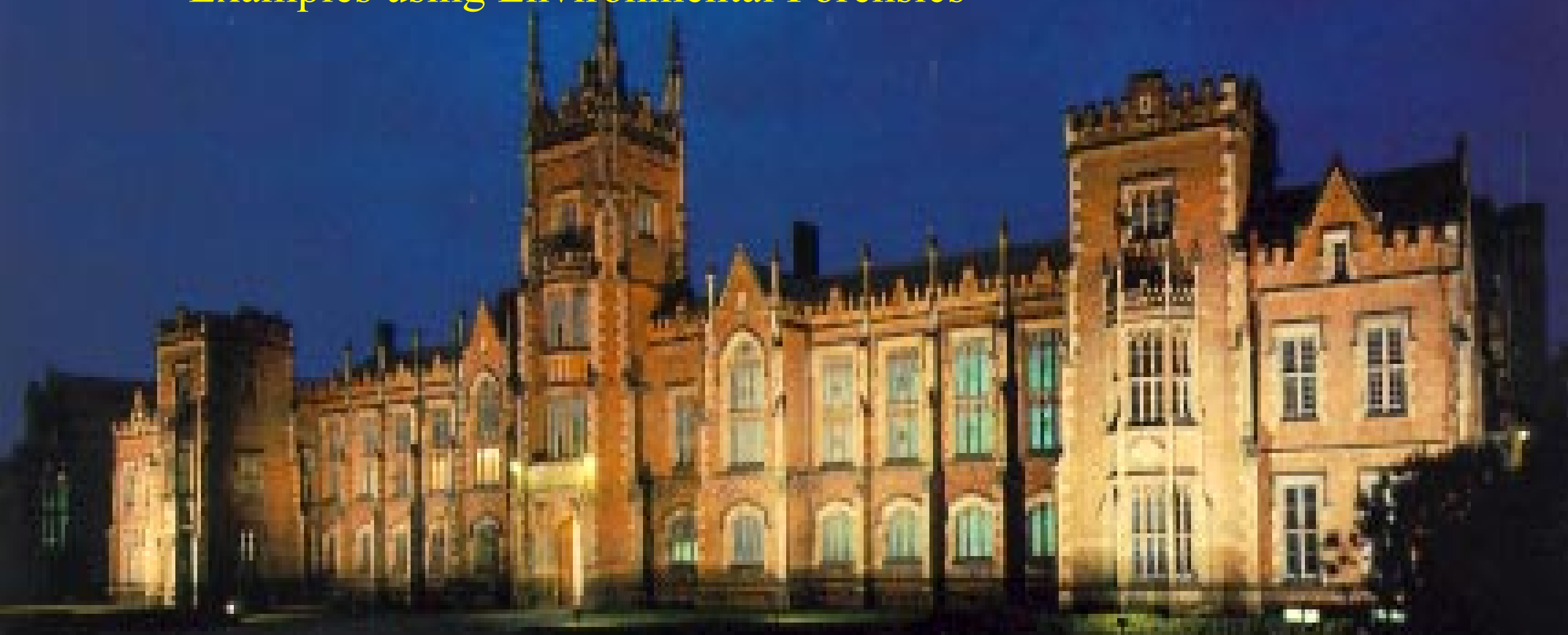


Isotopes as a Tool to Evaluate Abiotic and Biochemical Reactions

Complicating Issues for Forensic Applications of IRMS:

Examples using Environmental Forensics



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(with lots and lots of collaborators)



Forensics Applications:

Environment

^{14}C , ^{13}C , ^{18}O , D/H, ^{15}N , ^{34}S

Art

Carbonates ^{13}C , ^{18}O

Canvass ^{13}C , ^{18}O , D/H

Age ^{14}C , Bomb ^{14}C

Food Adulteration

^{14}C , ^{13}C , ^{18}O , D/H

Death

Bomb ^{14}C



Forensic Application

What is initial isotope content?

Does it change during abiotic or biological rxn?

If it does change, can this change be used?

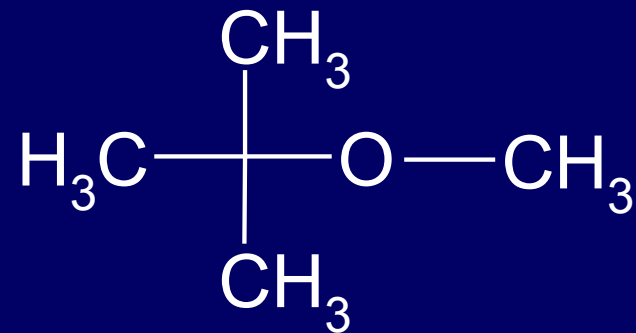
Does any change relate to a process that can be used
to understand a biologic mechanism?

Can we use these changes to confirm or refute
a hypothesised reaction?



Environmental Forensics

MTBE



First Example: Methyl Tert-Butyl Ether

Slight variation in MTBE ^{13}C from analysis
Of ca. 80 gasoline samples globally (few permil)

Is this conservative in nature?

Abiotic Reactions

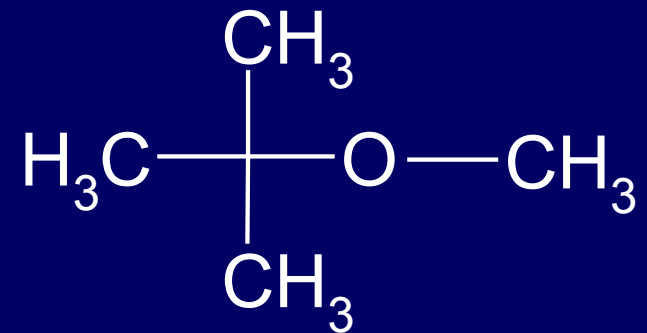
Microbial Reactions



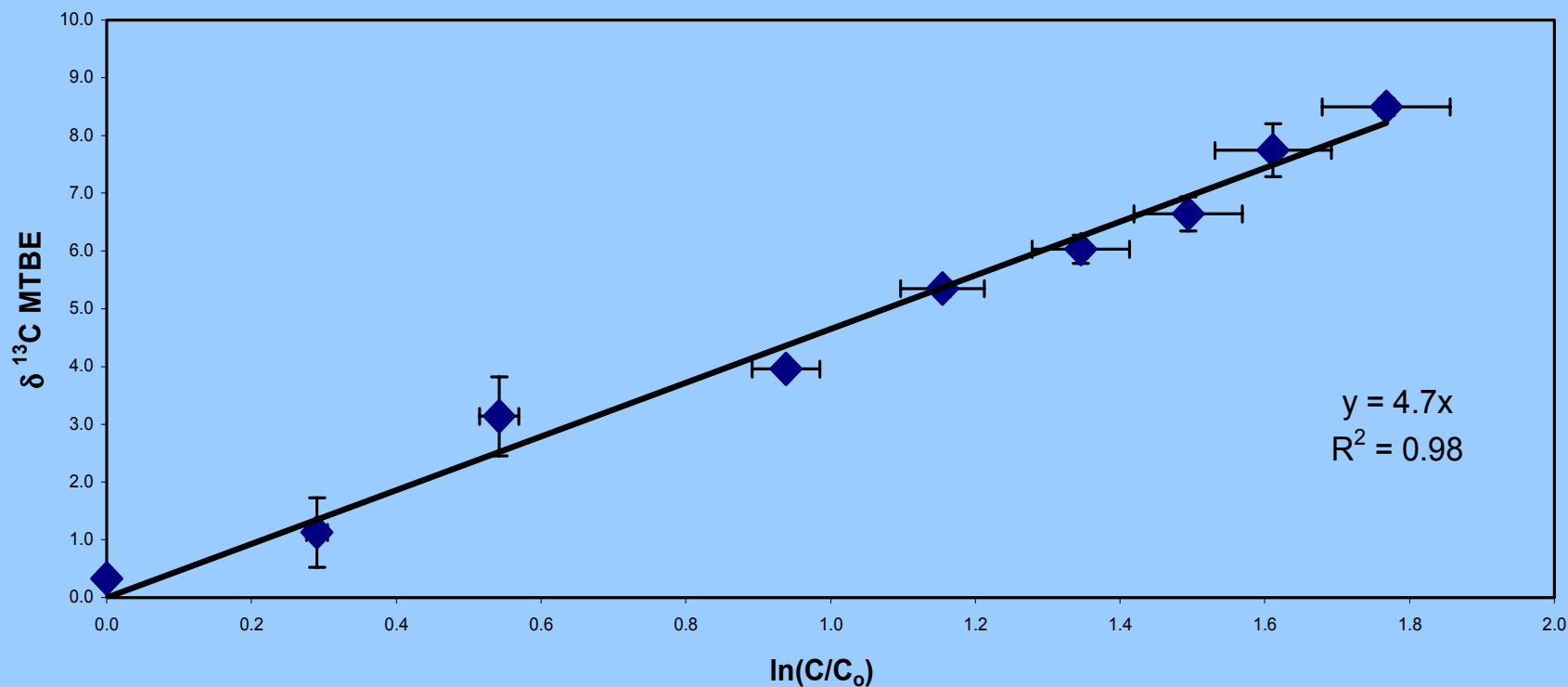


Environmental Forensics

MTBE Oxidation 10 permil change



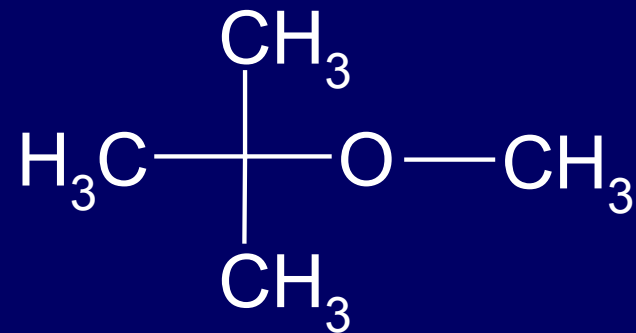
Abiotic Degradation of MTBE by KMnO_4





Environmental Forensics

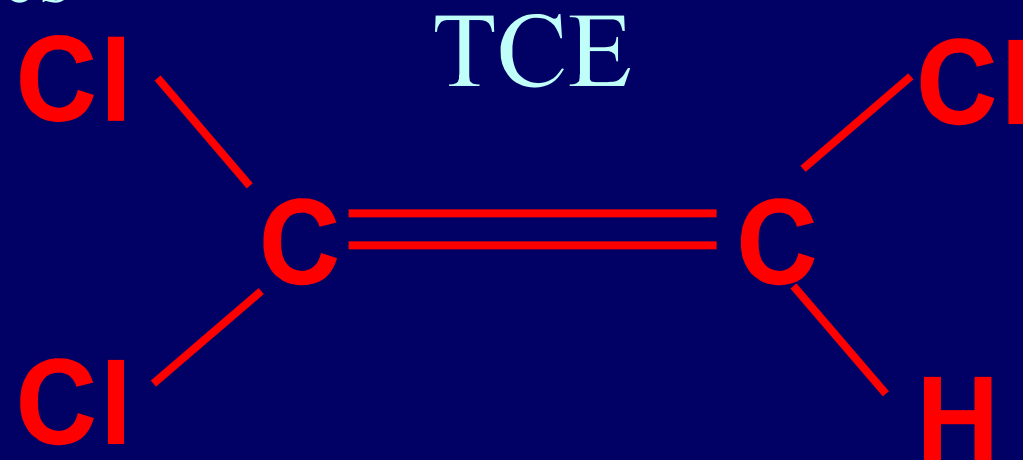
MTBE Carbon Isotopes



- Microbial Fractionation Waterloo
 - $\epsilon = 1.5$ to 2.0 (?) (5 permil)
- Microbial Fractionation UC Davis
 - $\epsilon = 2.0$ to 2.4 (pure culture) (8 permil)
 - $\epsilon = 1.5$ to 1.8 (consortia) (5 permil)
- Microbial Fractionation Belfast
 - $\epsilon = 0$ Field Isolated consortia (0 permil)
 - $\epsilon = 4.7$ abiotic reactions (10 permil)



Environmental Forensics



Globally quite a few studies

Abiotic

Anaerobic

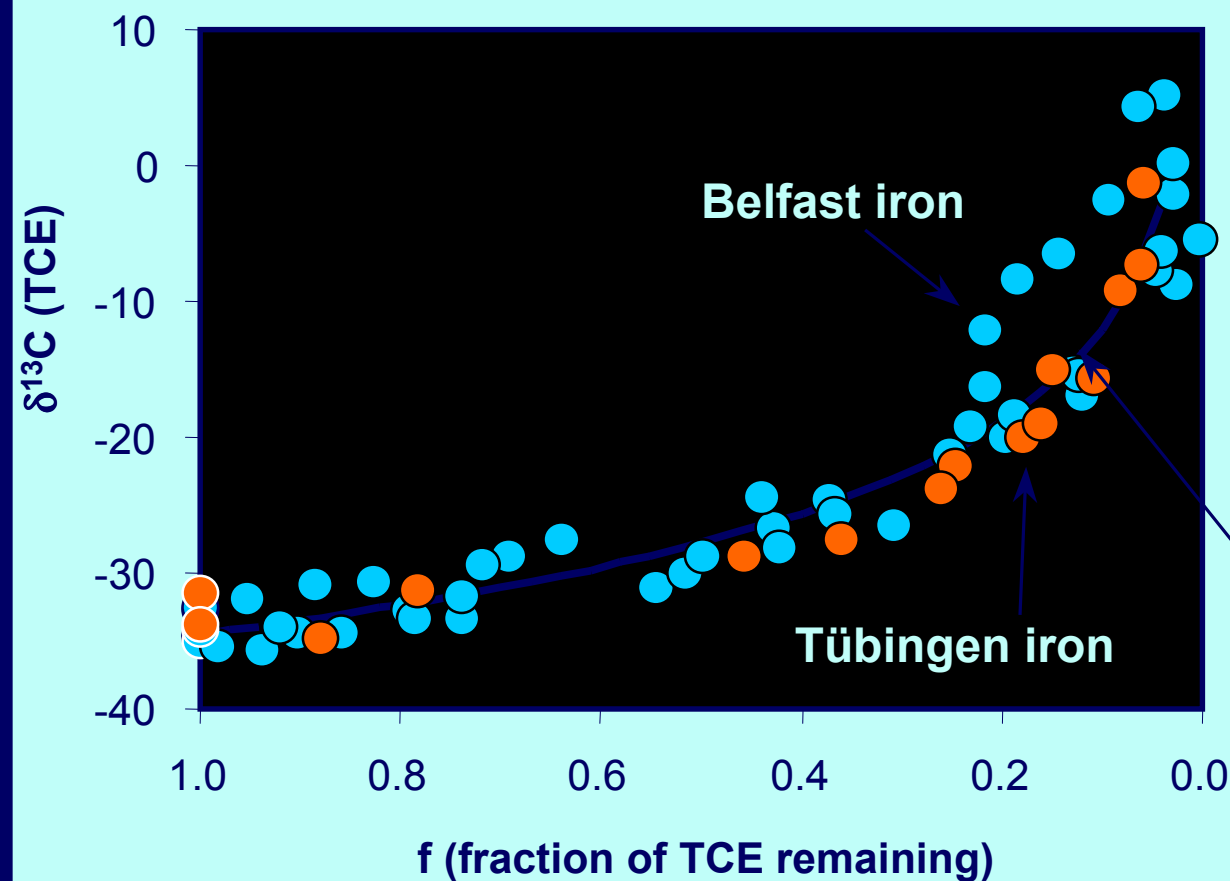
Aerobic

Field Based & Lab Based



Environmental Forensics

TCE Degradation with Fe^0 – Isotopes



9 independently performed experiments with different reaction rates and different types of iron

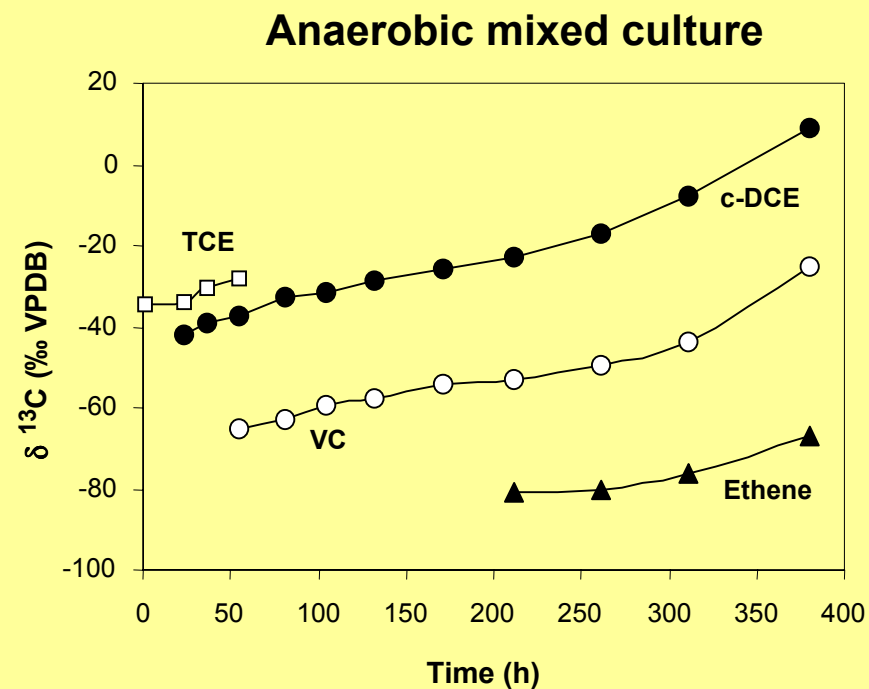
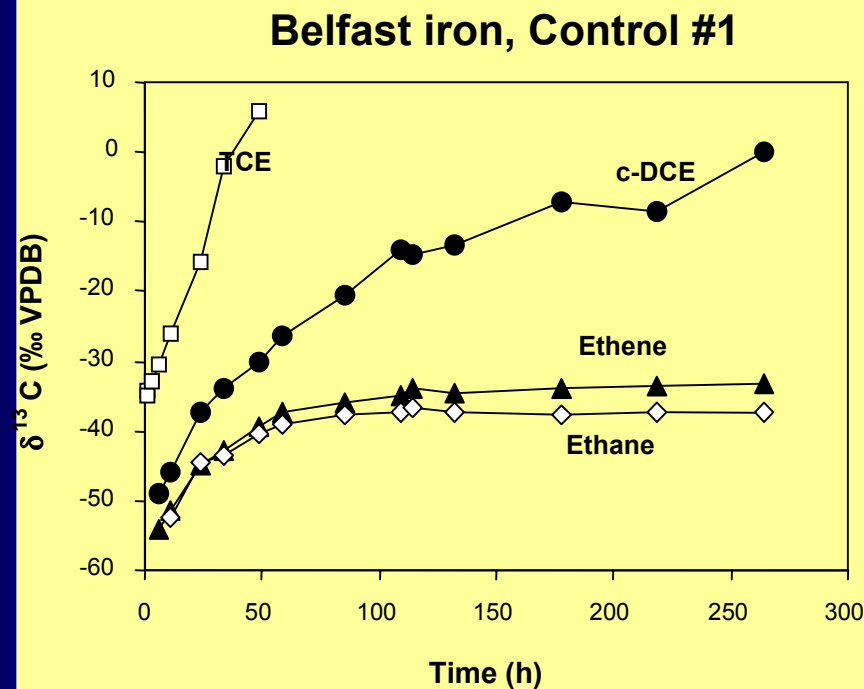
$$\varepsilon = \frac{1000 \cdot \ln \frac{10^{-3} \cdot \delta^{13}\text{C}_{\text{TCE}} + 1}{10^{-3} \cdot \delta^{13}\text{C}_{\text{TCE}(0)} + 1}}{\ln f}$$

$$\varepsilon = -10$$



Environmental Forensics

TCE Degradation with Fe^0 and Anaerobes



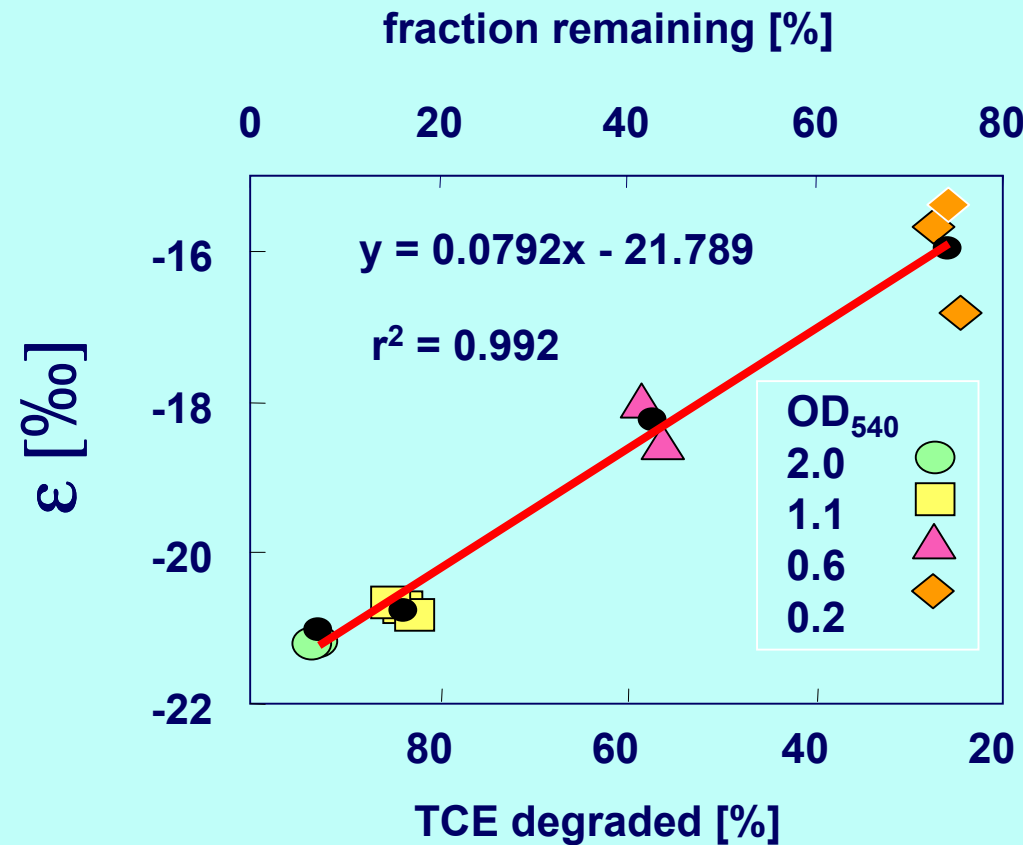
Abiotic anaerobic

Microbial anaerobic



Environmental Forensics

AEROBIC TCE DEGRADATION with *Burkholderia* *Cepacia G4*



Fractionation
f (cell biomass)



Environmental Forensics

TCE

- Abiotic different from microbial
- Anaerobic different from aerobic
- Co metabolic depends on cell biomass
(enzyme activity / concentration?)

How might we use this knowledge?





Environmental Forensics

What about more complicated systems?

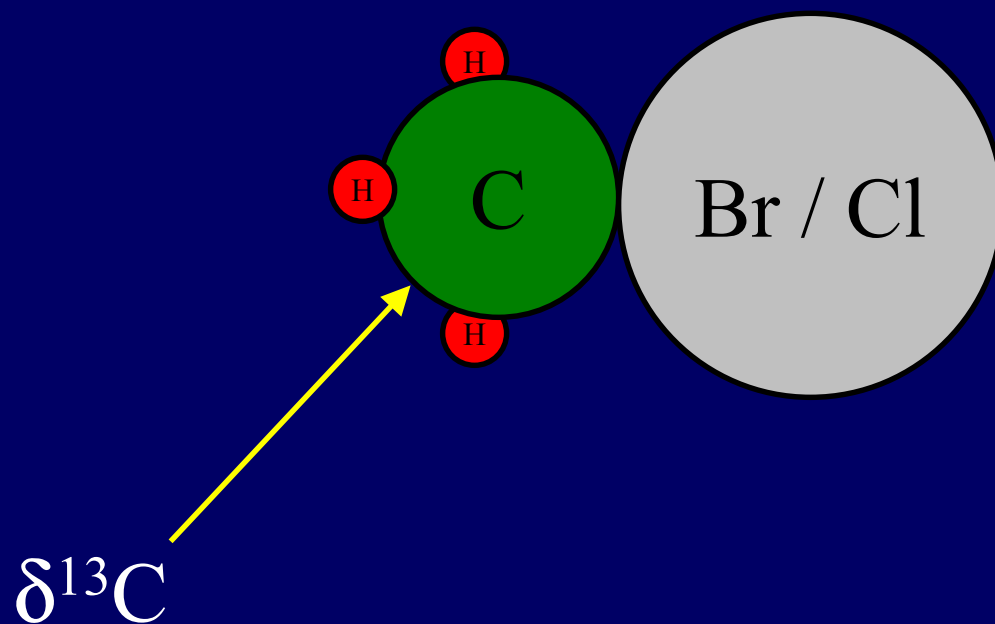
Need more knowledge of all abiotic and biologically mediated reactions to evaluate those reactions that have the greatest affect on the residual concentration and isotopic composition of the compound of interest.

Example: Halomethanes





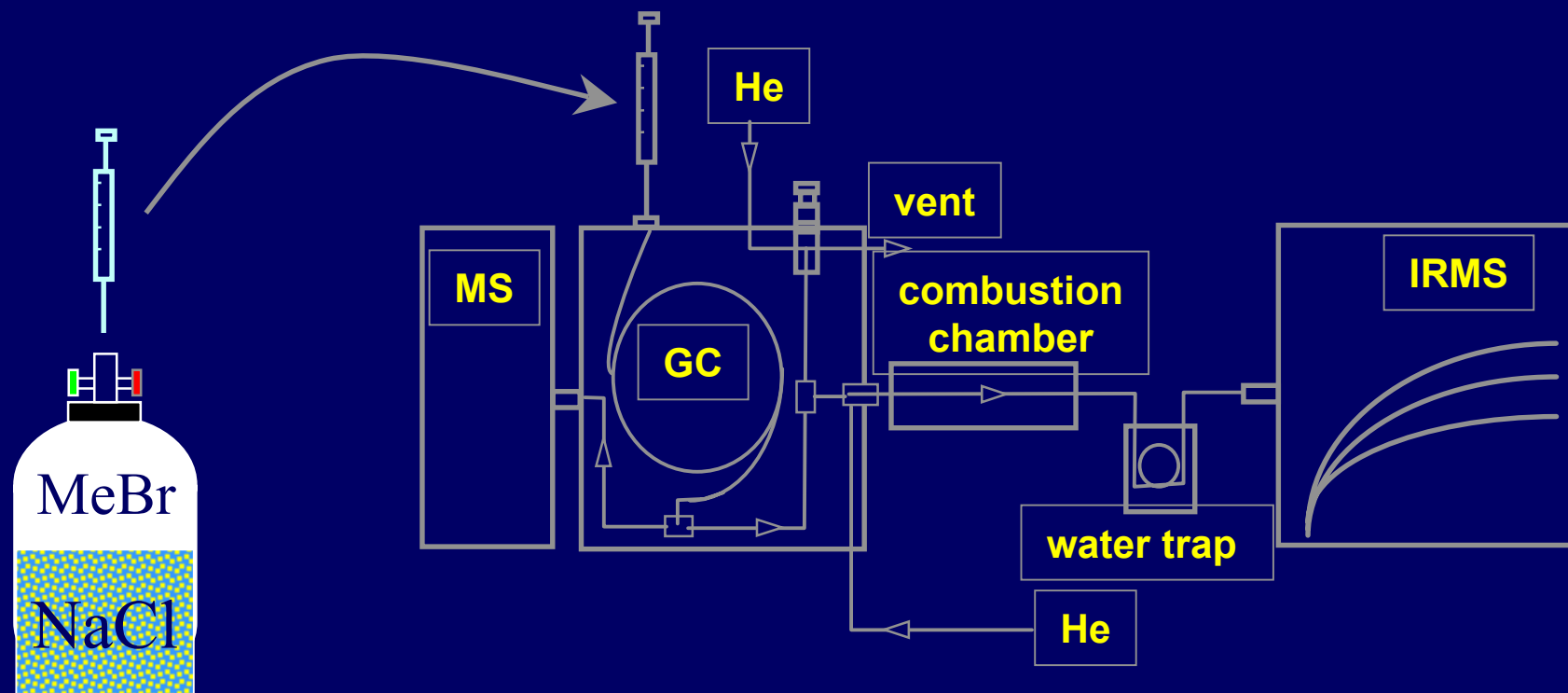
Environmental Forensics





Environmental Forensics

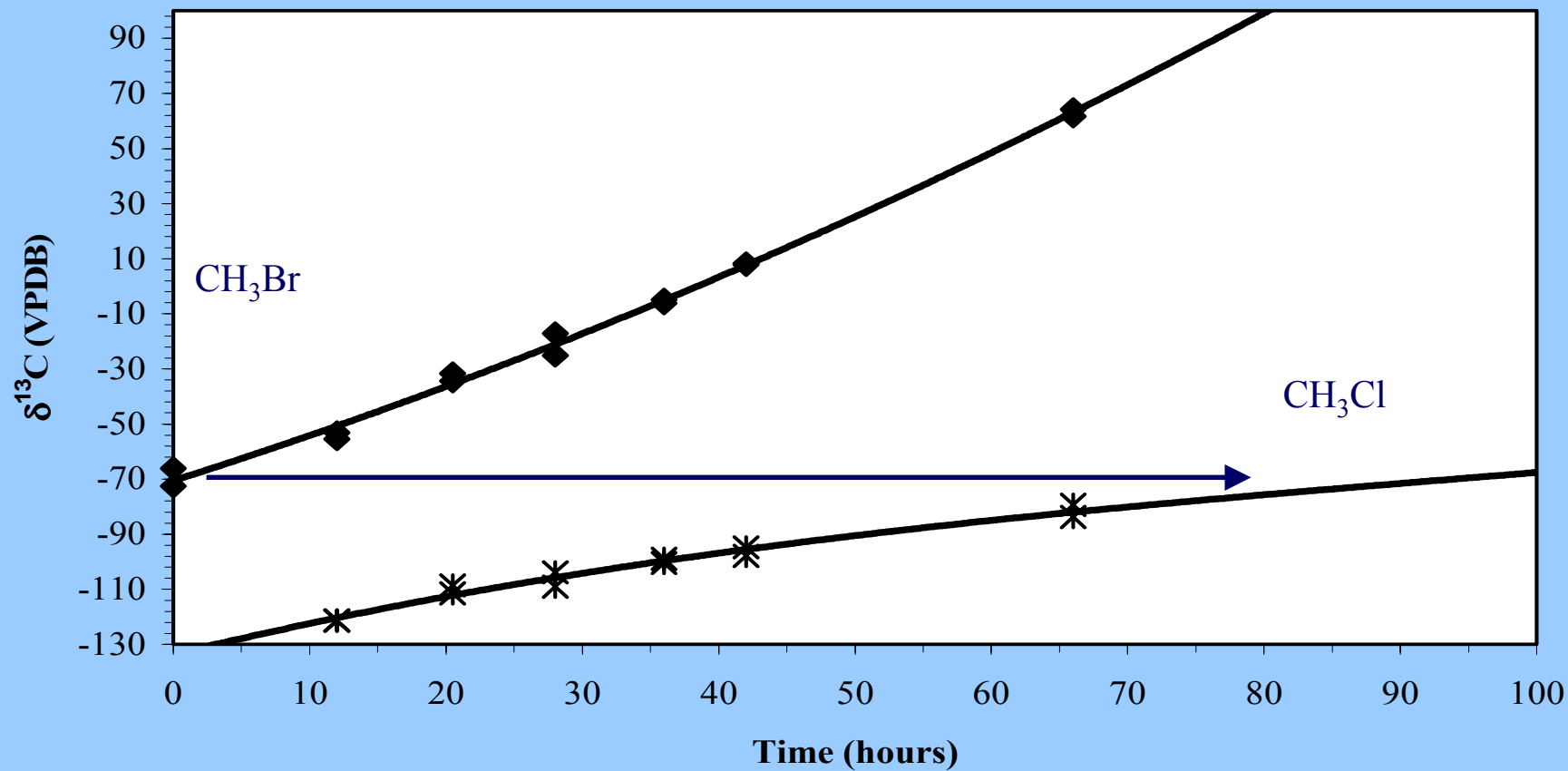
Abiotic Transhalogenation Experiments





Environmental Forensics

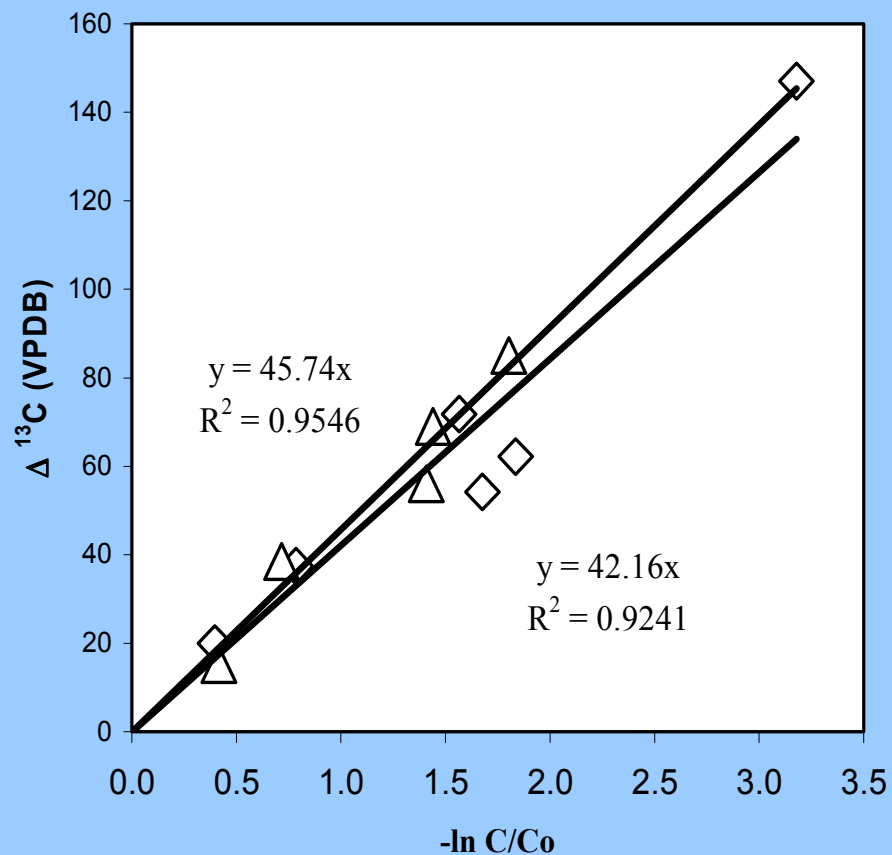
Abiotic Transhalogenation of CH_3Br to CH_3Cl



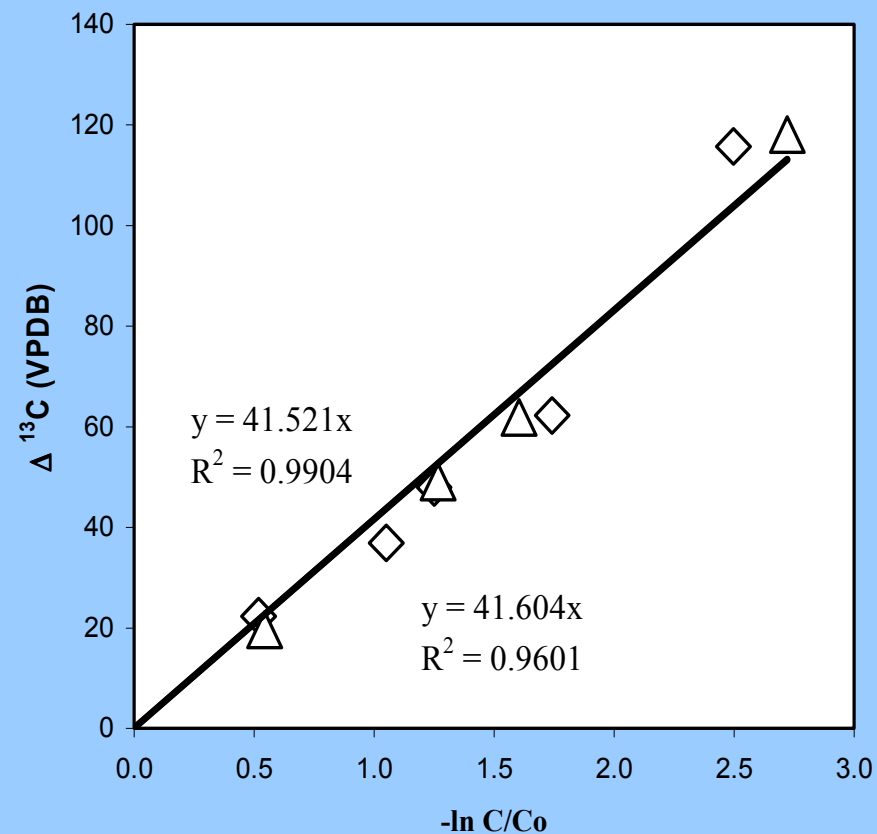


KIE – Replicate Experiments Reproducible

Abiotic Transhalogenation of CH_3Br to CH_3Cl
(35°C)

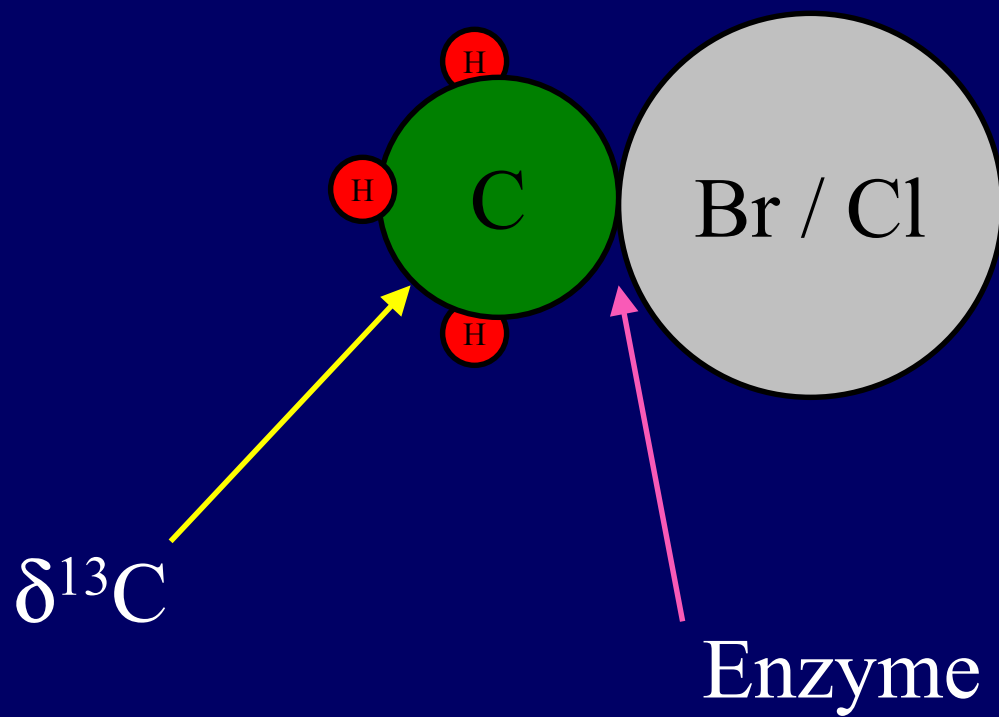


Abiotic Transhalogenation of CH_3Br to CH_3Cl
(35°C)





Environmental Forensics

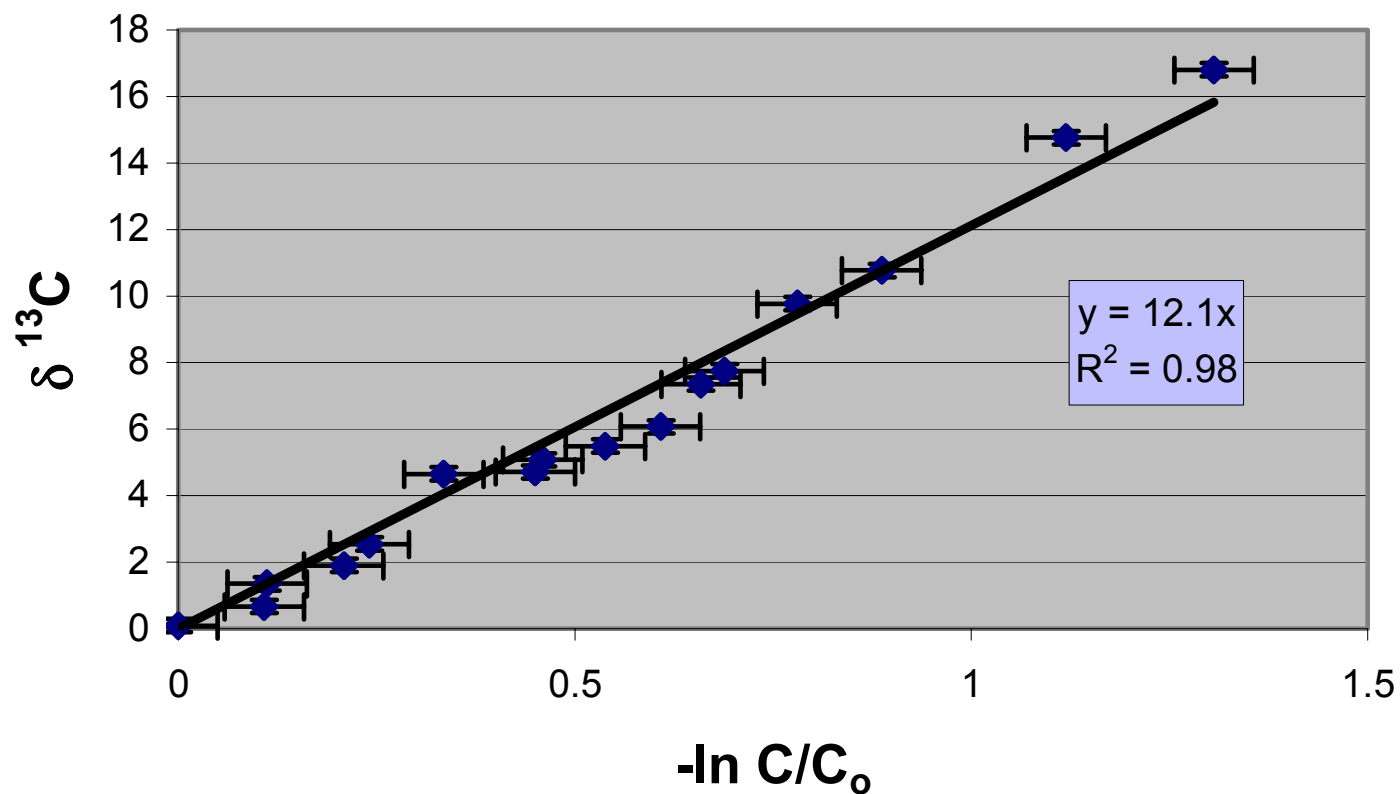


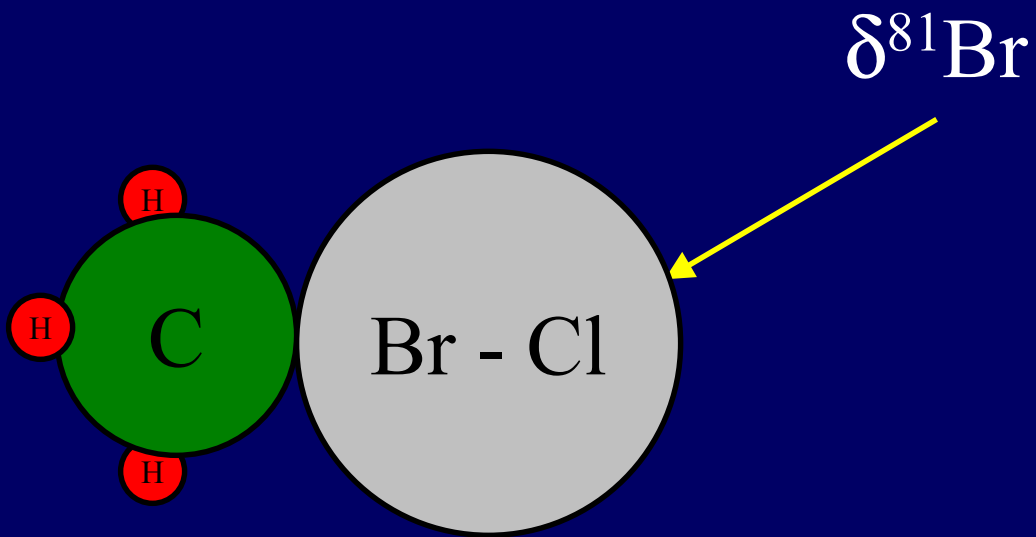


Abiotic ε – 42

Enzyme ε - 12

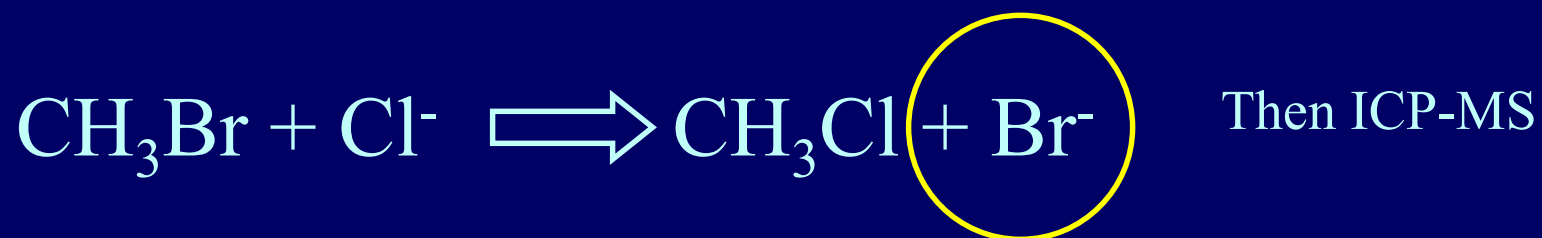
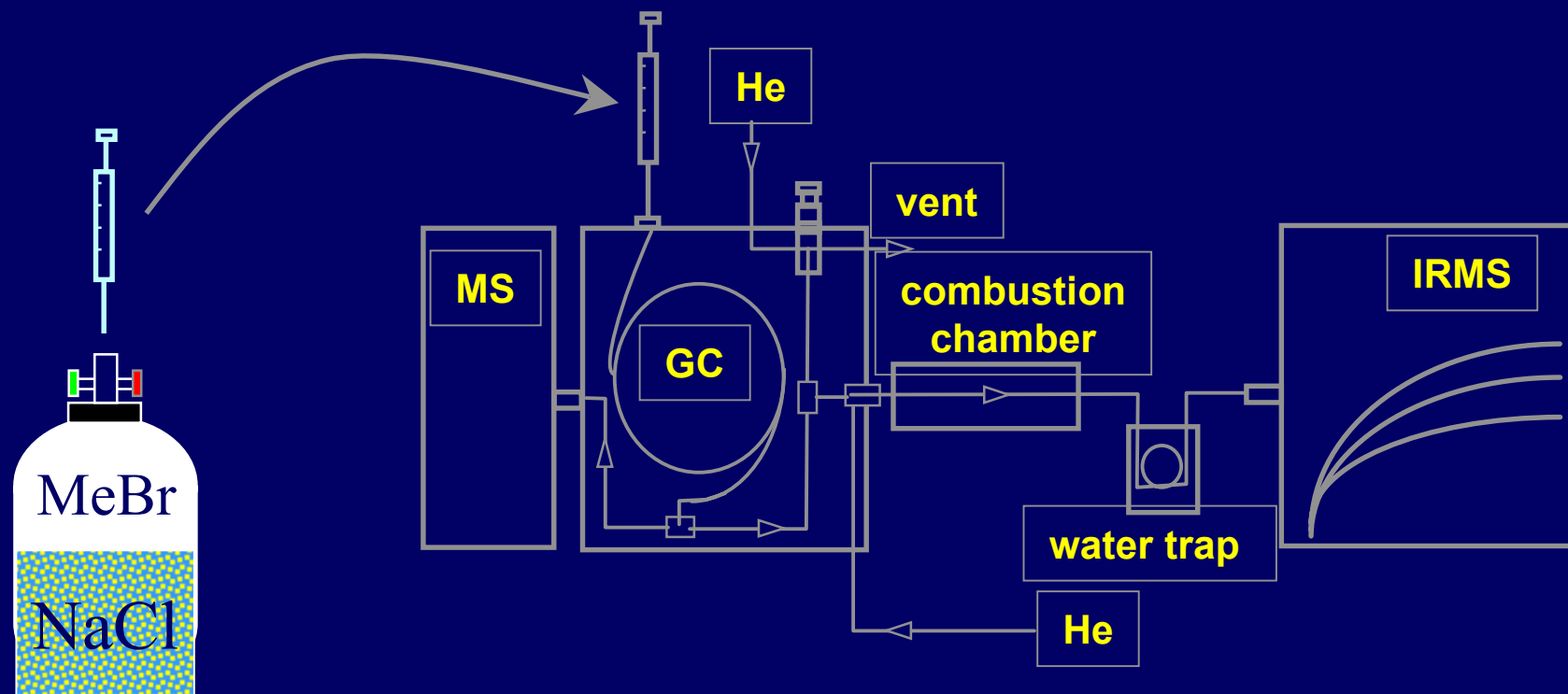
KIE MeBr to MeCl CC495 Enzyme







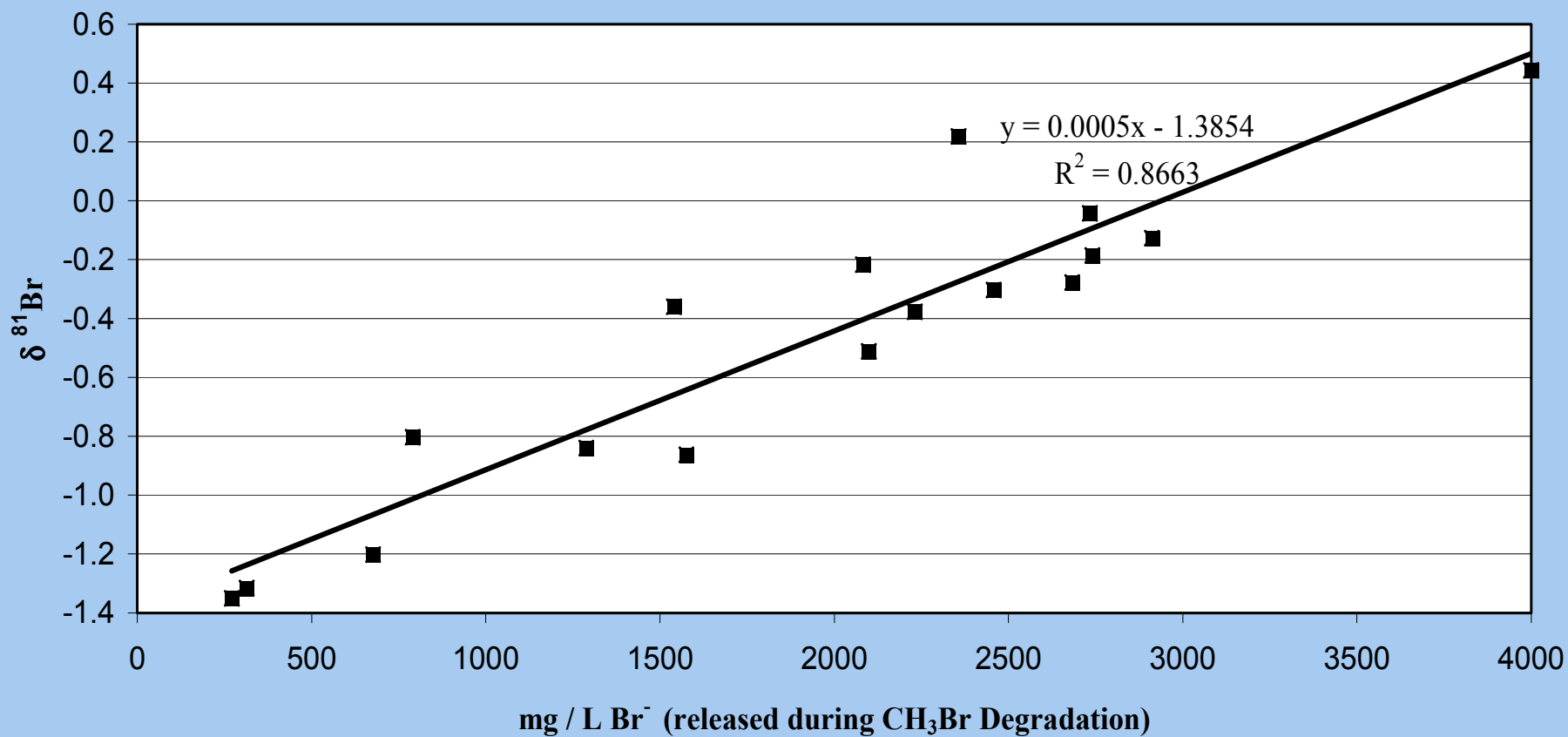
Abiotic Transhalogenation Experiments





Environmental Forensics

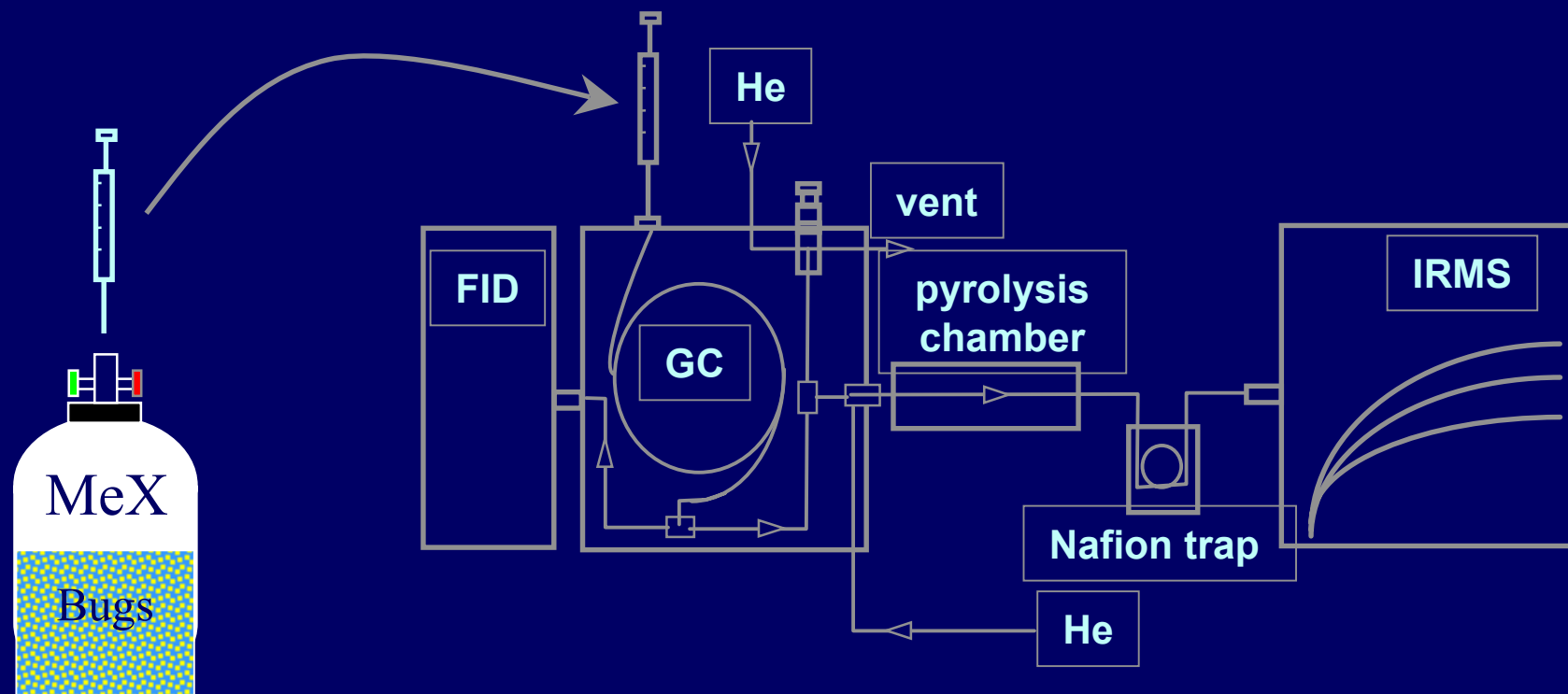
Bromine Isotope Fractionation During CH_3Br Abiotic Transhalogenation





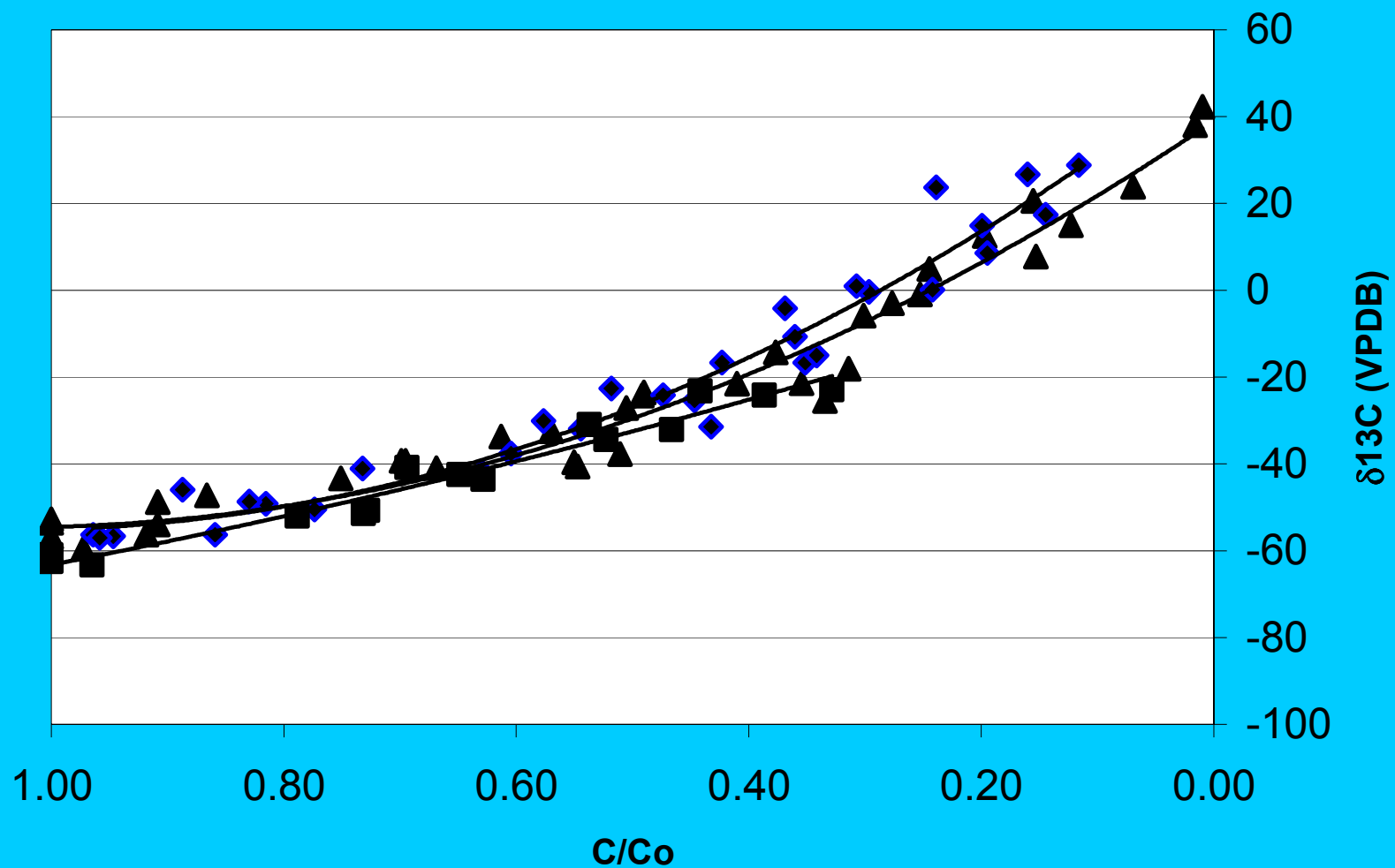
Environmental Forensics

Microbial Experiments



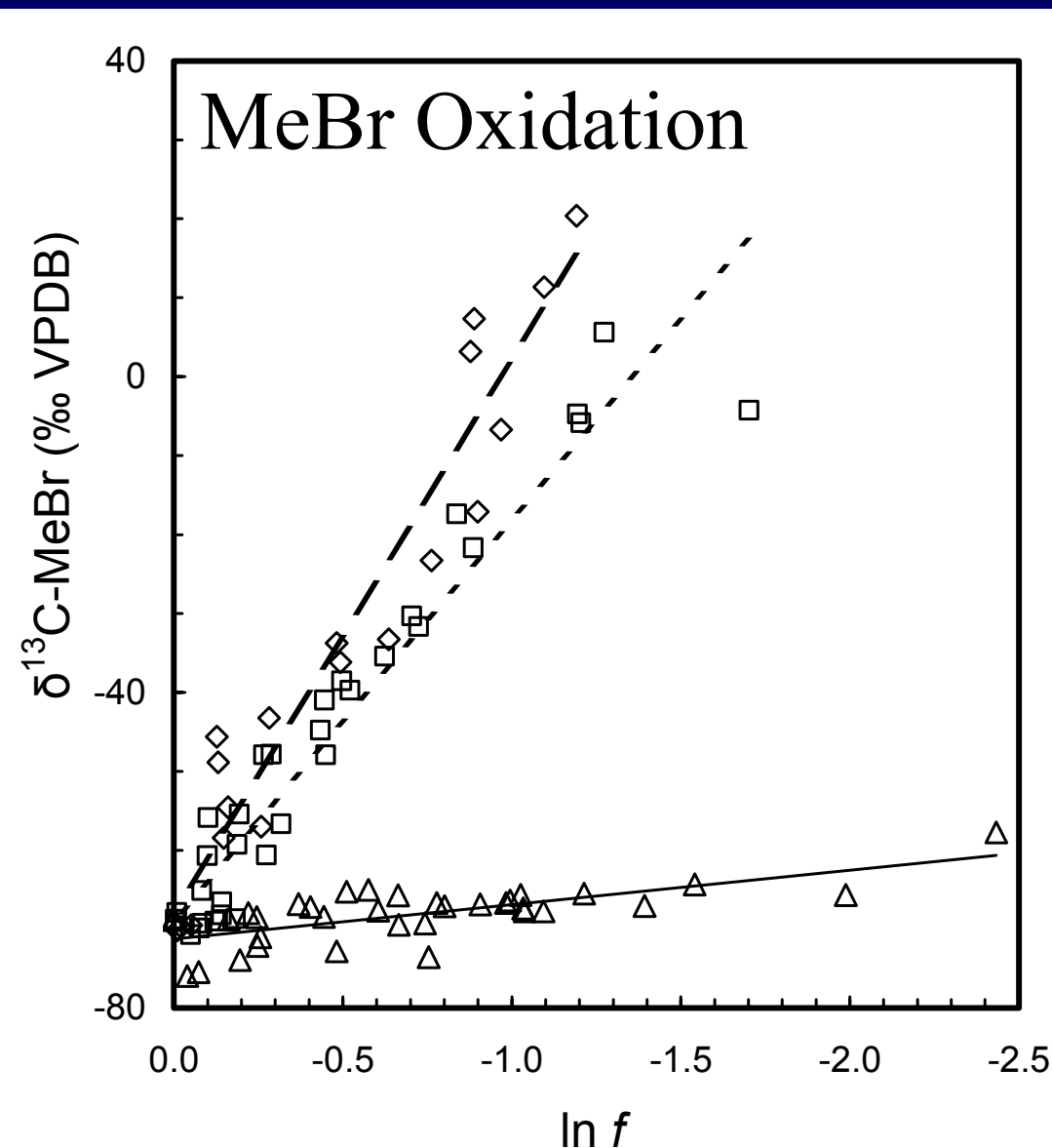


MeCl oxidation by IMB-1, CC495 & MB2





Rate limiting
Step is not
expressed in
CC495 for
MeBr
oxidation,
Thus isotope
Fractionation
is not
observed.





Abiotic and biologically mediated reactions can change the isotopic composition of target compounds

Care must be taken to determine if a degradation reaction has taken place or not

When degradation has taken place the changes in isotope composition should be evaluated

Isotope changes can be used as both positive and null hypothesis result.



Current research of interest & discussion here

P450s and human metabolism

Metabolite 'chain' studies

Specific functional groups

Better analysis for pg samples?

(eg. when can we do 0.1% on Quad or TOF?)



Current research direction at QUB 2002 - 2007

DNA Array – Microbial Genetics & Ecology

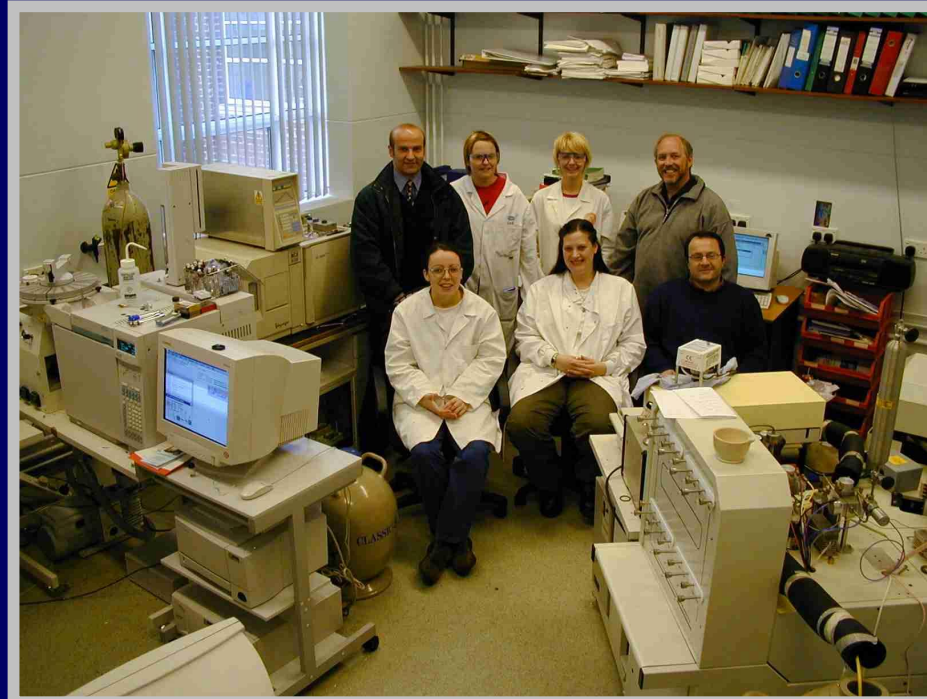
Biogeochemistry – Compounds and Metabolites

Isotope Biochemistry – Validation of Pathways

= Validated understanding of fate of compounds
in the natural environment



Any Questions



Acknowledgements:

This research has been supported by in part by the following UK EPSRC grants GR/L85183, GR/M26374, GR/M32139, GR/M91693, GR/N31856/01, and by UK NERC. Thanks to all those past and present who work at QUB in isotope biogeochemistry and who have provided help to this work.