　　期	地　　點	工作說明
105 年 10 月 16-17 日	桃園國際機場至美國阿默斯特多	啟程
105 年 10 月 18-21 日	麻州大學阿默斯特多分校	出席第 32 屆 (2016) 土壤、底泥、水和能源國際研討會
105 年 10 月 22 日	美國阿默斯特多至桃園國際機場	返程

二、會議紀要

會議內容包含專題研習（Workshops）、分類議題演講（Platforms Sessions）、壁報論文報告（Posters）、廠商儀器展示（Exhibits）等項進行。專題研習以環境鑑識與整治技術為目標開辦 9 個研習議題；分類議題演講分為 18 類議題；壁報論文報告共 60 篇。本研討會會議包含 5 個核心議題：

1. 創新的整治技術
2. 新興污染物的關切
3. 法規制度觀點
4. 環境鑑識

5. 當前敏感且重要的議題，包含蒸氣入侵 (Vapor Intrusion)、水力壓裂 (Hydraulic Fracking) 與自然資源破壞評估 (Natural Resource Damage Assessment, NRDA)

由這 5 個核心議題為基礎，延伸各項議題如下：

(一) 專題研習 (Workshops)

專題研習共分為 9 大項，講授研習題目如下：

1. Measuring Biological Exposure to Environmental Chemicals

   (量測生物暴露瞭解環境化學物質危害)

2. Vapor Intrusion Assessment and Mitigation in Massachusetts: Status of Sites, Findings from the Field, and Guidance for Practitioners

   (蒸氣入侵評估與減緩以麻州為例)

3. Building a Better Background Data Set

   (建立更好的背景資料庫)

4. Sustainable Remediation Principles & Practice

   (永續整治的原則與實例)

5. Environmental Forensics – Integration of Established and Evolving Techniques to Evaluate Who Was Responsible for the Spill or Release

   (環境鑑識－整合已建立與創新技術評估誰該為污染物排放負責)

6. Incremental Sampling Methodology (ISM)

   (增樣採樣方法)

7. Remediation Tools for Challenging Geology – Cutting Edge Technology for Cleanups in Clay & Fractured Bedrock

   (用於具挑戰性地質的整治工具-黏土與裂隙岩層的除污尖端技術)

8. Vapor Intrusion – Reducing Uncertainty in Investigations, Mitigation and Transactions – Tools for the Toolbox

   (蒸氣入侵-減少調查、緩解與處置的不確定度－「工具箱」的使用方法)

9. The Urban Background Dilemma: A Regional Study and Global Perspective

   (都市背景難題：區域性研究與全球觀點)

依本次參與研討會的目的、考量本所業務相關性以及課程行程表上的時間安排，筆者選擇第 5 個研習議題「環境鑑識－整合已建立與創新技術評估誰該為污染物排放負責」聆聽研習，進行方式為投影片簡報 4 小時，並提供簡報紙本給參與研習者參考。

(二) 分類議題演講 (Platforms Sessions)

分類議題演講分為 18 類議題共 106 個題目演講， 因議題眾多同時間會有 4 個議題進行，筆者考量參與研討會目的與本所業務相關性，其中 4 個議題與本所業務相關：

1. Risk Assessment (風險評估)
2. Advanced Analytical Tools for Management of Contaminated Sites

   (高階分析工具用於污染場址管理)

3. Environmental Forensics (環境鑑識)

4. Sediments (底泥)

演講者背景多以專家學者、廠商以及政府部門人員為主，進行方式以投影片簡報 30 分鐘，隨後進行約 5 分鐘問與答。

(三) 壁報論文報告 (Posters)

壁報展覽共有 60 篇，分別於 2 間會議室同時進行展覽，壁報作者以專家學者、廠商以及在學學生為主，60 篇壁報中以污染場址整治研究為多數，經筆者於會期空檔觀看共計 10 篇論文壁報與本所業務較為相關，10 篇題目如下：

1. Fractionation Effects on C, H and Cl Stable Isotopes of Chlorinated Solvents During Dissolution, Adsorption and Evaporation

   (含氯溶劑在溶解、吸附與揮發過程對碳、氫與氯穩定同位素的分化效應)

2. Two-Dimensional Compound Specific Isotope Analysis (2D-CSIA) Forensic Approach for Low ppb Level Emerging Contaminant 1,4-Dioxane

   (應用 2D-CSIA 鑑識方式檢測低濃度 ppb 等級的新興污染物 1,4-二氧環己烷)

3. Challenges and Options for the Analysis of 1,4-Dioxane

   (1,4-二氧環己烷分析的挑戰與選項)

4. 1, 4- Dioxane – A Review and Evaluation of the Available Analytical Methodologies Used in Support of the Latest State and Federal Standards

   (1,4-二氧環己烷-回顧與評估可行的分析方法用來輔助最新州與聯邦標準)

5. Performance Based Equivalency of Extract Clean-Ups for Dioxin and PCB Cogener Analysis

   (戴奧辛與多氯聯苯同族物萃取淨化分析)

6. **E**xamining PCB Concentrations in New Bedford Harbor Quahogs for Human Risk Implications

   (麻州新伯福港蚌蠣多氯聯苯濃度檢測隱含人類風險)

7. Chemical Evidence for Exposure of Red Crabs (Chaceon quinquedens) to Macondo Oil After the Deep Water Horizon Oil Spill

   (深水漏油後從五齒查氏蟹暴露馬康多油的化學證據)

8. The Analysis of Perfluorinated Compounds - Beyond UCMR3

   (全氟化物分析- UCMR3 之外的物種)

9. Detection of Water-Borne 4-Methylcyclohexanemethanol (MCHM) via Purge & Trap and Transportable, On-Site GC/MS

   (以移動式吹氣捕捉氣相層析質譜儀於現地偵測水中 4-甲基環己烷甲醇)

10. Environmental Sample Holding Time Studies: Chemical Preservation of Volatile and Semivolatile Compounds at Ambient Temperature

(環境樣品保存期限研究：在室溫下以化學方法保存揮發性與半揮發性化合物)

總觀這 10 篇論文，第 1 至 2 篇為發展同位素比值分析應用於環境鑑識之技術；第 2 至 4 篇為發展 1,4-二氧環己烷(1,4-Dioxane)分析檢測技術；第 5 至 6 篇為多氯聯苯 (PCBs) 技術發展；第 6 至 7 篇為應用水中生物來分析評估污染物；第 8 篇與第 9 篇分別為新興污染物分析技術發展；第 10 篇為多環芳香族碳氫化合物 (PAHs) 與 BTEX 樣品保存方法參數評估。另筆者以壁報論文發表者方式參與本次研討會，發表論文題目為「Identification of Source Relevance Using Isotopic Signatures of Multiple Contaminants」，分析方法同第 1 至 2 篇以同位素比值分析應用於環境鑑識。

(四) 廠商儀器展示 (Exhibits)

本次大會邀請了 50 家廠商參展，展出以現地整治技術之藥劑、開發整治技術零組件為主，而與本所業務應用相關的直讀式儀器有 2 家廠商，分別為 FLIR 公司展示 Griffin 460 移動式吹氣捕捉氣相層析串聯質譜儀 (GC/MS)、Defiant Technologies 公司展示 Frog-4000 攜帶式氣相層析串聯光離子偵測器 (GC/PID)，以上兩種直讀式儀器皆以揮發性有機物 (VOCs) 為目標物，適合各種基質 (包含水、土壤與空氣)，儀器設計訴求為快速、方便攜帶與偵測極限可低於現行美國環保法規標準。

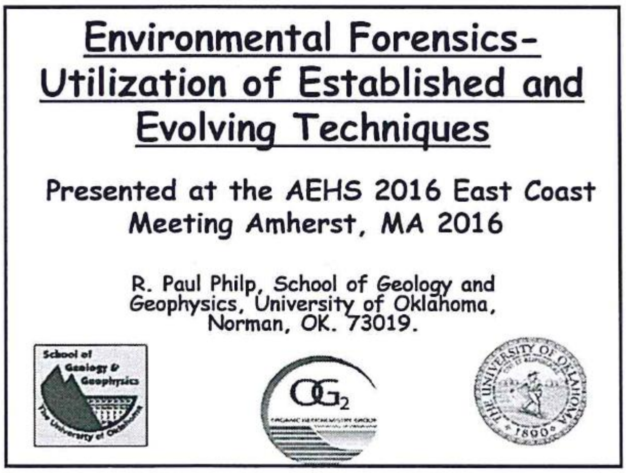
參、心得

本次筆者參加於麻薩諸塞州阿默斯特多市麻州大學阿默斯特多分校舉辦的第 32 屆 (2016) 土壤、底泥、水和能源國際研討會，很特別的是並沒有開幕與閉幕的行程，研討會第一天直接以專題研習(Workshops) 作為研討會的開頭，第二天至第四天從上午 8 時 30 分開始 4 個分類議題演講同時舉行，下午 1 時 30 分開始第二個時段接續 4 個分類議題演講同時舉行，並且海報展覽講解也在第二天與第三天下午與類議題演講同時舉行，因此整個大會行程是相當緊湊且內容豐富，詳細參與研討會心得將依會議內容逐項分享:

一、 專題研習 (Workshops)

筆者於九個專題研習中選擇「環境鑑識－整合已建立與創新技術評估誰該為污染物排放負責」聆聽。過往傳統的分析結果只顯示化合物物種以及化合物濃度，例如從查緝環保犯罪場所中採得的樣品經由分析瞭解已知化合物是否有超過環保法規標準，亦或是查到特定排放口是由已知不良廠商排放，偷排濃度經由分析是否有超過環保法規標準，因此物種與濃度分析得到答案就完成檢測。然而有一些情況是在資訊短缺下，無法單純從物種與濃度判斷抓到偷排廠商，那就必須要發展其它的方法串連已知的資訊協助判斷，環境鑑識的目的就是要知道是「誰」污染了環境。

奧克拉馬大學 (University of Oklahoma) Dr. Paul Philp 是這堂課的講師 (圖一) ，他本身的研究專長是做石油與環境地質分析，他介紹的環境鑑識技術就是穩定同位素比值 (Stable Isotope Ratio) 。穩定同位素比值是利用標準氣體標準值計算出來的比值，有機物可以用碳、氫、氧、氮、硫與氯分析，通常碳與氫是比較常被使用的兩個元素，近年來氯也被作為第三種穩定同位素比值的元素也被用來作為含氯溶劑污染場址的鑑識，圖二為同位素比值的表示方式。



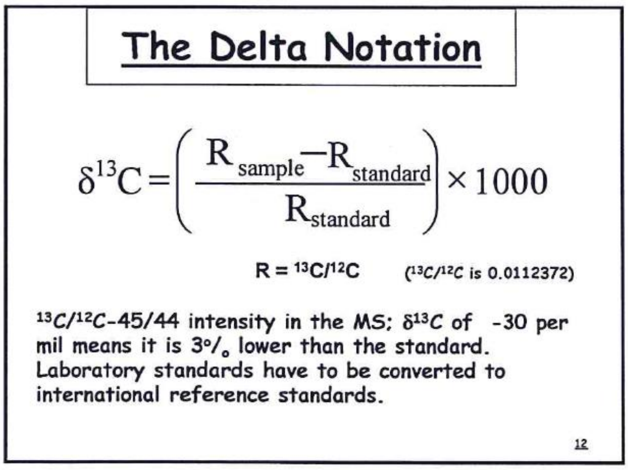
Environmental Forensics- Utilization of Established and Evolving Techniques

Presented at the AEHS 2016 East Coast Meeting Amherst, MA 2016

R. Paul Philp, School of Geology and Geophysics, University of Oklahoma, Norman, OK. 73019.

圖一 Workshop 投影片首頁標題

穩定同位素比值鑑別的理論在於分化作用（effects of fractionation），如三至圖五所示，分化作用可由兩種效應產生，第一種是平衡同位素效應（Equilibrium isotope effect），由於物化特性（如溫度、氣壓、化合物濃度或熔沸點等），元素同位素共振能量差異造成能階差，因此同位素比值會因不同相（固態、液態或氣態）出現偏差，如水在密閉容器達成平衡時，重的同位素（^{2}H、^{18}O）在水中會比空氣中比例來的高。第二種是動力學同位素效應（Kinetic isotope effect），由於鍵結共振能量的差異，影響反應速率，因此元素的鍵結力會有強弱分別，在有外在能量下鍵結被打斷或形成會使得原本的重同位素與輕同位素之間的比值產生差異。生物性或化學性的降解一般是經由動力學同位素效應造成的，因此這個效應通常被認為是主要同位素比值差異的原因。



The Delta Notation

$$\delta^{13}C = \left(\frac{R_{sample} - R_{standard}}{R_{standard}} \right) \times 1000$$

$R = {}^{13}C/{}^{12}C$ $({}^{13}C/{}^{12}C$ is 0.0112372)

${}^{13}C/{}^{12}C$-45/44 intensity in the MS; $\delta^{13}C$ of -30 per mil means it is $3^{o}/_{o}$ lower than the standard. Laboratory standards have to be converted to international reference standards.

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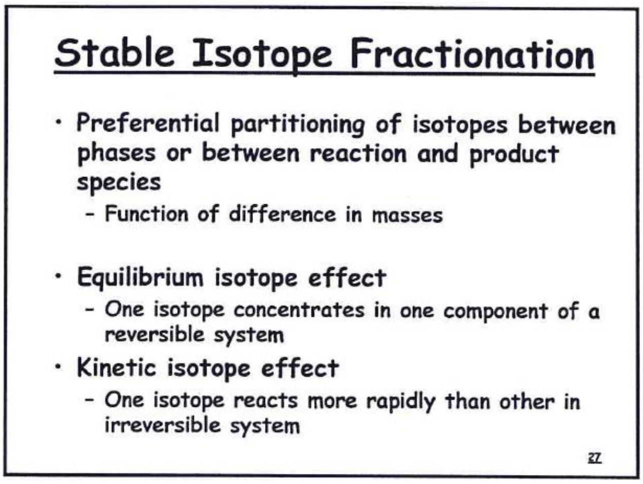
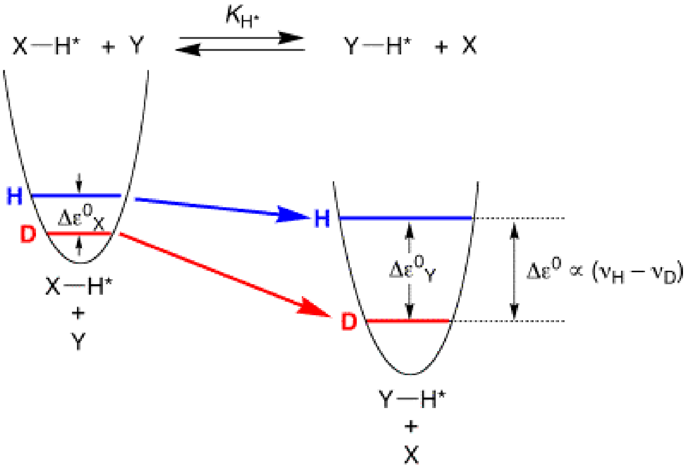
圖二 穩定同位素比值計算方式



Stable Isotope Fractionation

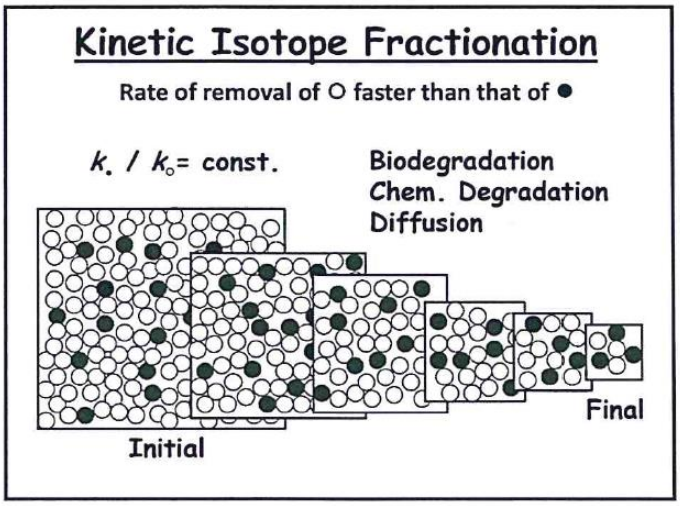
- Preferential partitioning of isotopes between phases or between reaction and product species
  - Function of difference in masses
- Equilibrium isotope effect
  - One isotope concentrates in one component of a reversible system
- Kinetic isotope effect
  - One isotope reacts more rapidly than other in irreversible system

圖三 分化作用造成穩定同位素比值產生差異



$K_H < K_D$, i.e. $K_H/K_D < 1$

圖四　氫與其同位素氘能量轉變 **(1)**



Kinetic Isotope Fractionation

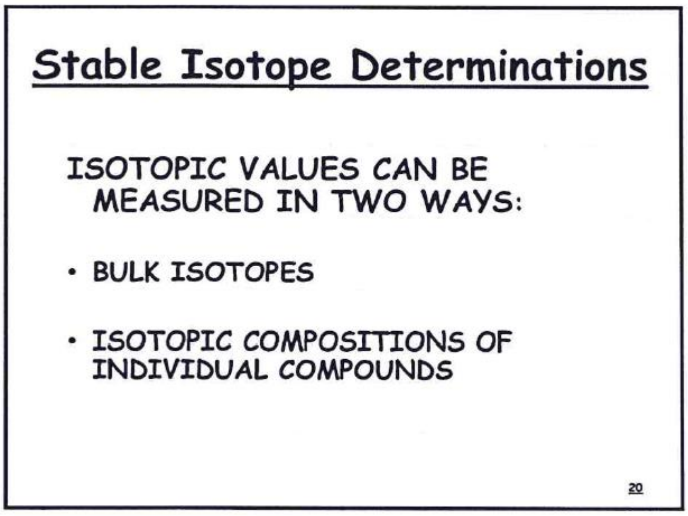
Rate of removal of ○ faster than that of ●

$k_\bullet / k_\circ$ = const.

Biodegradation
Chem. Degradation
Diffusion

圖五　動力學同位素效應

同位素比值可利用其特徵性辨別來源如圖六所示，有兩種分析方式可以提供同位素比值資訊，第一種是批量穩定同位素比值分析 (Bulk Stable Isotope Analysis, BSIA)，將所有樣品經由完全燃燒氧化後進入同位素比值質譜儀，可得到的圖譜是單一元素波峰與單一元素的同位素比值；第二種是特定化合物同位素分析 (Compound Specific Isotope Analysis, CSIA) ，將樣品先經由層析方式 (如氣相層析管柱或液相層析管柱)分離，隨後依分離順序氧化進入同位素比值質譜儀得到層析圖譜各個化合物波峰與同位素比值。以上兩種分析方式得到的資訊不同，使用的方向也不一樣，BSIA 因為只知道單一元素同位素比值，通常用來分析圖譜難以分離油或純物質，如果需要瞭解特定化合物的來源，則須使用 CSIA 方法分析，可以協助環境污染物追蹤。污染整治上，也可以利用同位素比值變化協助瞭解污染場址是否有生物降解的狀況，如果能以生物降解處理污染物可以減少額外化學藥劑使用，並且純化出生物降解的物種來增加菌量幫助加快污染物降解。



Stable Isotope Determinations

ISOTOPIC VALUES CAN BE MEASURED IN TWO WAYS:

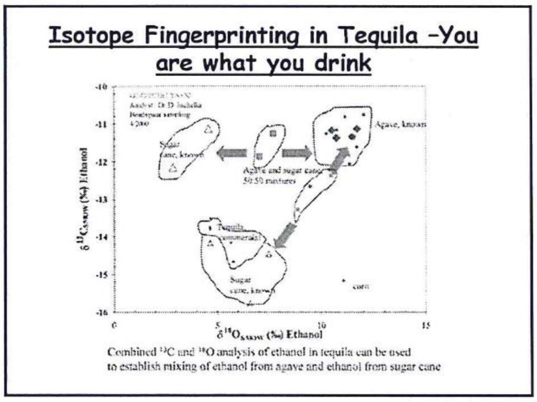
- BULK ISOTOPES
- ISOTOPIC COMPOSITIONS OF INDIVIDUAL COMPOUNDS

20

圖六 同位素比值分析分為 BSIA 與 CSIA

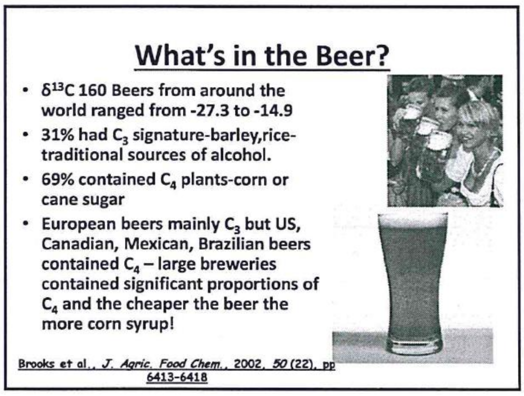
有關同位素比值分析的應用案例， Dr. Paul Philp 指出目前國外有同位素比值分析標準方法且已相當多檢測業使用的範圍以食品加工物為主，如圖七酒的產地檢驗、蜂蜜的真偽以及肉品與乳製品產地檢驗。同位素比值分析應用在環境污染鑑識上，目前各國並沒有一個標準方法，大多為學術研究文獻探討水體油污來源 (圖八)、底泥、土壤中或空氣中碳氫化合物如多環芳香烴 (PAHs) 來源辨識 (圖九) ，而且至少會用到兩種以上的元素進行結果分析，再搭配其它儀器分析結果 (如 GC/FID 或 GC/MS 等)綜合交叉比對，來比對出

污染來源，政府部門僅有美國環保署出版 CSIA 指引（圖十），內容針對地下水中工廠排放揮發性含氯有機物提供同位素比值分析技術與相關數據解釋方法指引。



Isotope Fingerprinting in Tequila –You are what you drink

Combined ^{13}C and ^{18}O analysis of ethanol in tequila can be used to establish mixing of ethanol from agave and ethanol from sugar cane

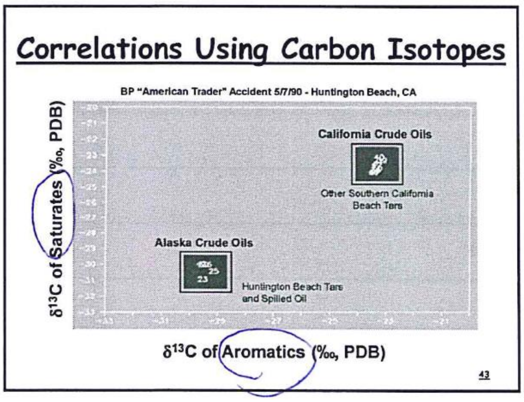


What's in the Beer?

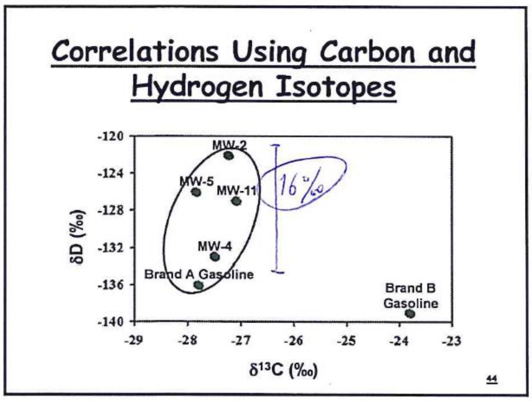
- $\delta^{13}C$ 160 Beers from around the world ranged from -27.3 to -14.9
- 31% had C_3 signature-barley,rice-traditional sources of alcohol.
- 69% contained C_4 plants-corn or cane sugar
- European beers mainly C_3 but US, Canadian, Mexican, Brazilian beers contained C_4 – large breweries contained significant proportions of C_4 and the cheaper the beer the more corn syrup!

Brooks et al., *J. Agric. Food Chem.*, 2002, *50* (22), pp 6413-6418

圖七 同位素比值運用於酒產地檢驗

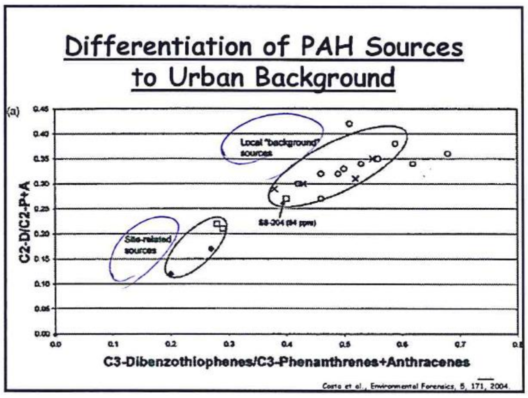


Correlations Using Carbon Isotopes



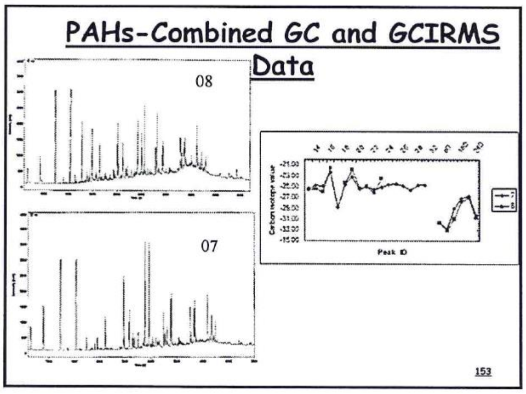
Correlations Using Carbon and Hydrogen Isotopes

圖八 洩漏油污比對



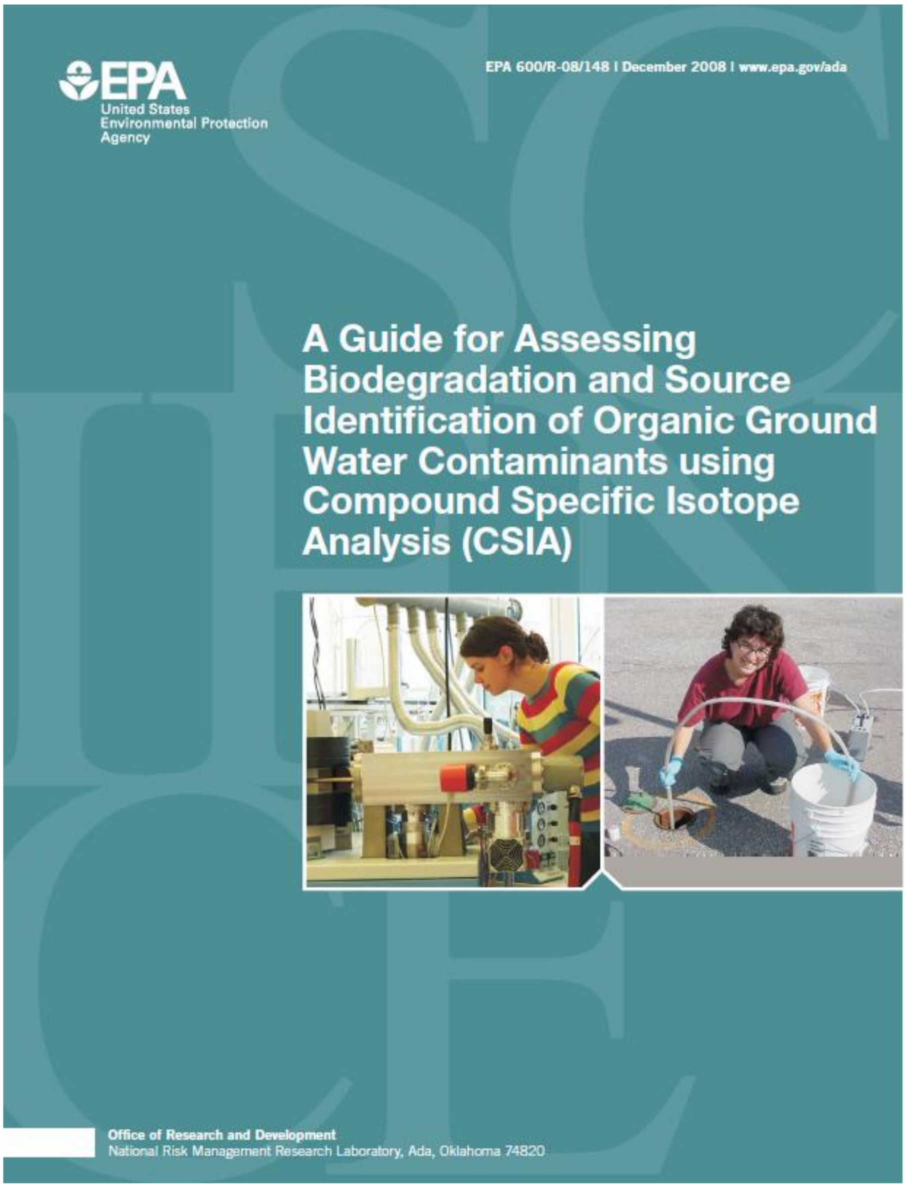
Differentiation of PAH Sources to Urban Background

Costa et al., Environmental Forensics, 5, 171, 2004.



PAHs-Combined GC and GCIRMS Data

圖九　PAHs 分析結合 GC/MS 與 GC/IRMS 比對



EPA
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Environmental Protection
Agency

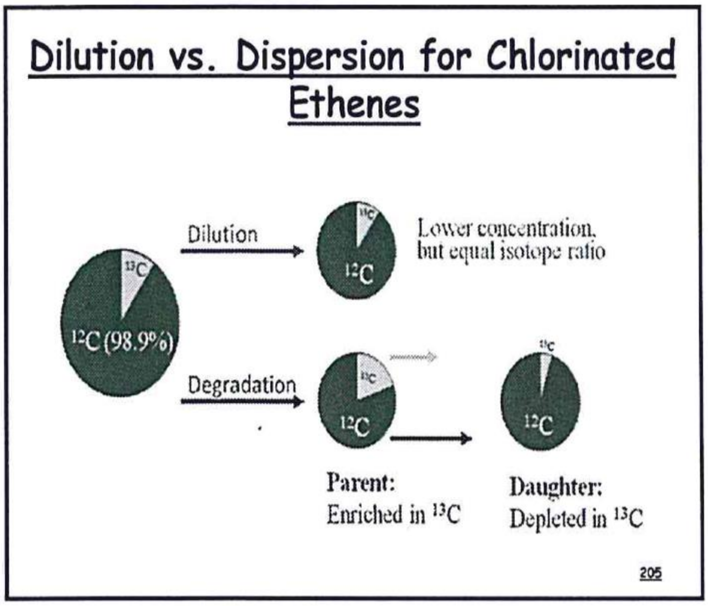
EPA 600/R-08/148 | December 2008 | www.epa.gov/ada

A Guide for Assessing Biodegradation and Source Identification of Organic Ground Water Contaminants using Compound Specific Isotope Analysis (CSIA)

Office of Research and Development
National Risk Management Research Laboratory, Ada, Oklahoma 74820

圖十 美國環保署出版有關 CSIA 分析指引 **(2)**

通常化合物進入到環境後會有兩種情況（圖十一），一種是因為稀釋導致濃度變低，另一種是降解成中間產物與最終產物造成原化合物濃度變低，兩種形式都會造成穩定同位素比值的改變，但是可以從穩定同位素比值改變的程度判斷是哪一種方式所導致化合物濃度改變的結果。稀釋化合物濃度造成的穩定同位素比值改變不大，通常會使用這樣的方式來找到儀器偵測極限，合理的穩定同位素比值變化範圍一般文獻建議在 ±0.5‰ ；化合物降解導致的穩定同位素比值改變的程度比較明顯，因為在降解過程會產生新的物種，佔有比例比較高的輕同位素被分化的比例也比較高，因此化合物的穩定同位素比值會越來越重，這個降解途徑的結果可以由雷利模式（Rayleigh Model）來模擬描述。



Dilution vs. Dispersion for Chlorinated Ethenes

圖十一　降解與稀釋作用分別在同位素比值上的表現

雷利模式（圖十二）之推導在此不贅述，最終公式可寫成：

$$\delta^{13}C_t = \delta^{13}C_0 + \epsilon \times \ln F$$

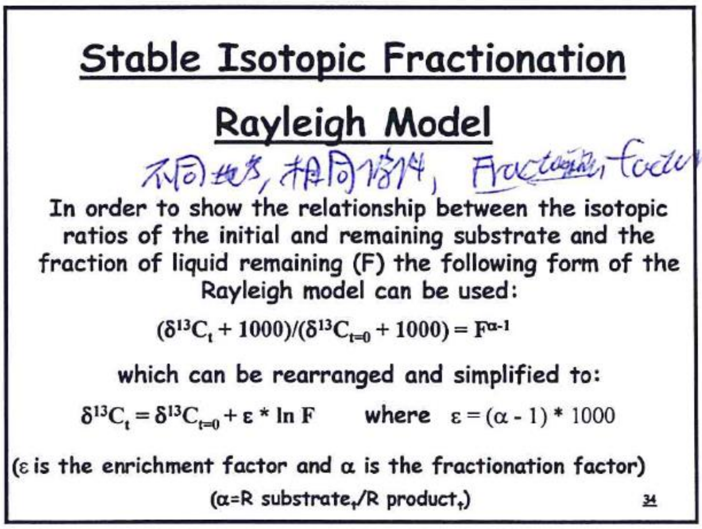
$\delta^{13}C_t$ ：代表化合物在時間 t 時的同位素比值

$\delta^{13}C_0$ ：代表化合物在初始的同位素比值

ϵ ：濃化因子，與化合物與其降解產物之同位素比值差值有關

F ：代表在時間 t 時化合物濃度相對於初始時化合物濃度比例

由公式可知，理想狀態下完全反應完後（F=0），降解產物的同位素比值會與化合物在初始的同位素比值相同，因此可由此判斷是否有降解情形以及降解的程度。如圖以三氯乙烯降解為例（圖十三），一般熟知的三氯乙烯降解產物為 1,2-二氯乙烯，三氯乙烯初始同位素比值會與三氯乙烯完全降解後產物 1,2-二氯乙烯的同位素比值接近，而中間反應過程分化因子（ϵ）會決定降解及生成速率。一般而言同一種化合物在相同外在環境條件會 ϵ 相近（圖十四），濃度影響同位素變化過程但不影響最終結果，以這樣的描述模式來觀察生物降解是很常使用的同位素比值分析方法。



Stable Isotopic Fractionation

Rayleigh Model

不同地方, 相同條件, Fractionation factor

In order to show the relationship between the isotopic ratios of the initial and remaining substrate and the fraction of liquid remaining (F) the following form of the Rayleigh model can be used:

$$(\delta^{13}C_t + 1000)/(\delta^{13}C_{t=0} + 1000) = F^{\alpha-1}$$

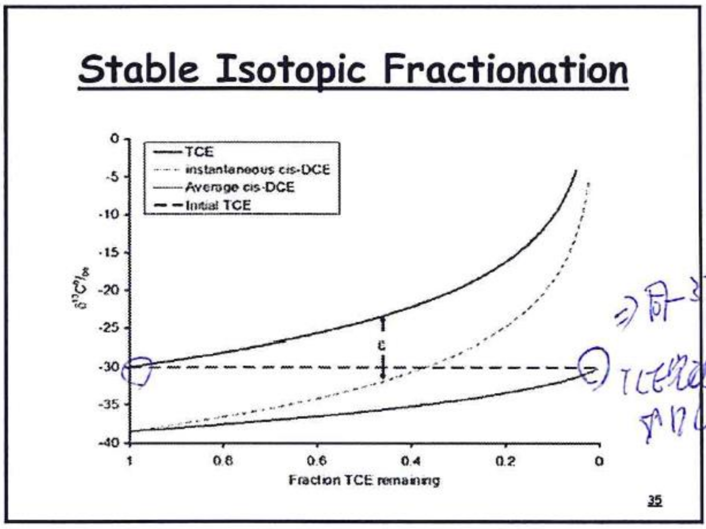
which can be rearranged and simplified to:

$$\delta^{13}C_t = \delta^{13}C_{t=0} + \varepsilon * \ln F \qquad \text{where} \quad \varepsilon = (\alpha - 1) * 1000$$

(ε is the enrichment factor and α is the fractionation factor)

(α=R substrate$_t$/R product$_t$)

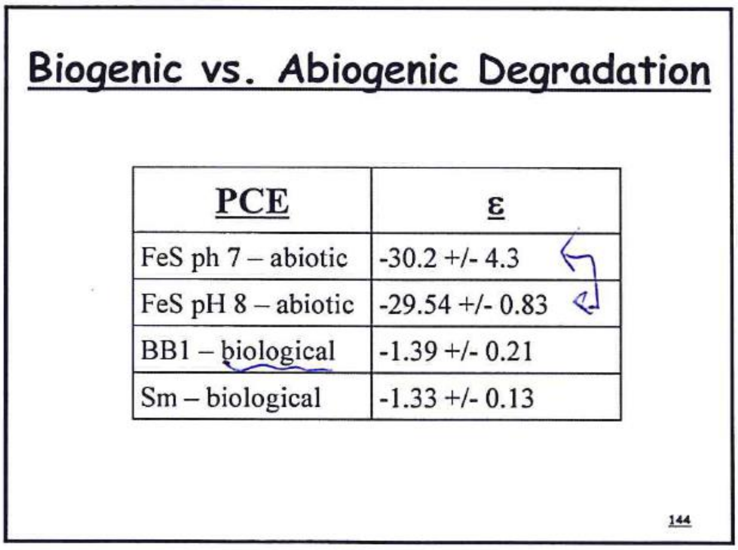
圖十二 雷利模式



Stable Isotopic Fractionation

⇒同一點 TCE完全降解為DCE.

圖十三 以三氯乙烯為例模擬雷利模式

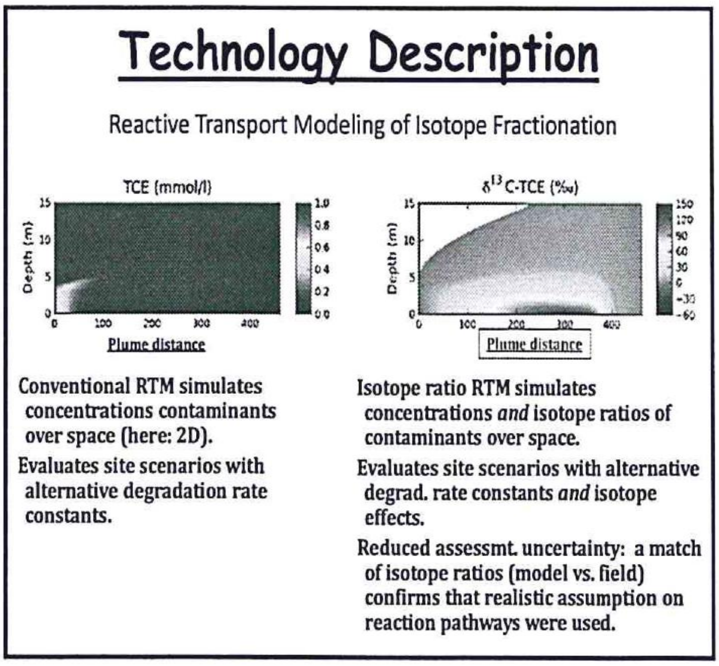


Biogenic vs. Abiogenic Degradation

PCE	**ε**
FeS ph 7 – abiotic	-30.2 +/- 4.3
FeS pH 8 – abiotic	-29.54 +/- 0.83
BB1 – biological	-1.39 +/- 0.21
Sm – biological	-1.33 +/- 0.13

圖十四 降解途徑差異造成 ϵ 不同

最後一個部分筆者認為是分析技術突破的亮點，但是很可惜 Dr. Paul Philp 提到比較少的部分，有關雷利模式再衍生出比較貼近真實傳輸狀況的模式建立。早期對於化合物降解的瞭解只有濃度上的監測，實質上無法得知中間的反應如何降低化合物濃度，到了 1990 末期同位素比值的技術已逐漸應用在環境鑑識上，2008 年美國環保署出版一本指引內容有關使用同位素比值去評估污染場址是否有降解，因此從化合物同位素比值的變化來瞭解是由自然衰減 (Natural Attenuation) 還是稀釋效應，但是這樣的評估方式只適合小範圍的污染，實際上污染蔓延到下游處時，在中間會有許多的物理、化學與生物反應或是混雜其它的物質，是否同樣能從同位素比值的變化判斷因而近年來發展出一套的模式-反應性傳輸模式 (Reactive Transportation Model, RTM) (圖十五)。影響 RTM 的因素包含了水力因素的平流 (Advection)、分散流 (Dispersion) 、 外來水體的稀釋 、 水體中的擴散、介質吸附與阻礙流動 (Sorption/Retardation) 、化學性 (氧化還原) 與生物性降解、化合物揮發性等，這些都是在應用時 RTM 會遇到的參數，才能貼近評估污染物流動的真實情況 (3)。RTM 對於同位素比值應用的方向又更為實際面取向，然而要完成此模是評估是需要多個領域的人才合作才有可能將此模式解釋的更客觀更具說服力。



Technology Description

Reactive Transport Modeling of Isotope Fractionation

Conventional RTM simulates concentrations contaminants over space (here: 2D).

Evaluates site scenarios with alternative degradation rate constants.

Isotope ratio RTM simulates concentrations *and* isotope ratios of contaminants over space.

Evaluates site scenarios with alternative degrad. rate constants *and* isotope effects.

Reduced assessmt. uncertainty: a match of isotope ratios (model vs. field) confirms that realistic assumption on reaction pathways were used.

圖十五　反應性傳輸模式 (RTM)

二、 分類議題演講 (Platforms Sessions)

分類議題演講分為 18 類議題共 106 個題目演講，議題都涵蓋到目前環境關切問題，尤其是在環境鑑識上的技術，以下為 5 個演講題目分享內容與心得：

(一) Forensic Sediment Evaluation - Differentiating Basin Derived Media from Anthropogenic Sources Using Multivariate Statistics

演講者為 Hexagon Environmental Solutions 公司的 Eric Cherry ，演講有關底泥鑑識分析來源的多變數統計方法，傳統方法對於底泥鑑識多半以濃度分布來判別，但是這樣的判斷方式會有太過單純地考量，也缺乏整體性的評估，因此在實行鑑識從採樣到分析應有一套先後程序的執行方式，分析的結果以物種類別去分類底泥來源，接續以多變數統計方式執行，Eric Cherry 提供四種統計方式提供分辨物種來源：迴歸分析 (Regression Analysis)、分層群集分析（ Regression Analysis ）、PCA 與異常值分析。實際上還有其它統計方法，但使用統計方法的前提是目標要明確，假設要定義清楚，方法使用要適當並且合乎一開始的假設，分析的結果才有可信度。

(二) Integrating Compound Specific Isotope Analysis (CSIA) in Forensic Investigations and Conceptual Site Models

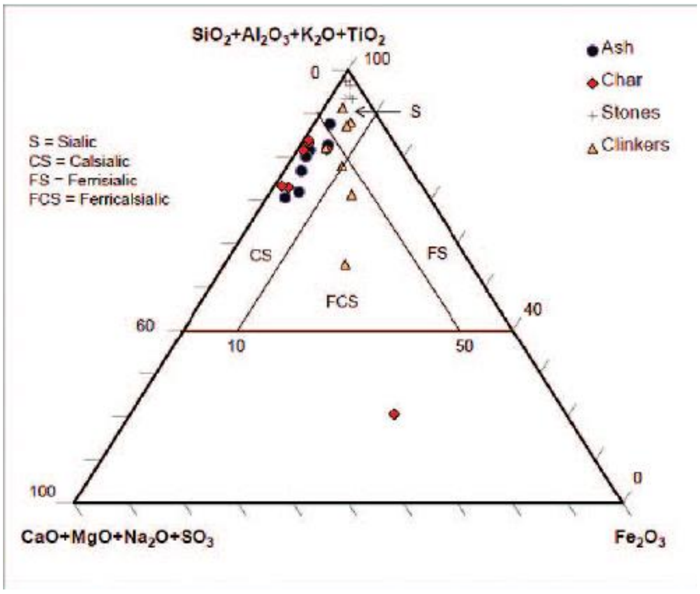
演講者為 Geosyntec Consultants 公司的 Dr. Silvia Mancini，主要內容是將 CSIA 分析技術導入概念場址模型 (Conceptual Site Models, CSM) 中，CSM 是描述受體的可能暴露來源與暴露途徑以及污染物對受體的影響，由於 CSIA 技術可以作為來源辨識與污染物降解途徑，Dr. Silvia Mancini 以巴西東北的兩個污染場址為例，第一個場址是氯苯污染土壤與地下水，利用碳、氫與氯同位素比值導入到 CSM 去區別污染來源與暴露途徑；而第二個場址是評估氯仿與四氯化碳的降解途徑，利用同位素比值在整治前後的變化瞭解最適合場址整治的方法。而 CSM 的概念最終是要計算風險評估，CSIA 在其中扮演了協助的角色。

圖十六 Dr. Silvia Mancini 演講

(三) Water Quality Signatures for CCR Management Sites

演講者為加州 Electric Power Research Institute（EPRI）研究員 Bruce Hensel，本篇主要闡述地下水污染水質鑑識的方法，污染源來自煤碳燃燒殘留物 (Coal Combustion Residuals, CCRs) 如無機物，Dr. Bruce Hensel 提供他們鑑識的三個程序概要：

1. 從水體背景資料中比對 CCRs 的指標物種如飛灰中的硼、氟、鉬、銻等以及脫硫石膏（FGD gypsum）中的氟、溴、氯等，由此瞭解 CCRs 的物質哪些是需要進一步釐清的。
2. 把前述的指標物種彼此的比例 （compound or ion ratio) 繪製成三角圖，不同來源的飛灰或脫硫石膏所組成的物種比例關係會有所差異，如圖十七與十八所示 。



圖十七 物種三角圖比例 (無機) (4)

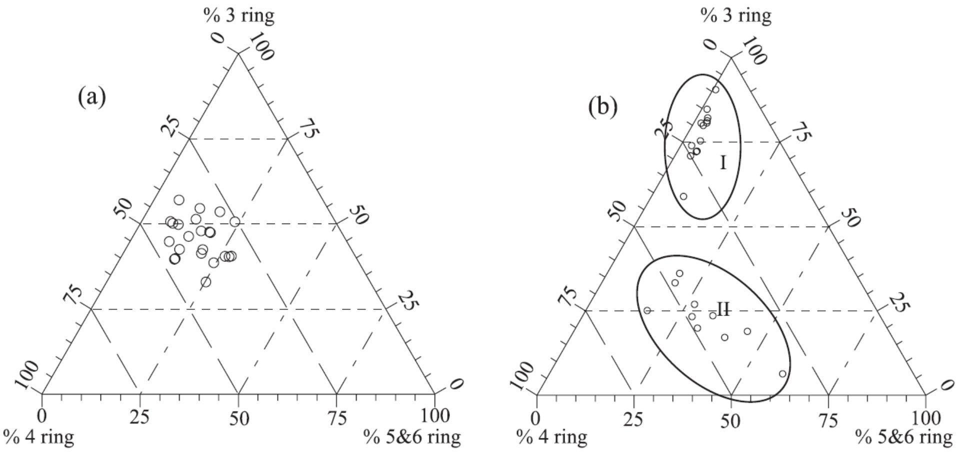
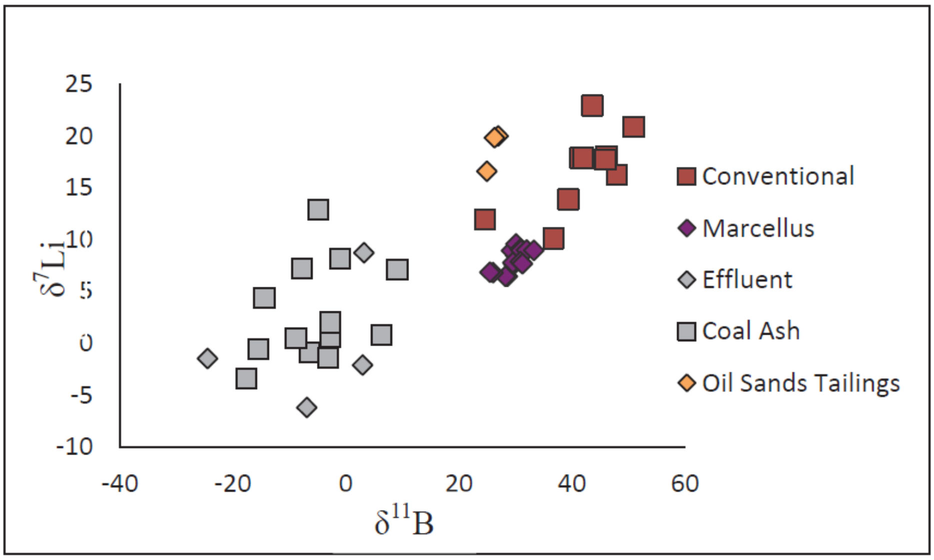


Fig. 3. Triangular comparison of PAHs in the dustfall of Tianjin in (a) heating season and (b) nonheating season.

圖十八 PAHs 不同環組成比例三角圖，顯示不同環境條件下產生的差異 (5)

3. 從三角圖可以瞭解哪些物種可用來辨別不同來源，因此可進一步以兩種或兩種以上的同位素比值分析來源，如圖十九所示。



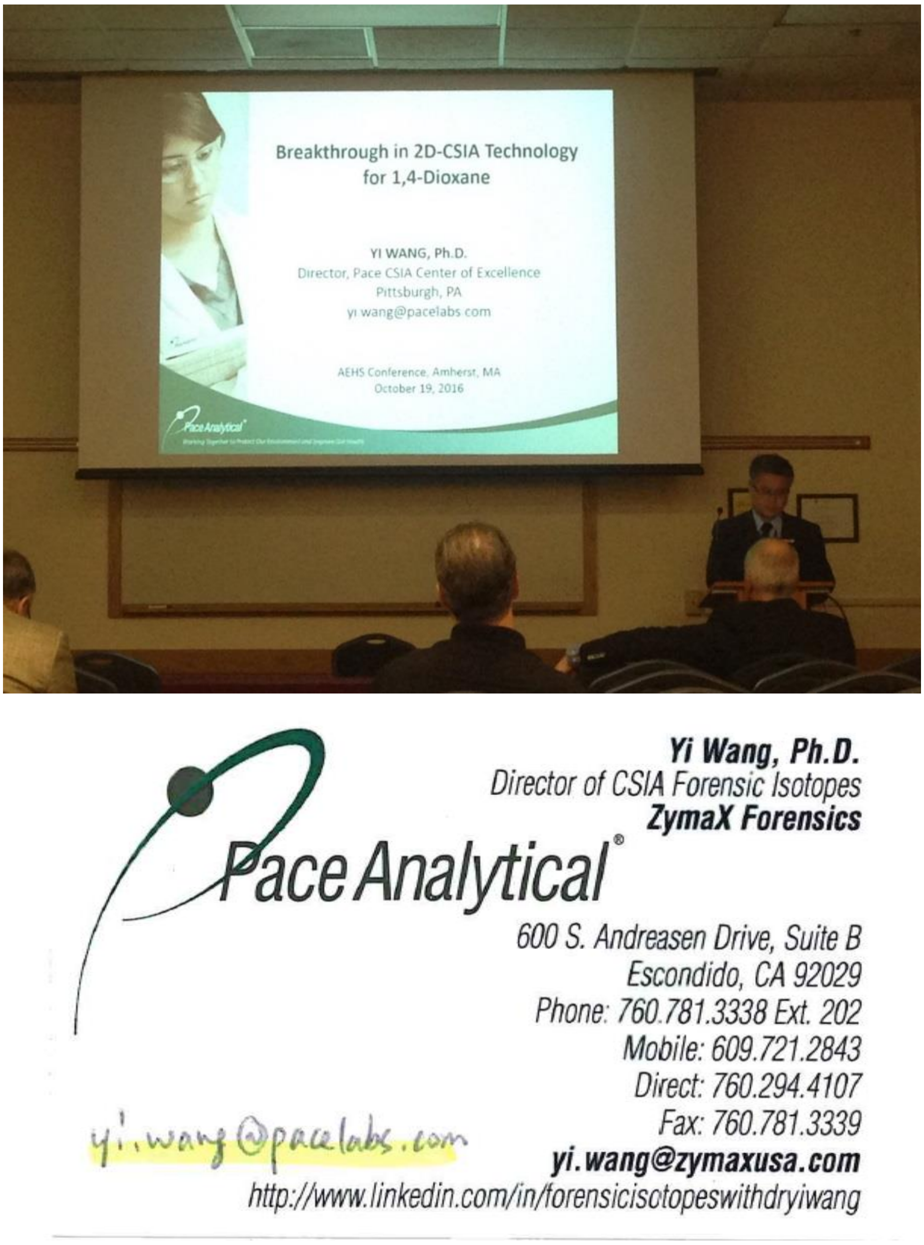
圖十九 二維同位素比值比對 **(6)**

這是目前 EPRI 他們針對 CCRs 提供的鑑識建議流程，不同場址是否能夠運用相同的程序執行無法確定，但類似的概念是可以提供參考，畢竟鑑識方法很多種，要尋找一套適合的評估方式是需要時間與人力來嘗試運作。

(四) Two-Dimensional Compound Specific Isotope Analysis (2D-CSIA) Forensic Approach for Low ppb Level Emerging Contaminant 1,4-Dioxane

演講者為任職美國 Pace Analytical 公司華裔學者 Dr. Yi Wang，Dr. Yi Wang 專長為同位素比值技術分析，目前也為該公司 CSIA 鑑識部門的領導，本篇演講的主題主要針對以二維同位素比值技術分析新興污染物 1,4-二氧環已烷 (1,4-Dioxane)。在本次研討會中 1,4-二氧環已烷被論述的頻率很高，從其背景論述，1,4-二氧環已烷為合成的化合物，容易溶於水中且不易被生物降解，主要是作為三氯乙烯 (1,1,1- TCA)或其它含氯溶劑的穩定劑，所以含氯溶劑的污染場址發現到 1,4-二氧環已烷的機率很高。此外 1,4-二氧環已烷也是生活用品中的添加物，如油漆、石蠟、油脂、染料甚至化妝品都有其蹤跡 (參考資料)。根據美國環保署整合風險資訊系統 (Integrated Risk Information System, IRIS) 1,4-二氧環已烷具有致癌性 **(7)**，風險評估值為當暴露濃度為 0.35 µg/L 致癌風險為百萬分之一，目前美國環保署尚未正式將 1,4-二氧環已烷列入列管規範，但是各州已各自有水體中濃度規範，如科羅拉多州地下水整治後濃度不可超過 0.35 µg/L；加州飲用水中告示濃度為 1 µg/L ； 新罕布夏州對於所

有水體規範不可超過 0.25 μg/L；麻州則對於飲用水公告指示值為 0.3 μg/L。由以上背景資料可知，1,4-二氧環己烷在水體中存在濃度低且具致癌性，而要追溯到其污染來源首先需要克服的是分析技術。Dr. Yi Wang 以美國 EPA method 522 固相萃取匣進行萃取，隨後進行碳與氫的二維同位素比值分析，實場數據分析結果針對目前方法偵測極限為 1 μg/L，檢測全國 32740 個場址中有 3796 處檢測出 1,4-二氧環己烷的蹤跡，其檢出率為 12%。筆者也在會前與 Dr. Yi Wang 交換名片交流，希望未來有機會能在同位素比值技術分析議題上能更進一步交流。



Breakthrough in 2D-CSIA Technology
for 1,4-Dioxane

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AEHS Conference, Amherst, MA
October 19, 2016

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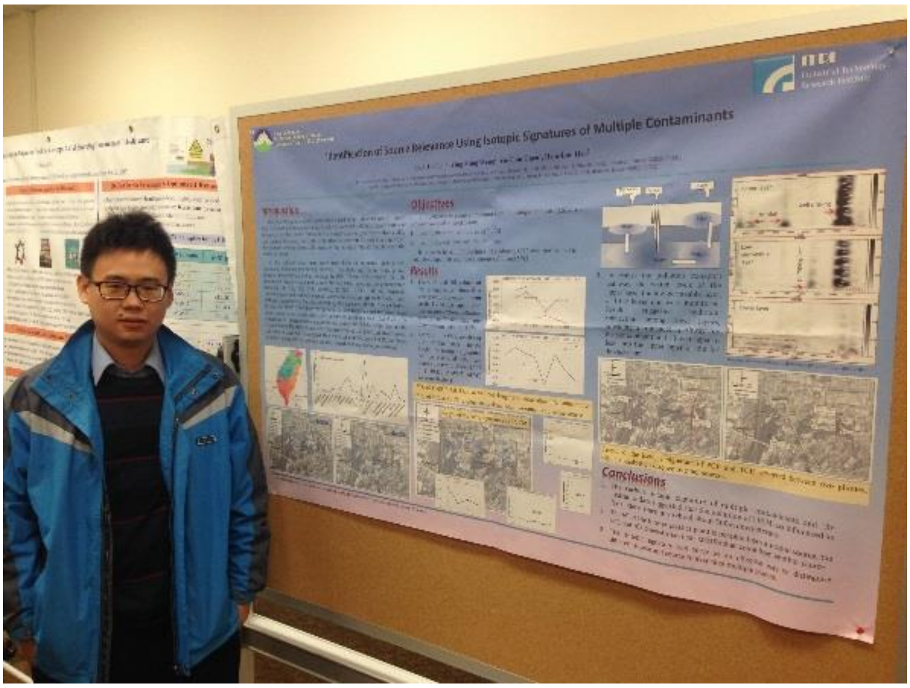
圖二十 演講者 Dr. Yi Wang (上) 交換名片 (下)

(五) Using Advanced Microbiological Sequencing and Analysis for Remedial Design of a CVOC Contaminated Site

演講者為 Haley & Aldrich 公司的 Elizabeth Bishop ，本篇不同於前面所提以同位素比值技術瞭解場址降解方式，而是直接分析微生物瞭解是否有生物降解。Elizabeth Bishop 以紐澤西州北部一個場址設計一套計畫瞭解是否該場址有潛在生物降解可能性，目標場址為含氯揮發性有機物 (CVOC) 中的四氯乙烯 (PCE) 以及其相關降解的產物，污染分布在表土與床岩上，要觀察的微生物物種為可降解含氯物種的 *Dehalococoides* (DHC)，因此以 qPCR 去定性與定量場址 *Dehalococoides* 濃度，除了 DHC 之外也運用 16S ribosomal rRNA 引子去定性是否有其它可能降解污染物的微生物存在，結果發現在這個場址中的 DHC 濃度低於 qPCR 定量極限 (8.12×10^2 gene copies/mL) 並且沒有找到其它可以降解氯物種的微生物，但是定性出其它可以降解碳氫化合物的微生物物種，表示在這個場址中有機會以生物降解進行整至，因此可以進一步將菌種純化。以結合特定目標物種定量與菌種定性兩種方式以及同位素比值協助尋找適當的生物降解方式以達到自然衰減，都是目前整治監測技術中較為新的作法。

三、 壁報論文報告 (Posters)

研討會本次壁報共 60 篇， 分在兩間會議室舉行，筆者本次投稿論文為與工研院綠能所許心蘭博士合作共同發表「 Identification of Source Relevance Using Isotopic Signatures of Multiple Contaminants 」，主要是以碳、氫與氯同位素比值去比對三氯乙烯污染場址與附近地下水井的污染物，由於場址污染時間較久，因此除了原先的三氯乙烯還有其它降解後的產物，包含二氯乙烯與氯乙烯等，碳、氫同位素比值主要以氣相層析串連同位素比值質譜分析儀 (GC/IRMS)，氯同位素比值主要以氣相層析串連質譜儀 (GC/MS)分析其同位素離子碎片比例計算，結果顯示附近污染地下水井經分析推測來自該三氯乙烯污染場址，筆者認為本研究可以 RTM 來強化污染來源與下游的關聯性。



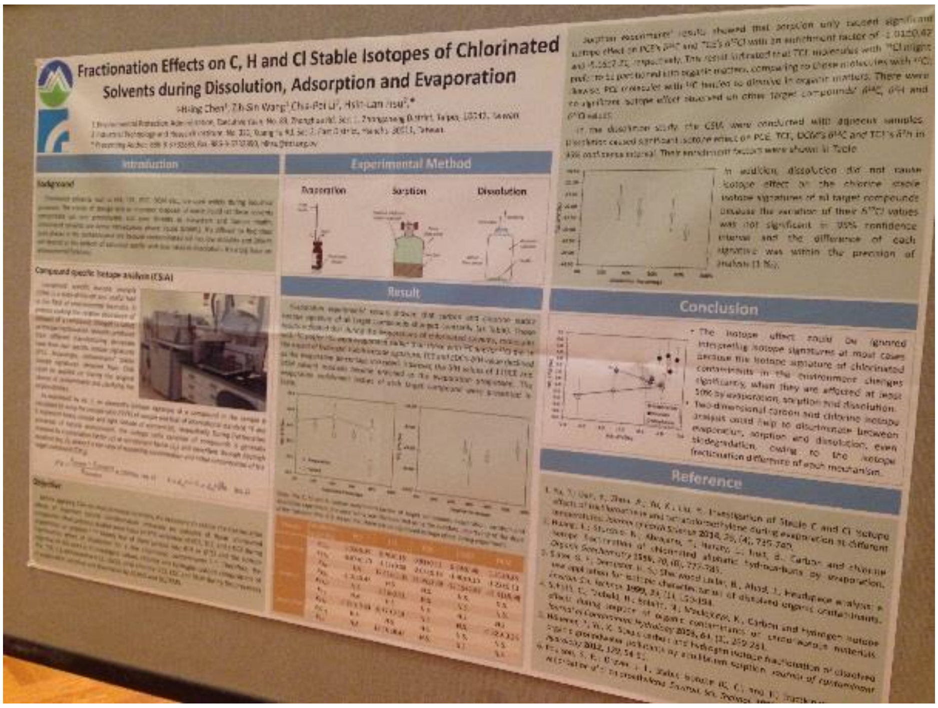
圖二十一 筆者與本次發表之壁報

60 篇壁報中以污染場址整治研究為多數，其中分享 5 篇心得如下：

(一) Fractionation Effects on C, H and Cl Stable Isotopes of Chlorinated Solvents During Dissolution, Adsorption and Evaporation

本篇由工研院綠能所許心蘭博士與本署土基會共同合作探討有關含氯物種（ PCE、DCE、EDC 與 DCM ）在揮發、吸附與溶解作用下，對於同位素比值的影響。在實際環境下這些途徑很可能會有分化作用徑而影響同位素比值

的比對，過往文獻多為探討碳同位素比值的分化作用，在此研究中又增加對氫與氯同位素比值的探討。雷利模式中的濃化因子（ϵ, Enrichment Factor) 可以用來觀察溶劑中含氯物種較輕同位素是否會受到影響，如當濃化因子小於 0，代表輕同位素容易留在溶劑中，濃化因子大於 0，代表輕同位素容易分離到其它介質中。研究結果顯示，吸附與溶解作用幾乎不影響三種元素同位素比值，揮發會影響同位素比值，但影響程度要至少 50% 才有明顯變化，這研究結果對於污染場址中含氯化合物物種的同位素比值研究可以提供解釋排除三種作用因子對評估同位素比值的影響。



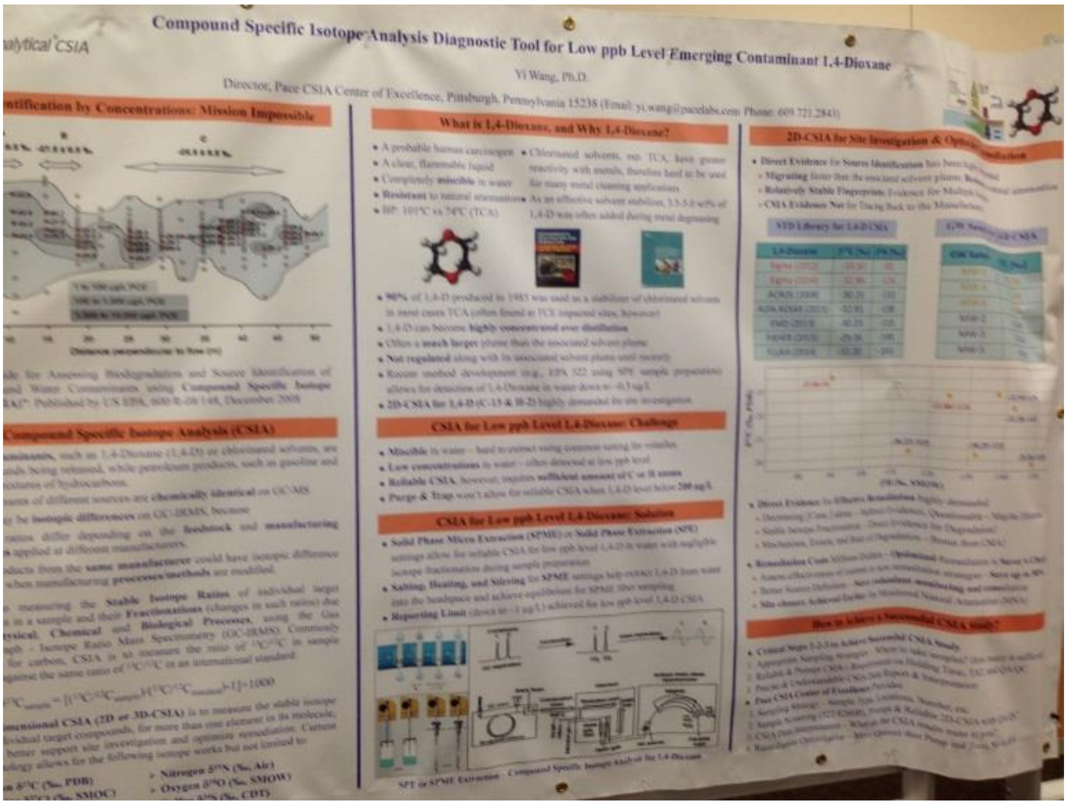
Fractionation Effects on C, H and Cl Stable Isotopes of Chlorinated Solvents during Dissolution, Adsorption and Evaporation

圖二十二　Fractionation Effects on C, H and Cl Stable Isotopes of Chlorinated Solvents During Dissolution, Adsorption and Evaporation 壁報論文

(二)　Two-Dimensional Compound Specific Isotope Analysis (2D-CSIA) Forensic Approach for Low ppb Level Emerging Contaminant 1,4-Dioxane

本壁報研究同樣由 Dr. Yi Wang 發表，針對 1,4-二氧環己烷(1,4-Dioxane) 發展碳與氫同位素比值分析方法，以 6 個來自不同廠牌 1,4-二氧環己烷標準品分析其碳與氫同位素比值，並且取樣地下水污染水樣進行比對，由於 1,4-二氧環己烷易溶於水，先經由固相萃取後再進行分析，研究結果指出分析方法偵測極限約 1 μg/L，分析的結果不代表能直接追溯到廠牌，因為同一廠牌不

同年代生產很可能同位素比值會有差異，因此應直接至污染場址取樣分析比較才能比較正確地連結關聯性。



Compound Specific Isotope Analysis Diagnostic Tool for Low ppb Level Emerging Contaminant 1,4-Dioxane

Yi Wang, Ph.D.

Director, Pace CSIA Center of Excellence, Pittsburgh, Pennsylvania 15238 (Email: yi.wang@pacelabs.com Phone: 609 721 2843)

ntification by Concentrations: Mission Impossible

Compound Specific Isotope Analysis (CSIA)

What is 1,4-Dioxane, and Why 1,4-Dioxane?

CSIA for Low ppb Level 1,4-Dioxane: Challenge

CSIA for Low ppb Level 1,4-Dioxane: Solution

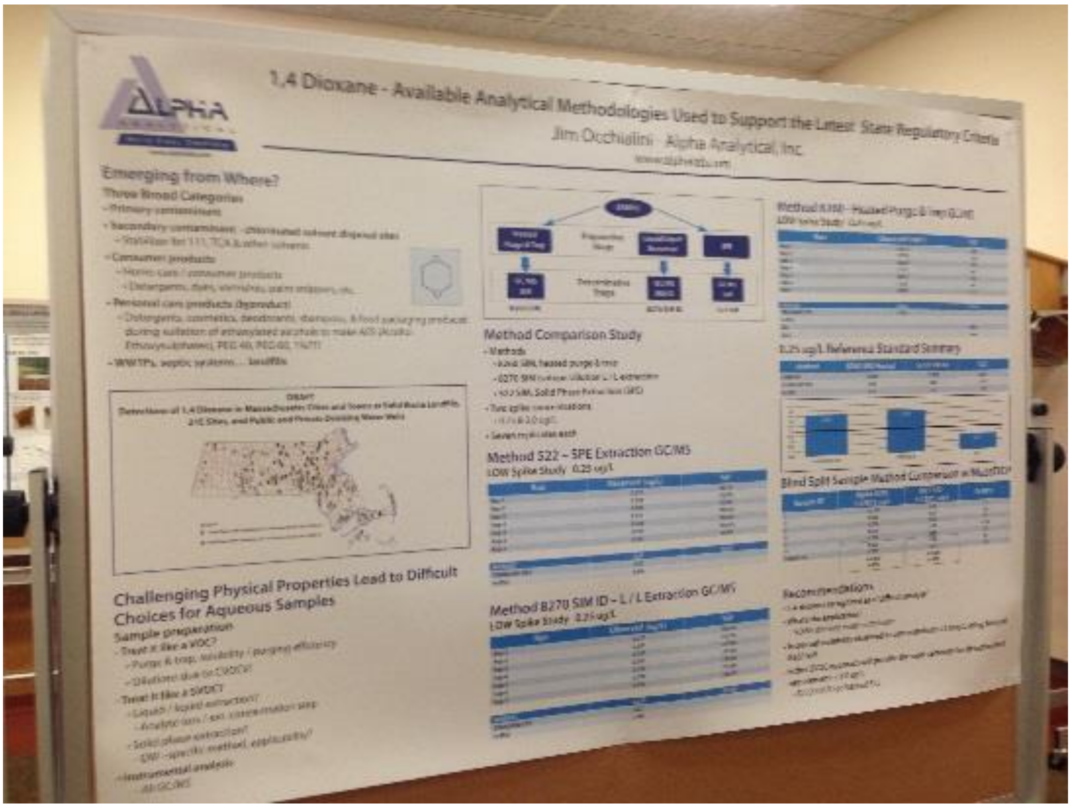
2D-CSIA for Site Investigation & Opt

圖二十三 Two-Dimensional Compound Specific Isotope Analysis (2D-CSIA) Forensic Approach for Low ppb Level Emerging Contaminant 1,4-Dioxane 壁報論文

(三) 1, 4- Dioxane – A Review and Evaluation of the Available Analytical Methodologies Used in Support of the Latest State and Federal Standards

這是另一篇關於 1,4-二氧環己烷(1,4-Dioxane) 的分析方法研究，由 Alpha Analytical 公司的 Dr. James Occhialini 所發表，他以目前美國環保署三種分析方法進行比較，第一種為 EPA method 8260 以吹氣捕捉方式作為前處理，以 GC/MS SIM mode 分析，第二種為 EPA method 522 以固相萃取匣前處理萃取，以 GC/MS SIM mode 分析；第三種為 EPA method 8270 以二氯甲烷液相萃取，以 GC/MS SIM mode 分析。研究結果顯示 EPA method 8260 在小於 1 μg/L 的標準偏差較大，EPA method 522 與 EPA method 8270 在小於 1 μg/L 的較為接近標

準偏差也較 EPA method 8260 小，很可能是因為吹氣捕捉方式每次分析並未能一致的把 1,4-二氧環己烷從水體中帶出，因此產生分析差別。



1,4 Dioxane - Available Analytical Methodologies Used to Support the Latest State Regulatory Criteria

Jim Occhialini · Alpha Analytical, Inc.

Emerging from Where?

Method Comparison Study

Method 522 – SPE Extraction GC/MS

Method 8270 SIM ID – L / L Extraction GC/MS

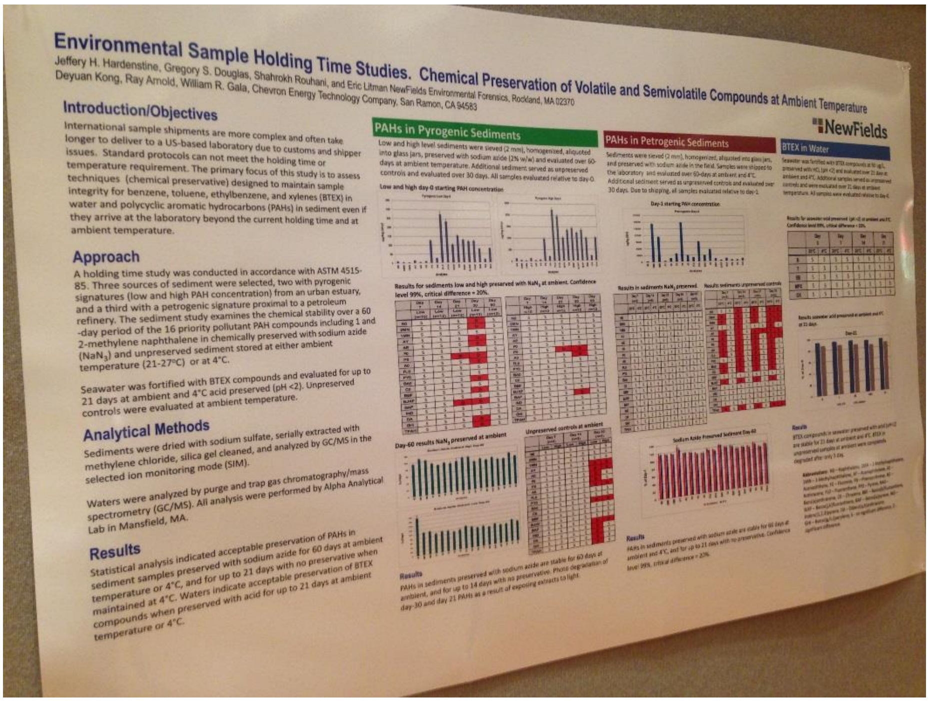
Challenging Physical Properties Lead to Difficult Choices for Aqueous Samples

圖二十四 1, 4- Dioxane – A Review and Evaluation of the Available Analytical Methodologies Used in Support of the Latest State and Federal Standards 壁報論文

(四) Environmental Sample Holding Time Studies: Chemical Preservation of Volatile and Semivolatile Compounds at Ambient Temperature

這篇由 NewFields、Chevron Energy Technology 公司聯合發表的壁報論文，不像其它篇探討環境鑑識技術，著重於探討樣品室溫下保存方式，以環境常見的多環芳香烴 (1,4-Dioxane) 與 BTEX 為例，其中 PAHs 樣品分為石油燃燒產生 (Petrogenic) 與煤灰燃燒產生 (Pyrogenic) 利用有無保存劑疊氮化鈉 (NaN_3) 以及放置室溫 (21-27℃) 與 4℃ 下的比較，每 7、14、21、30 與 60 天分析一批次樣品；BTEX 水體樣品加酸使其 pH 值小於 2，在室溫與 4℃ 下保存比較，每 7、14 與 21 分析一批次樣品，各個樣品保存天數分析出來的濃度與第 0 天比較。結果顯示有加保存劑可在室溫下保存 60 天，沒有加保存劑在室溫下容易降解，即使在 4℃ 下也僅能保存 14 天；BTEX 則在室溫下與 4

℃ 下，並不影響濃度變化，顯示加酸即可使 BTEX 穩定保存在樣品中，此篇研究結果可知樣品保存只要處置得當不一定要在 4℃ 下保存。



Environmental Sample Holding Time Studies. Chemical Preservation of Volatile and Semivolatile Compounds at Ambient Temperature

Jeffery H. Hardenstine, Gregory S. Douglas, Shahrokh Rouhani, and Eric Litman NewFields Environmental Forensics, Rockland, MA 02370
Deyuan Kong, Ray Arnold, William R. Gala, Chevron Energy Technology Company, San Ramon, CA 94583

NewFields

Introduction/Objectives

International sample shipments are more complex and often take longer to deliver to a US-based laboratory due to customs and shipper issues. Standard protocols can not meet the holding time or temperature requirement. The primary focus of this study is to assess techniques (chemical preservative) designed to maintain sample integrity for benzene, toluene, ethylbenzene, and xylenes (BTEX) in water and polycyclic aromatic hydrocarbons (PAHs) in sediment even if they arrive at the laboratory beyond the current holding time and at ambient temperature.

Approach

A holding time study was conducted in accordance with ASTM 4515-85. Three sources of sediment were selected, two with pyrogenic signatures (low and high PAH concentration) from an urban estuary, and a third with a petrogenic signature proximal to a petroleum refinery. The sediment study examines the chemical stability over a 60-day period of the 16 priority pollutant PAH compounds including 1 and 2-methylene naphthalene in chemically preserved with sodium azide (NaN_3) and unpreserved sediment stored at either ambient temperature (21-27°C) or at 4°C.

Seawater was fortified with BTEX compounds and evaluated for up to 21 days at ambient and 4°C acid preserved (pH <2). Unpreserved controls were evaluated at ambient temperature.

Analytical Methods

Sediments were dried with sodium sulfate, serially extracted with methylene chloride, silica gel cleaned, and analyzed by GC/MS in the selected ion monitoring mode (SIM).

Waters were analyzed by purge and trap gas chromatography/mass spectrometry (GC/MS). All analysis were performed by Alpha Analytical Lab in Mansfield, MA.

Results

Statistical analysis indicated acceptable preservation of PAHs in sediment samples preserved with sodium azide for 60 days at ambient temperature or 4°C, and for up to 21 days with no preservative when maintained at 4°C. Waters indicate acceptable preservation of BTEX compounds when preserved with acid for up to 21 days at ambient temperature or 4°C.

PAHs in Pyrogenic Sediments

Low and high level sediments were sieved (2 mm), homogenized, aliquoted into glass jars, preserved with sodium azide (2% w/w) and evaluated over 60-days at ambient temperature. Additional sediment served as unpreserved controls and evaluated over 30 days. All samples evaluated relative to day-0.

Low and high day-0 starting PAH concentration

Day-60 results NaN_3 preserved at ambient

Results

PAHs in sediments preserved with sodium azide are stable for 60 days at ambient, and for up to 14 days with no preservative. Photo degradation of day-30 and day 21 PAHs as a result of exposing extracts to light.

PAHs in Petrogenic Sediments

Sediments were sieved (2 mm), homogenized, aliquoted into glass jars, and preserved with sodium azide in the field. Samples were shipped to the laboratory and evaluated over 60-days at ambient and 4°C. Additional sediment served as unpreserved controls and evaluated over 30 days. Due to shipping, all samples evaluated relative to day-1.

Day-1 starting PAH concentration

Results in sediments NaN_3 preserved

Results sediments unpreserved controls

Sodium Azide Preserved Sediment

Results

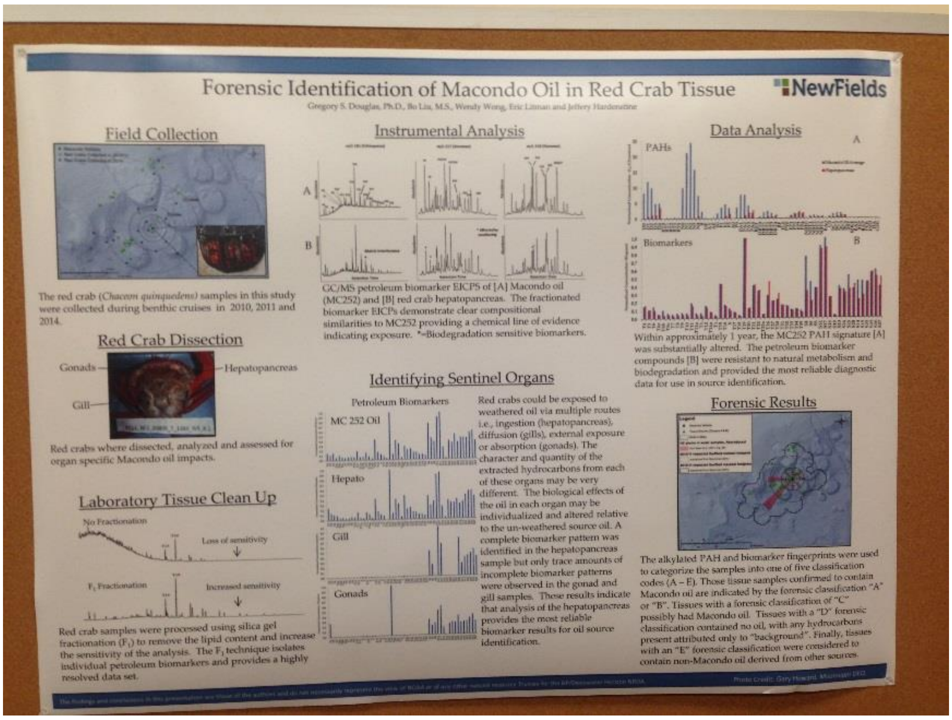
PAHs in sediments preserved with sodium azide are stable for 60 days at ambient and 4°C, and for up to 21 days with no preservative. Confidence level 99%, critical difference = 20%.

BTEX in Water

圖二十五 Environmental Sample Holding Time Studies: Chemical Preservation of Volatile and Semivolatile Compounds at Ambient Temperature 壁報論文

(五) Chemical Evidence for Exposure of Red Crabs (Chaceon quinquedens) to Macondo Oil After the Deep Water Horizon Oil Spill

這篇是由 NewFields 公司的 Eric Litman 與 Jeff Hardenstine 共同發表一篇關於使用海洋生物的組織與器官瞭解油污污染來源，這是在 2010 年爆發墨西哥灣馬康多油井深水油管漏油事件後，油污對生態的影響陸續有很多學術進行研究，本篇是從五齒查氏蟹（ Chaceon quinquedens ）的肝胰腺 (Hepatopancreas)、鰓 (Gill) 與生殖腺 (Gonad) 瞭解海洋生物暴露漏油的化學證據，以矽膠進行淨化降低基質干擾，以 GC/MS 分析得到的層析圖譜與離子碎片比對，比對結果發現肝胰腺的圖譜幾乎與油原料一致，根據作者解釋肝胰腺為五齒查氏蟹消化系統中的組織，因此攝取食物時油污會跟著進入到消化系統。一般而言我們會直接分析環境基質，然而海洋生物在這裡也可以作為污染的直接證據。



Forensic Identification of Macondo Oil in Red Crab Tissue

NewFields

Gregory S. Douglas, Ph.D., Bo Liu, M.S., Wendy Wong, Eric Litman and Jeffery Hardenstine

Field Collection

The red crab (*Chaceon quinquedens*) samples in this study were collected during benthic cruises in 2010, 2011 and 2014.

Red Crab Dissection

Red crabs where dissected, analyzed and assessed for organ specific Macondo oil impacts.

Laboratory Tissue Clean Up

Red crab samples were processed using silica gel fractionation (F_1) to remove the lipid content and increase the sensitivity of the analysis. The F_1 technique isolates individual petroleum biomarkers and provides a highly resolved data set.

Instrumental Analysis

GC/MS petroleum biomarker EICPS of [A] Macondo oil (MC252) and [B] red crab hepatopancreas. The fractionated biomarker EICPs demonstrate clear compositional similarities to MC252 providing a chemical line of evidence indicating exposure. *=Biodegradation sensitive biomarkers.

Identifying Sentinel Organs

Red crabs could be exposed to weathered oil via multiple routes i.e., ingestion (hepatopancreas); diffusion (gills), external exposure or absorption (gonads). The character and quantity of the extracted hydrocarbons from each of these organs may be very different. The biological effects of the oil in each organ may be individualized and altered relative to the un-weathered source oil. A complete biomarker pattern was identified in the hepatopancreas sample but only trace amounts of incomplete biomarker patterns were observed in the gonad and gill samples. These results indicate that analysis of the hepatopancreas provides the most reliable biomarker results for oil source identification.

Data Analysis

Within approximately 1 year, the MC252 PAH signature [A] was substantially altered. The petroleum biomarker compounds [B] were resistant to natural metabolism and biodegradation and provided the most reliable diagnostic data for use in source identification.

Forensic Results

The alkylated PAH and biomarker fingerprints were used to categorize the samples into one of five classification codes (A – E). Those tissue samples confirmed to contain Macondo oil are indicated by the forensic classification "A" or "B". Tissues with a forensic classification of "C" possibly had Macondo oil. Tissues with a "D" forensic classification contained no oil, with any hydrocarbons present attributed only to "background". Finally, tissues with an "E" forensic classification were considered to contain non-Macondo oil derived from other sources.

圖二十六 Chemical Evidence for Exposure of Red Crabs (Chaceon quinquedens) to Macondo Oil After the Deep Water Horizon Oil Spill 壁報論文

四、　廠商儀器展示 (Exhibits)

由於研討會重心在場址整治，廠商展覽多為整治工具，因此一般環境分析研討會常見的儀器商如安捷倫 (Agilent)、賽默飛世爾 (Thermo Fisher) 等並未在大會中設攤位。而現場採樣經常需要進行快篩現地直接瞭解狀況，因此廠商所展示的檢測儀器都是直讀式，其中有兩家廠商的產品符合本所業務需求：

(一)　Griffin 460 移動式吹氣捕捉氣相層析串聯質譜儀：

Griffin 460 移動式吹氣捕捉氣相層析串聯質譜儀是由 FLIR 公司開發，儀器的外觀像一個大箱子且相當堅固，向我們介紹產品的 Dr. Philip Tackett 表示，Griffin 460 目前美國軍方有向 FLIR 公司購買，多為偵測爆裂物或具揮發性毒性物質為主，儀器本體內部有個大烘箱放有 15 公尺長的層析管柱，後端質譜儀可偵測質荷比 (m/Z) 範圍 35-425，也與一般桌上型的氣相層析儀偵測範圍相仿；而前方進樣方式以吹氣捕捉為主，因此水體樣品可以直接進樣，揮發性有機物偵測極限可達 1 μg/L，一個樣品分析時間可在 15 分鐘內完成。然而儀器最大的缺點筆者認為是儀器本體體積與重量，雖然儀器是號稱移動式，實際上本體的重量達到 40 公斤，對於地勢無法很穩固放置進行採樣的位置可能會受到限制。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FLIR Systems, Inc.
3000 Kent Avenue
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USA

圖二十七　FLIR 公司產品 Griffin 460 移動式吹氣捕捉氣相層析串聯質譜儀與交換名片

(二) Frog-4000 攜帶式氣相層析串聯光離子偵測器

Frog-4000 攜帶式氣相層析串聯光離子偵測器的外型看起來很可愛，就像一隻活生生的青蛙蹲著，所以它的型號就以青蛙為代號。體積小重量輕（大約兩公斤），可用於分析水體、土壤與空氣中的揮發性有機物，向我們介紹產品的 Patrick Lewis 表示，他們的機器可以微型化在於他們研發的奈米材質製作的層析微型管柱 (micro column) 以及微型前濃縮器 (micro preconcentrator) ，可使化合物濃縮並可集中加熱協助升溫脫附分析，因此雖然後端偵測器並非為感度更好的質譜儀，但是偵測極限也可以達到 1 μg/L。一個樣品分析約 5 分鐘，電力也可以持續使用 6 小時，而且不像一般氣相層析串聯質譜儀，儀器可以直接使用空氣作為攜帶氣體 (carrier gas)，因此相對於 FLIR 公司出產的儀器的確賣相較佳，也比較符合實際採樣時所要求的攜帶便利與快速。

Defiant Technologies
A Systems Approach to Chemical Detection

Patrick Lewis
Senior Scientist

FROG 4000

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圖二十八 Frog-4000 攜帶式氣相層析串聯光離子偵測器與交換名片

圖二十九 Frog-4000 層析微管柱

肆、建議

本次筆者參加在美國舉辦的第 32 屆 (2016) 土壤、底泥、水和能源國際研討會，看到了國外辦理研討會的方式以及國外在環境鑑識技術的發展，尤其是同位素比值的分析技術與其簡報同位素比值品管的方式，都有更深一層的瞭解與值得學習的地方，希望這次學習到新的技術透過蒐集的資訊以及未來能與國內專家交流，能實際應用到國內的環境鑑識上。關於這次研討會後，以下有幾點建議如下：

1. 環境鑑識技術是一門跨領域的學門，整合地質學、海洋學、大氣學、環境工程學、化學分析、統計學、資訊科學等，可諮詢這些學門的專家先建立大方向的執行流程，再針對不同地理條件與氣候因素等環境差異的鑑識場址制定出適當的採樣計畫，搭配具可信度的後端統計模式來比對污染源。
2. 同位素比值分析技術在土水整治上越來越多應用上的實例，在美國每年約有 1200 萬美元的產值運用在環境整治，然而目前國內同位素比值分析大多以辨識食品摻假與產地來源辨別為主。在環境領域上礙於市場小與儀器價格昂貴，在污染場址整治這部份仍需要找到優勢推行，目前環境鑑識應用可先嘗試建立分析方法與模式建立以辨別污染物來源為優先考量。
3. 參加國外研討會瞭解國外關切的環境議題（如新興污染物 1,4-二氧環己烷)，因此每年持續的派員至國外參與研討會，將國外專家提出的新技術以及國外最新關切議題帶回國內，可增進本所技術突破。

伍、參考文獻

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附件一 大會議程

Monday, October 17, 2016 (Monday is workshops only)

Registration: 10:00am – 4:00pm

Workshop 1 (1:00pm - 5:00pm) Measuring Biological Exposure to Environmental Chemicals, *Cape Cod Lounge*

Workshop 2 (1:00pm - 5:00pm) Vapor Intrusion Assessment and Mitigation in Massachusetts: Status of Sites, Findings from the Field, and Guidance for Practitioners, *Rm. 164*

Workshop 3 (1:00pm - 5:00pm) Building a Better Background Data Set, *Rm. 165*

Workshop 4 (1:00pm - 5:00pm) Sustainable Remediation Principles & Practice, *Rm. 168*

Workshop 5 (1:00pm - 4:00pm) Environmental Forensics – Integration of Established and Evolving Techniques to Evaluate Who Was Responsible for the Spill or Release, *Rm. 176*

Tuesday, October 18, 2016

Registration: 7:30am – 7:00pm | **Exhibit Hall Hours:** 9:00am – 7:00pm

Morning Platform Sessions

8:30/9:00am – 12:00pm, *Sessions are concurrent*

Session 1: Intersection of Transportation & the Environment, *Rm. 176*
Session 2: Use of Decision Analysis and Probabalistic Tools to Manage Evironmental Risk, *Rm. 164*
Session 3: New England's Regulatory Perspective on Greener Cleanups, *Rm. 168*
Session 4: Remediation, *Rm. 165*

Afternoon Platform Sessions

1:30pm – 5:00/5:30pm, *Sessions are concurrent*

Session 1: Building Resilience to Climate Impacts: Local Efforts to Implement Adaptation Plans, *Rm. 164*
Session 2: Risk Assessment, *Rm. 165*
Session 3: In-Situ Chemical Oxidation, *Rm. 168*
Session 4: Sustainability and Sustainable Remediation, *Rm. 176*

Poster Session 3:00pm – 6:00pm, *CCA and Rm. 162*

Wine/Welcome Reception 5:00pm – 7:00pm, exhibit areas, 1st floor

Evening Workshops

Workshop 6 (6:30pm – 9:30pm) Incremental Sampling Methodology (ISM), *Rm. 168*

Workshop 7 (6:30pm – 9:30pm) Remediation Tools for Challenging Geology – Cutting Edge Technology for Cleanups in Clay & Fractured Bedrock, *Rm. 176*

LUNCHEON:
12:00pm – 1:30pm
Amherst Room, 10th Floor

Speaker: Robert Haddad, Ph.D., Corporate Vice President and Principal Scientist, Exponent, Menlo Park, CA

NRDA - Past, Present, and Future

Wednesday, October 19, 2016

Registration: 7:30am – 7:00pm | **Exhibit Hall Hours:** 9:00am – 7:00pm

Morning Platform Sessions

8:30/9:00am – 12:00pm, *Sessions are concurrent*

Session 1: Innovative & Sustainable Soil, Sediment, Water & Energy Solutions, *Rm. 176*
Session 2: Toward a Sustainable Energy Future, *Rm. 168*
Session 3: Advanced Analytical Tools for Management of Contaminated Sites, *Rm. 164*
Session 4: Bioremediation, *Rm. 165*

Afternoon Platform Sessions

1:30pm – 5:00/6:00pm, *Sessions are concurrent*

Session 1: PFAS (Poly & Perfluoroalkyl Substances), *Rm. 164*
Session 2: Environmental Forensics, *Rm. 176*
Session 3: Innovative Remedial Approaches, *Rm. 168*

Poster Session 3:00pm – 6:00pm, *CCA and Rm. 162*

Social 5:00pm – 7:00pm, exhibit areas, 1st floor

Evening Workshops

Workshop 8 (6:30pm – 9:30pm) Vapor Intrusion – Reducing Uncertainty in Investigations, Mitigation and Transactions – Tools for the Toolbox, *Rm. 176*

Workshop 9 (7:00pm – 9:00pm) The Urban Background Dilemma: A Regional Study and Global Perspective, *Rm. 168*

LUNCHEON:
12:00pm – 1:30pm
Amherst Room, 10th Floor

Speaker: David W. Cash, PhD, Dean, John W. McCormack Graduate School of Policy and Global Studies, University of Massachusetts Boston

Science and Policy in the Crucible: Exploring the Interface in Contentious, Uncertain and Complex Arenas

Thursday, October 20, 2016

Registration: 7:30am – 12:00pm | **Exhibit Hall Hours:** 9:00am – 12:00pm

Morning Platform Sessions

8:30am – 12:00pm, *Sessions are concurrent*

Session 1: Advancing the Practice of In-Situ Remediation, *Rm. 164*
Session 2: Sediments, *Rm. 176*
Session 3: Vapor Intrusion, *Rm. 168*

Who Should Attend

- Environmental science educators and students
- Federal, state, county, and municipal officials responsible for the development and implementation of environmental regulatory programs
- Agencies and organizations responsive to issues arising from contaminated soils, sediments, water, and air
- Consultants providing environmental contaminant assessment, advice, and guidance
- Attorneys concerned with client environmental contaminant issues
- Environmental scientists, engineers, managers, and consultants
- Analytical laboratory staff specializing in environmental contamination
- Real estate, insurance, and banking representatives

Conference Highlights

- Strong technical presentations for immediate application
- Excellent networking opportunities
- Active participation from military, academia, regulatory agencies and the oil and gas industry.

Regulator Friendly

State and federal regulators receive:

- Special reduced registration
- Complimentary workshops (see registration form for details)

Socials

- Tuesday evening Wine Reception from 5:00pm – 7:00pm in the exhibit areas.
- Wednesday evening Social from 5:00pm – 7:00pm in the exhibit areas.
- Poster session socials

STUDENT COMPETITION/ AWARD PROGRAM

We are proud to announce the 13th Annual Student Competition for best student presentation at the conference. One $1000.00 cash prize and two $500.00 cash prizes will be awarded to the three best student presentations. Winners will be announced on Wednesday. See posting at registration desk.

Must be entered prior to the conference in order to compete. Open to all full and part-time students (post-docs excluded).

See www.AEHSFoundation.org for full details and previous winners.

AEHS Foundation

附件二　投稿論文摘要

Identification of Source Relevance Using Isotopic Signatures of Multiple Contaminants

Shih-Lin Lo[1,*], Ying-Ming Weng[1], Yu-Chin Chen[2], Hsin-Lan Hsu[2]

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[2] Industrial Technology and Research Institute. No. 321, Kuang Fu Rd. Sec.2, East District, Hsinchu, Taiwan 30011, R.O.C.

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Chlorinated organic solvents were widely used in the industrial area in Taiwan. Due to clustering of many factories which are potential polluters, identification of the source and the source relevance is a critical issue in order to resolve liability and conduct the remediation efficiently.

The studied case is a polluted area of about 250 acres located across two towns at the central Taiwan. Multiple plumes containing more than ten chlorinated organic compounds were detected above the regulated levels in the groundwater. One chemical manufacturer has been identified as one source, but it was not clear whether there exist other sources.

To resolve the source relevance issue, compound-specific isotope ratios of carbon and chlorine were analyzed for several contaminants. Interpretation of the isotopic signatures was based on the degradation potential of the compound. For the pollutants which are less likely degraded under the associated aquatic environment, their isotopic ratios were compared; for those likely degraded, the variation trend of their isotopic ratios was used instead to signal the existence of other sources. Long term monitoring of the water table and the geological strata were also studied to provide insight of the pollution migration. The multiple lines of evidence showed that in a certain downstream area the pollution might have come from the chemical manufacturer while there shall exist other pollution sources responsible for the further downstream pollution.

Keywords：stable isotope、environmental forensics

附件三　投稿論文壁報

Environmental
Protection Administration
Executive Yuan, R.O.C. (Taiwan)

ITRI
Industrial Technology
Research Institute

Identification of Source Relevance Using Isotopic Signatures of Multiple Contaminants

Shih-Lin Lo[1]*, Ying-Ming Weng[1], Yu-Chin Chen[2], Hsin-Lan Hsu[2]

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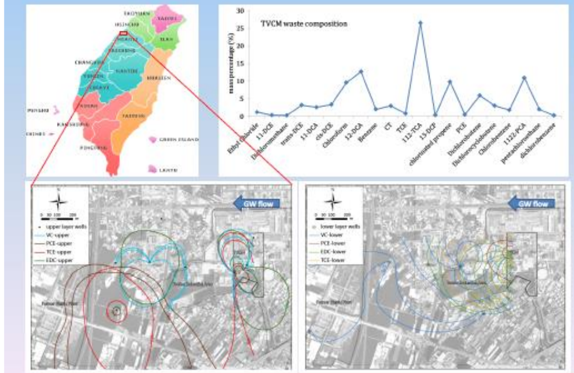
[2] Green Energy and Environment Laboratory, Industrial Technology Research Institute. No. 321, Kuang Fu Rd. Sec.2, East District, Hsinchu, Taiwan 30011, R.O.C.

Introduction

Chlorinated organic solvents were widely used in the industrial area in Taiwan. Due to clustering of many factories which are potential polluters, identification of the source and the source relevance is a critical issue in order to resolve liability and conduct the remediation efficiently. Here we presented a case study, in which the polluted area is about 250 acres at the north of Miaoli County near the northern Taiwan.

In this polluted area, there were many historical industrial plants with operations including machining, chemical manufacturing, metal working and plastics manufacturing and processing. In 1994, Taiwan EPA detected multiple chlorinated organic compounds above the regulated levels in the groundwater, including 112-TCA, PCE, TCE, cis-DCE, 11-DCE, 12-DCA, VC and benzene. Chlorobenzene and dichlorobenzene were also detected up to 0.29mg/L and 0.04mg/L, respectively, but not exceeding the regulated levels. The geological setting was sandy gravel from the ground surface to 25m deep (referred to as upper layer), under which was a low permeable layer of about 15m thick. The underlying was alternations of sandstone and mudstone till 90m deep (referred to as lower level). Multiple plumes were characterized at the upper and lower levels, and some of them were comingled. One chemical manufacturer, TVCM, has been identified as one source, but it was not clear whether there exist other sources.



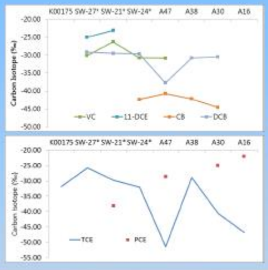
Objectives

The purpose is using compound-specific isotope analysis (CSIA) to achieve two goals stated below.

1. Identify the responsible area of TVCM.
2. Identify the existence of other sources.

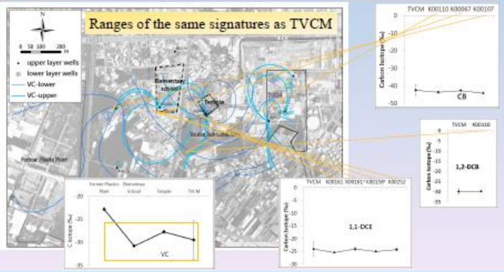
In order to have multiple lines of evidence, CSIA was performed for multiple compounds and two elements, $\delta^{13}C$ and $\delta^{37}Cl$.

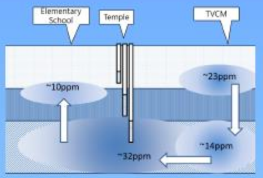
Results



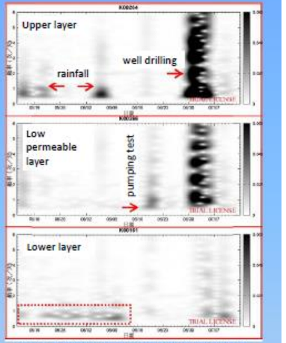
1. The ORP and DO values of the groundwater showed a strong reducing environment inside TVCM, perhaps due to the ongoing bioremediation, and a mild reducing one downstream outside TVCM.
2. Based on the CSIA results of the contaminants inside TVCM, the isotopic signature can be classified into two kinds (the two outliers (A47 of 11-DCE and SW-21 of VC) were neglected):

- $\delta^{13}C$ of 11-DCE, CB, DCB, or VC not changing → same signature, same source
- $\delta^{13}C$ of PCE and TCE varying due to degradation → same trend, same source

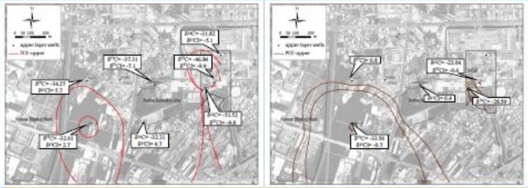




3. To realize the pollution transport pathway, the water levels of the upper layer, the low permeable layer, and the lower one were monitored. Results suggested hydraulic connection among these layers, providing a transport pathway for the contaminant in the lower layer to leak into the upper layer at the far downstream.



Source: Above hydraulic data was provided by Apollo Inc.



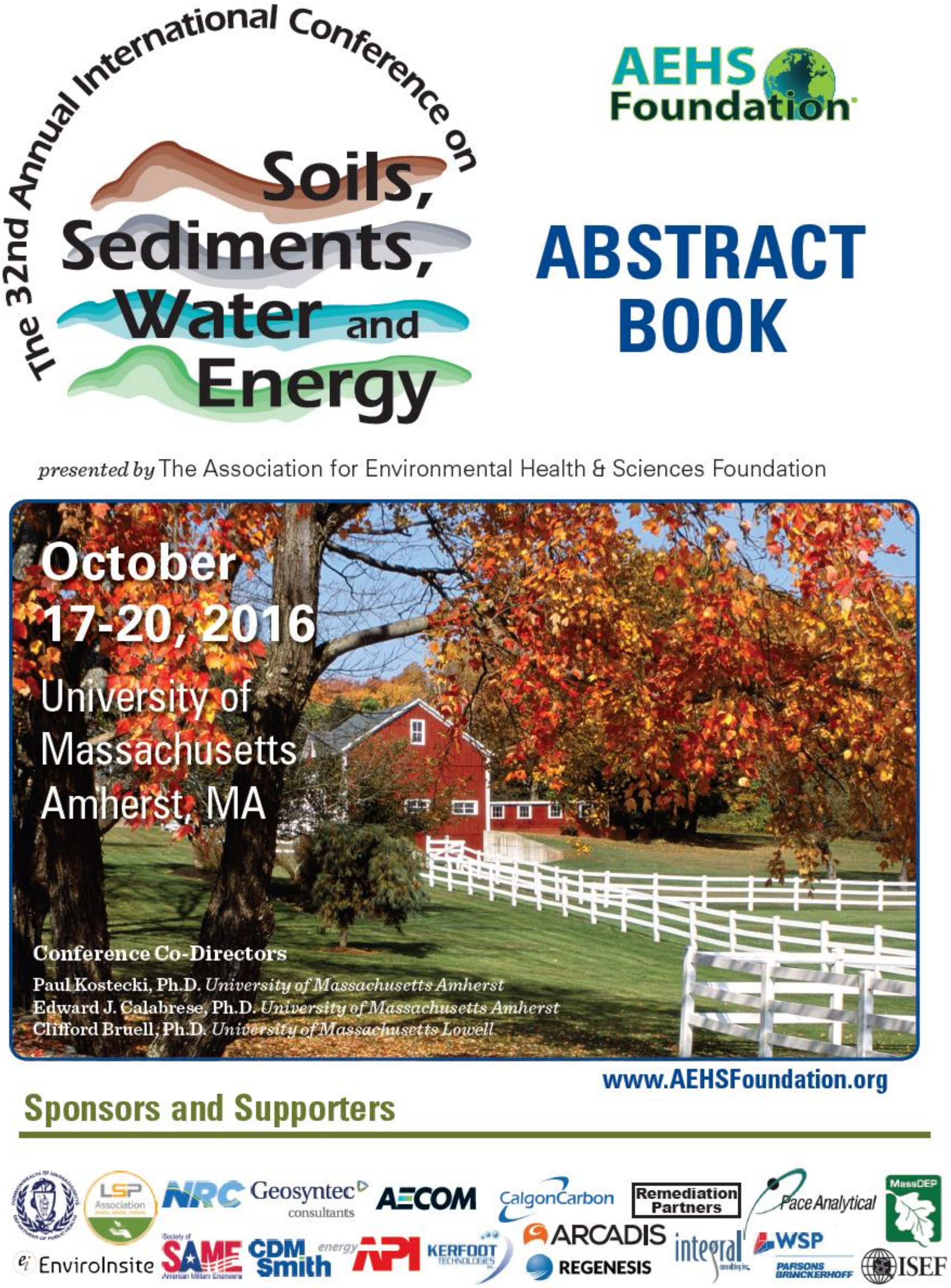
Trends of the isotopic signature of PCE and TCE reversed between two plumes, which signals the existence of other sources.

Conclusions

1. The carbon isotopic signature of multiple contaminants and the hydraulic data suggested that the pollution of TVCM has influenced as far as the elementary school about 500m downstream.
2. The VC at the former plastics plant is possible from a second source; the PCE and TCE downstream near K00156 shall come from another source.
3. The isotopic signature can serve as an effective way to distinguish different source and source relevance of multiple plumes.

Acknowledgement: This work was supported by the Environmental Protection Administration of Taiwan.

附件四　大會論文摘要書



The 32nd Annual International Conference on

Soils, Sediments, Water and Energy

AEHS Foundation

ABSTRACT BOOK

presented by The Association for Environmental Health & Sciences Foundation

October 17-20, 2016

University of Massachusetts Amherst, MA

Conference Co-Directors

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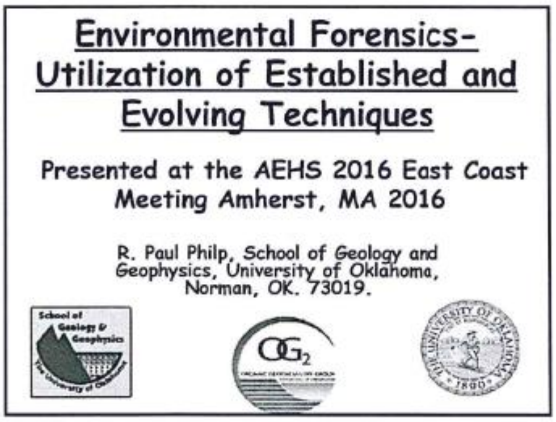
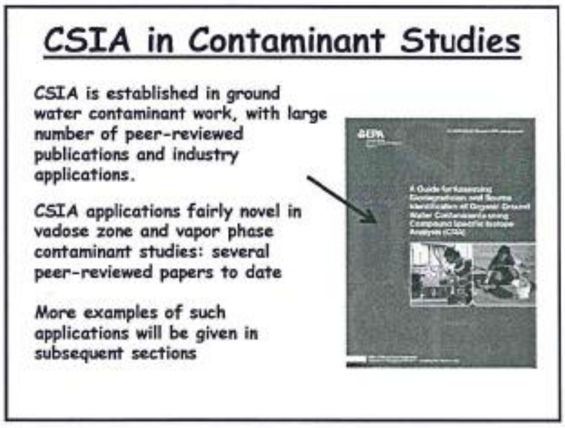
附件五 Workshops 講義



Environmental Forensics-Utilization of Established and Evolving Techniques

Presented at the AEHS 2016 East Coast Meeting Amherst, MA 2016

R. Paul Philp, School of Geology and Geophysics, University of Oklahoma, Norman, OK. 73019.

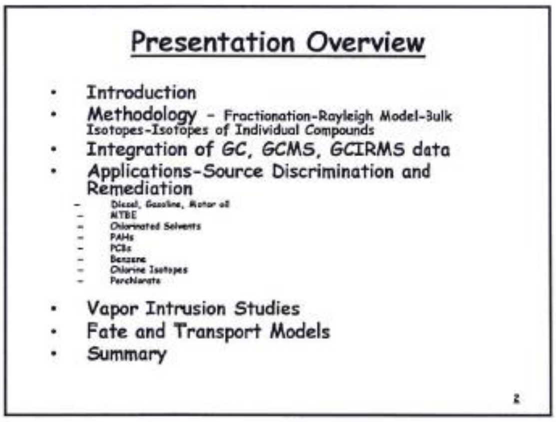


CSIA in Contaminant Studies

CSIA is established in ground water contaminant work, with large number of peer-reviewed publications and industry applications.

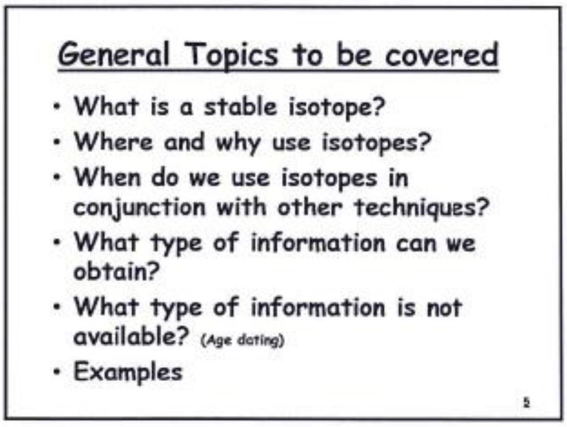
CSIA applications fairly novel in vadose zone and vapor phase contaminant studies: several peer-reviewed papers to date

More examples of such applications will be given in subsequent sections



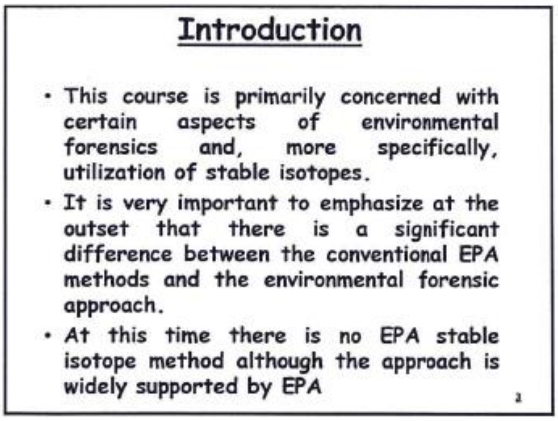
Presentation Overview

- Introduction
- Methodology - Fractionation-Rayleigh Model-Bulk Isotopes-Isotopes of Individual Compounds
- Integration of GC, GCMS, GCIRMS data
- Applications-Source Discrimination and Remediation
  - Diesel, Gasoline, Motor oil
  - MTBE
  - Chlorinated Solvents
  - PAHs
  - PCBs
  - Benzene
  - Chlorine Isotopes
  - Perchlorate
- Vapor Intrusion Studies
- Fate and Transport Models
- Summary



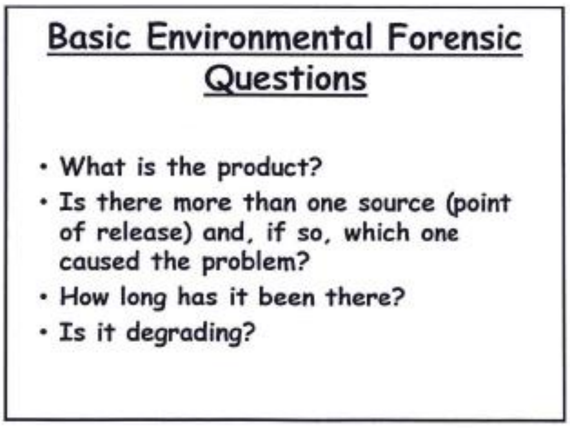
General Topics to be covered

- What is a stable isotope?
- Where and why use isotopes?
- When do we use isotopes in conjunction with other techniques?
- What type of information can we obtain?
- What type of information is not available? (Age dating)
- Examples



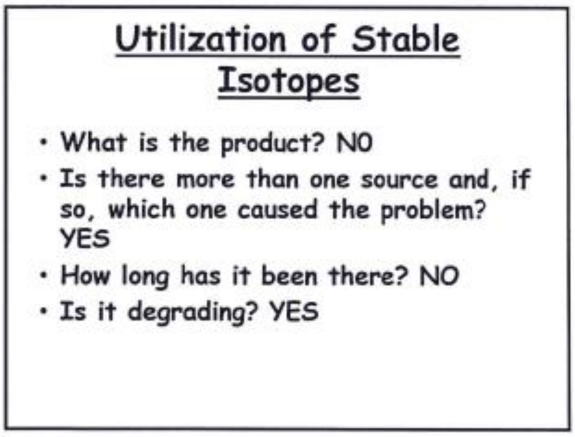
Introduction

- This course is primarily concerned with certain aspects of environmental forensics and, more specifically, utilization of stable isotopes.
- It is very important to emphasize at the outset that there is a significant difference between the conventional EPA methods and the environmental forensic approach.
- At this time there is no EPA stable isotope method although the approach is widely supported by EPA



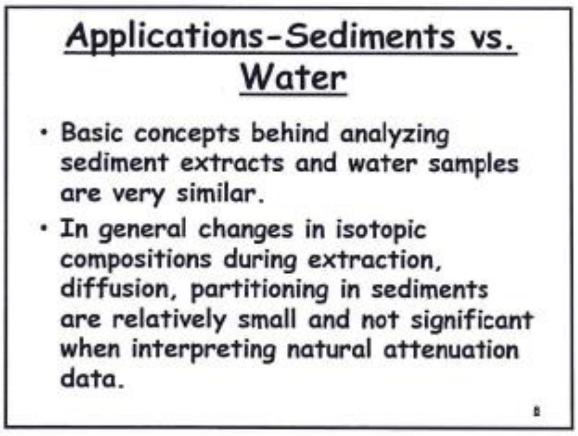
Basic Environmental Forensic Questions

- What is the product?
- Is there more than one source (point of release) and, if so, which one caused the problem?
- How long has it been there?
- Is it degrading?



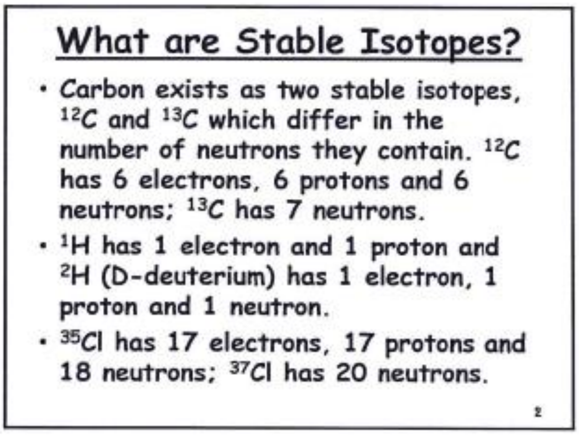
Utilization of Stable Isotopes

- What is the product? NO
- Is there more than one source and, if so, which one caused the problem? YES
- How long has it been there? NO
- Is it degrading? YES



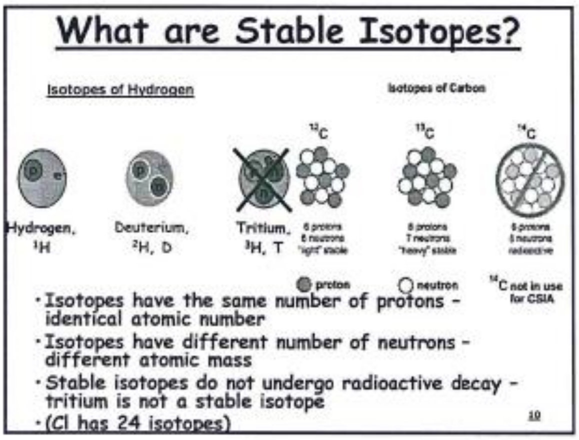
Applications-Sediments vs. Water

- Basic concepts behind analyzing sediment extracts and water samples are very similar.
- In general changes in isotopic compositions during extraction, diffusion, partitioning in sediments are relatively small and not significant when interpreting natural attenuation data.



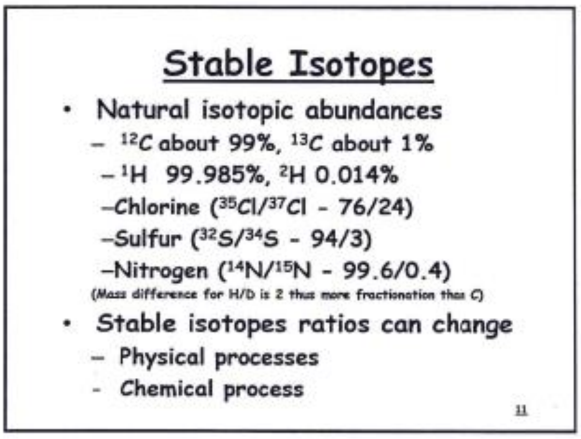
What are Stable Isotopes?

- Carbon exists as two stable isotopes, ^{12}C and ^{13}C which differ in the number of neutrons they contain. ^{12}C has 6 electrons, 6 protons and 6 neutrons; ^{13}C has 7 neutrons.
- ^{1}H has 1 electron and 1 proton and ^{2}H (D-deuterium) has 1 electron, 1 proton and 1 neutron.
- ^{35}Cl has 17 electrons, 17 protons and 18 neutrons; ^{37}Cl has 20 neutrons.



What are Stable Isotopes?

- Isotopes have the same number of protons - identical atomic number
- Isotopes have different number of neutrons - different atomic mass
- Stable isotopes do not undergo radioactive decay - tritium is not a stable isotope
- (Cl has 24 isotopes)

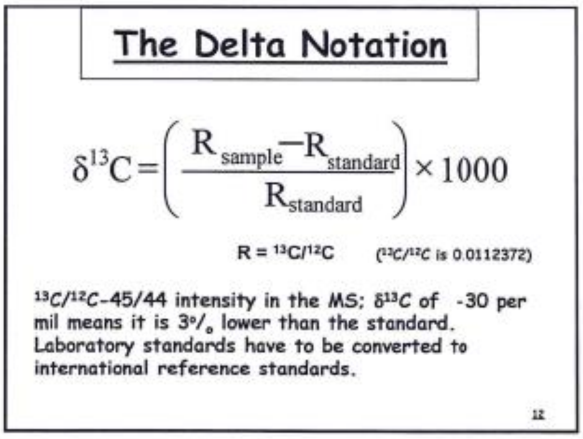


Stable Isotopes

- Natural isotopic abundances
  - ^{12}C about 99%, ^{13}C about 1%
  - ^{1}H 99.985%, ^{2}H 0.014%
  - Chlorine ($^{35}Cl/^{37}Cl$ - 76/24)
  - Sulfur ($^{32}S/^{34}S$ - 94/3)
  - Nitrogen ($^{14}N/^{15}N$ - 99.6/0.4)

(Mass difference for H/D is 2 thus more fractionation than C)

- Stable isotopes ratios can change
  - Physical processes
  - Chemical process

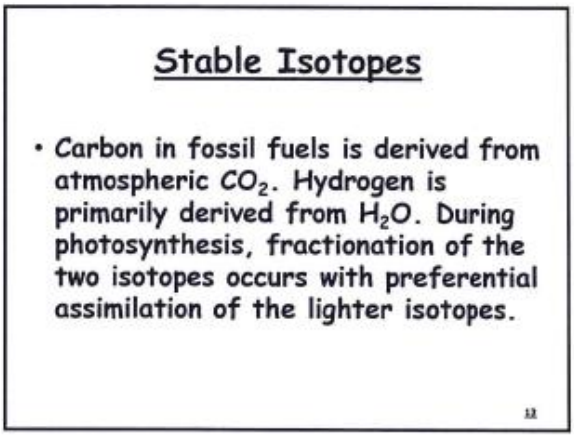


The Delta Notation

$$\delta^{13}C = \left(\frac{R_{sample} - R_{standard}}{R_{standard}} \right) \times 1000$$

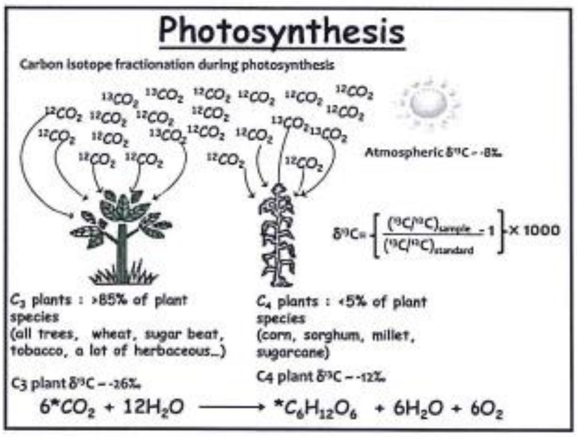
$R = {}^{13}C/{}^{12}C$ ($^{13}C/^{12}C$ is 0.0112372)

$^{13}C/^{12}C$-45/44 intensity in the MS; $\delta^{13}C$ of -30 per mil means it is 3°/ₒ lower than the standard. Laboratory standards have to be converted to international reference standards.



Stable Isotopes

- Carbon in fossil fuels is derived from atmospheric CO_2. Hydrogen is primarily derived from H_2O. During photosynthesis, fractionation of the two isotopes occurs with preferential assimilation of the lighter isotopes.



Photosynthesis

Carbon isotope fractionation during photosynthesis

Atmospheric $\delta^{13}C$ ~ -8‰

$$\delta^{13}C = \left[\frac{(^{13}C/^{12}C)_{sample}}{(^{13}C/^{12}C)_{standard}} - 1 \right] \times 1000$$

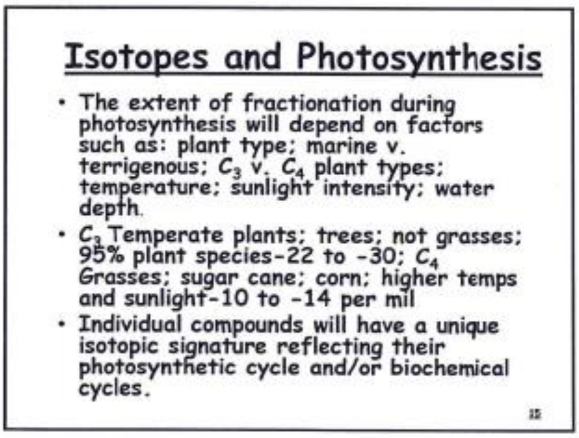
C_3 plants : >85% of plant species (all trees, wheat, sugar beat, tobacco, a lot of herbaceous…)

C_4 plants : <5% of plant species (corn, sorghum, millet, sugarcane)

C3 plant $\delta^{13}C$ ~ -26‰

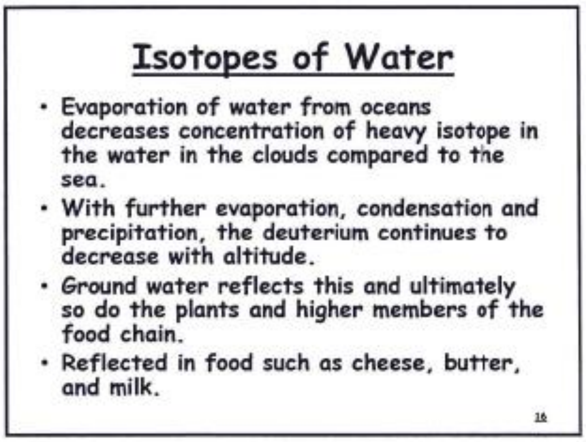
C4 plant $\delta^{13}C$ ~ -12‰

$$6{*}CO_2 + 12H_2O \longrightarrow {*}C_6H_{12}O_6 + 6H_2O + 6O_2$$



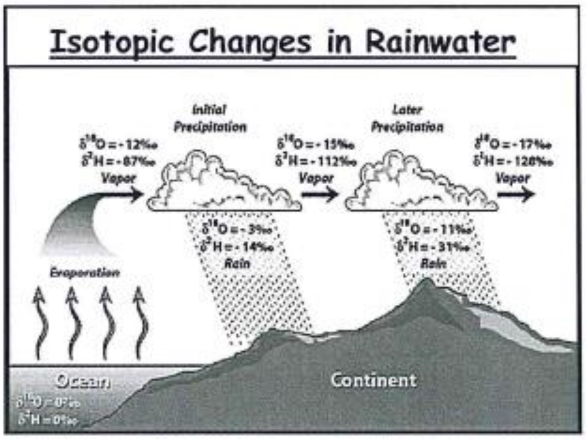
Isotopes and Photosynthesis

- The extent of fractionation during photosynthesis will depend on factors such as: plant type; marine v. terrigenous; C_3 v. C_4 plant types; temperature; sunlight intensity; water depth.
- C_3 Temperate plants; trees; not grasses; 95% plant species-22 to -30; C_4 Grasses; sugar cane; corn; higher temps and sunlight-10 to -14 per mil
- Individual compounds will have a unique isotopic signature reflecting their photosynthetic cycle and/or biochemical cycles.

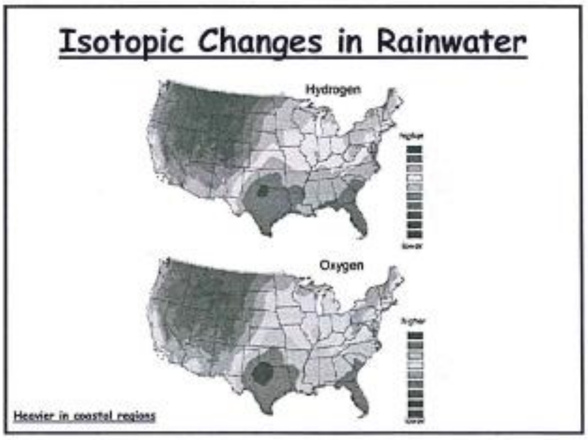


Isotopes of Water

- Evaporation of water from oceans decreases concentration of heavy isotope in the water in the clouds compared to the sea.
- With further evaporation, condensation and precipitation, the deuterium continues to decrease with altitude.
- Ground water reflects this and ultimately so do the plants and higher members of the food chain.
- Reflected in food such as cheese, butter, and milk.

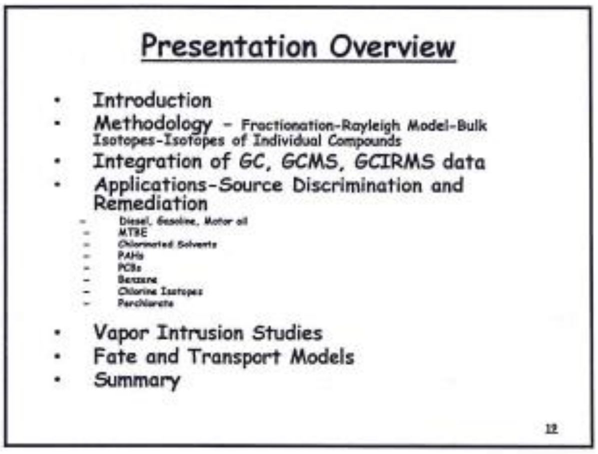


Isotopic Changes in Rainwater



Isotopic Changes in Rainwater

Heavier in coastal regions



Presentation Overview

- Introduction
- Methodology - Fractionation-Rayleigh Model-Bulk Isotopes-Isotopes of Individual Compounds
- Integration of GC, GCMS, GCIRMS data
- Applications-Source Discrimination and Remediation
  - Diesel, Gasoline, Motor oil
  - MTBE
  - Chlorinated Solvents
  - PAHs
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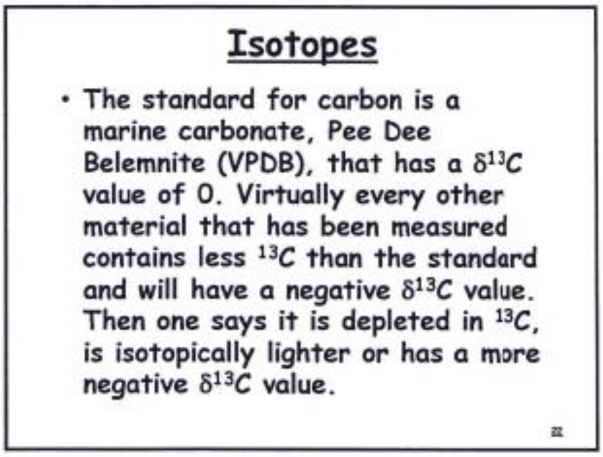
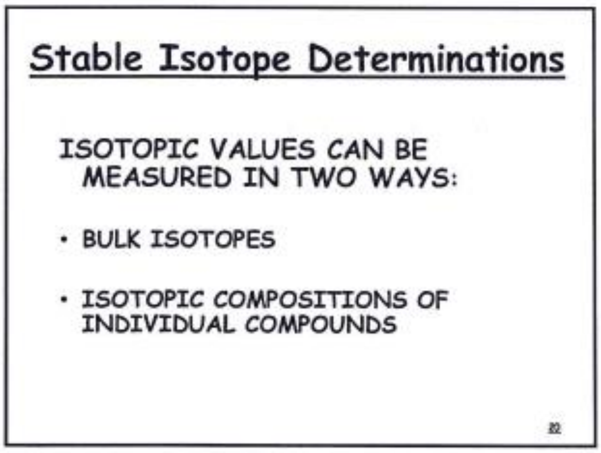
  - Chlorine Isotopes
  - Perchlorate
- Vapor Intrusion Studies
- Fate and Transport Models
- Summary



Isotopes

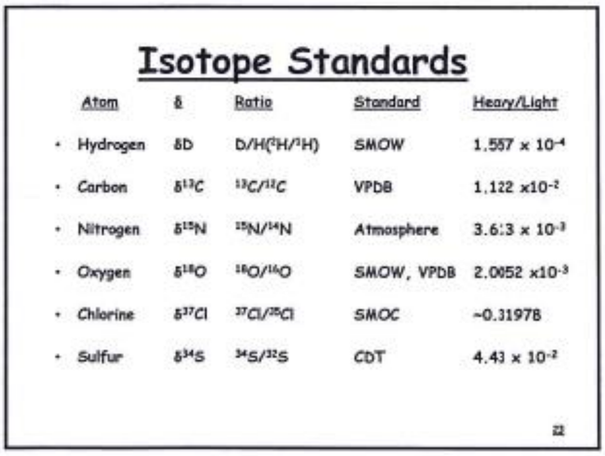
- The standard for carbon is a marine carbonate, Pee Dee Belemnite (VPDB), that has a $\delta^{13}C$ value of 0. Virtually every other material that has been measured contains less ^{13}C than the standard and will have a negative $\delta^{13}C$ value. Then one says it is depleted in ^{13}C, is isotopically lighter or has a more negative $\delta^{13}C$ value.



Stable Isotope Determinations

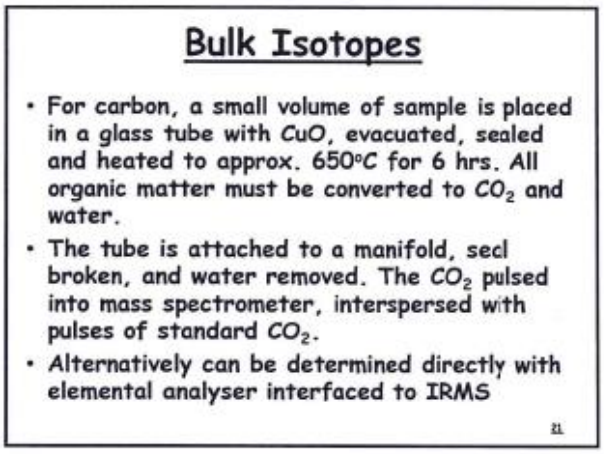
ISOTOPIC VALUES CAN BE MEASURED IN TWO WAYS:

- BULK ISOTOPES
- ISOTOPIC COMPOSITIONS OF INDIVIDUAL COMPOUNDS



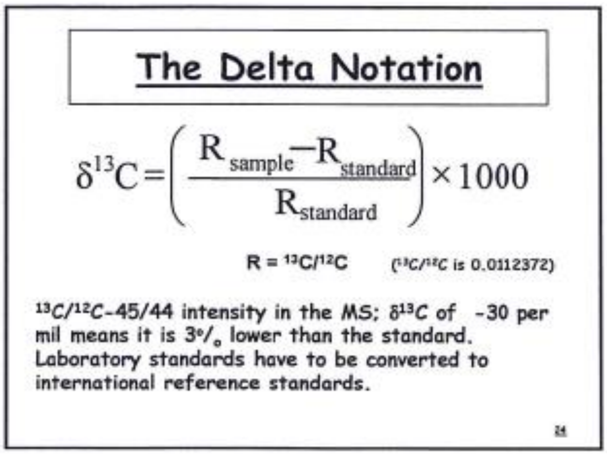
Isotope Standards

Atom	δ	Ratio	Standard	Heavy/Light
• Hydrogen	δD	D/H($^2H/^1H$)	SMOW	1.557×10^{-4}
• Carbon	$\delta^{13}C$	$^{13}C/^{12}C$	VPDB	1.122×10^{-2}
• Nitrogen	$\delta^{15}N$	$^{15}N/^{14}N$	Atmosphere	3.613×10^{-3}
• Oxygen	$\delta^{18}O$	$^{18}O/^{16}O$	SMOW, VPDB	2.0052×10^{-3}
• Chlorine	$\delta^{37}Cl$	$^{37}Cl/^{35}Cl$	SMOC	~0.31978
• Sulfur	$\delta^{34}S$	$^{34}S/^{32}S$	CDT	4.43×10^{-2}



Bulk Isotopes

- For carbon, a small volume of sample is placed in a glass tube with CuO, evacuated, sealed and heated to approx. 650°C for 6 hrs. All organic matter must be converted to CO_2 and water.
- The tube is attached to a manifold, seal broken, and water removed. The CO_2 pulsed into mass spectrometer, interspersed with pulses of standard CO_2.
- Alternatively can be determined directly with elemental analyser interfaced to IRMS



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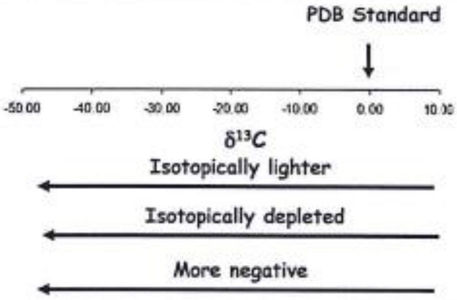
$R = {}^{13}C/{}^{12}C$ $\quad$ (${}^{13}C/{}^{12}C$ is 0.0112372)

$^{13}C/^{12}C$-45/44 intensity in the MS; $\delta^{13}C$ of -30 per mil means it is 3°/₀ lower than the standard. Laboratory standards have to be converted to international reference standards.

Data Output-Isotope Scale

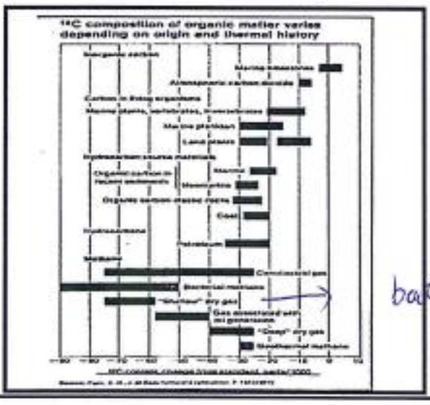


Equilibrium Isotope Effect

- Evaporation of water in closed container (equilibrium)
  - Lighter isotopes (^{1}H, ^{16}O) partition to higher energy phase (vapor)

[illegible]

Variations in Bulk Isotope Values



bakerul

Kinetic Isotope Effect

- Hydrocarbon molecules are comprised primarily of ^{12}C-^{12}C bonds; lesser amounts of ^{12}C-^{13}C bonds and even fewer ^{13}C-^{13}C bonds. The kinetic isotope effect can be thought of as the cleavage of the weaker bonds, ^{12}C-^{12}C, which will ultimately lead to an enrichment of the residual substrate.
- Similar effects occur in chlorinated compounds where the ^{12}C-^{35}Cl bonds are preferentially cleaved

(37Cl) 的 [illegible]

Stable Isotope Fractionation

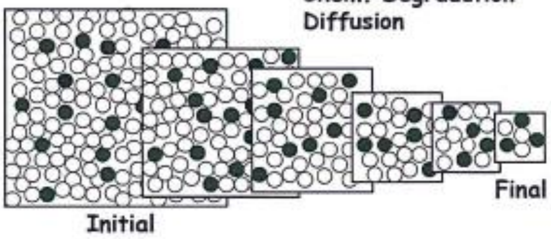
- Preferential partitioning of isotopes between phases or between reaction and product species
  - Function of difference in masses
- Equilibrium isotope effect
  - *One isotope concentrates in one component of a reversible system*
- Kinetic isotope effect
  - *One isotope reacts more rapidly than other in irreversible system*

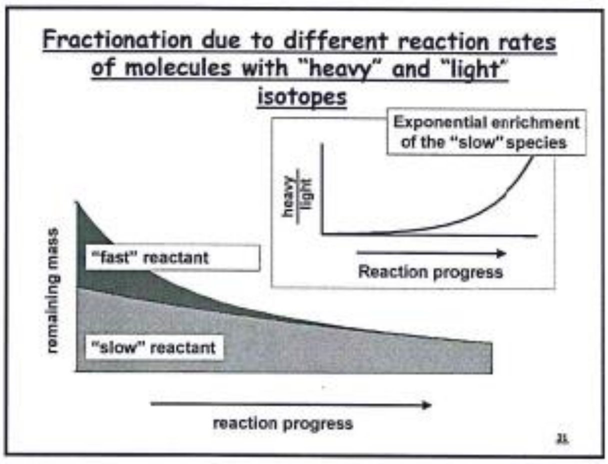
Kinetic Isotope Fractionation

Rate of removal of ○ faster than that of ●

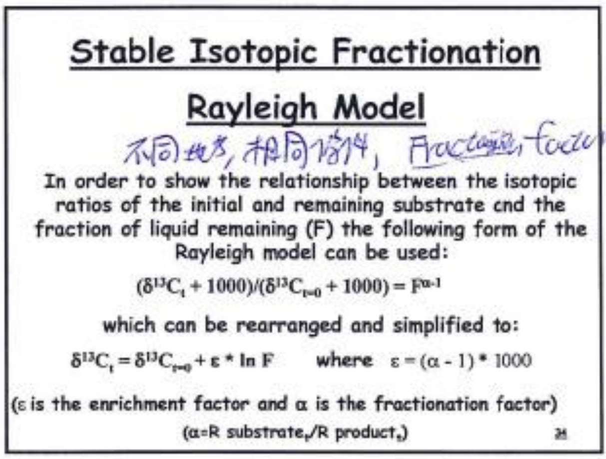
$k_{○} / k_{●}$ = const.

Biodegradation
Chem. Degradation
Diffusion





Fractionation due to different reaction rates of molecules with "heavy" and "light" isotopes



Stable Isotopic Fractionation

Rayleigh Model

不同物质，相同条件，Fractionation factor

In order to show the relationship between the isotopic ratios of the initial and remaining substrate cnd the fraction of liquid remaining (F) the following form of the Rayleigh model can be used:

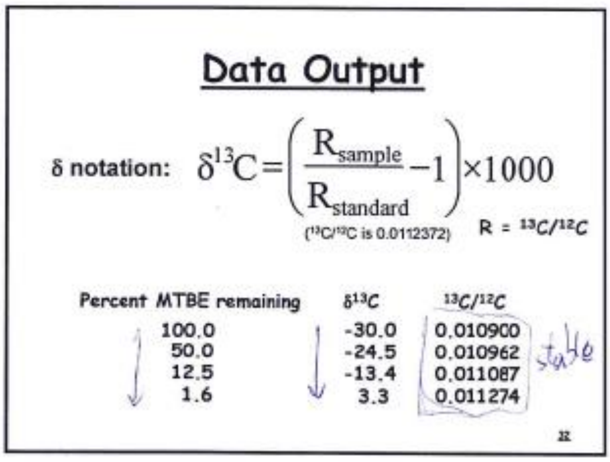
$$(\delta^{13}C_t + 1000)/(\delta^{13}C_{t=0} + 1000) = F^{\alpha-1}$$

which can be rearranged and simplified to:

$$\delta^{13}C_t = \delta^{13}C_{t=0} + \varepsilon * \ln F \quad \text{where} \quad \varepsilon = (\alpha - 1) * 1000$$

(ε is the enrichment factor and α is the fractionation factor)

(α=R substrate$_t$/R product$_t$)



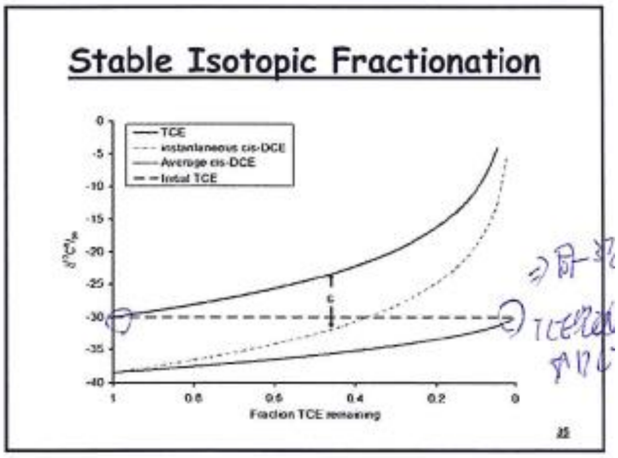
Data Output

δ notation: $$\delta^{13}C = \left(\frac{R_{sample}}{R_{standard}} - 1\right) \times 1000$$

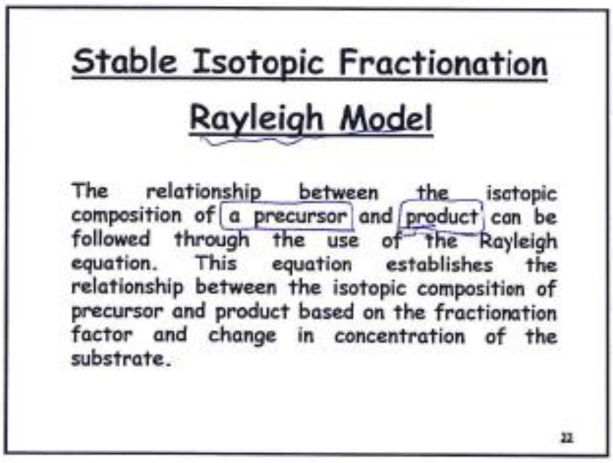
($^{13}C/^{12}C$ is 0.0112372) R = $^{13}C/^{12}C$

Percent MTBE remaining	$\delta^{13}C$	$^{13}C/^{12}C$
100.0	-30.0	0.010900
50.0	-24.5	0.010962
12.5	-13.4	0.011087
1.6	3.3	0.011274

stable



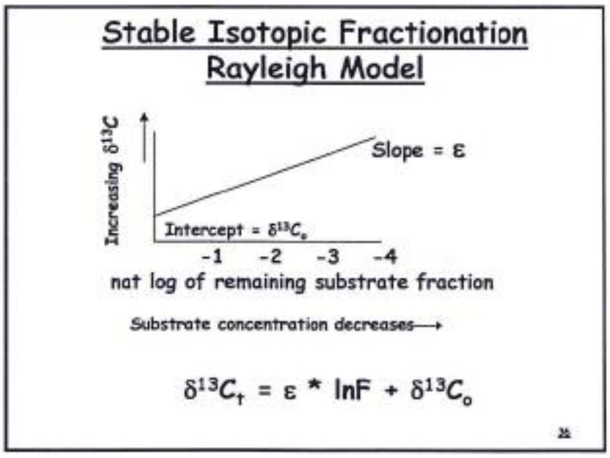
Stable Isotopic Fractionation



Stable Isotopic Fractionation

Rayleigh Model

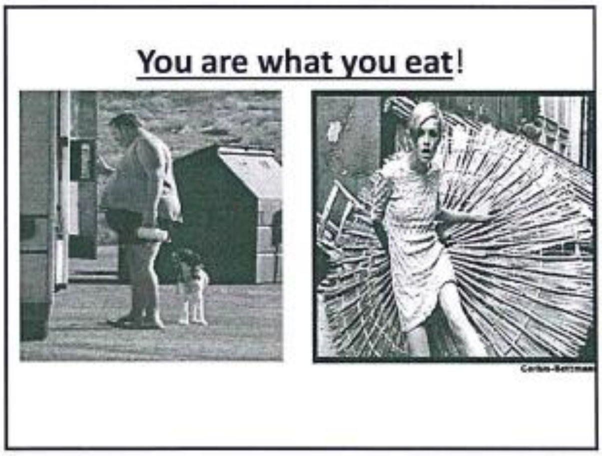
The relationship between the isotopic composition of a precursor and product can be followed through the use of the Rayleigh equation. This equation establishes the relationship between the isotopic composition of precursor and product based on the fractionation factor and change in concentration of the substrate.



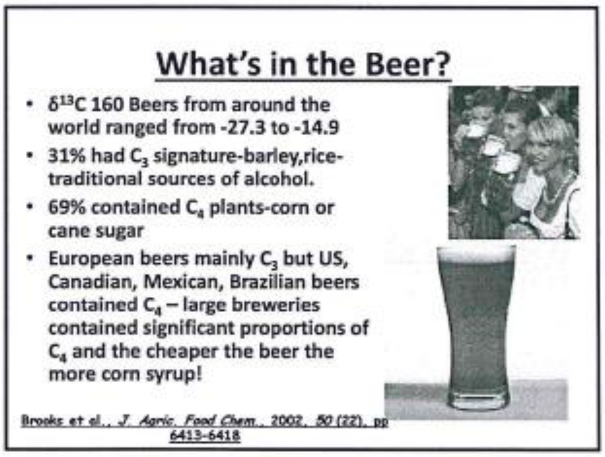
Stable Isotopic Fractionation

Rayleigh Model

$$\delta^{13}C_t = \varepsilon * \ln F + \delta^{13}C_o$$



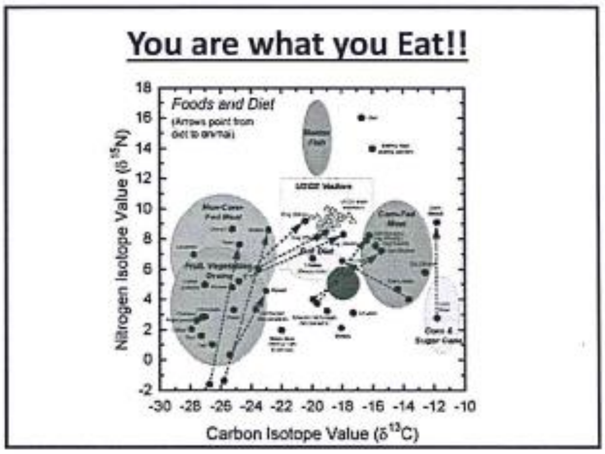
You are what you eat!



What's in the Beer?

- $\delta^{13}C$ 160 Beers from around the world ranged from -27.3 to -14.9
- 31% had C_3 signature-barley,rice-traditional sources of alcohol.
- 69% contained C_4 plants-corn or cane sugar
- European beers mainly C_3 but US, Canadian, Mexican, Brazilian beers contained C_4 – large breweries contained significant proportions of C_4 and the cheaper the beer the more corn syrup!

Brooks et al., *J. Agric. Food Chem.*, 2002, *50 (22)*, pp 6413-6418



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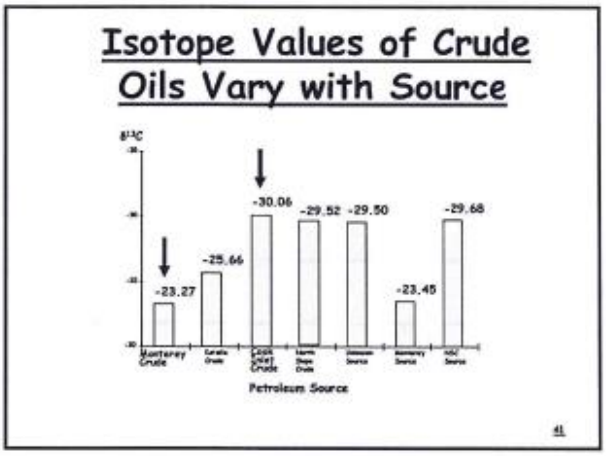
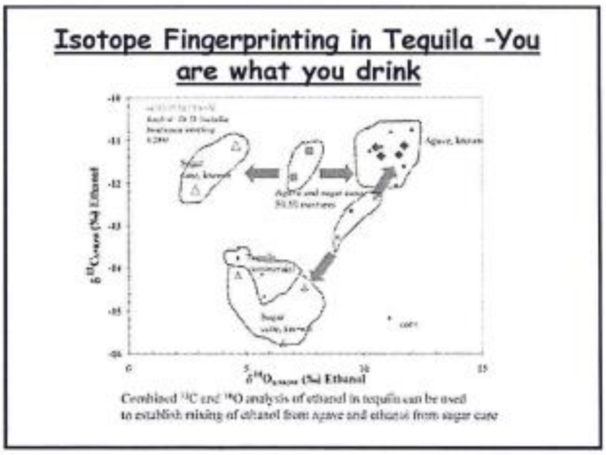
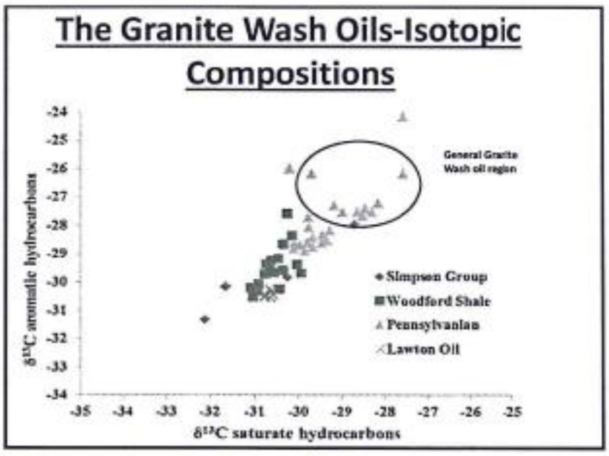


Isotope Values of Crude Oils Vary with Source

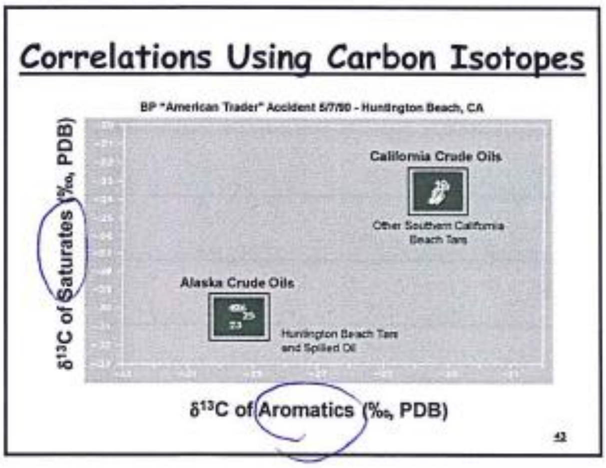


Isotope Fingerprinting in Tequila -You are what you drink

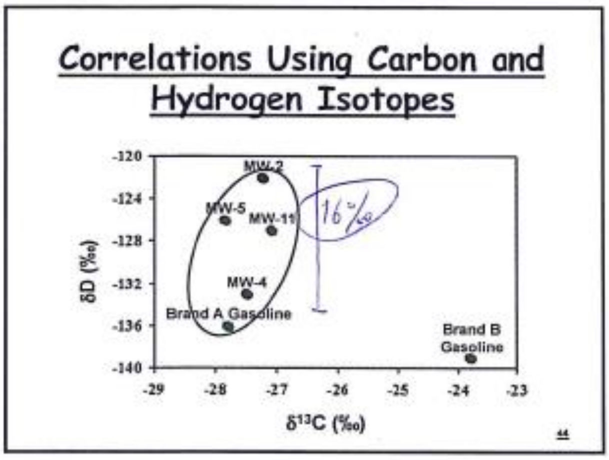
Combined ^{13}C and ^{18}O analysis of ethanol in tequila can be used to establish mixing of ethanol from agave and ethanol from sugar cane



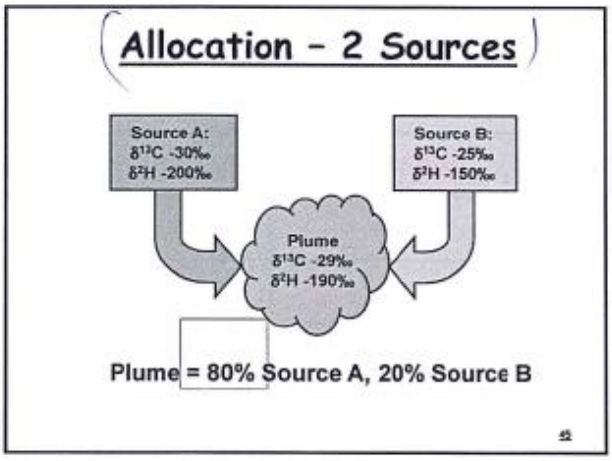
The Granite Wash Oils-Isotopic Compositions



Correlations Using Carbon Isotopes



Correlations Using Carbon and Hydrogen Isotopes



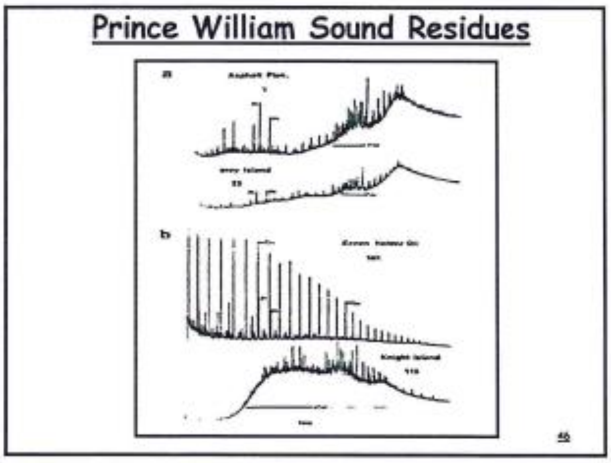
Allocation – 2 Sources

Source A:
$\delta^{13}C$ -30‰
$\delta^{2}H$ -200‰

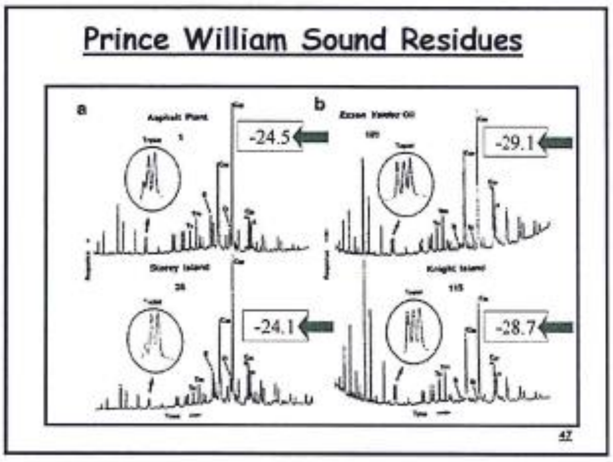
Source B:
$\delta^{13}C$ -25‰
$\delta^{2}H$ -150‰

Plume
$\delta^{13}C$ -29‰
$\delta^{2}H$ -190‰

Plume = 80% Source A, 20% Source B



Prince William Sound Residues



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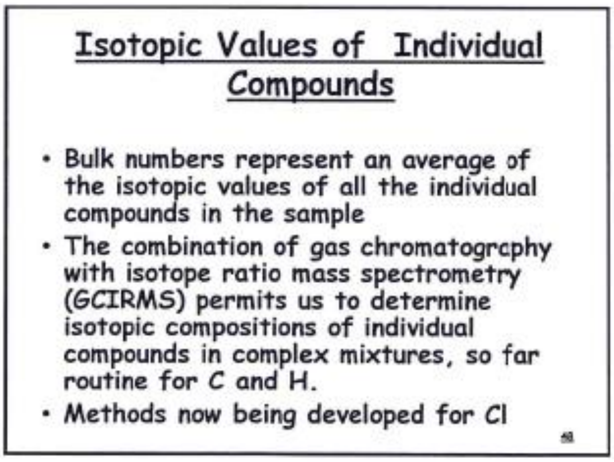
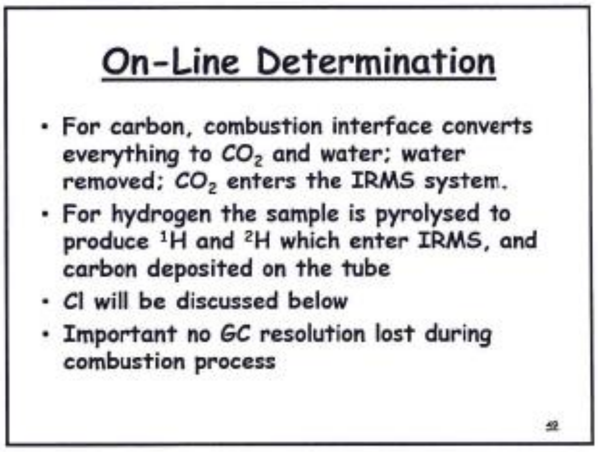


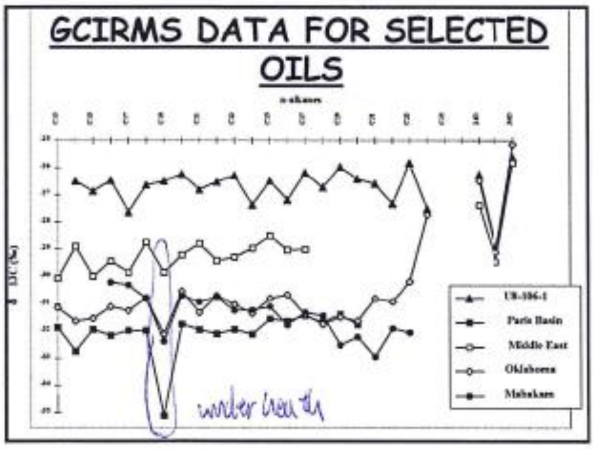
Isotopic Values of Individual Compounds

- Bulk numbers represent an average of the isotopic values of all the individual compounds in the sample
- The combination of gas chromatography with isotope ratio mass spectrometry (GCIRMS) permits us to determine isotopic compositions of individual compounds in complex mixtures, so far routine for C and H.
- Methods now being developed for Cl

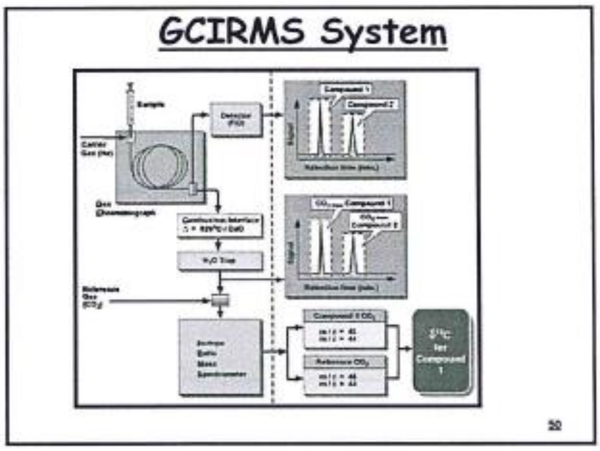


On-Line Determination

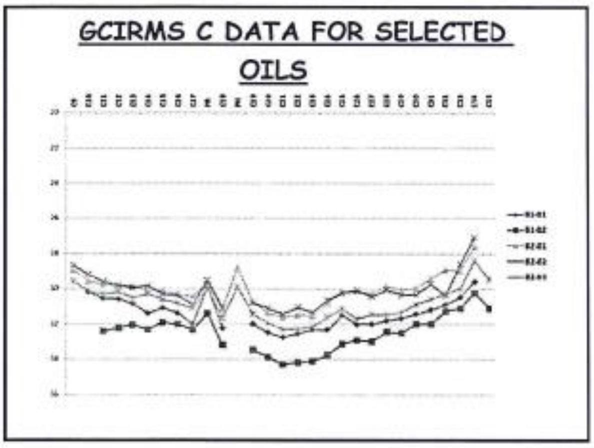
- For carbon, combustion interface converts everything to CO_2 and water; water removed; CO_2 enters the IRMS system.
- For hydrogen the sample is pyrolysed to produce ^1H and ^2H which enter IRMS, and carbon deposited on the tube
- Cl will be discussed below
- Important no GC resolution lost during combustion process



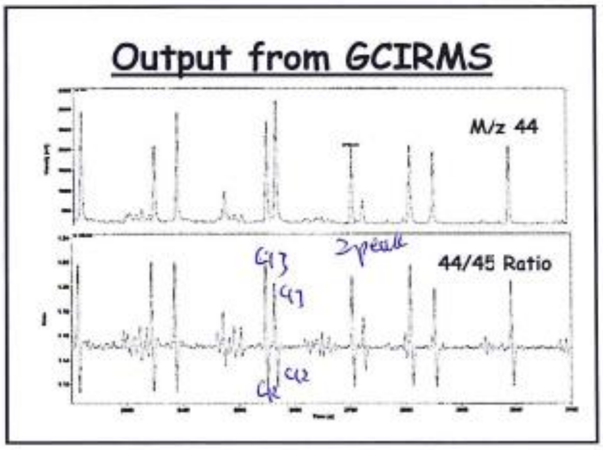
GCIRMS DATA FOR SELECTED OILS



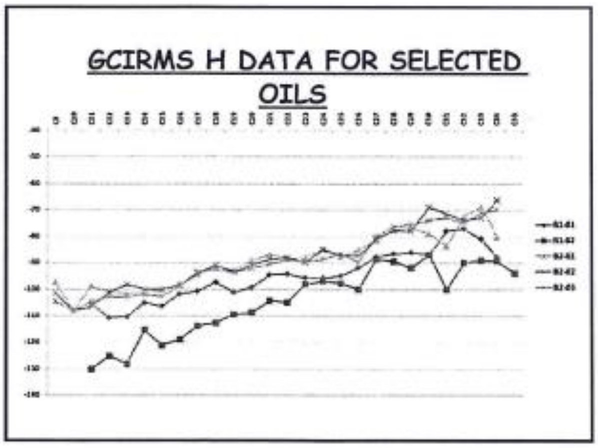
GCIRMS System



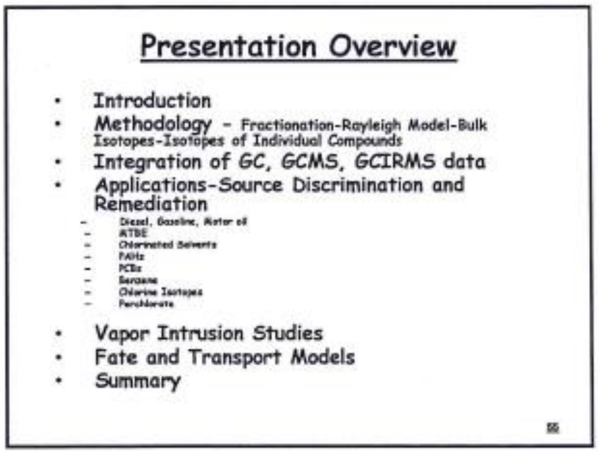
GCIRMS C DATA FOR SELECTED OILS



Output from GCIRMS



GCIRMS H DATA FOR SELECTED OILS



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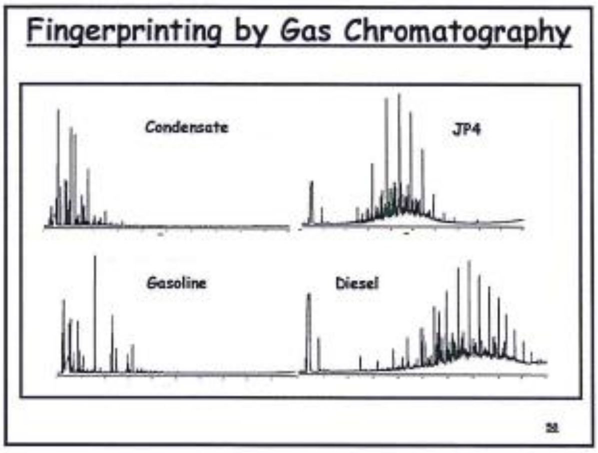
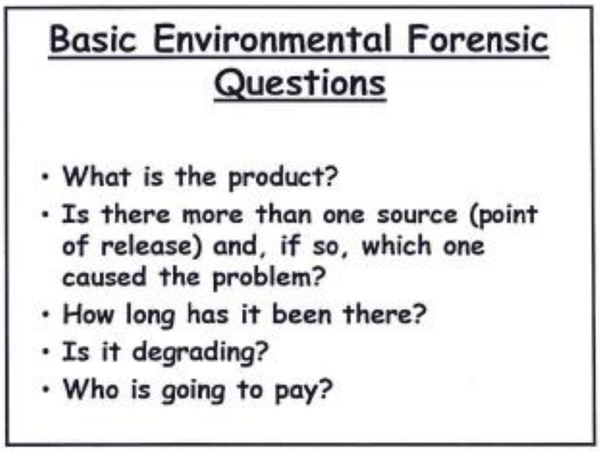
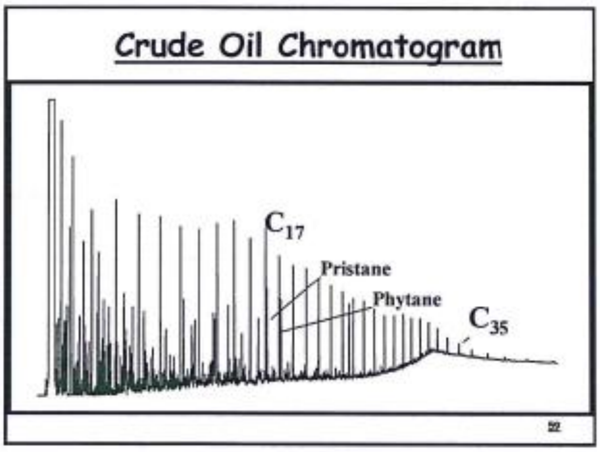


Fingerprinting by Gas Chromatography

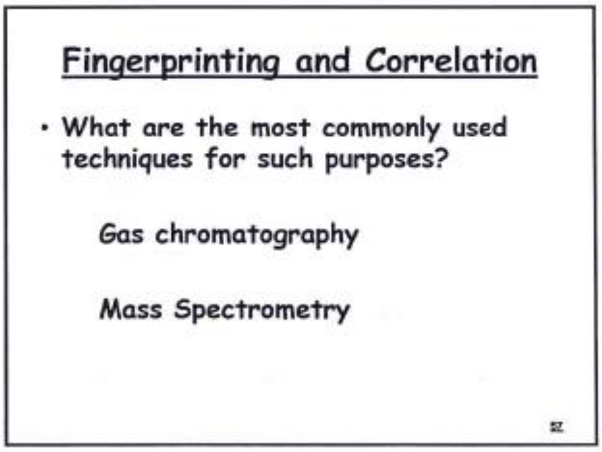


Basic Environmental Forensic Questions

- What is the product?
- Is there more than one source (point of release) and, if so, which one caused the problem?
- How long has it been there?
- Is it degrading?
- Who is going to pay?



Crude Oil Chromatogram

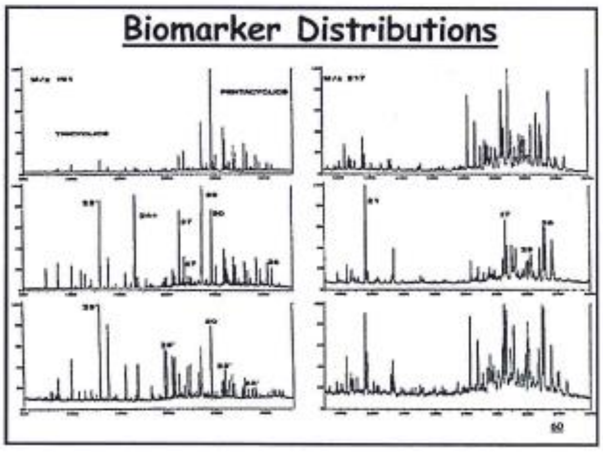


Fingerprinting and Correlation

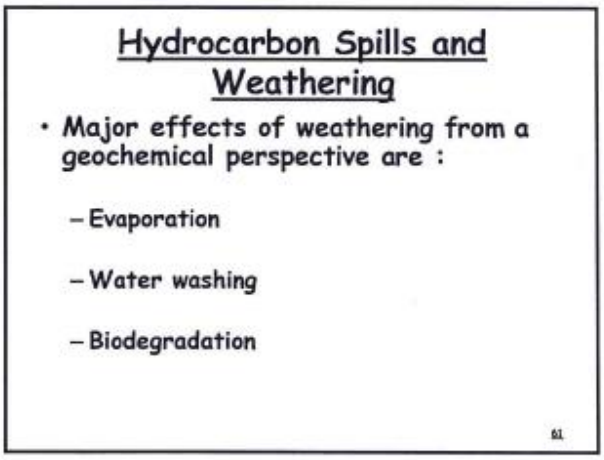
- What are the most commonly used techniques for such purposes?

Gas chromatography

Mass Spectrometry

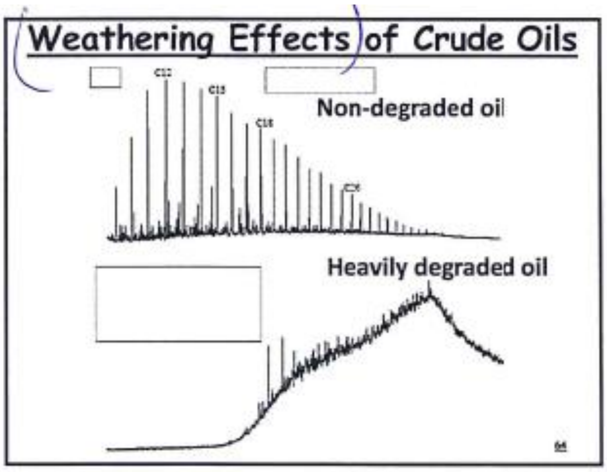


Biomarker Distributions

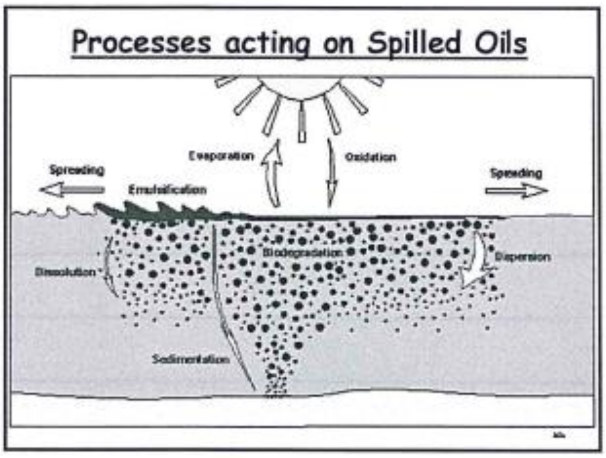


Hydrocarbon Spills and Weathering

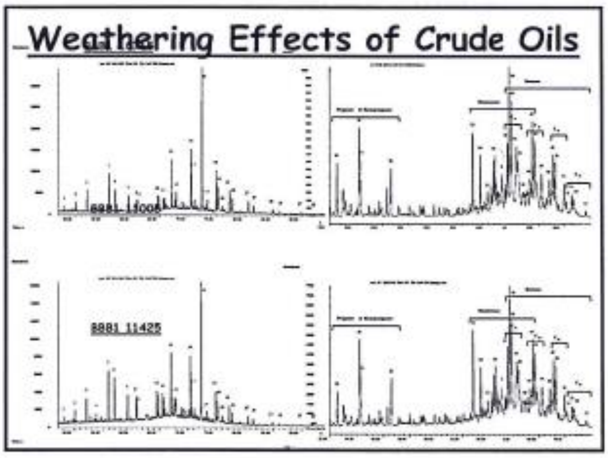
- Major effects of weathering from a geochemical perspective are :
  - Evaporation
  - Water washing
  - Biodegradation



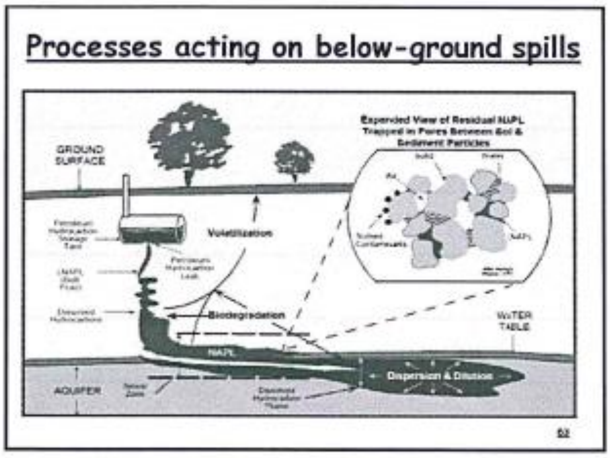
Weathering Effects of Crude Oils



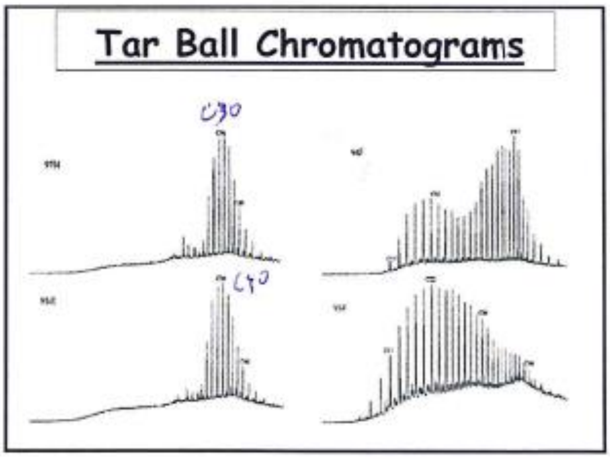
Processes acting on Spilled Oils



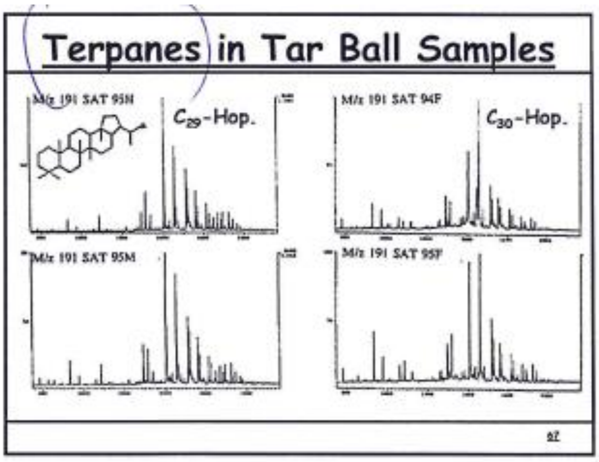
Weathering Effects of Crude Oils



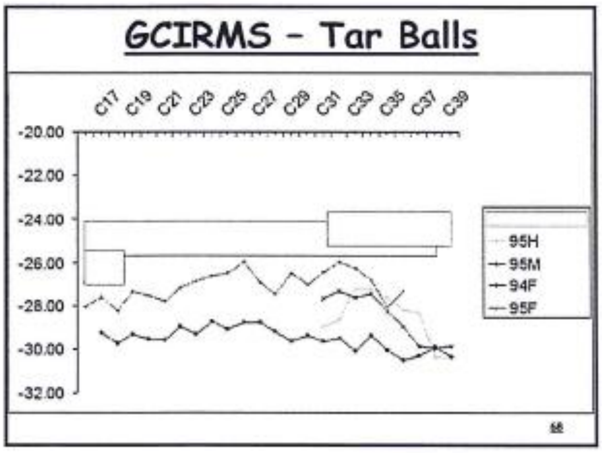
Processes acting on below-ground spills



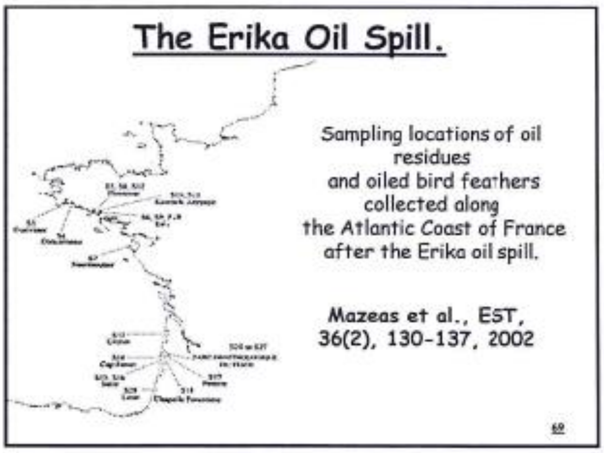
Tar Ball Chromatograms



Terpanes in Tar Ball Samples



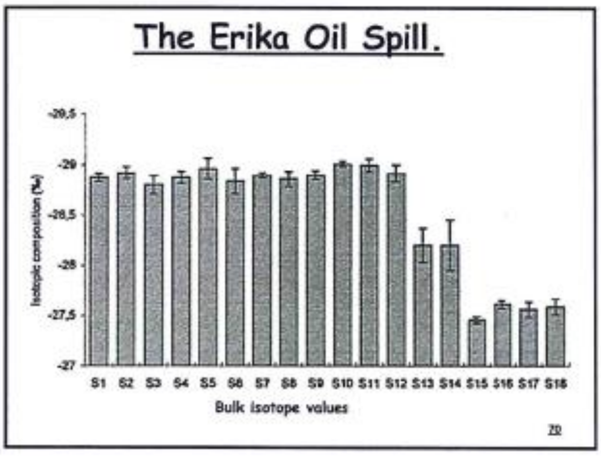
GCIRMS – Tar Balls



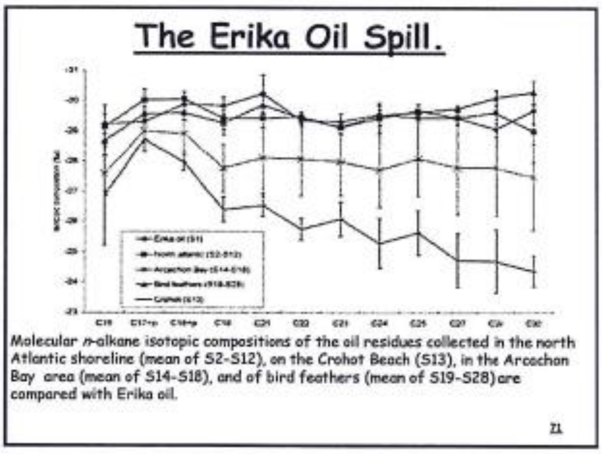
The Erika Oil Spill.

Sampling locations of oil
residues
and oiled bird feathers
collected along
the Atlantic Coast of France
after the Erika oil spill.

**Mazeas et al., EST,
36(2), 130-137, 2002**

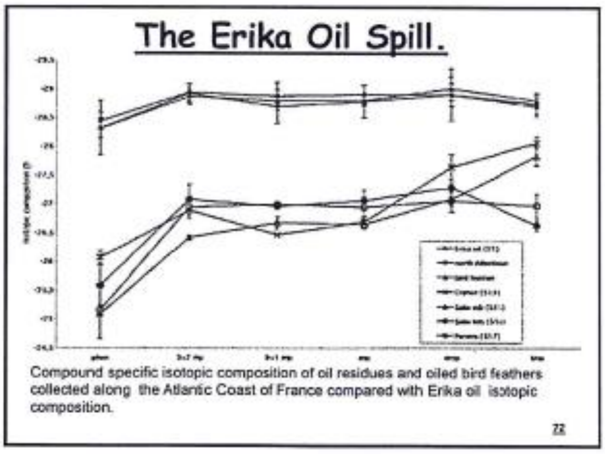


The Erika Oil Spill.



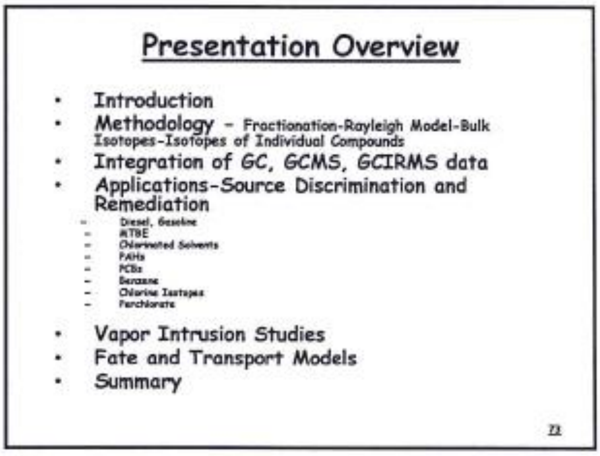
The Erika Oil Spill.

Molecular n-alkane isotopic compositions of the oil residues collected in the north Atlantic shoreline (mean of S2-S12), on the Crohot Beach (S13), in the Arcachon Bay area (mean of S14-S18), and of bird feathers (mean of S19-S28) are compared with Erika oil.



The Erika Oil Spill.

Compound specific isotopic composition of oil residues and oiled bird feathers collected along the Atlantic Coast of France compared with Erika oil isotopic composition.



Presentation Overview

- Introduction
- Methodology - Fractionation-Rayleigh Model-Bulk Isotopes-Isotopes of Individual Compounds
- Integration of GC, GCMS, GCIRMS data
- Applications-Source Discrimination and Remediation
  - Diesel, Gasoline
  - MTBE
  - Chlorinated Solvents
  - PAHs
  - PCBs
  - Benzene
  - Chlorine Isotopes
  - Perchlorate
- Vapor Intrusion Studies
- Fate and Transport Models
- Summary

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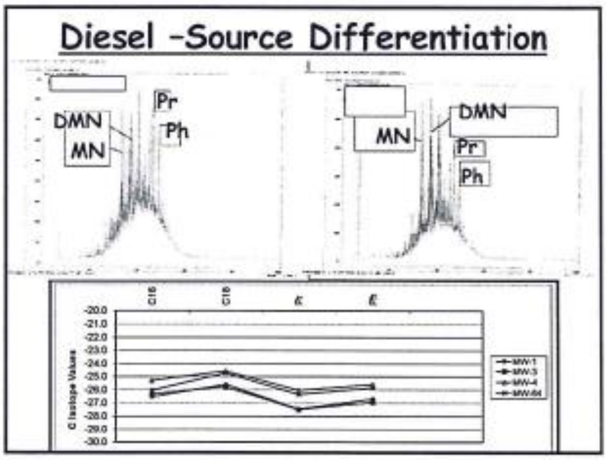
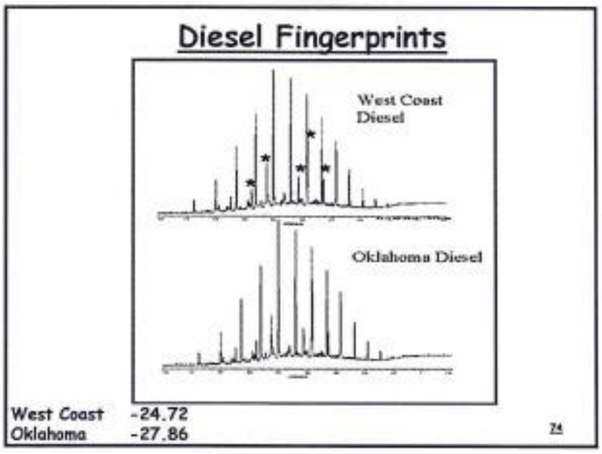


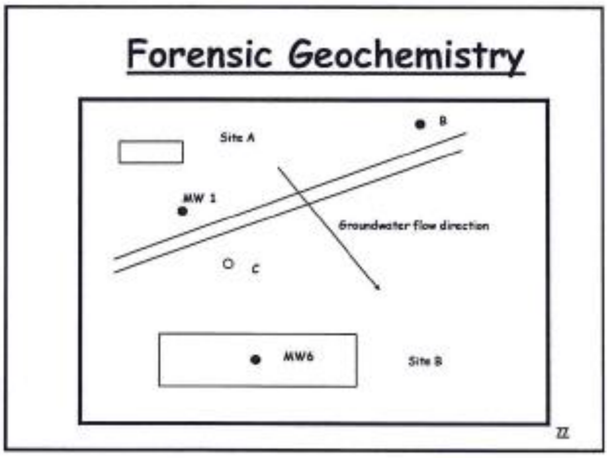
Diesel -Source Differentiation



Diesel Fingerprints

West Coast -24.72
Oklahoma -27.86

74



Forensic Geochemistry

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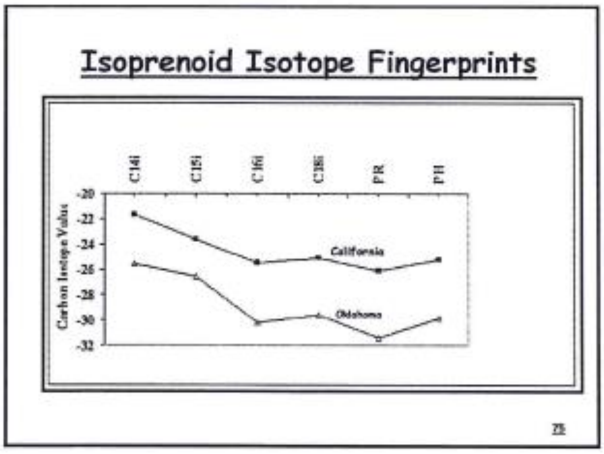
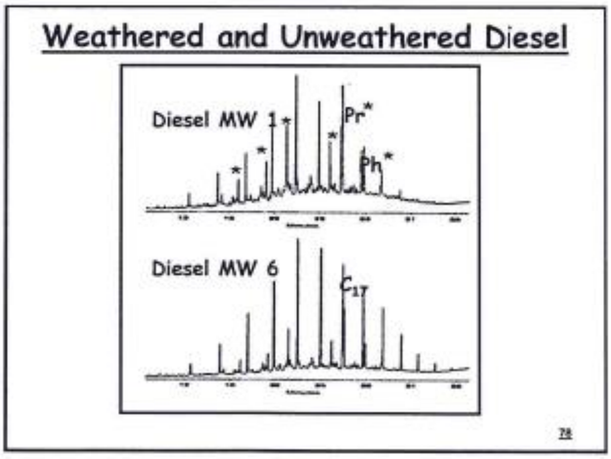


Isoprenoid Isotope Fingerprints

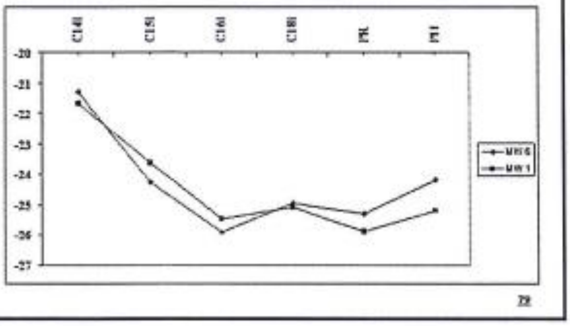
75



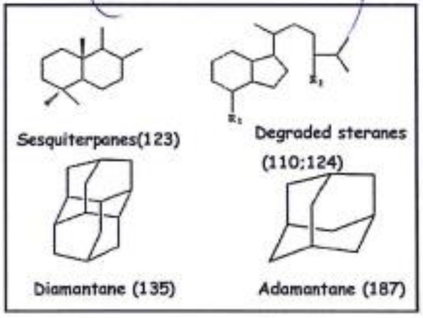
Weathered and Unweathered Diesel

78

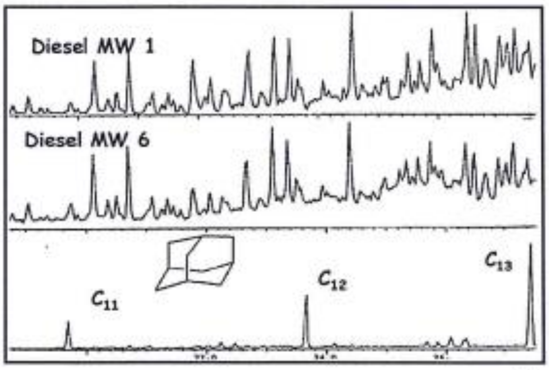
Carbon Isotope Values for Isoprenoids



Diesel Correlations



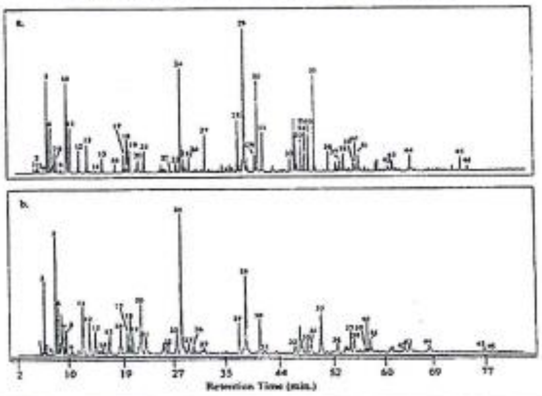
Adamantanes in Diesel Fuels

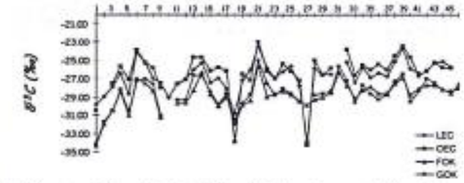


Gasolines

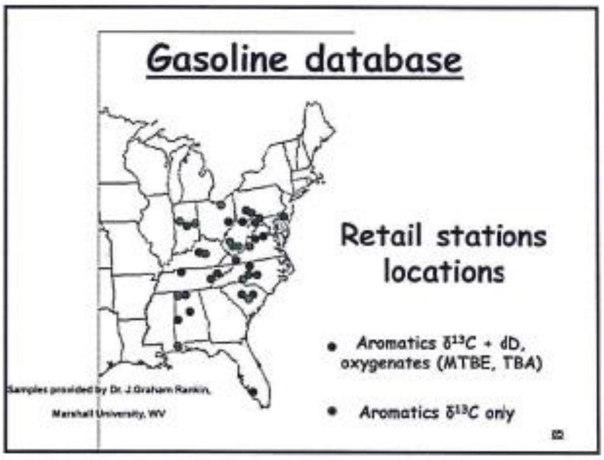
- Gasolines from different sources often have very similar chromatograms, making it difficult to distinguish such samples. Gasolines are also devoid of biomarkers, further limiting correlation possibilities.
- One solution here is to use GCIRMS for both the hydrocarbons and additives.

Comparison of Gasolines by GC




Carbon Isotopic Composition of Gasolines from Oklahoma (FOK, GOK) and the East Coast (LEC, OEC)

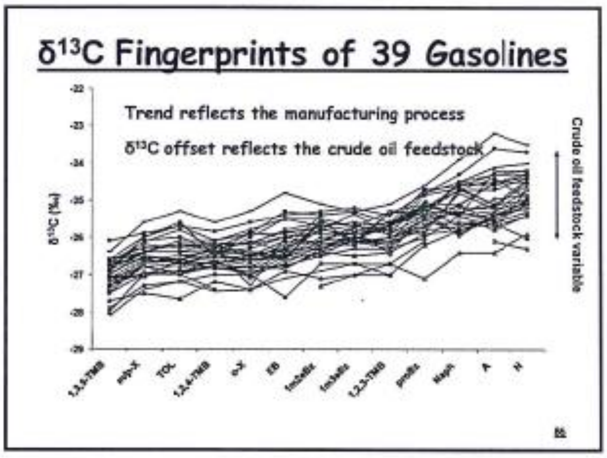
This figure shows the carbon isotopic fingerprint of gasolines sampled from Oklahoma and from the East Coast and demonstrates that these gasolines are significantly different in terms of isotopic composition and can be discriminated from each other on this basis. The peak numbers are identified in the section above.



Gasoline database

Retail stations locations

- Aromatics $\delta^{13}C$ + dD, oxygenates (MTBE, TBA)
- Aromatics $\delta^{13}C$ only



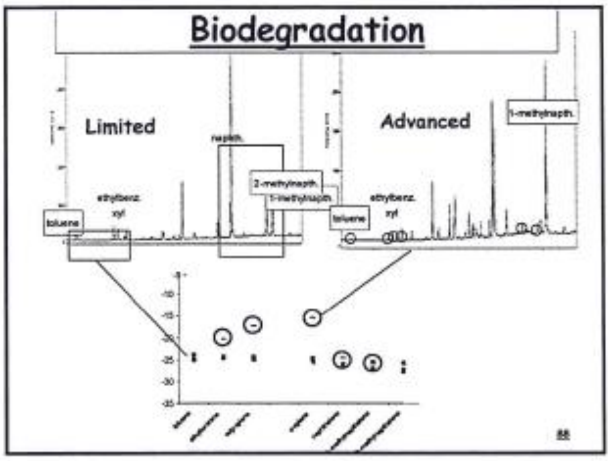
$\delta^{13}C$ Fingerprints of 39 Gasolines

Trend reflects the manufacturing process

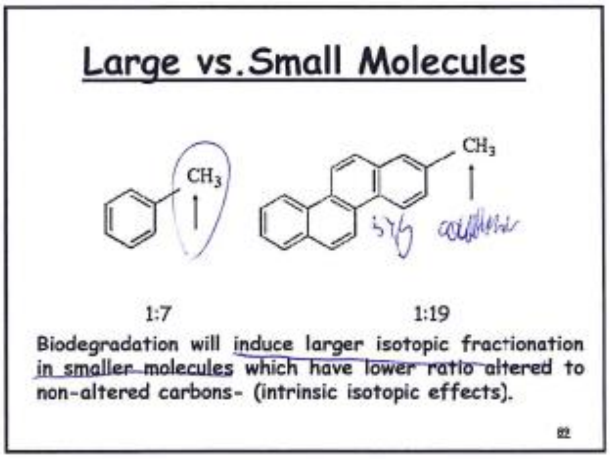
$\delta^{13}C$ offset reflects the crude oil feedstock

When are Two Fingerprints Different?

- Factors causing differences:
  - Source
  - Precision and Accuracy
  - Fresh samples vs. Environmental samples
  - Weathering and biodegradation



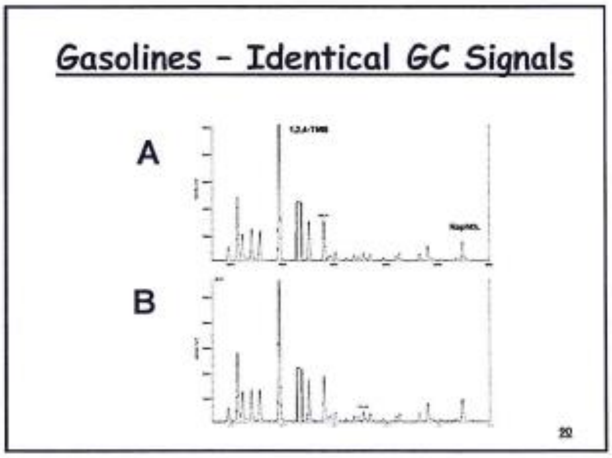
Biodegradation



Large vs.Small Molecules

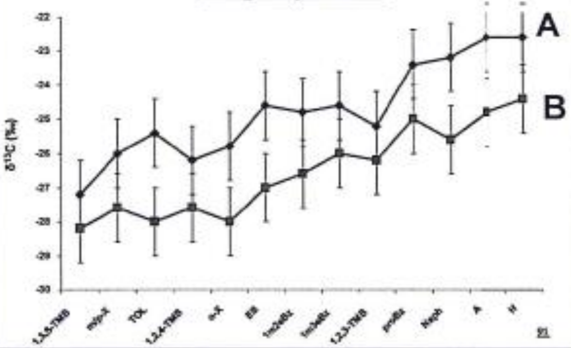
1:7 1:19

Biodegradation will induce larger isotopic fractionation in smaller molecules which have lower ratio altered to non-altered carbons- (intrinsic isotopic effects).

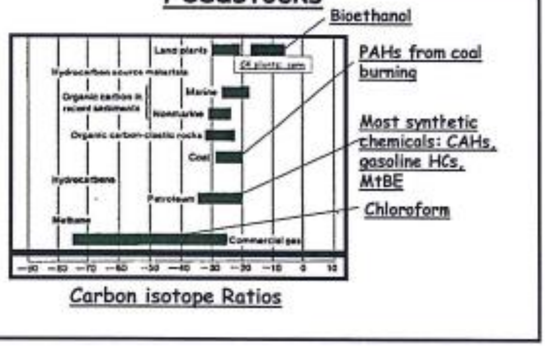


Gasolines – Identical GC Signals

Gasolines - Different δ¹³C Fingerprints



The Isotopes in Manufactured Chemicals are Inherited from Synthetic Feedstocks



Bioethanol

PAHs from coal burning

Most synthetic chemicals: CAHs, gasoline HCs, MtBE

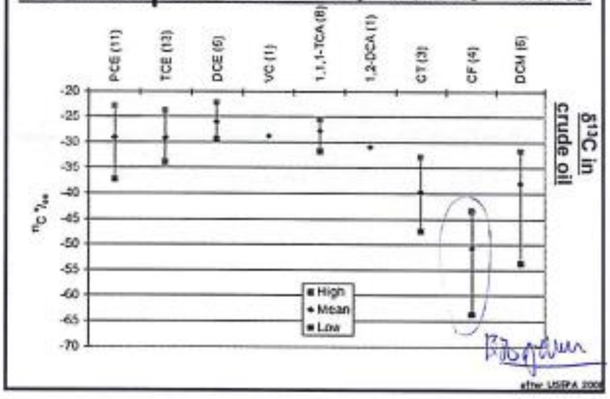
Chloroform

Carbon isotope Ratios

Source Discrimination- Ground-water Problems

- Source discrimination
  - Stable isotopes provide a tool that can be used to discriminate source of common ground water and sediment contaminants.
  - Particularly valuable for single component contaminants
  - Volatile compound source signatures may be affected by "weathering"
  - Relatively narrow range of signatures

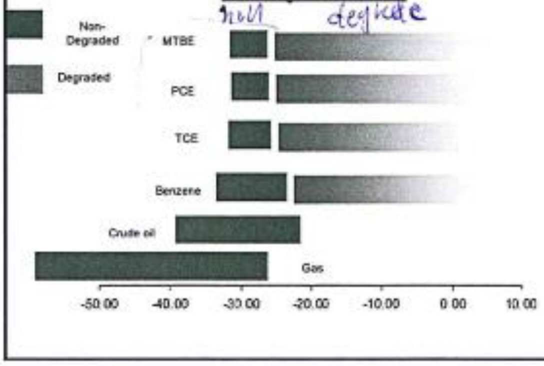
C Isotope Ratios of Misc. CAHs



after USEPA 200

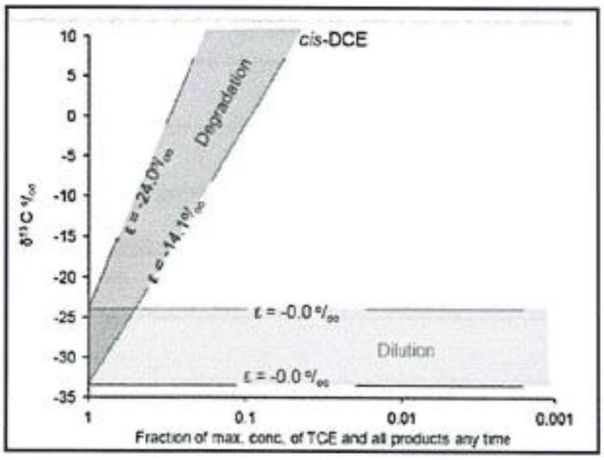
Non-degraded v. Degraded Components

non degrade



Remediation Studies

- How can isotopes assist in remediation studies?
- Provide independent verification that attenuation is taking place
- Provide estimates of extent of attenuation
- Distinguish mechanisms of degradation
- Distinguish non-degradative processes that may be taking place



Remediation - Summary

- Provide estimates of extent of attenuation
- Conservative estimates of the extent of degradation can be obtained from the Rayleigh equation
- Information can also be incorporated into flow transport models

$\Delta\delta = \varepsilon \ln F$

Isotopes in Remediation Studies

- Provide independent verification that attenuation is taking place
- Basically looking for isotopic enrichment such that the substrate is isotopically enriched relative to the original source material
- Enrichment magnitude should exceed that of abiotic (physical) processes
- Ranges of source signatures established for most common contaminants

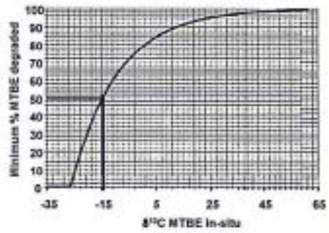
Use of CSIA data to determine the progress of in-situ degradation (anaerobic)

Simplified Rayleigh equation: $\delta^{13}C_{insitu} = \delta^{13}C_{initial} + \varepsilon * \ln F$

Mixing with less degraded MTBE will lower the degradation estimate

Calculation is made using a conservative value of $\delta^{13}C_{initial}$

This is a conservative approach



Isotopes in Remediation Studies

- Provide independent verification that attenuation is taking place
- Ideally 2D or even 3D isotope monitoring will provide more reliable evidence for attenuation
- Mechanism specific since one isotope may be enriched, but little change in the others depending on mechanism.

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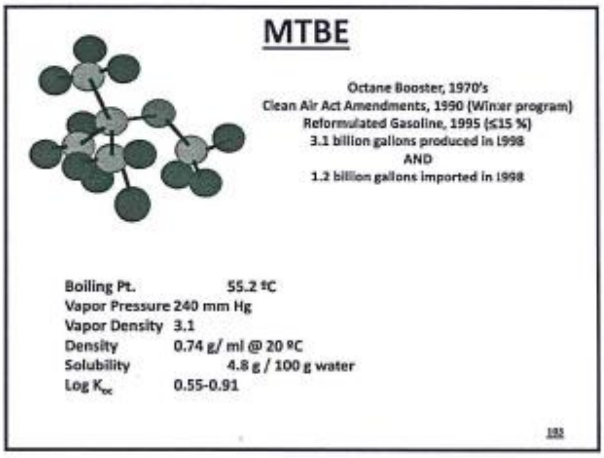
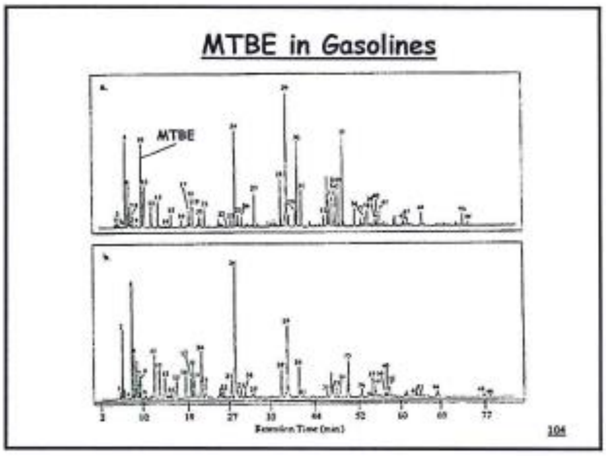


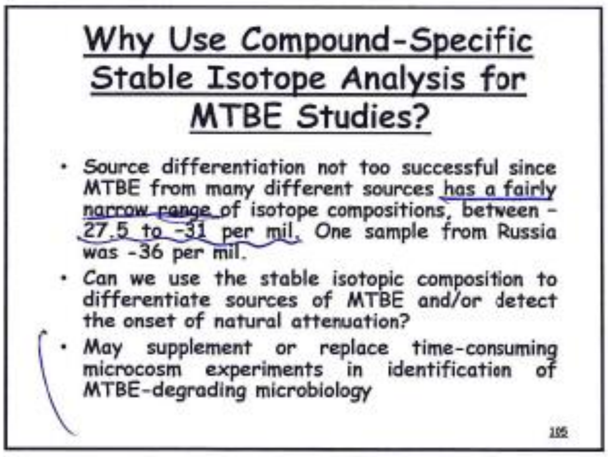
MTBE

Octane Booster, 1970's
Clean Air Act Amendments, 1990 (Winter program)
Reformulated Gasoline, 1995 (≤15 %)
3.1 billion gallons produced in 1998
AND
1.2 billion gallons imported in 1998

Boiling Pt.	55.2 ºC
Vapor Pressure	240 mm Hg
Vapor Density	3.1
Density	0.74 g/ ml @ 20 ºC
Solubility	4.8 g / 100 g water
Log K_{oc}	0.55-0.91

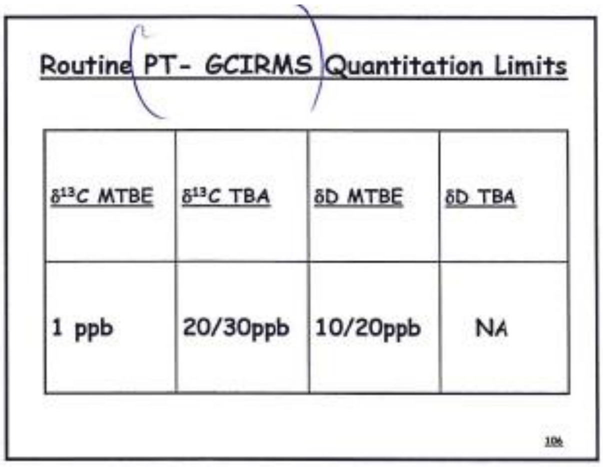


MTBE in Gasolines



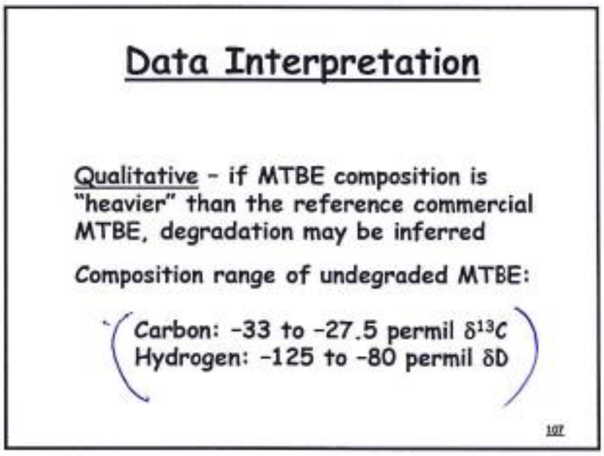
Why Use Compound-Specific Stable Isotope Analysis for MTBE Studies?

- Source differentiation not too successful since MTBE from many different sources has a fairly narrow range of isotope compositions, between -27.5 to -31 per mil. One sample from Russia was -36 per mil.
- Can we use the stable isotopic composition to differentiate sources of MTBE and/or detect the onset of natural attenuation?
- May supplement or replace time-consuming microcosm experiments in identification of MTBE-degrading microbiology



Routine PT- GCIRMS Quantitation Limits

$\delta^{13}C$ MTBE	$\delta^{13}C$ TBA	δD MTBE	δD TBA
1 ppb	20/30ppb	10/20ppb	NA

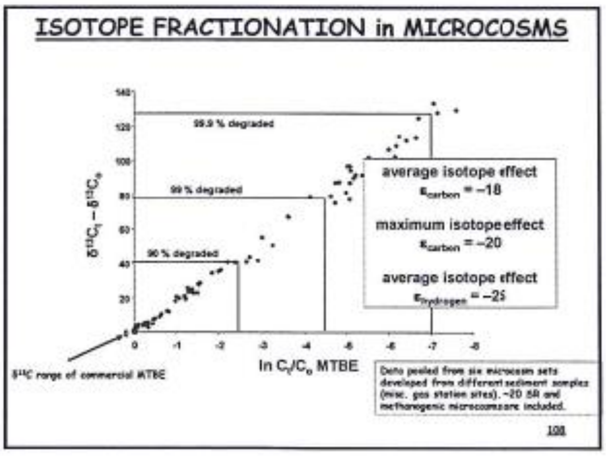


Data Interpretation

Qualitative - if MTBE composition is "heavier" than the reference commercial MTBE, degradation may be inferred

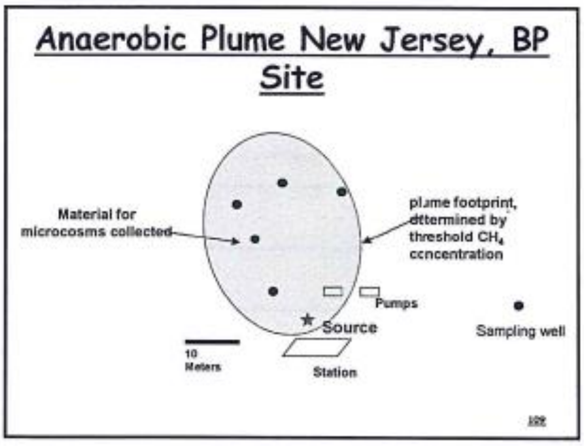
Composition range of undegraded MTBE:

Carbon: -33 to -27.5 permil $\delta^{13}C$
Hydrogen: -125 to -80 permil δD

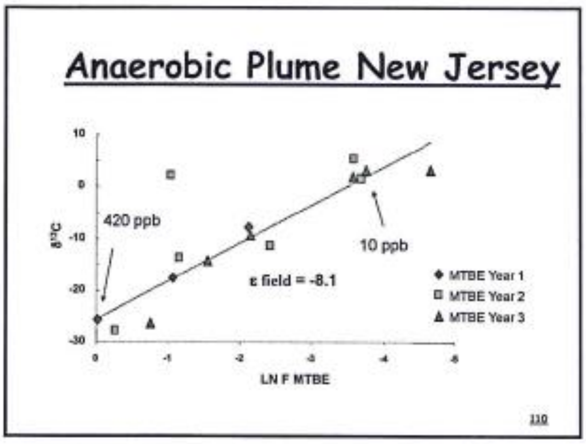


ISOTOPE FRACTIONATION in MICROCOSMS

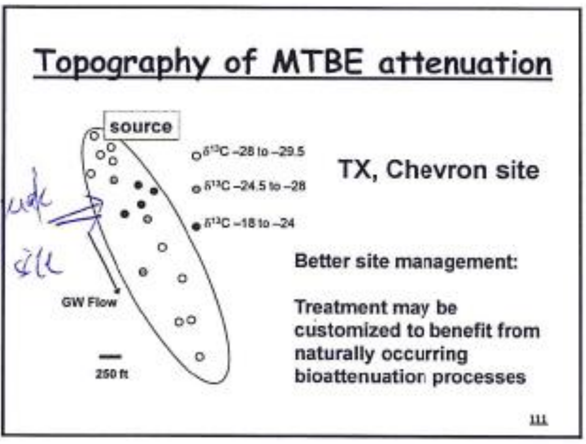
Data pooled from six microcosm sets developed from different sediment samples (misc. gas station sites). ~20 SR and methanogenic microcosms are included.



Anaerobic Plume New Jersey, BP Site



Anaerobic Plume New Jersey



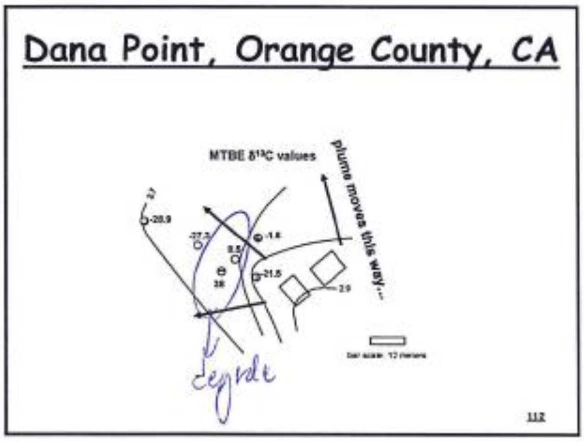
Topography of MTBE attenuation

TX, Chevron site

Better site management:

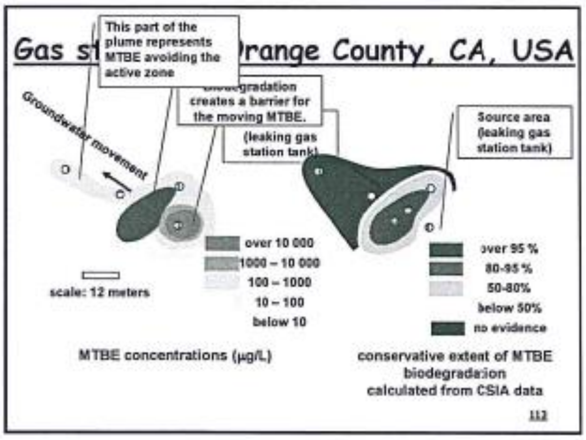
Treatment may be customized to benefit from naturally occurring bioattenuation processes

degrade site



Dana Point, Orange County, CA

degrade



Gas st… Orange County, CA, USA

This part of the plume represents MTBE avoiding the active zone

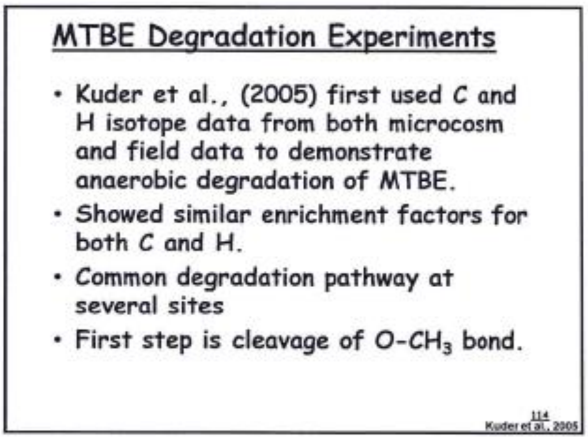
…degradation creates a barrier for the moving MTBE.

(leaking gas station tank)

Source area (leaking gas station tank)

MTBE concentrations (μg/L)

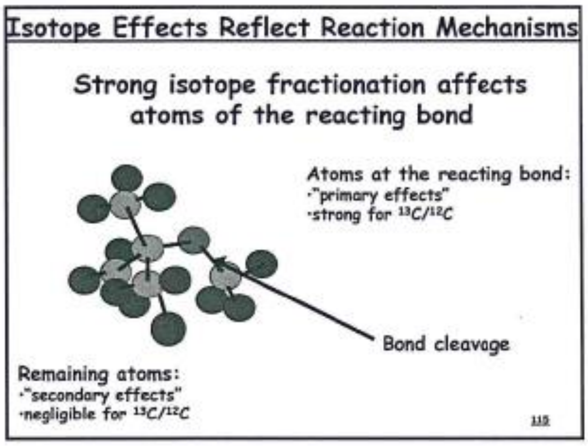
conservative extent of MTBE biodegradation calculated from CSIA data



MTBE Degradation Experiments

- Kuder et al., (2005) first used C and H isotope data from both microcosm and field data to demonstrate anaerobic degradation of MTBE.
- Showed similar enrichment factors for both C and H.
- Common degradation pathway at several sites
- First step is cleavage of O-CH_3 bond.

Kuder et al. 2005



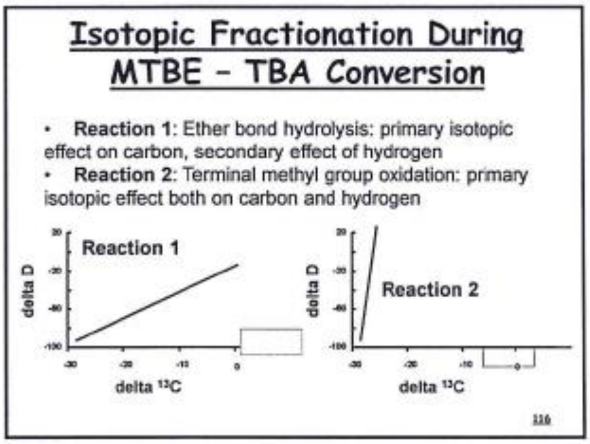
Isotope Effects Reflect Reaction Mechanisms

Strong isotope fractionation affects atoms of the reacting bond

Atoms at the reacting bond:
- "primary effects"
- strong for $^{13}C/^{12}C$

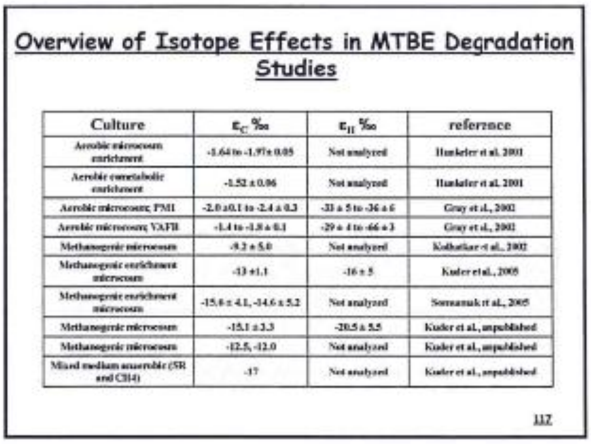
Bond cleavage

Remaining atoms:
- "secondary effects"
- negligible for $^{13}C/^{12}C$



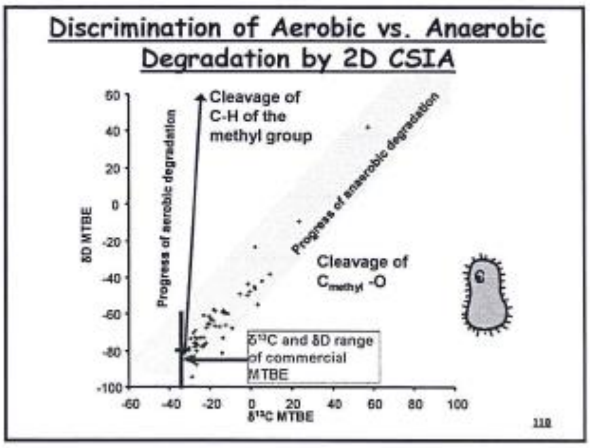
Isotopic Fractionation During MTBE – TBA Conversion

- **Reaction 1**: Ether bond hydrolysis: primary isotopic effect on carbon, secondary effect of hydrogen
- **Reaction 2**: Terminal methyl group oxidation: primary isotopic effect both on carbon and hydrogen

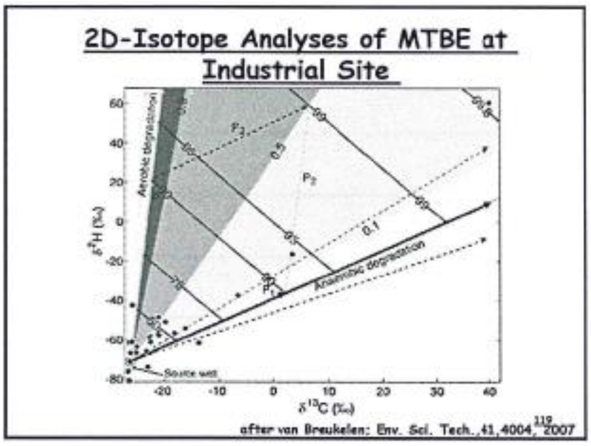


Overview of Isotope Effects in MTBE Degradation Studies

Culture	ε_C ‰	ε_H ‰	referznce
Aerobic microcosm enrichment	-1.64 to -1.97± 0.05	Not analyzed	Hunkeler et al. 2001
Aerobic cometabolic enrichment	-1.52 ± 0.06	Not analyzed	Hunkeler et al. 2001
Aerobic microcosm; PM1	-2.0 ±0.1 to -2.4 ± 0.3	-33 ± 5 to -36 ± 6	Gray et al., 2002
Aerobic microcosm; VAFB	-1.4 to -1.8 ± 0.1	-29 ± 4 to -66 ± 3	Gray et al., 2002
Methanogenic microcosm	-9.2 ± 5.0	Not analyzed	Kolhatkar et al., 2002
Methanogenic enrichment microcosm	-13 ±1.1	-16 ± 5	Kuder et al., 2005
Methanogenic enrichment microcosm	-15.6 ± 4.1, -14.6 ± 5.2	Not analyzed	Somsamak et al., 2005
Methanogenic microcosm	-15.1 ± 3.3	-20.5 ± 5.5	Kuder et al., unpublished
Methanogenic microcosm	-12.5, -12.0	Not analyzed	Kuder et al., unpublished
Mixed medium anaerobic (SR and CH4)	-17	Not analyzed	Kuder et al., unpublished

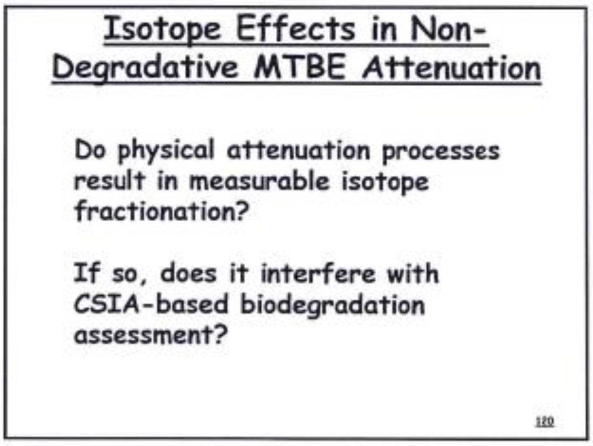


Discrimination of Aerobic vs. Anaerobic Degradation by 2D CSIA



2D-Isotope Analyses of MTBE at Industrial Site

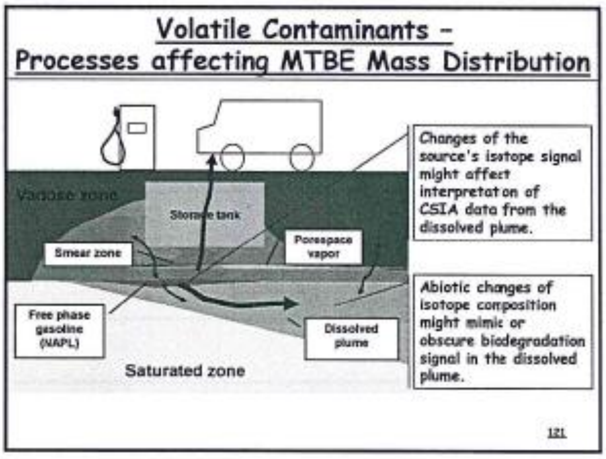
after van Breukelen: Env. Sci. Tech., 41, 4004, 2007



Isotope Effects in Non-Degradative MTBE Attenuation

Do physical attenuation processes result in measurable isotope fractionation?

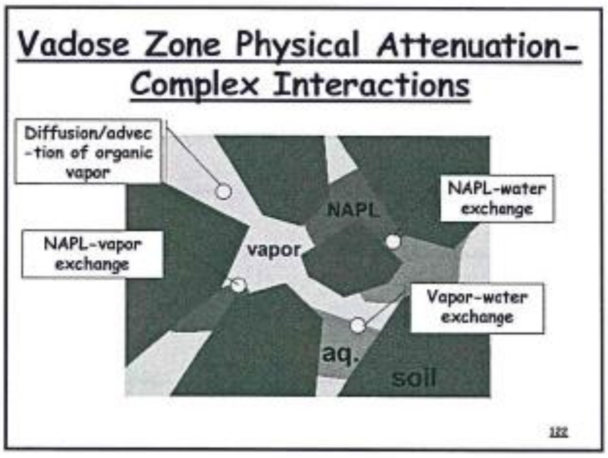
If so, does it interfere with CSIA-based biodegradation assessment?



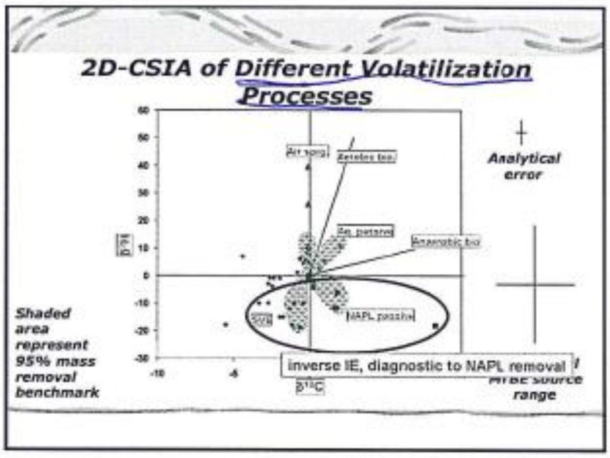
Volatile Contaminants – Processes affecting MTBE Mass Distribution

Changes of the source's isotope signal might affect interpretation of CSIA data from the dissolved plume.

Abiotic changes of isotope composition might mimic or obscure biodegradation signal in the dissolved plume.



Vadose Zone Physical Attenuation-Complex Interactions



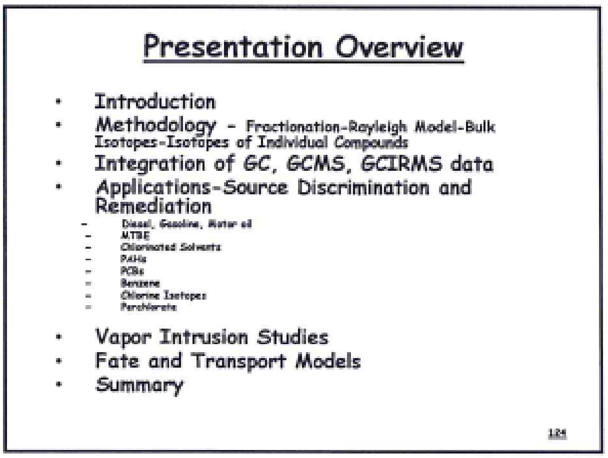
2D-CSIA of Different Volatilization Processes

Analytical error

Shaded area represent 95% mass removal benchmark

inverse IE, diagnostic to NAPL removal

MTBE source range



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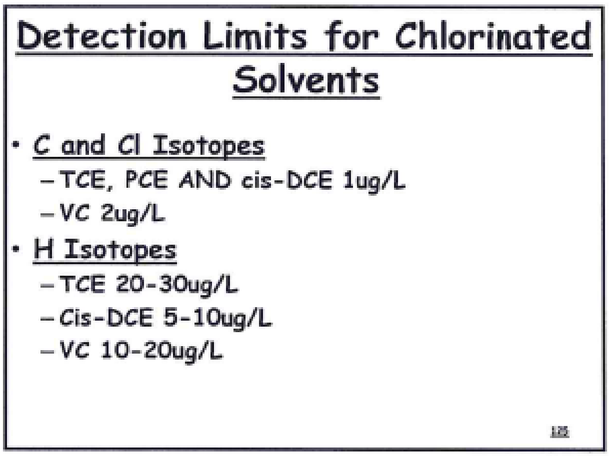
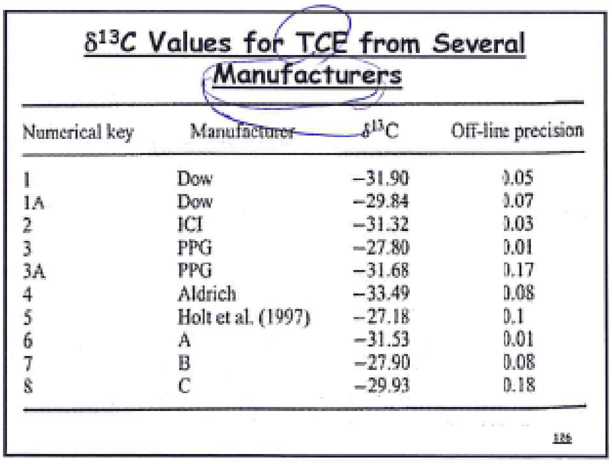


Detection Limits for Chlorinated Solvents

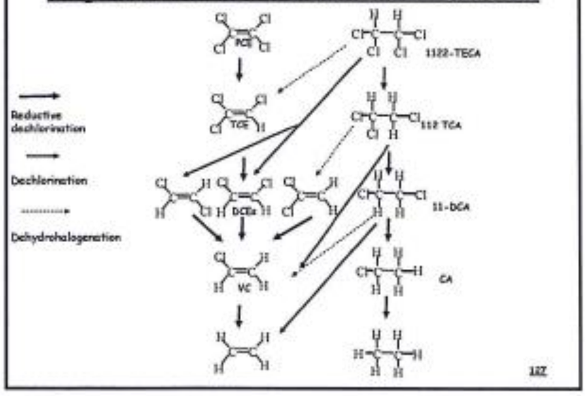
- C and Cl Isotopes
  - TCE, PCE AND cis-DCE 1ug/L
  - VC 2ug/L
- H Isotopes
  - TCE 20-30ug/L
  - Cis-DCE 5-10ug/L
  - VC 10-20ug/L



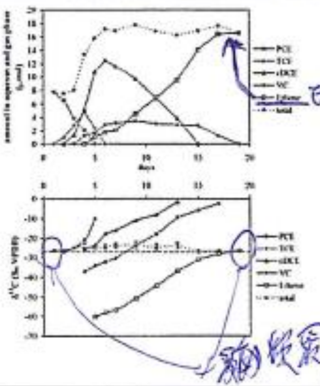
$\delta^{13}C$ Values for TCE from Several Manufacturers

Numerical key	Manufacturer	$\delta^{13}C$	Off-line precision
1	Dow	−31.90	0.05
1A	Dow	−29.84	0.07
2	ICI	−31.32	0.03
3	PPG	−27.80	0.01
3A	PPG	−31.68	0.17
4	Aldrich	−33.49	0.08
5	Holt et al. (1997)	−27.18	0.1
6	A	−31.53	0.01
7	B	−27.90	0.08
8	C	−29.93	0.18

Degradation of Chlorinated Solvents



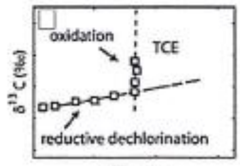
Degradation of Chlorinated Solvents



Ethene

開始與最終 isotope value 一樣

Discrimination of Reaction Mechanisms by Isotope Effects



After Hunkeler et al., 2009

In different reaction types, the proportions between C, Cl and H isotope effects are different. These differences can be visualized by collecting data on 2 or 3 isotopes (e.g., C+Cl).

The same principles apply to biodegradation, chemical degradation and physical mass remediation.

Isotopic Enrichment Factors

Compound	ε(‰)	Conditions	References
PCE	-2	batch, anaerobic	Hunkeler et al, 1999
	-5.2	batch, methanogenic	Slater et al, 2001
TCE	-2.5	batch, methanogenic	Bloom et al, 2000
	-4	batch, anaerobic	Hunkeler et al, 1999
	-6.6	batch, methanogenic	Bloom et al., 2000
	-7.1	batch, anaerobic	Sherwood-Lollar et al, 1999
	-13.8	batch, anaerobic	Slater et al, 2001
cDCE	-12	batch, anaerobic	Hunkeler et al, 1999
	-14.1	batch, methanogenic	Bloom et al., 2000
	-16.1	batch, methanogenic	Bloom et al., 2000
	-20.4	batch, anaerobic	Slater et al, 2001
VC	-21.5	batch, methanogenic	Bloom et al., 2000
	-22.4	batch, anaerobic	Slater et al, 2001
	-26.6	batch, methanogenic	Bloom et al., 2000
	-26	batch, anaerobic	Hunkeler et al, 1999

The last two steps of degradation are the slowest. During these processes, the enrichment factor is the highest highlighting an important degradation at this time.

Degradation of Chlorinated Solvents

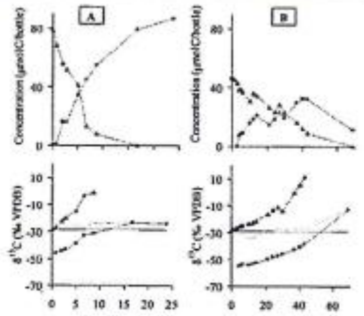
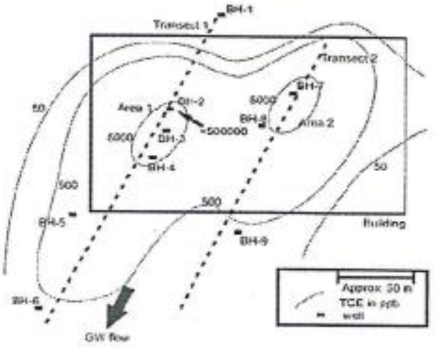


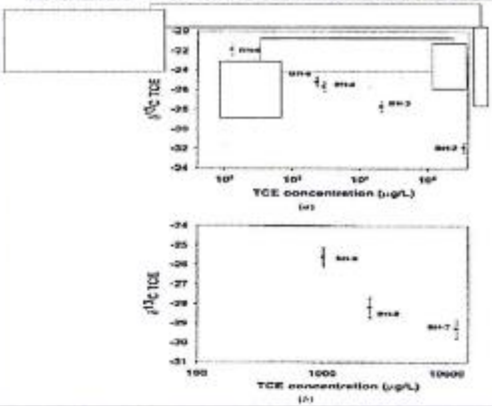
FIGURE 3. Concentration and stable carbon isotope data for experiment A and B, VC culture (VC —▲—, ETH —●—, initial value —, isotope balance ---).

Bloom et al., Environ. Sci. Technol. 34 (13) 2768 -2772, 2000.

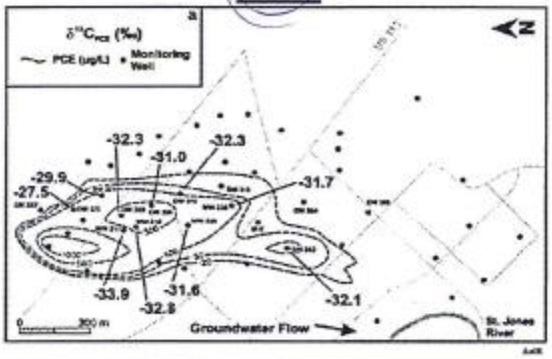
Source Discrimination of PCE and TCE



Source Discrimination of PCE and TCE



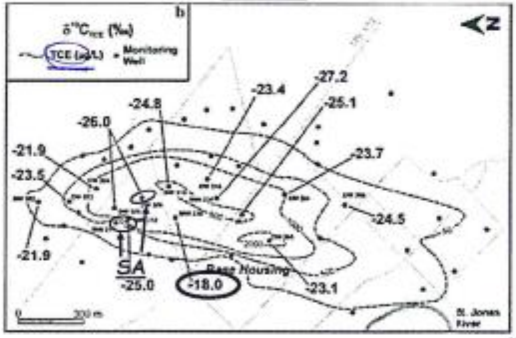
Reductive Dechlorination of PCEs



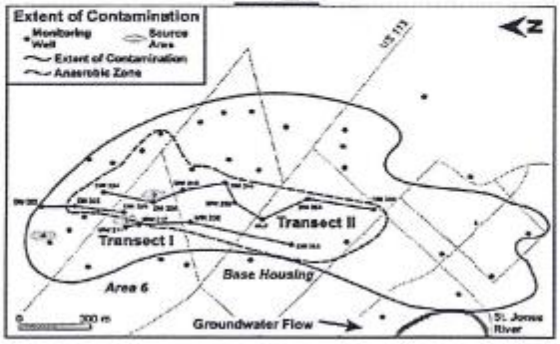
Reductive Dechlorination of PCEs

- Sherwood Lollar et al., EST 2001,35,261-269-first showed that during anaerobic reductive dechlorination of chlorinated hydrocarbons,isotopic enrichment of PCE and TCE was observed at Area 6 Dover AFB.

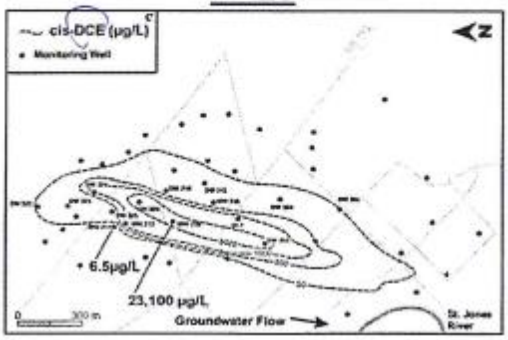
Reductive Dechlorination of PCEs



Reductive Dechlorination of PCEs



Reductive Dechlorination of PCEs



PCE Degradation Site Study

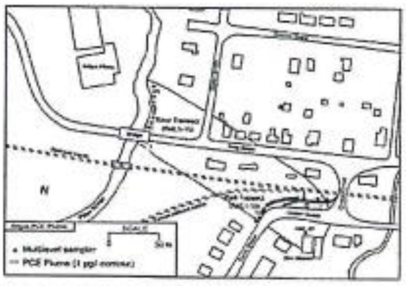
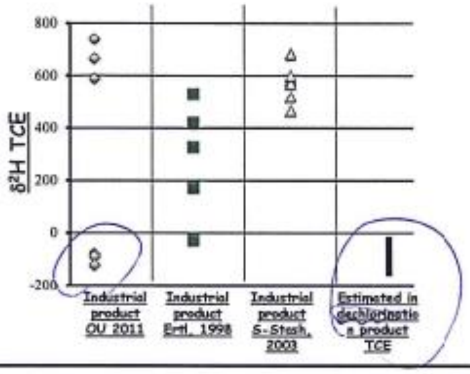


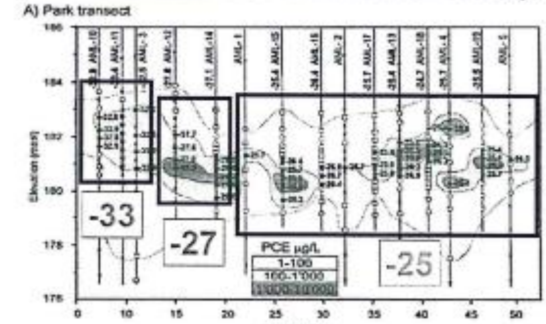
Fig. 2. Map of Angus field site with locations of multilevel samplers (circles) in park and river transects. The southern margin of the plume in the vicinity of the river is not known due to the absence of sampling locations outside of the plume.

Hunkeler et al., J. Contaminant Hydrology, 74, 265-282,2004.

H Isotope Ratios of Manufactured TCE



PCE Source Evaluation Study



Hunkeler et al., J. Contaminant Hydrology, 74, 265-282,2004.

解釋上
須加以，之說

Abiotic and Microbial Transformation of PCE and TCE

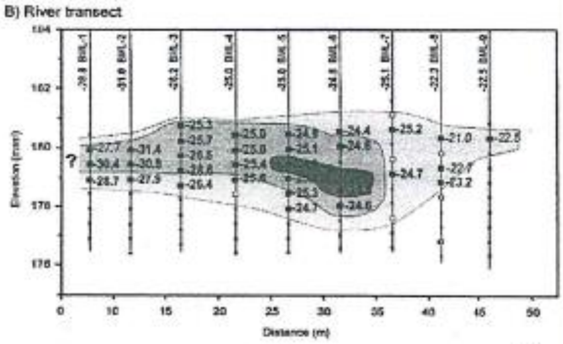
Microbial processes are most rapid transformation of PCE and TCE in the field and should be exploited for this purpose where appropriate.

Abiotic processes can contribute to transformation of PCE and TCE where significantly higher mass loadings of reactive minerals are generated in situ as part of a remediation technology or where the activity of dechlorinating bacteria is low.

Abiotic processes can also play a significant role in cases where complete microbial degradation of PCE or TCE to ethene does not occur.

Under these conditions, although slow, abiotic processes may still contribute to the complete transformation of PCE and TCE to benign products at contaminated sites.

PCE Degradation Site Study



Hunkeler et al., J. Contaminant Hydrology, 74, 265-282,2004

Biogenic vs. Abiogenic Degradation

PCE	ε
FeS ph 7 – abiotic	-30.2 +/- 4.3
FeS pH 8 – abiotic	-29.54 +/- 0.83
BB1 – biological	-1.39 +/- 0.21
Sm – biological	-1.33 +/- 0.13

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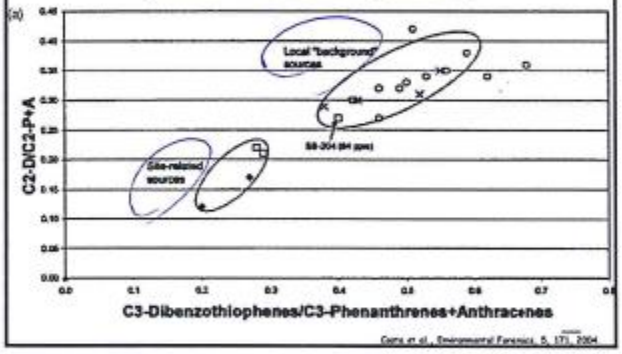
Differentiation of PAH Sources to Urban Background



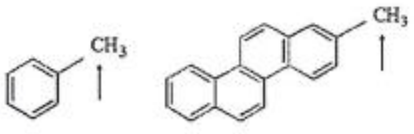
Costa et al., Environmental Forensics, 5, 171, 2004

Sources of PAHs to Urban Background

- Natural background
  - Pre-existing and naturally produced
- Atmospheric fallout
  - Transportation, heating systems, power generation, industries
- Fill
  - Building materials
  - Debris, ash, trash
- Spills and sprays

Are the isotope ratios different for different sources? Can they be sorted out?

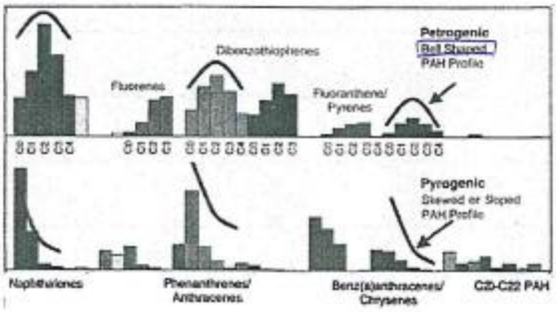
Large vs.Small Molecules



1:7 1:19

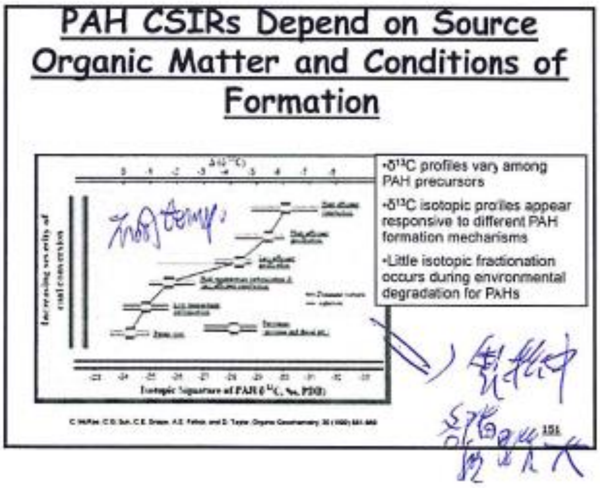
Biodegradation will induce larger isotopic fractionation in smaller molecules which have lower ratio altered to non-altered carbons- (intrinsic isotopic effects).

Petrogenic vs. Pyrogenic



PAHs and Stable Isotopes

- Current interest is centered around whether carbon isotopes can be used to discriminate PAHs derived from former manufactured gas plant (MGP) wastes versus those from general urban background aromatics
- Urban backgrounds have a fairly narrow range and small differences may be related to source differences



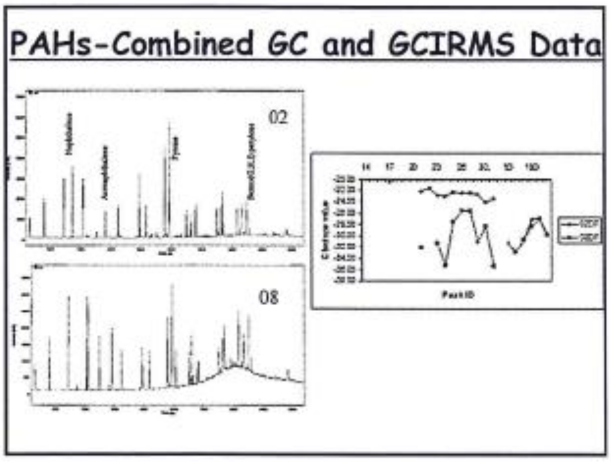
PAH CSIRs Depend on Source Organic Matter and Conditions of Formation

- δ13C profiles vary among PAH precursors
- δ13C isotopic profiles appear responsive to different PAH formation mechanisms
- Little isotopic fractionation occurs during environmental degradation for PAHs

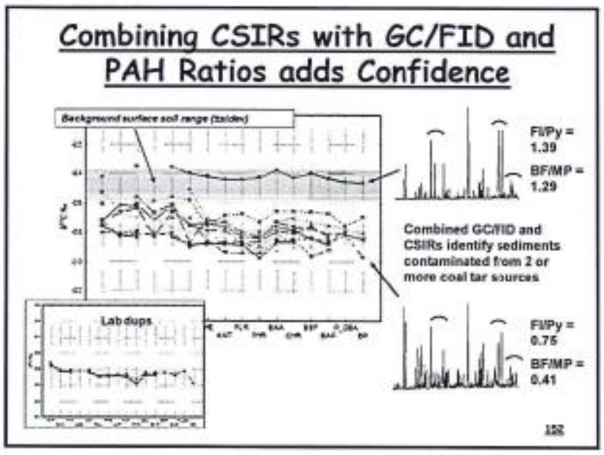
[illegible] temp.

[illegible]

C. McRae, C.G. Sun, C.E. Snape, A.E. Fallick and D. Taylor, Organic Geochemistry 30 (1999) 881-889

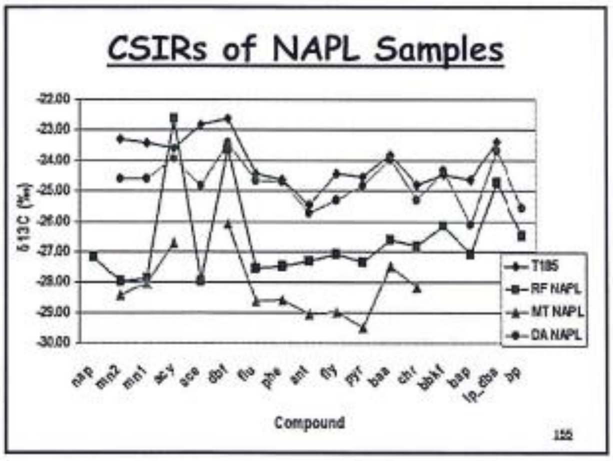


PAHs-Combined GC and GCIRMS Data

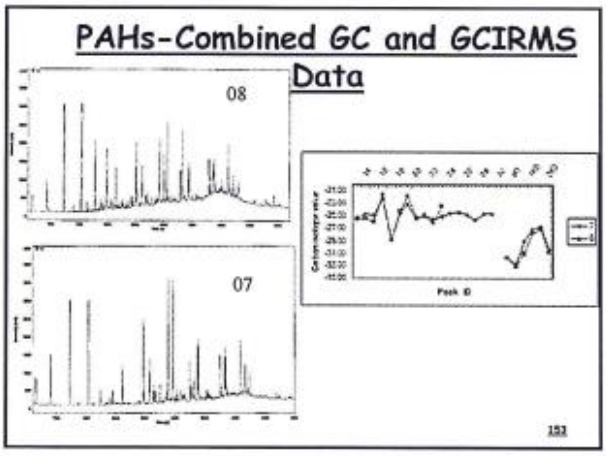


Combining CSIRs with GC/FID and PAH Ratios adds Confidence

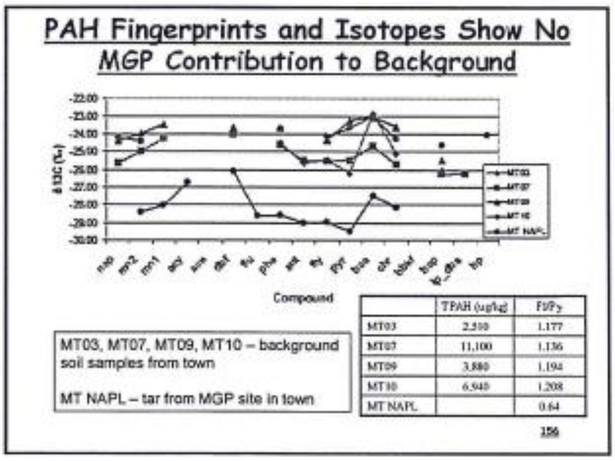
Combined GC/FID and CSIRs identify sediments contaminated from 2 or more coal tar sources



CSIRs of NAPL Samples



PAHs-Combined GC and GCIRMS Data

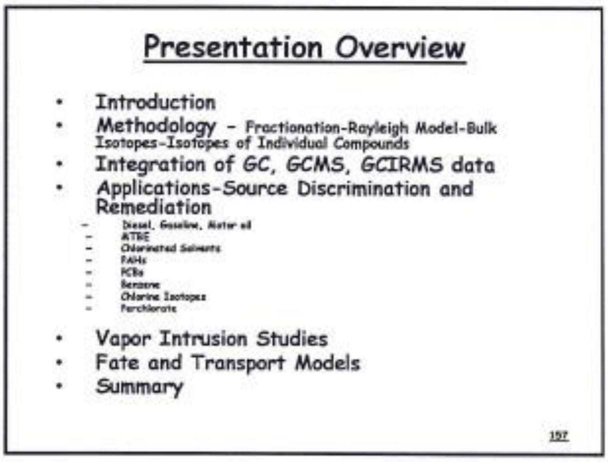


PAH Fingerprints and Isotopes Show No MGP Contribution to Background

MT03, MT07, MT09, MT10 – background soil samples from town

MT NAPL – tar from MGP site in town

	TPAH (ug/kg)	Fl/Py
MT03	2,510	1.177
MT07	11,100	1.136
MT09	3,880	1.194
MT10	6,940	1.208
MT NAPL		0.64



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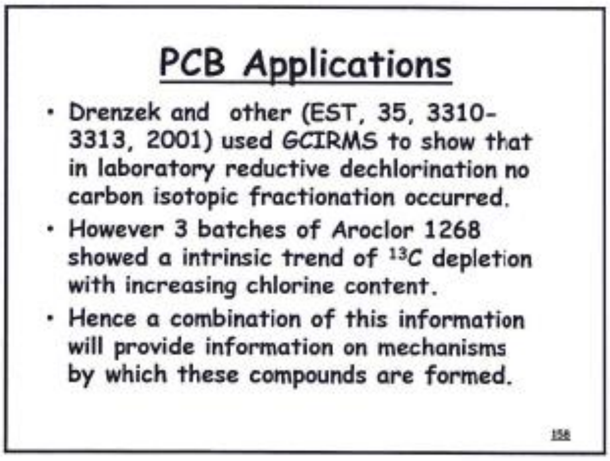
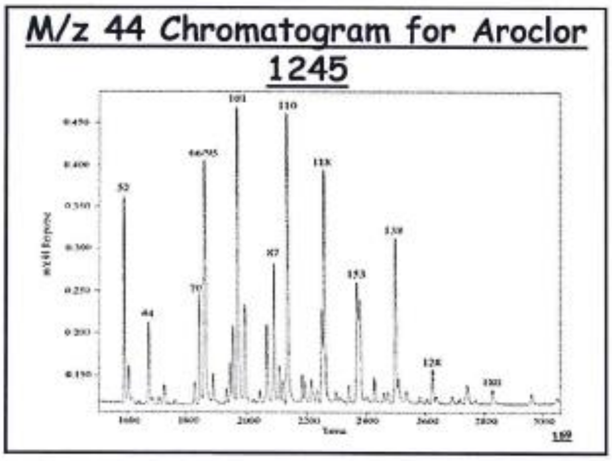
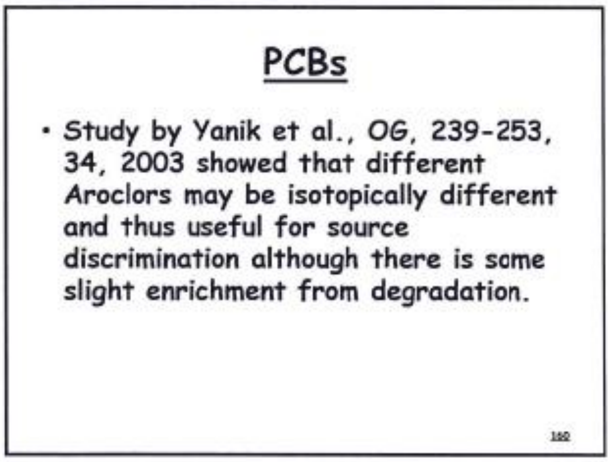


PCB Applications

- Drenzek and other (EST, 35, 3310-3313, 2001) used *GCIRMS* to show that in laboratory reductive dechlorination no carbon isotopic fractionation occurred.
- However 3 batches of Aroclor 1268 showed a intrinsic trend of ^{13}C depletion with increasing chlorine content.
- Hence a combination of this information will provide information on mechanisms by which these compounds are formed.

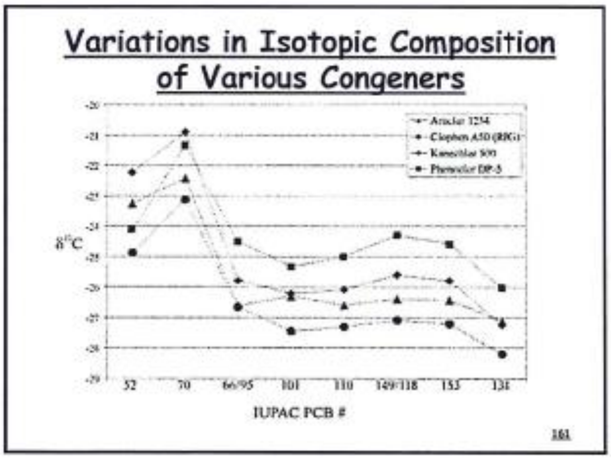


M/z 44 Chromatogram for Aroclor 1245

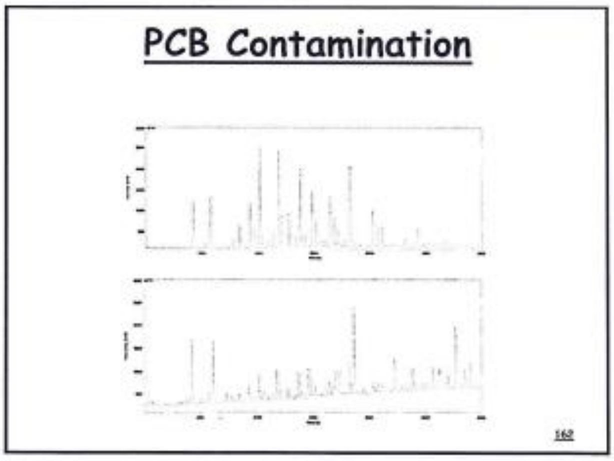


PCBs

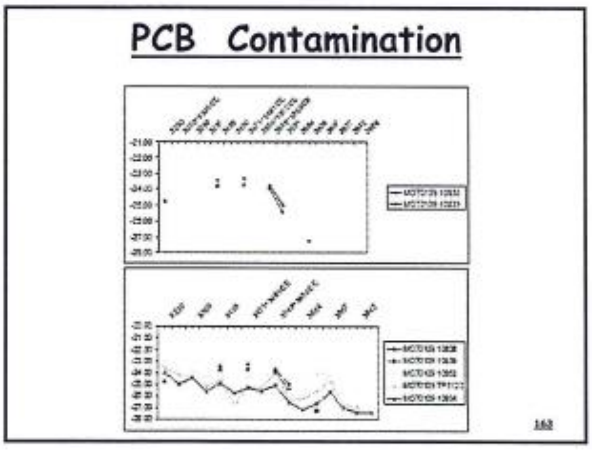
- Study by Yanik et al., *OG*, 239-253, 34, 2003 showed that different Aroclors may be isotopically different and thus useful for source discrimination although there is some slight enrichment from degradation.



Variations in Isotopic Composition of Various Congeners



PCB Contamination



PCB Contamination

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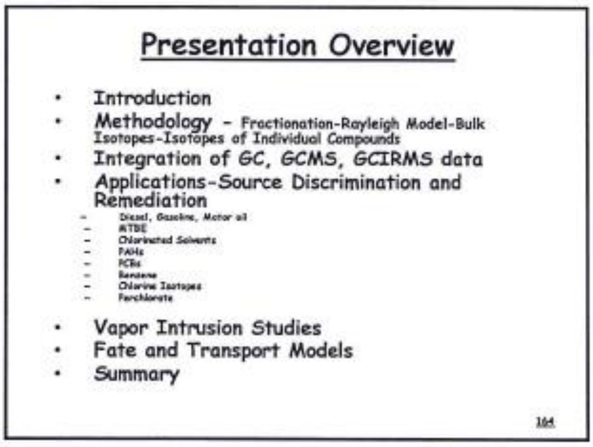

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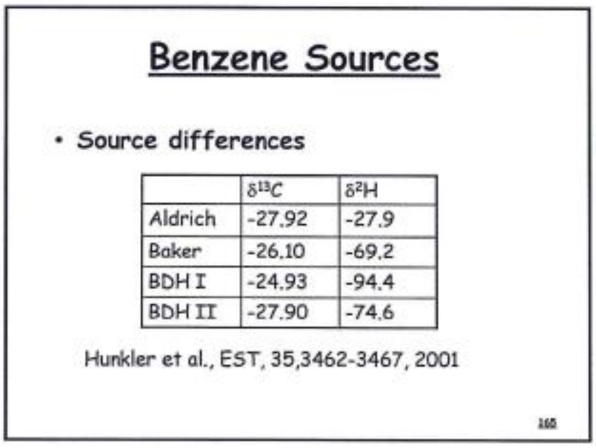

Benzene Sources

- Source differences

	δ13C	δ2H
Aldrich	-27.92	-27.9
Baker	-26.10	-69.2
BDH I	-24.93	-94.4
BDH II	-27.90	-74.6

Hunkler et al., EST, 35,3462-3467, 2001

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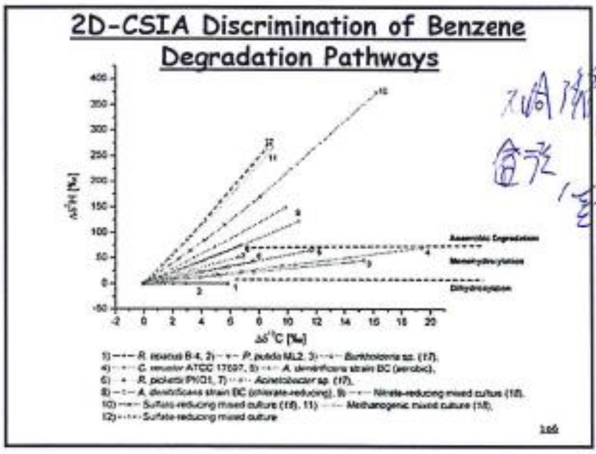

2D-CSIA Discrimination of Benzene Degradation Pathways

1) R. opacus B-4, 2) P. putida ML2, 3) Burkholderia sp. (17),
4) C. necator ATCC 17697, 5) A. denitrificans strain BC (aerobic),
6) R. pickettii PKO1, 7) Acinetobacter sp. (17),
8) A. denitrificans strain BC (chlorate-reducing), 9) Nitrate-reducing mixed culture (18),
10) Sulfate-reducing mixed culture (18), 11) Methanogenic mixed culture (18),
12) Sulfate-reducing mixed culture

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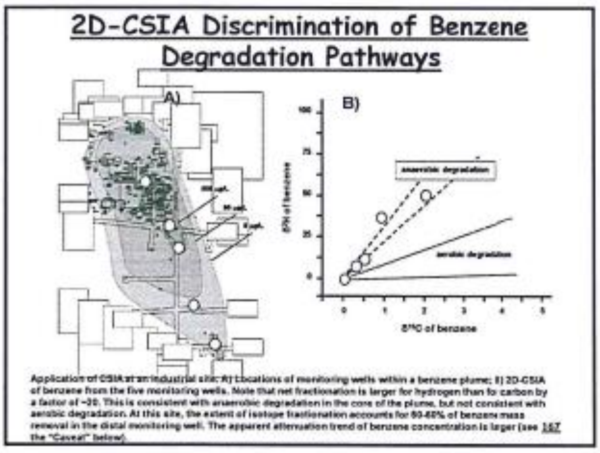
不同降解
途徑，C/氫



2D-CSIA Discrimination of Benzene Degradation Pathways

Application of CSIA at an industrial site: A) Locations of monitoring wells within a benzene plume; B) 2D-CSIA of benzene from the five monitoring wells. Note that net fractionation is larger for hydrogen than fo carbon by a factor of ~20. This is consistent with anaerobic degradation in the core of the plume, but not consistent with aerobic degradation. At this site, the extent of isotope fractionation accounts for 60-80% of benzene mass removal in the distal monitoring well. The apparent attenuation trend of benzene concentration is larger (see the "Caveat" below).

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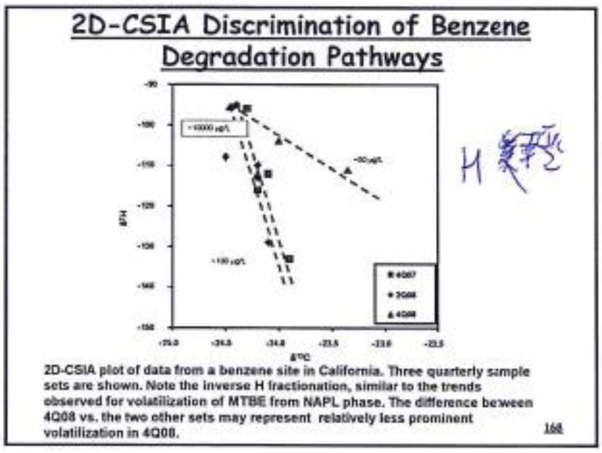

2D-CSIA Discrimination of Benzene Degradation Pathways

2D-CSIA plot of data from a benzene site in California. Three quarterly sample sets are shown. Note the inverse H fractionation, similar to the trends observed for volatilization of MTBE from NAPL phase. The difference beween 4Q08 vs. the two other sets may represent relatively less prominent volatilization in 4Q08.

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Presentation Overview

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  - MTBE
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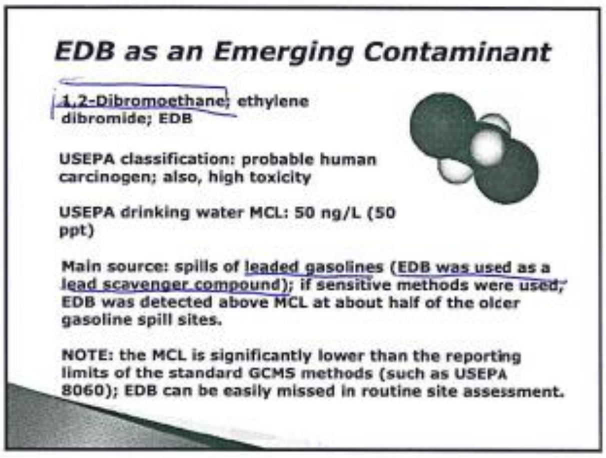
  - PAHs
  - PCBs
  - Benzene
  - Chlorine Isotopes
  - Perchlorate
- Vapor Intrusion Studies
- Fate and Transport Models
- Summary



EDB as an Emerging Contaminant

1,2-Dibromoethane; ethylene dibromide; EDB

USEPA classification: probable human carcinogen; also, high toxicity

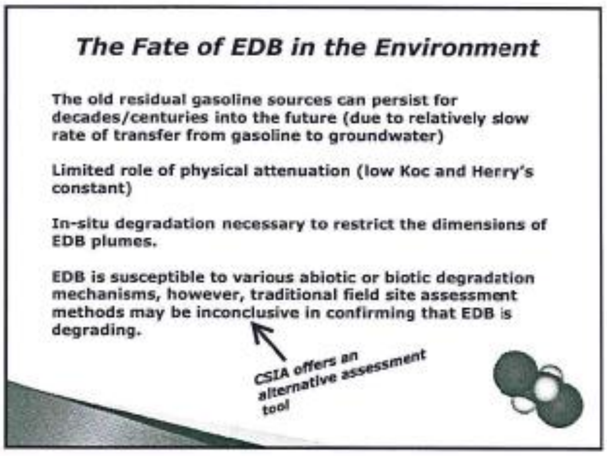
USEPA drinking water MCL: 50 ng/L (50 ppt)

Main source: spills of leaded gasolines (EDB was used as a lead scavenger compound); if sensitive methods were used, EDB was detected above MCL at about half of the older gasoline spill sites.

NOTE: the MCL is significantly lower than the reporting limits of the standard GCMS methods (such as USEPA 8060); EDB can be easily missed in routine site assessment.

1,4-Dioxane

- 1,4-Dioxane used as a stabilizer for chlorinated solvents and an ingredient in personal care products and printer inks.
- Probable carcinogen.
- Highly water soluble and spreads more extensively than the chlorinated solvents.
- Can be degraded in advance water treatment methods.
- Degrades relatively slowly *in-situ*



The Fate of EDB in the Environment

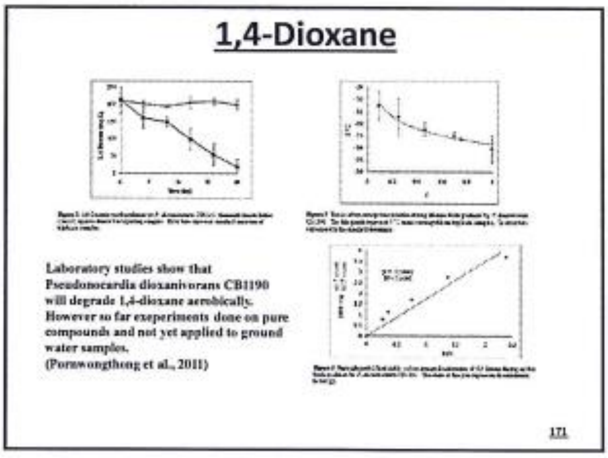
The old residual gasoline sources can persist for decades/centuries into the future (due to relatively slow rate of transfer from gasoline to groundwater)

Limited role of physical attenuation (low Koc and Herry's constant)

In-situ degradation necessary to restrict the dimensions of EDB plumes.

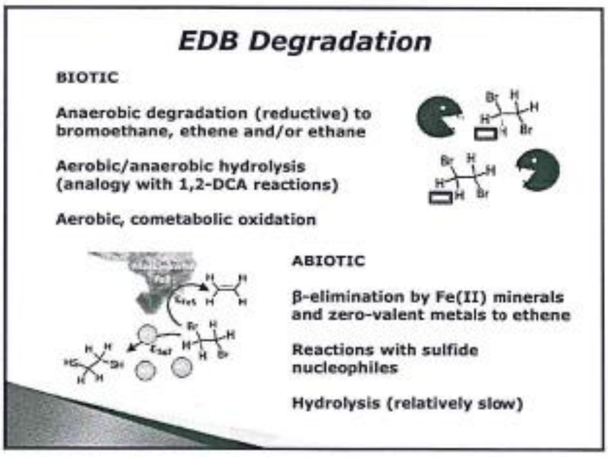
EDB is susceptible to various abiotic or biotic degradation mechanisms, however, traditional field site assessment methods may be inconclusive in confirming that EDB is degrading.

CSIA offers an alternative assessment tool



1,4-Dioxane

Laboratory studies show that Pseudonocardia dioxanivorans CB1190 will degrade 1,4-dioxane aerobically. However so far exeperiments done on pure compounds and not yet applied to ground water samples. (Pornwongthong et al., 2011)



EDB Degradation

BIOTIC

Anaerobic degradation (reductive) to bromoethane, ethene and/or ethane

Aerobic/anaerobic hydrolysis (analogy with 1,2-DCA reactions)

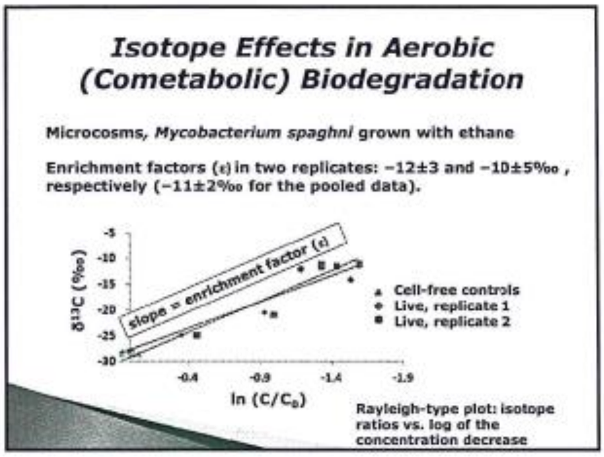
Aerobic, cometabolic oxidation

ABIOTIC

β-elimination by Fe(II) minerals and zero-valent metals to ethene

Reactions with sulfide nucleophiles

Hydrolysis (relatively slow)



Isotope Effects in Aerobic (Cometabolic) Biodegradation

Microcosms, *Mycobacterium spaghni* grown with ethane

Enrichment factors (ε) in two replicates: −12±3 and −10±5‰, respectively (−11±2‰ for the pooled data).

Rayleigh-type plot: isotope ratios vs. log of the concentration decrease

Problems that can be investigated

- As with carbon and hydrogen the two problems that, potentially, can be investigated with chlorine are:
  - Source
  - Natural Attenuation

Conclusions: Implications for the Use of CSIA in EDB Attenuation Assessment

Significant C isotope effects were observed in all degradation pathways studied to date.

So far, the few biodegrading organisms examined exhibited no significant dampening of the isotope effect (e.g., via commitment to catalysis)

Good perspective for the assessment of degradation of EDB by CSIA methods (if degradation were occurring at the site, the isotope enrichments should be readily detectable)

Unlike in most traditional CSIA work, abiotic pathways must be considered as viable mechanisms leading to isotope fractionation

With C-CSIA data alone, differentiation of alternative degradation mechanisms may be difficult. Awaiting progress in Br-CSIA to permit dual C-Br isotope approach

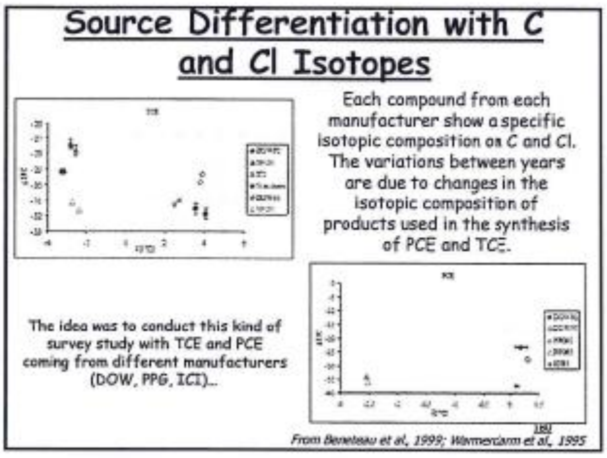
Chlorine Isotopes

- Heraty et al., (*OG.*, 30, 793-799, 1999) first showed that both chlorine and carbon were enriched in laboratory microbial degradation experiments of dichloromethane (DCM).
- Determination of the kinetic fractionation factors for microbial degradation could be important in distinguishing microbial from abiogenic degradation processes.

What can be done with Chlorine Isotopes?

- First the stable isotopes are-^{35}Cl (75.77%) and ^{37}Cl (24.23%).
- Standard-SMOW but some disagreement re. absolute ratio of these isotopes in the OW

(SMOW-Standard Mean Ocean Water; OW Ocean Water)

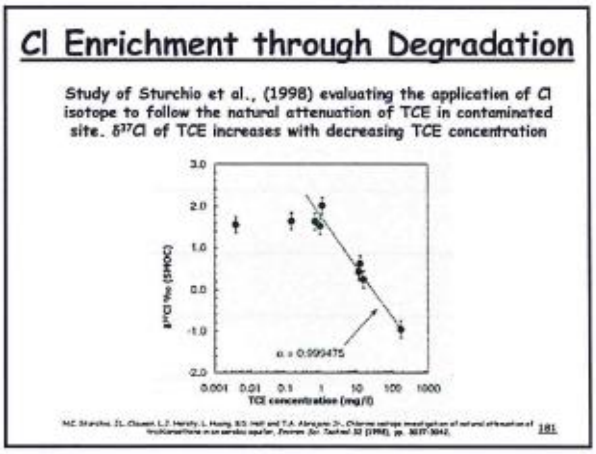


Source Differentiation with C and Cl Isotopes

Each compound from each manufacturer show a specific isotopic composition on C and Cl. The variations between years are due to changes in the isotopic composition of products used in the synthesis of PCE and TCE.

The idea was to conduct this kind of survey study with TCE and PCE coming from different manufacturers (DOW, PPG, ICI)...

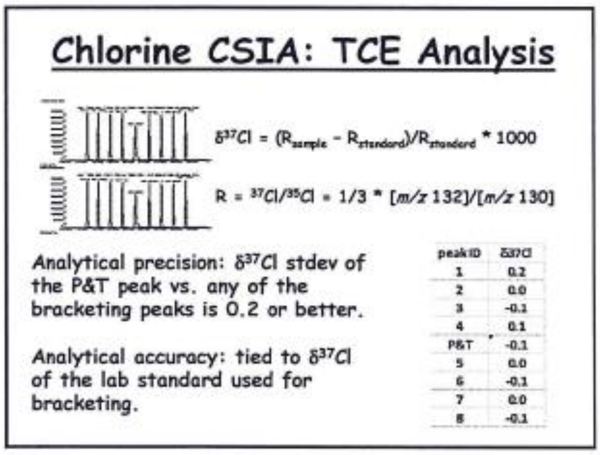
From Beneteau et al, 1999; Warmerdam et al, 1995



Cl Enrichment through Degradation

Study of Sturchio et al., (1998) evaluating the application of Cl isotope to follow the natural attenuation of TCE in contaminated site. $\delta^{37}Cl$ of TCE increases with decreasing TCE concentration

M.C. Sturchio, J.L. Clausen, L.J. Heraty, L. Huang, B.D. Holt and T.A. Abrajano Jr., Chlorine isotope investigation of natural attenuation of trichloroethene in an aerobic aquifer, Environ. Sci. Technol. 32 (1998), pp. 3037-3042.



Chlorine CSIA: TCE Analysis

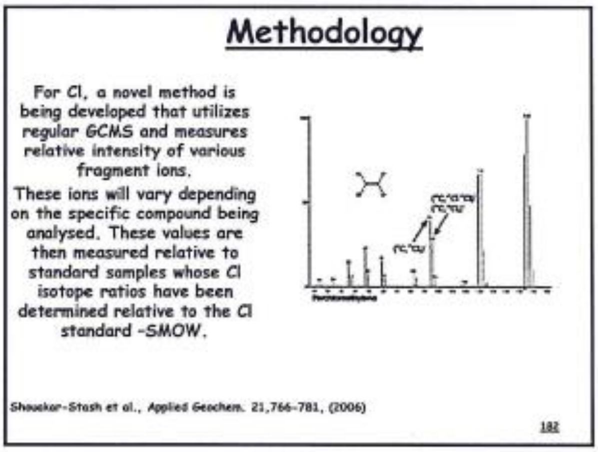
$\delta^{37}Cl = (R_{sample} - R_{standard})/R_{standard} * 1000$

$R = {}^{37}Cl/{}^{35}Cl = 1/3 * [m/z\ 132]/[m/z\ 130]$

Analytical precision: $\delta^{37}Cl$ stdev of the P&T peak vs. any of the bracketing peaks is 0.2 or better.

Analytical accuracy: tied to $\delta^{37}Cl$ of the lab standard used for bracketing.

peak ID	$\delta 37Cl$
1	0.2
2	0.0
3	-0.1
4	0.1
P&T	-0.1
5	0.0
6	-0.1
7	0.0
8	-0.1

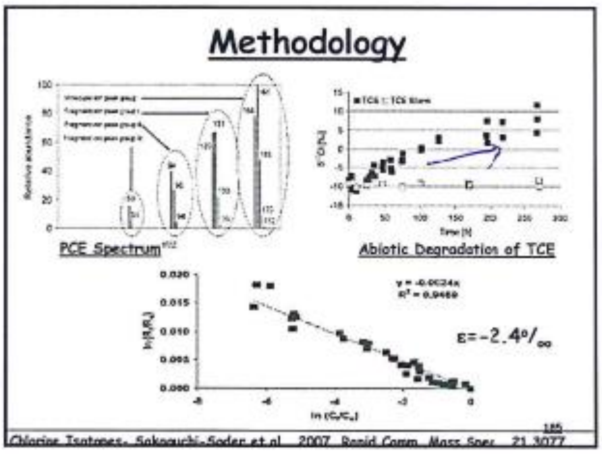


Methodology

For Cl, a novel method is being developed that utilizes regular GCMS and measures relative intensity of various fragment ions.

These ions will vary depending on the specific compound being analysed. These values are then measured relative to standard samples whose Cl isotope ratios have been determined relative to the Cl standard -SMOW.

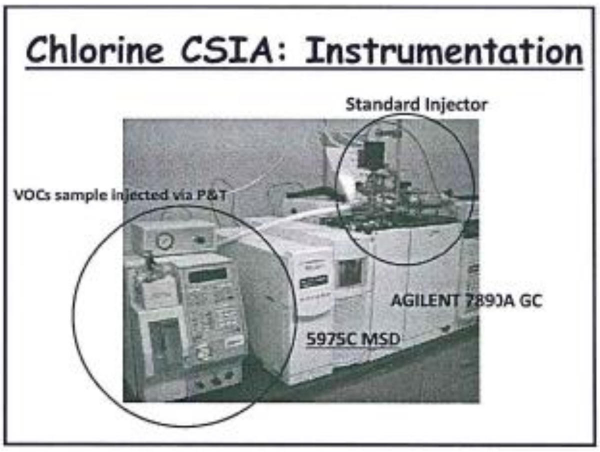
Shouakar-Stash et al., Applied Geochem. 21,766-781, (2006)



Methodology

$\varepsilon = -2.4 ^{o}/_{oo}$

Chlorine Isotopes- Sakaguchi-Soder et al 2007 Rapid Comm. Mass Spec. 21 3077



Chlorine CSIA: Instrumentation

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Perchlorate

Perchlorate taints water in 22 states. The main sources of this contamination are users of perchlorate salts: military bases, aerospace installations, and defense contractors that build rockets-such as the Massachusetts Military Reservation on Cape Cod or Lockheed Propulsion in Redlands, Calif., which manufactured rockets. A small amount of perchlorate pollution in the U.S. is believed to have stemmed from a sodium nitrate fertilizer made in Chile.
Since 1992, EPA has recommended safe levels ranging from 4 to 18 ppb
Perchlorate can cause adverse effects by blocking the uptake of iodine by the thyroid

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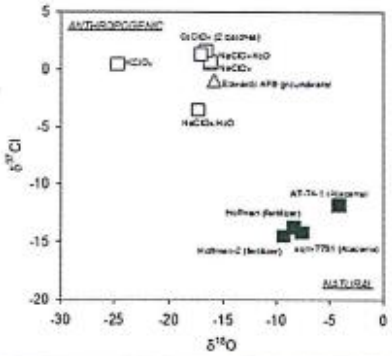
Perchlorate Problems

- Source-source variability must be characterized first; natural (fertilizer) *vs.* anthropogenic (oxidant)?
- Natural Attenuation (microbial degradation has large (~15‰) KIE for Cl)

Are Perchlorate Sources Isotopically Distinct?



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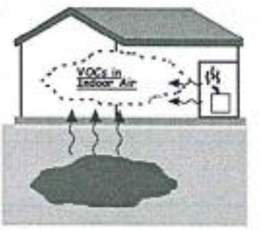
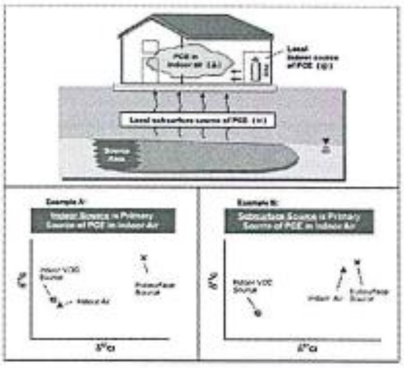
Vapor Intrusion

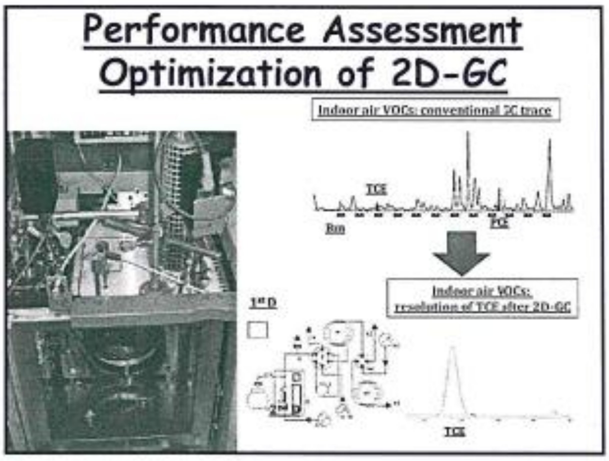
- At vapor intrusion site, testing of indoor air is most direct way to identify VI impacts.
- Indoor sources of VOCs are ubiquitous: cleaners, glues, plastic, etc
- Detection of VOCs in indoor air does not necessarily indicate vapor intrusion.



Key Point: *Critical need for reliable methods to distinguish between vapor intrusion and indoor sources of VOCs.*

Vapor Intrusion

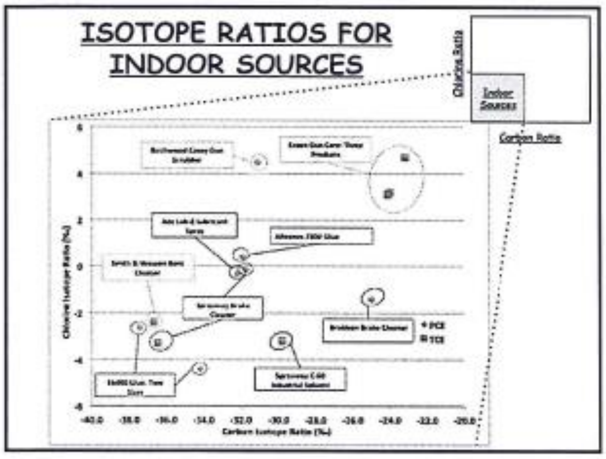




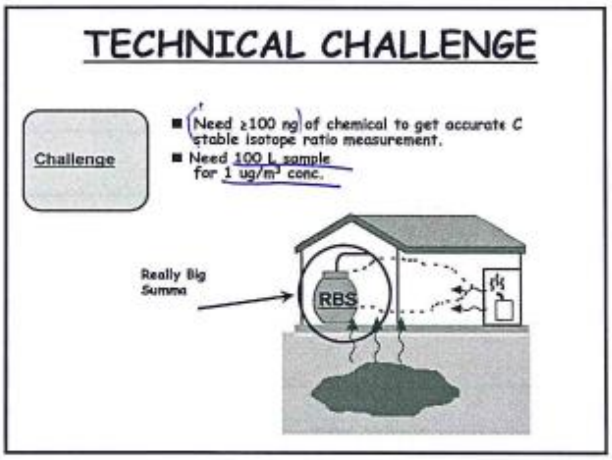
Performance Assessment Optimization of 2D-GC

Indoor air VOCs: conventional GC trace

Indoor air VOCs: resolution of TCE after 2D-GC



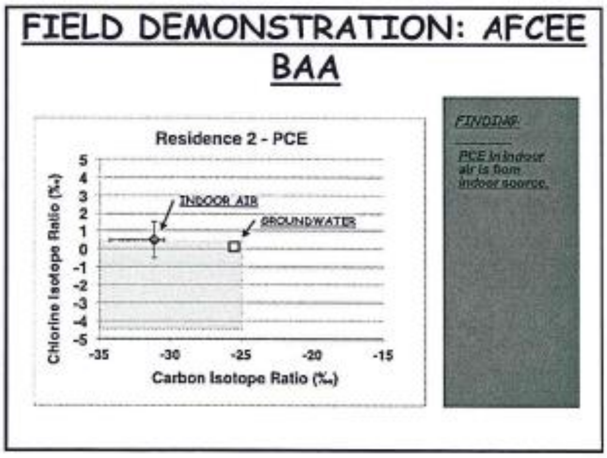
ISOTOPE RATIOS FOR INDOOR SOURCES



TECHNICAL CHALLENGE

Challenge

- Need ≥100 ng of chemical to get accurate C stable isotope ratio measurement.
- Need 100 L sample for 1 ug/m³ conc.

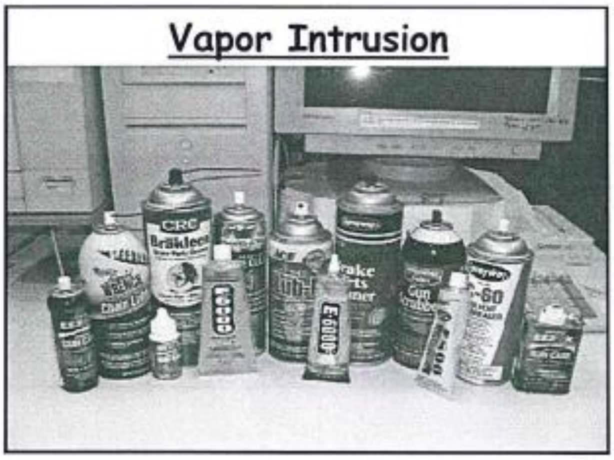


FIELD DEMONSTRATION: AFCEE BAA

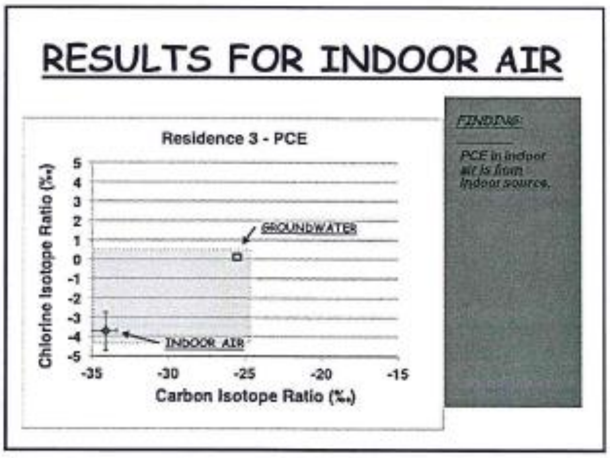
Residence 2 - PCE

FINDING:

PCE in indoor air is from indoor source.



Vapor Intrusion



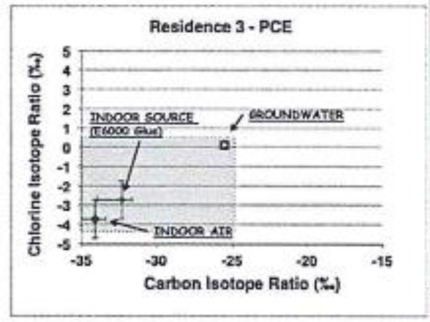
RESULTS FOR INDOOR AIR

Residence 3 - PCE

FINDING:

PCE in indoor air is from indoor source.

RESULTS FOR INDOOR AIR

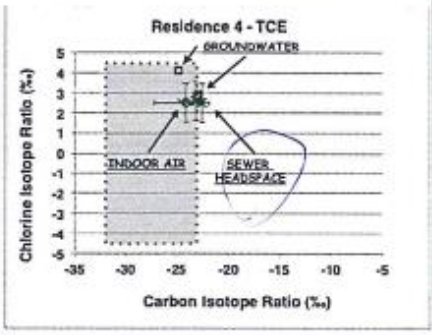


FINDING:

PCE in indoor air is from indoor source.

(Source later identified as E6000 glue)

RESULTS FOR INDOOR AIR



FINDING:

GW with TCE discharged into sewers.

TCE is moving from sewer into house.

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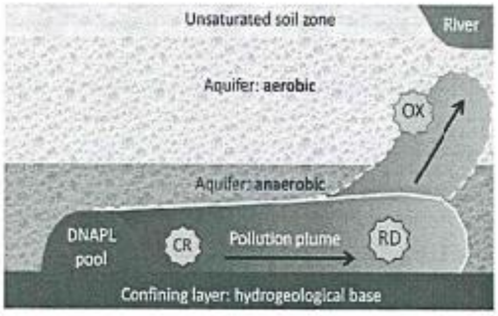
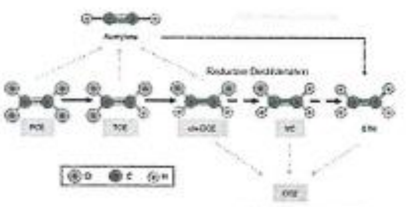
Reactive Transport Model (RTM) Incorporating Isotope Fractionation

- *Success and acceptance of MNA depends on strong conceptual site model (CSM) documenting attenuation processes and contaminant mass removal using multiple lines of evidence*
- For many sites, decreasing mass, the presence of intermediate degradation products, low oxygen concentrations, and favorable geochemical indicators (e.g., nitrate, sulfate, alkalinity etc.) are sufficient to support selection of a full or partial MNA remedy.
- In the absence of some or all of these lines of evidence, MNA remedies can be difficult to implement.
- CSIA provides strong evidence to support MNA assessment and strengthen CSMs.

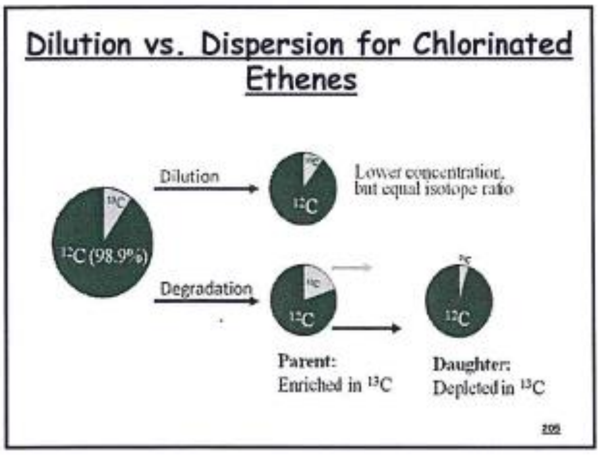
Potential Degradation Pathways for Chlorinated Ethenes



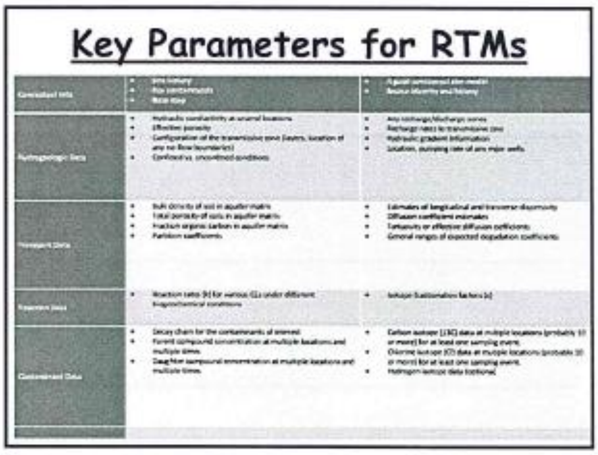
Degradation Pathways of Chlorinated Ethenes



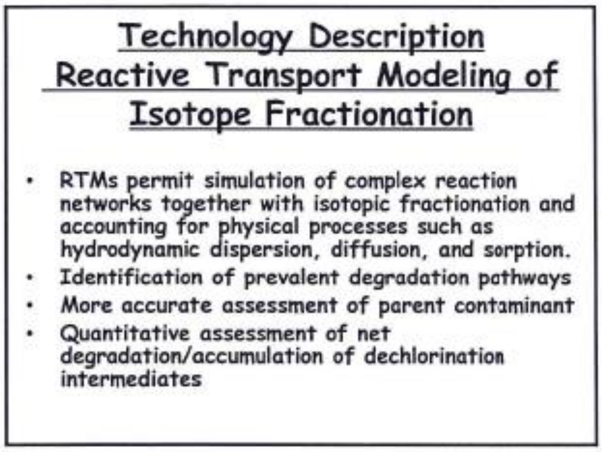
Primary degradation processes in a reaction network for chlorinated ethene degradation. Anaerobic degradation pathway is dominant for most sites with MNA remedies. Each pathway needs to be quantified.



Dilution vs. Dispersion for Chlorinated Ethenes

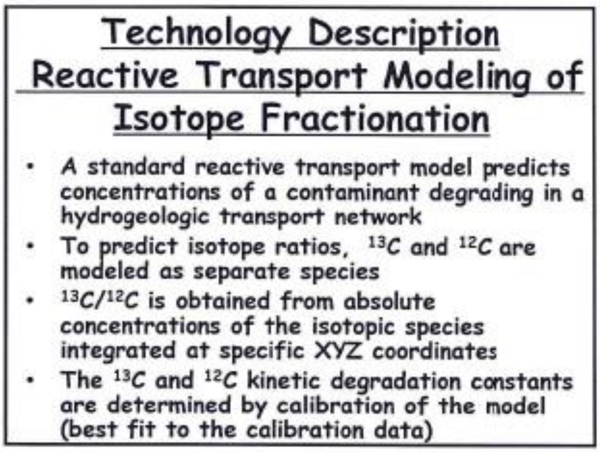


Key Parameters for RTMs



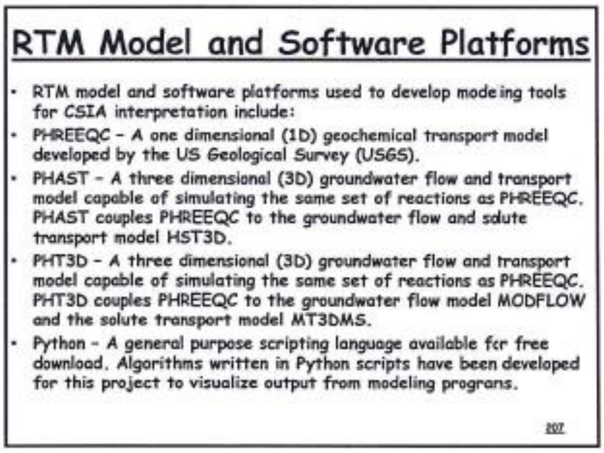
Technology Description
Reactive Transport Modeling of Isotope Fractionation

- RTMs permit simulation of complex reaction networks together with isotopic fractionation and accounting for physical processes such as hydrodynamic dispersion, diffusion, and sorption.
- Identification of prevalent degradation pathways
- More accurate assessment of parent contaminant
- Quantitative assessment of net degradation/accumulation of dechlorination intermediates



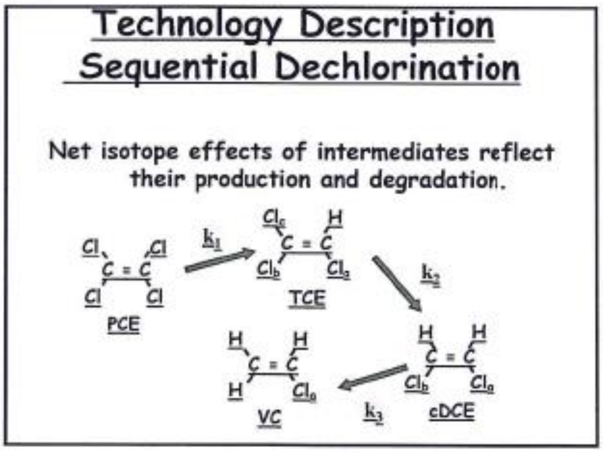
Technology Description
Reactive Transport Modeling of Isotope Fractionation

- A standard reactive transport model predicts concentrations of a contaminant degrading in a hydrogeologic transport network
- To predict isotope ratios, ^{13}C and ^{12}C are modeled as separate species
- $^{13}C/^{12}C$ is obtained from absolute concentrations of the isotopic species integrated at specific XYZ coordinates
- The ^{13}C and ^{12}C kinetic degradation constants are determined by calibration of the model (best fit to the calibration data)



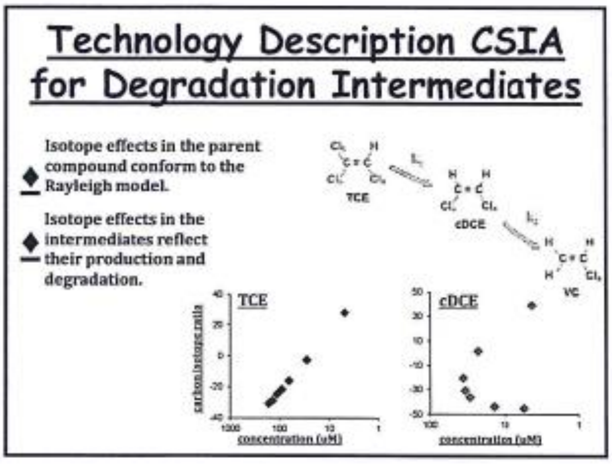
RTM Model and Software Platforms

- RTM model and software platforms used to develop modeling tools for CSIA interpretation include:
- PHREEQC – A one dimensional (1D) geochemical transport model developed by the US Geological Survey (USGS).
- PHAST – A three dimensional (3D) groundwater flow and transport model capable of simulating the same set of reactions as PHREEQC. PHAST couples PHREEQC to the groundwater flow and solute transport model HST3D.
- PHT3D – A three dimensional (3D) groundwater flow and transport model capable of simulating the same set of reactions as PHREEQC. PHT3D couples PHREEQC to the groundwater flow model MODFLOW and the solute transport model MT3DMS.
- Python – A general purpose scripting language available for free download. Algorithms written in Python scripts have been developed for this project to visualize output from modeling programs.



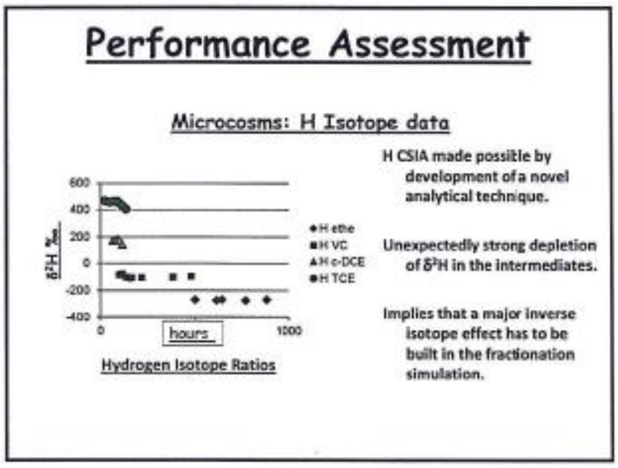
Technology Description
Sequential Dechlorination

Net isotope effects of intermediates reflect their production and degradation.



Technology Description CSIA for Degradation Intermediates

- Isotope effects in the parent compound conform to the Rayleigh model.
- Isotope effects in the intermediates reflect their production and degradation.



Performance Assessment

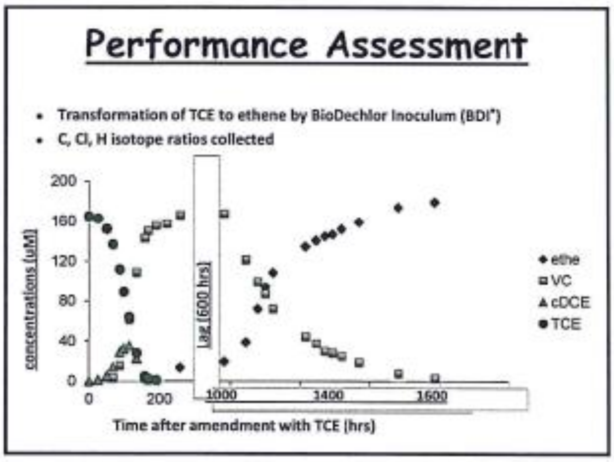
Microcosms: H Isotope data

H CSIA made possible by development of a novel analytical technique.

Unexpectedly strong depletion of δ^2H in the intermediates.

Implies that a major inverse isotope effect has to be built in the fractionation simulation.

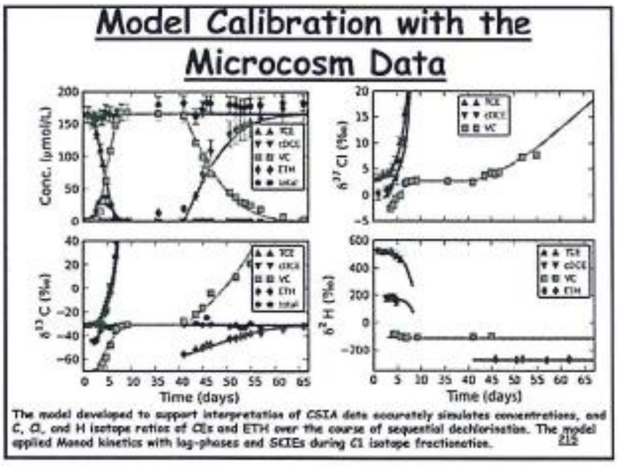
Hydrogen Isotope Ratios



Performance Assessment

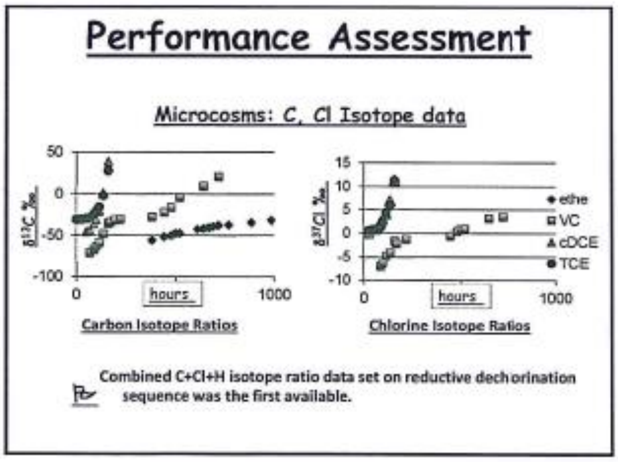
- Transformation of TCE to ethene by BioDechlor Inoculum (BDI®)
- C, Cl, H isotope ratios collected

Time after amendment with TCE (hrs)



Model Calibration with the Microcosm Data

The model developed to support interpretation of CSIA data accurately simulates concentrations, and C, Cl, and H isotope ratios of CEs and ETH over the course of sequential dechlorination. The model applied Monod kinetics with lag-phases and SKIEs during Cl isotope fractionation. 215



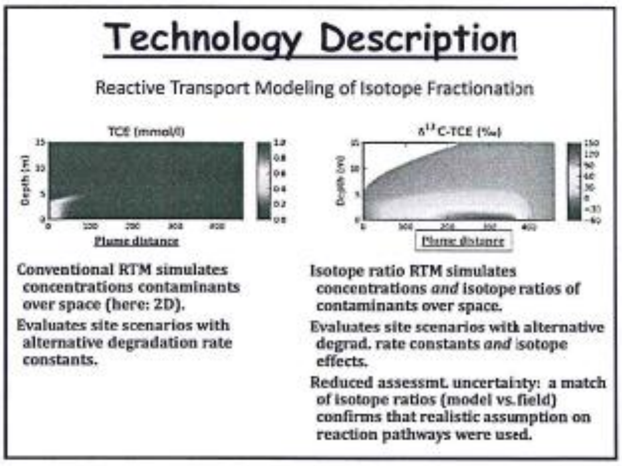
Performance Assessment

Microcosms: C, Cl Isotope data

Carbon Isotope Ratios

Chlorine Isotope Ratios

Combined C+Cl+H isotope ratio data set on reductive dechorination sequence was the first available.



Technology Description

Reactive Transport Modeling of Isotope Fractionation

TCE (mmol/l)

δ^{13}C-TCE (‰)

Conventional RTM simulates concentrations contaminants over space (here: 2D).

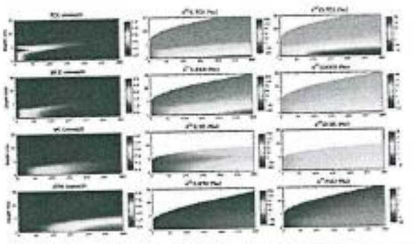
Evaluates site scenarios with alternative degradation rate constants.

Isotope ratio RTM simulates concentrations *and* isotope ratios of contaminants over space.

Evaluates site scenarios with alternative degrad. rate constants *and* isotope effects.

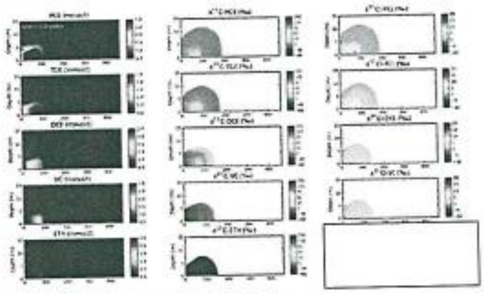
Reduced assessmt. uncertainty: a match of isotope ratios (model vs. field) confirms that realistic assumption on reaction pathways were used.

Model Simulation Results

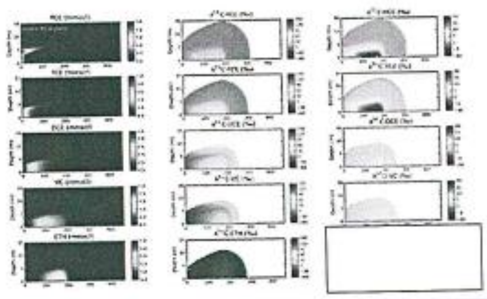


Results of 2-D PHT3D simulation for C-Cl isotope fractionation following reductive dechlorination (TCE to ETH) in the core of the plume and aerobic oxidation of VC at the fringe.

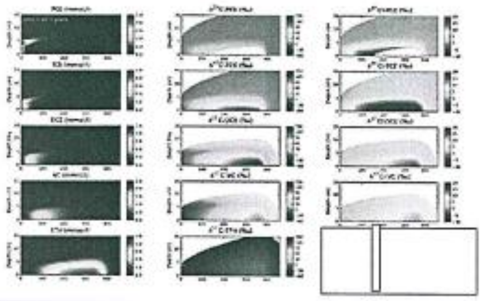
2-D PHAST Simulation.Time=5 yrs



2-D PHAST Simulation.Time=10yrs



2-D PHAST Simulation.Time=20 yrs



SUMMARY

GC, GCMS
IRMS combine

- Stable isotopes provide a powerful complimentary tool for the correlation of spilled products in the environment with suspected sources.
- Can be used to evaluate onset of natural attenuation and extent of degradation.
- Isotopes can play a valuable role in remediation studies in furthering the understanding of degradation mechanisms.
- Can distinguish biogenic, abiogenic mechanisms from non-degradative processes causing concentration changes.

SUMMARY

- GC and GCMS already widely used techniques in forensic geochemistry
- For refined products, or those not containing biomarkers, need an alternative approach
- Stable isotopes (C,H, and Cl) of individual compounds are, and will continue to develop as, extremely important tools for forensic studies