Structure and reactivity of dissolved organic matter as determined by ultra-high resolution electrospray ionization mass spectrometry

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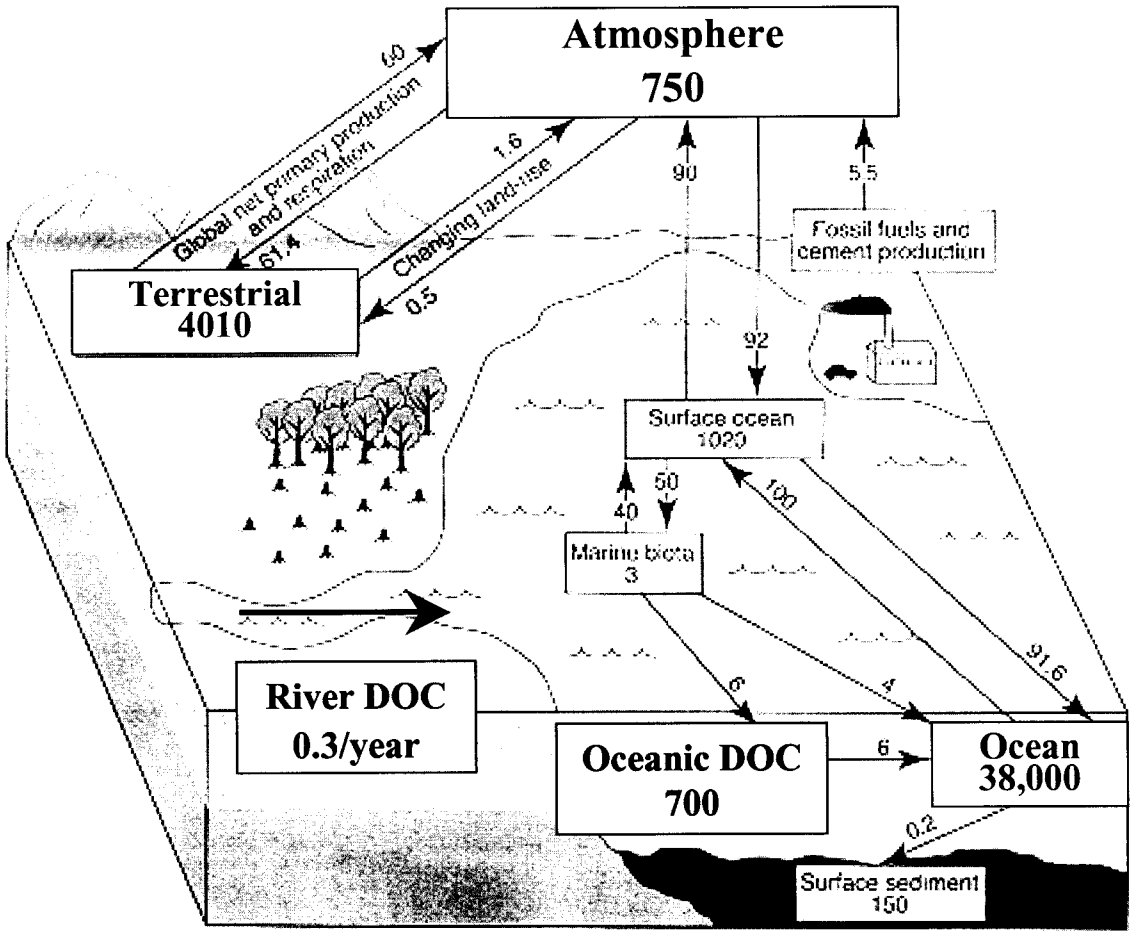
Overview

- Understanding of the riverine dissolved organic matter (DOM) is important however little is known about this material in a molecular level.
- Riverine DOM is a major source of carbon flow to the oceans and plays an important role in the global cycle of carbon.

A riddle in a global carbon cycle



- **0.3 Gt of carbon is large enough to sustain the turnover of the entire ocean**
- **However, a little resemblance was found between two carbon pools.**
- **Low amount of lignin phenol (terrestrial bio-marker) exists in oceanic DOC pool.***
- **$\delta^{13}C$ isotope signatures are different.**

(units: Gt)

Adapted from Houghton *et. al.* Climate change 1994 (1995), Cambridge Press, New York

* Meyers-Schuttle & Hedges, Nature (1986), **321**, 61-63

Isolation of DOM from natural river water samples

How to isolate the DOM?

XAD extraction	Established method	Final elution include salt – dialysis necessary Large volume of chemical
Ultrafiltration	Fractionation possible	Large amount of sample Requires instrument
Freezedrying	Not-selective	Takes a long time Concentrate salts too

How to isolate DOM from river water?

- Disk type C_{18} solid phase extraction

Benefits

1. Faster extraction
2. Simple experiment setup
3. easily handle small amount of sample

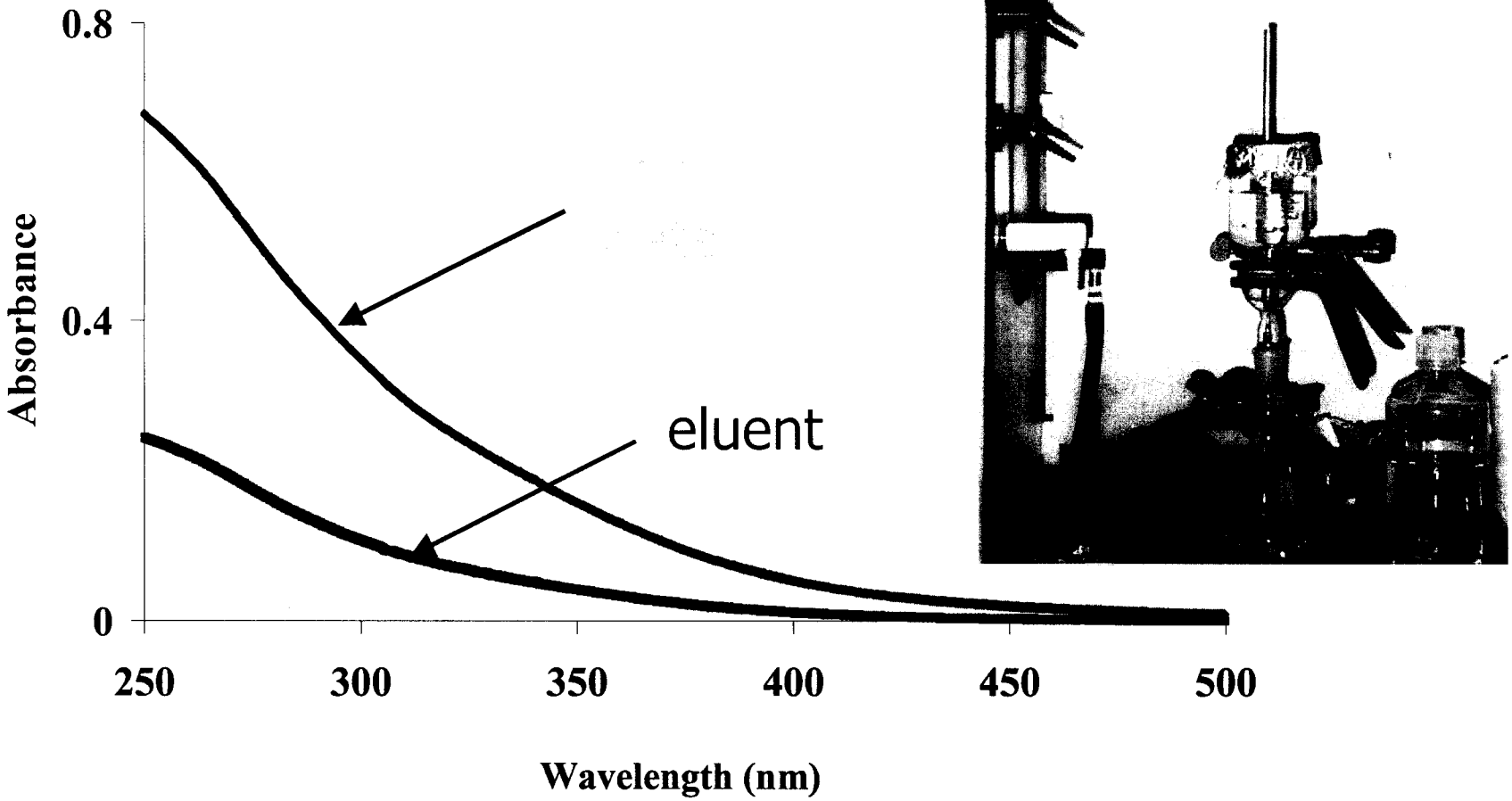
Questions to be answered

1. Retention rate?
2. Does collected sample reflect DOM in river?

Louchouarn, P.; Opsahl, S.; Benner, R.;(2000), Anal. Chem. 72, 2780-2787

Retention rate?

Retention rate of ~ 70 %



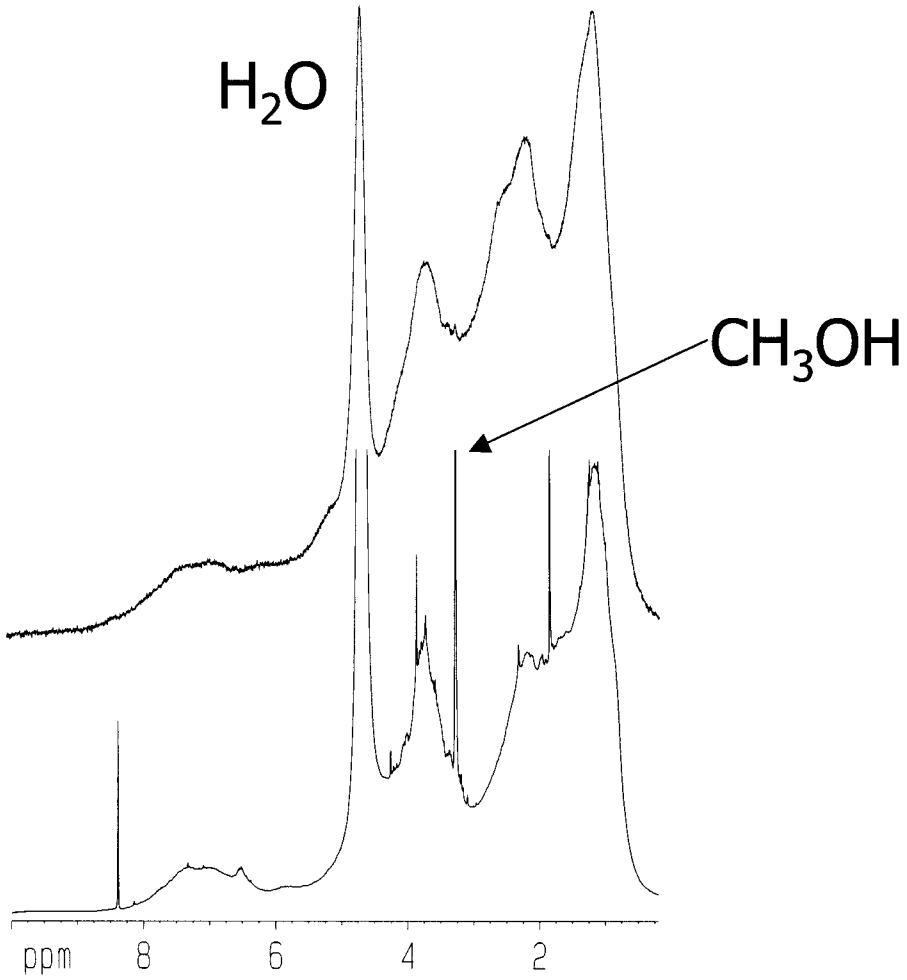
Does final eluent reflect the DOM in river?

DOM acquired

by freeze drying

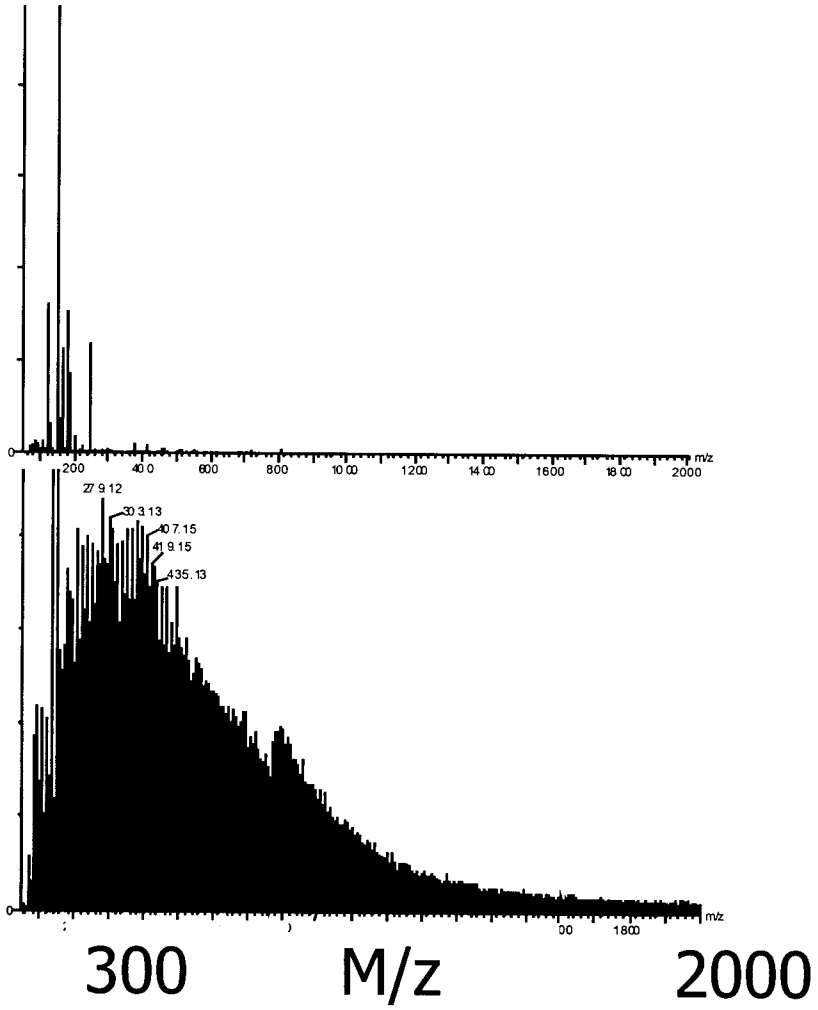
DOM acquired

by SPE



ESI-MS data on DOM

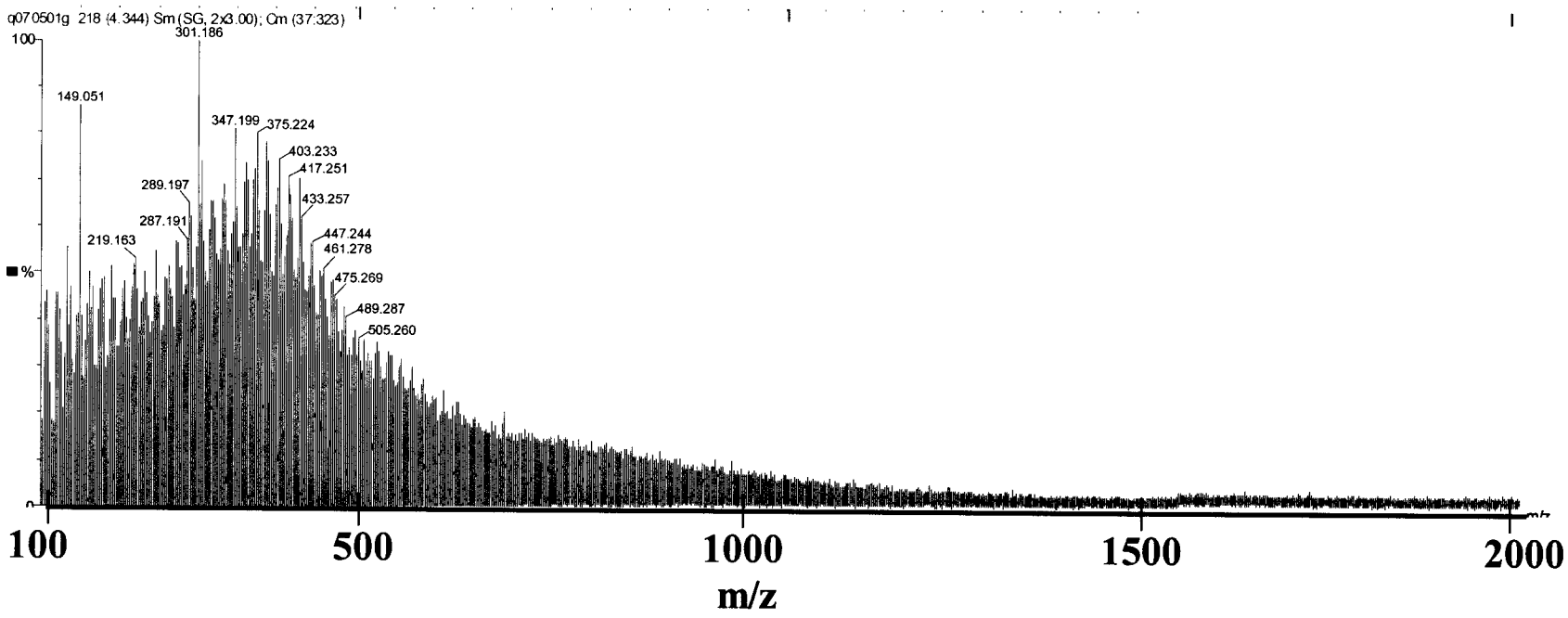
(quadrupole time of flight mass spectrometry)



MS spectrum from control (ultra-high purity water processed with same procedure)

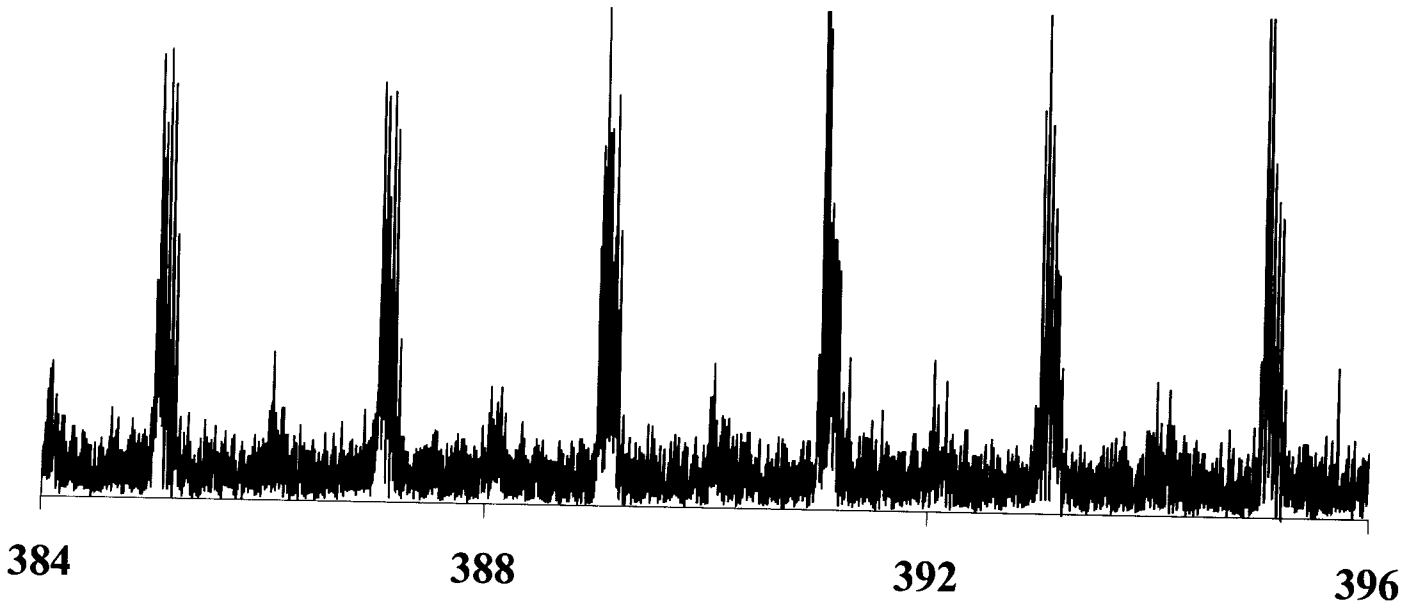
MS spectrum from DOM isolated by C_{18} SDE

Spectrum of DOM from Rio Tempisquito at Costa Rica



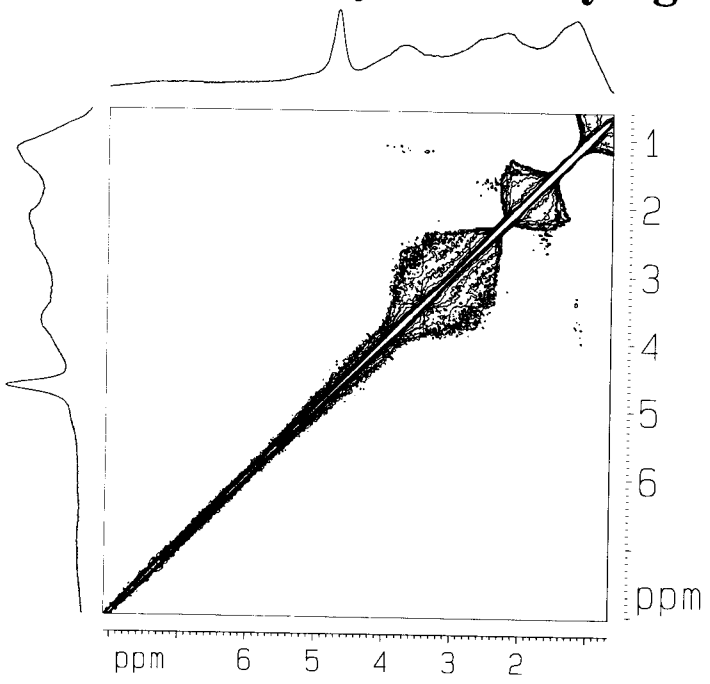
High resolution mass spectrum

Resolution ~ 80,000

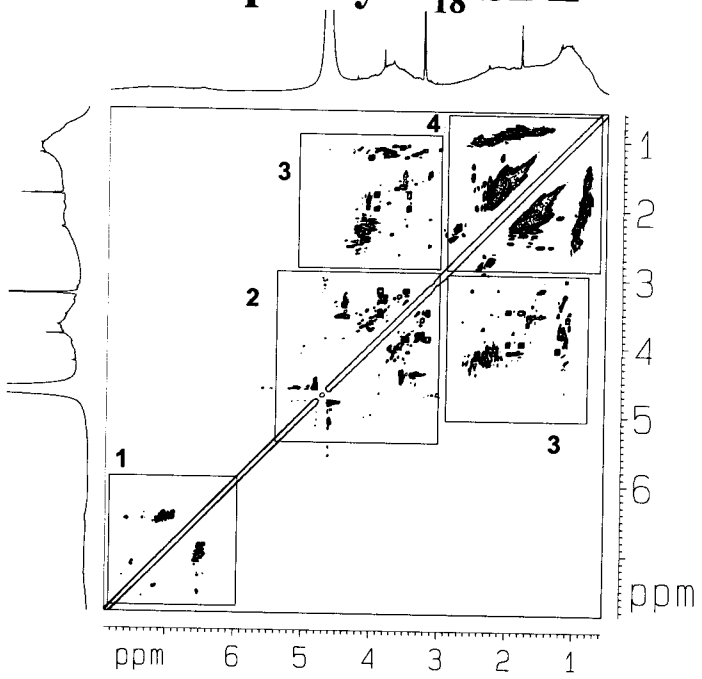


2D NMR (TOCSY) data on DOM

Sample by freezedrying



Sample by C_{18} SDE



(1) aromatics; (2) sugars; aliphatic units bridging lignin aromatics; amino acids (α-β couplings); (3) methylene units adjacent to ethers, esters, and hydroxyls in aliphatic chains; amino acids (α-β-γ couplings); (4) methylene in aliphatic chains; and methyl units in amino acids and aliphatic chains.

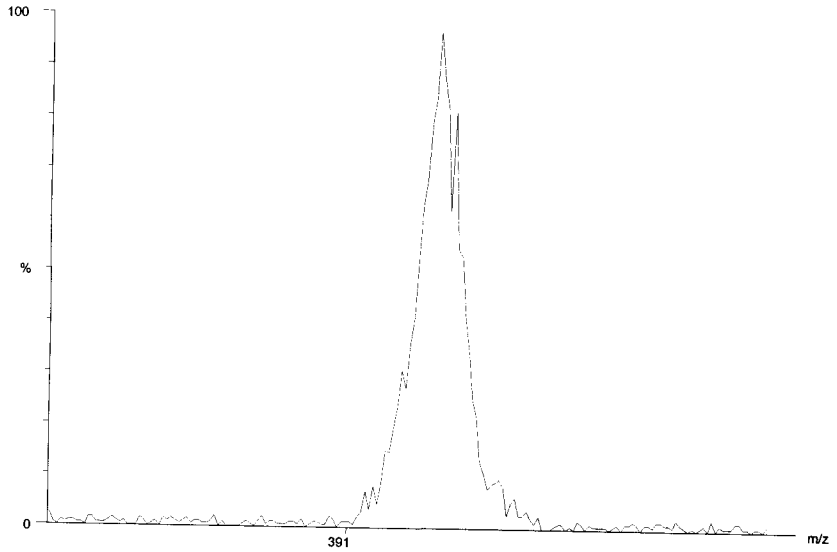
Conclusion

- 1. DOM can be extracted with C_{18} solid phase disk extraction in a shorter time with simple equipment.

- 2. Extracted DOM was successfully analyzed by high resolution ESI-MS resulting high resolution spectra.

Sunghwan Kim *et. al* submitted to Organic Geochemistry

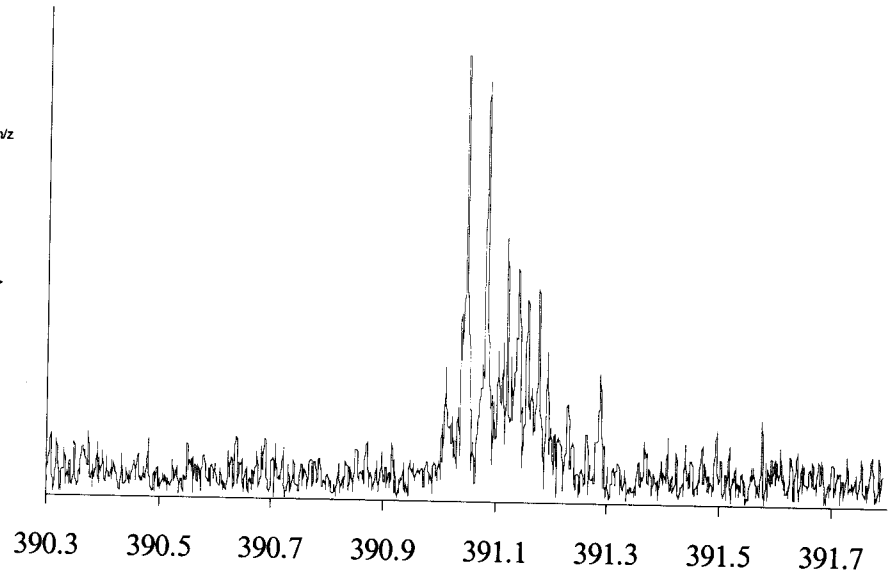
Resolving power is very critical



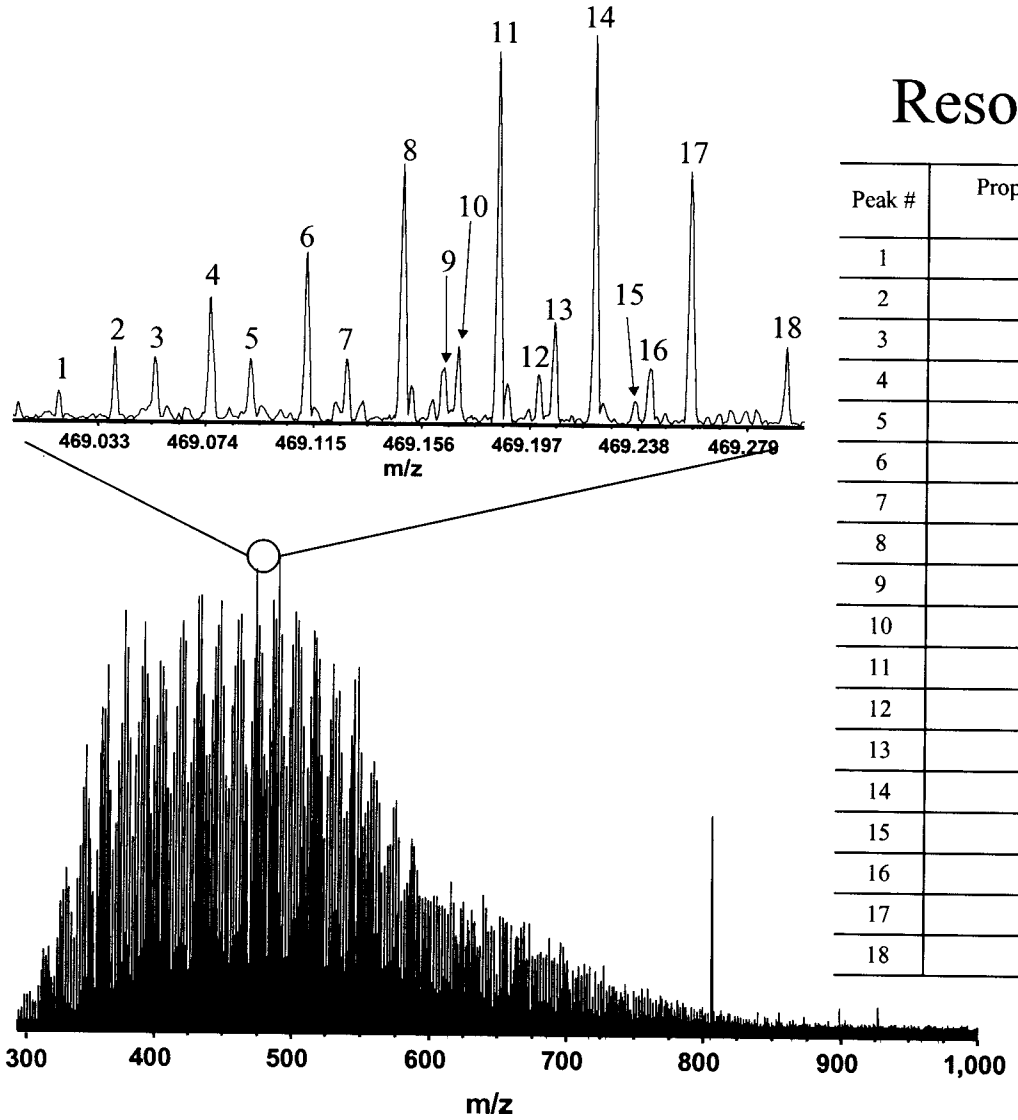
← Q-TOF analysis of DOM
Resolving power ~10,000

7 T FT-ICR analysis of DOM
Resolving power ~80,000

→



Ultra-high resolution spectrum of DOM

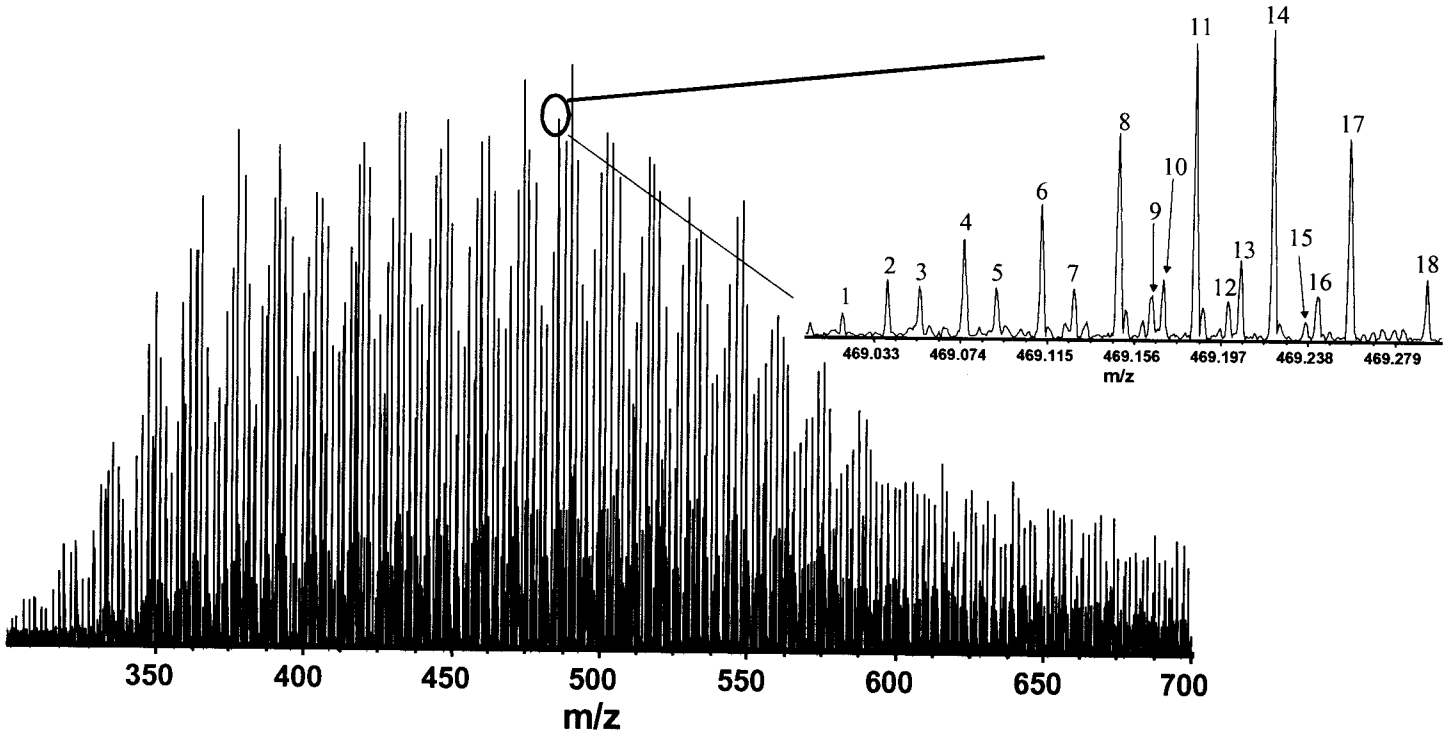


Resolving power ~ 200,000

Peak #	Proposed molecular formula	Observed values	Theoretical values	Difference from Theoretical value (ppm)
1	$C_{25}H_{10}O_{10}$	469.02018	469.02012	-0.1
2	$C_{22}H_{14}O_{12}$	469.04118	469.04125	0.1
3	$C_{26}H_{14}O_{9}$	469.05646	469.05651	0.1
4	$C_{23}H_{18}O_{11}$	469.07763	469.07764	0
5	$C_{27}H_{18}O_{8}$	469.09288	469.09289	0
6	$C_{24}H_{22}O_{10}$	469.11401	469.11402	0
7	$C_{28}H_{22}O_{7}$	469.1293	469.12928	0
8	$C_{25}H_{26}O_{9}$	469.15042	469.15041	0
9	$C_{29}H_{26}O_{6}$	469.16576	469.16566	-0.2
10	$C_{22}H_{30}O_{11}$	469.17151	469.17154	0.1
11	$C_{26}H_{30}O_{8}$	469.18681	469.18679	0
12	$C_{30}H_{30}O_{5}$	469.20201	469.20205	0.1
13	$C_{23}H_{34}O_{10}$	469.20789	469.20792	0.1
14	$C_{27}H_{34}O_{7}$	469.22316	469.22318	0
15	$C_{31}H_{34}O_{4}$	469.23838	469.23843	0.1
16	$C_{24}H_{38}O_{9}$	469.24423	469.24431	0.2
17	$C_{28}H_{38}O_{6}$	469.25949	469.25956	0.2
18	$C_{29}H_{42}O_{5}$	469.29584	469.29595	0.2

9.4 T FT-ICR at NHMFL

Trees or forest ?



Graphical-statistical method for the study of structure and reaction processes of coal

D. W. VAN KREVELEN, D.Sc., M.A.I.Ch.E.

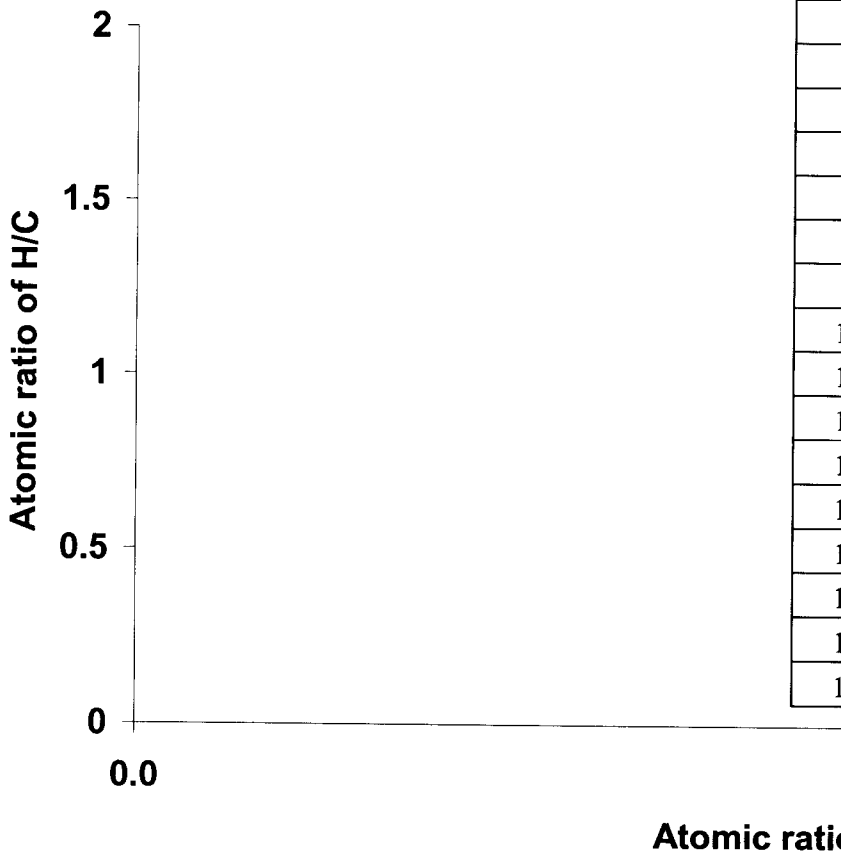
A graphical-statistical method is developed for the study of problems connected with structure and reaction processes of coal. In this method use is made of a diagram in which the atomic hydrogen-to-carbon ratio has been plotted versus the atomic oxygen-to-carbon ratio. This graphical method offers the advantage that the principal reactions such as decarboxylation, demethanation, dehydration, dehydrogenation, hydrogenation and oxidation in the aforementioned diagram can be represented by straight lines. Furthermore, an auxiliary diagram is used where the hydrogen-to-carbon ratio of hydrocarbons has been plotted as a function of the number of carbon atoms per molecule. From a combination of the two diagrams valuable information can be drawn as regards the structure of oxygen containing organic products e.g. high polymers, such as cellulose. These ideas are applied to the coalification series. The skeleton structure of lignin evolved in the literature proves to be in conformity with the results of the graphical statistical method. The conversion of lignite to bituminous coal is found to be based on a decarboxylation: the conversion from high rank bituminous coal to anthracite is a reaction process in which methane is removed almost exclusively in the transition from low rank to high rank bituminous coal a decarboxylation as well as a demethanation and a dehydration occur. The stoichiometry of the coalification is expressed in formulae. A correlation is made between the coalification of various vegetable components and the rank of coal in which the product formed cannot be distinguished from vitrain. Finally the formation process of fusain is studied in more detail and this leads to the construction of a fusinization band by the side of the coal band (=vitrinization band). The principal reaction processes of coal, namely carbonization, hydroconversion, solvent extraction, hydrogenolysis and oxidation, are investigated by a graphical-statistical method. It proves that both in carbonization and in oxidation with gaseous oxygen all coalification products show a tendency to yield a uniform final product; in the carbonization this product has the composition $(C_8H_2O_{0\cdot16})_x$, in the case of oxidation the composition is $(C_8H_2O_3)_x$. Further carbonization results in a graphitization, while an oxidation beyond the above composition gives a complete conversion to carbon dioxide and water. Thermal decomposition in the presence of water vapour under pressure must be based on a reaction mechanism which is closely related with the coalification. In hydrogenation the character of the final products depends both on the character of the starting material and on the conditions under which the hydrogenation is carried out. In oxidation with nitric acid, two stages can be distinguished: in the first stage hydrogen is removed while oxygen is absorbed, in the second stage both hydrogen and oxygen are absorbed and this in the approximate proportion of 1 : 1. Solvent extraction of coal shows that coal is not a homogeneous macromolecule: there is either a differentiation in molecular size or such a configuration that fragments of a relatively low molecular weight are split off rather easily.

van Krevelen, D.W. (1950) Fuel 29, 269-284

van Krevelen plot: An informative graphical method for analysis of ultrahigh-resolution broadband spectra of natural organic matter

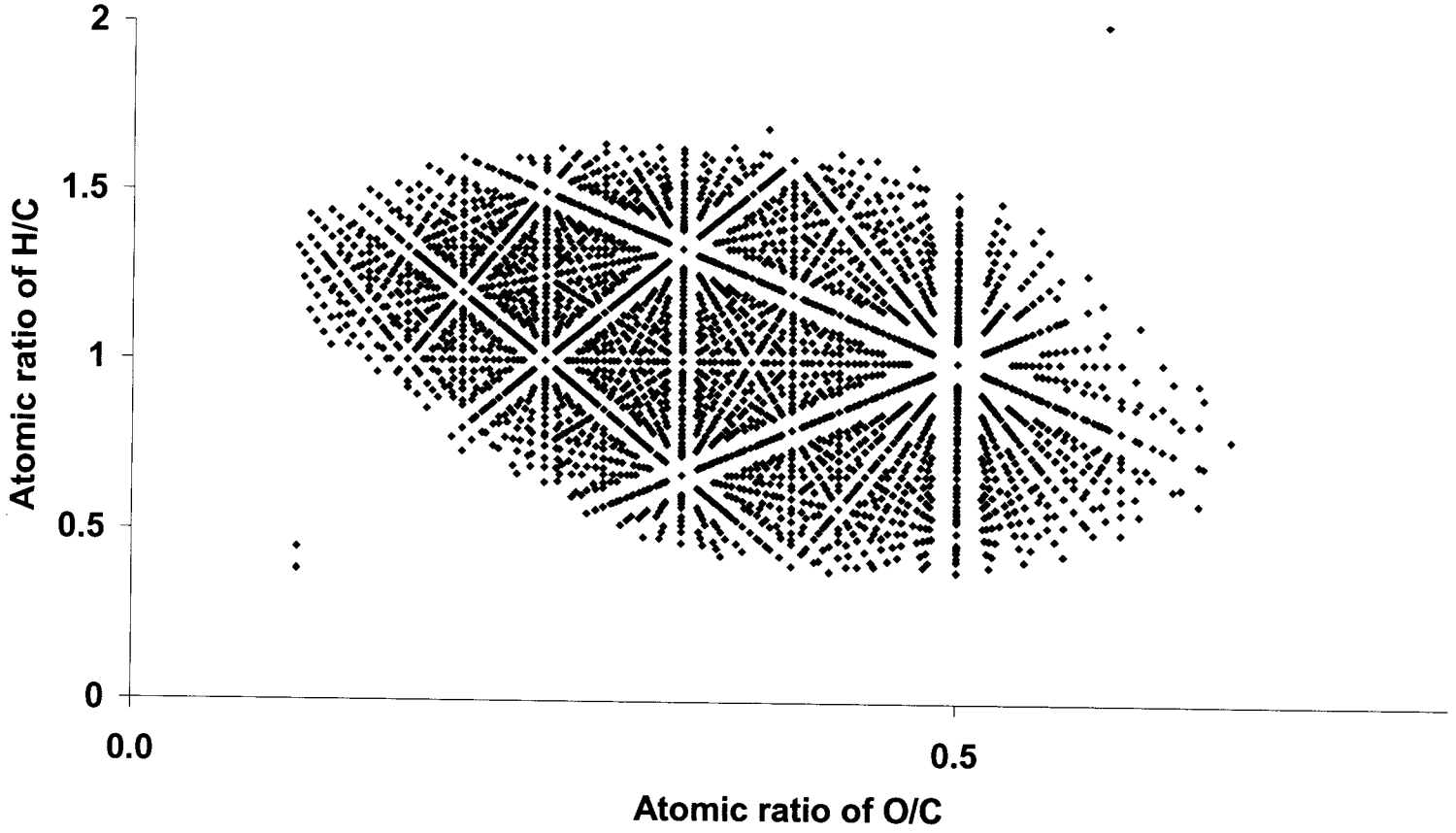
A visual tool to study complicated spectra.

van Krevelen Plot



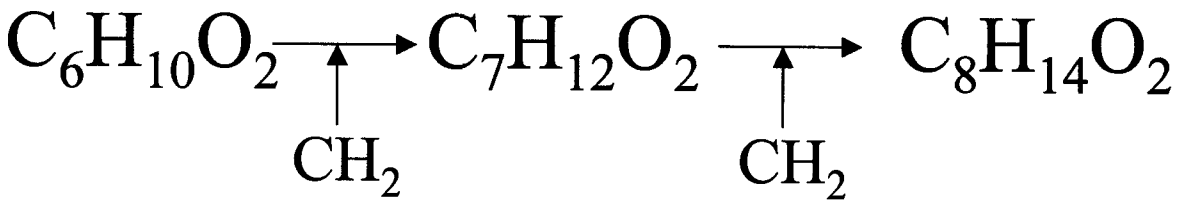
peak number	Observed value	Proposed molecular	Atomic ratio of H/C	Atomic ratio of O/C
1	469.02018	$C_{25}H_{10}O_{10}$	0.40	0.40
2	469.04118	$C_{22}H_{14}O_{12}$	0.64	0.55
3	469.05646	$C_{26}H_{14}O_{12}$	0.54	0.46
4	469.07763	$C_{23}H_{18}O_{11}$	0.78	0.48
5	469.09288	$C_{27}H_{18}O_{8}$	0.67	0.30
6	469.11401	$C_{24}H_{22}O_{10}$	0.92	0.42
7	469.1293	$C_{28}H_{22}O_{7}$	0.79	0.25
8	469.15042	$C_{25}H_{26}O_{9}$	1.04	0.36
9	469.16576	$C_{29}H_{26}O_{6}$	0.90	0.21
10	469.17151	$C_{22}H_{30}O_{11}$	1.36	0.50
11	469.18681	$C_{26}H_{30}O_{8}$	1.15	0.31
12	469.20201	$C_{30}H_{30}O_{8}$	1.00	0.27
13	469.20789	$C_{23}H_{34}O_{10}$	1.48	0.43
14	469.22316	$C_{27}H_{34}O_{7}$	1.26	0.26
15	469.23838	$C_{31}H_{34}O_{4}$	1.10	0.13
16	469.24423	$C_{24}H_{38}O_{9}$	1.58	0.38
17	469.25949	$C_{28}H_{38}O_{6}$	1.36	0.21
18	469.29584	$C_{29}H_{42}O_{5}$	1.45	0.17

van Krevelen Plot of DOM



van Krevelen plot as a tool to identify and display series of molecules possibly from various chemical reactions

Reaction	Characteristic of a line
De-carboxylation	pass (2,0)
Hydration or dehydration	slope of 2
Oxidation	horizontal line
Hydrogenation or dehydrogenation	vertical line
oxidation alcohol to aldehyde	slope of -2
oxidation of alcohol to acid	slope of -1
Addition of CH_2	pass (0,2)



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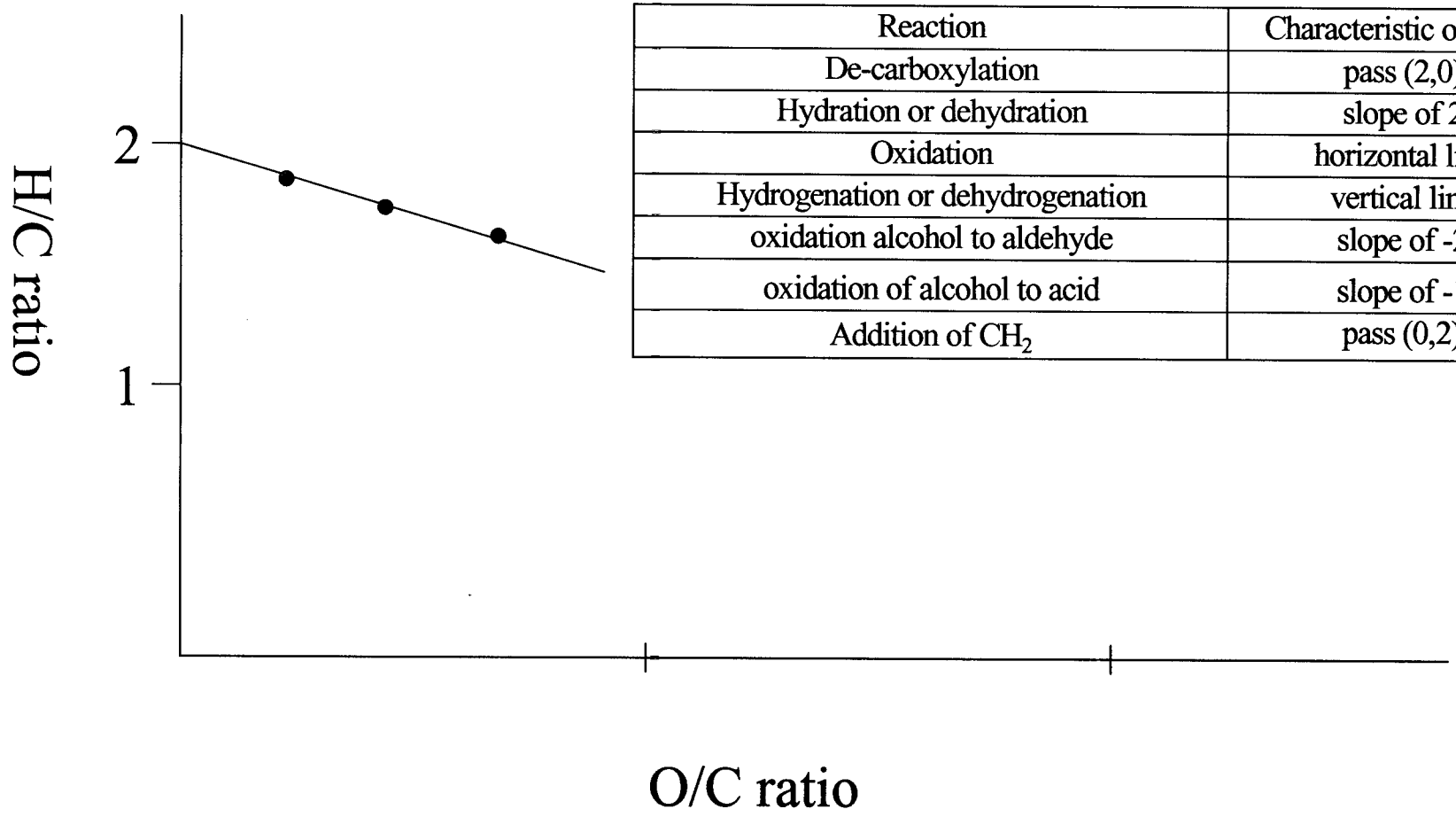
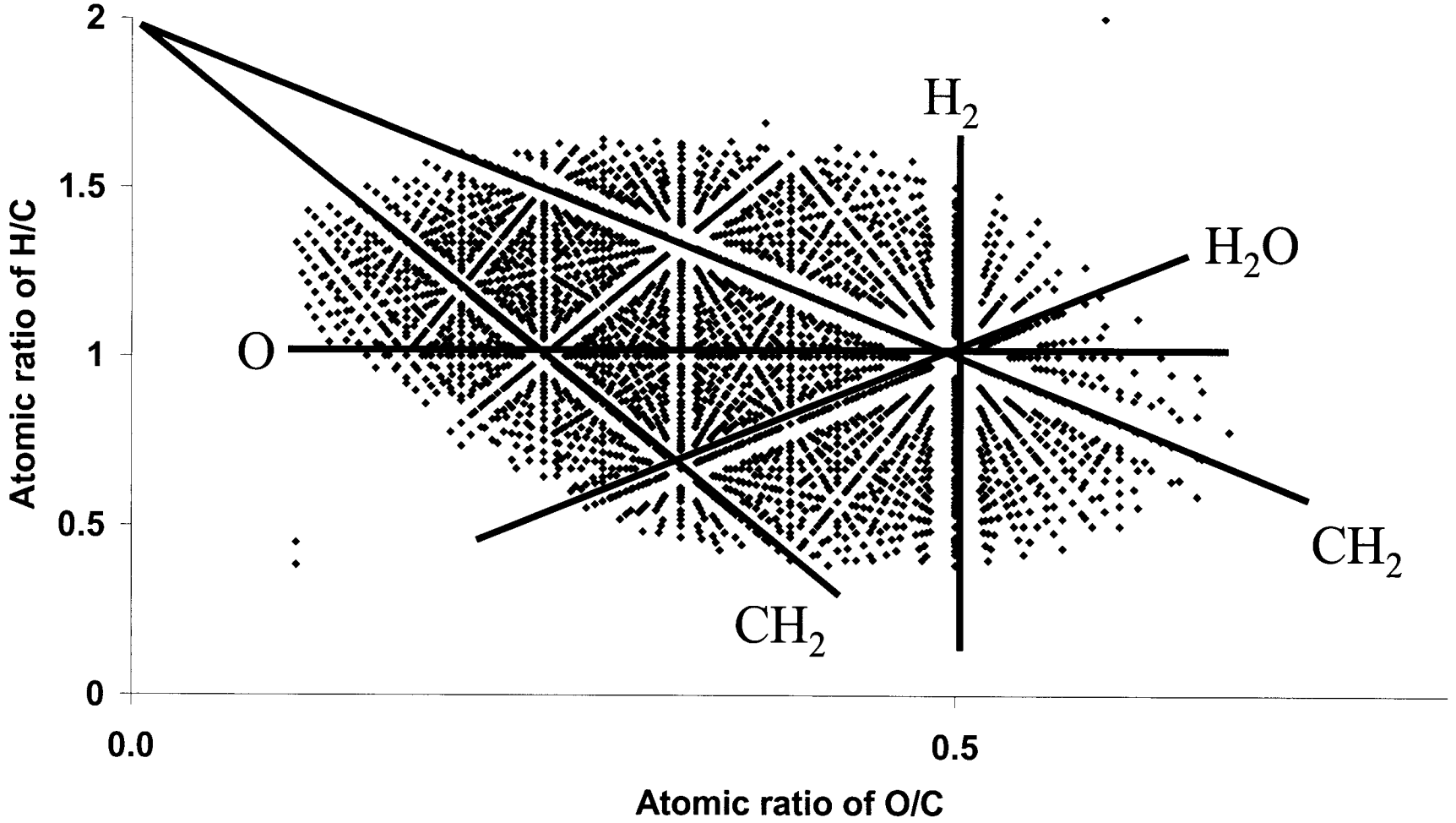
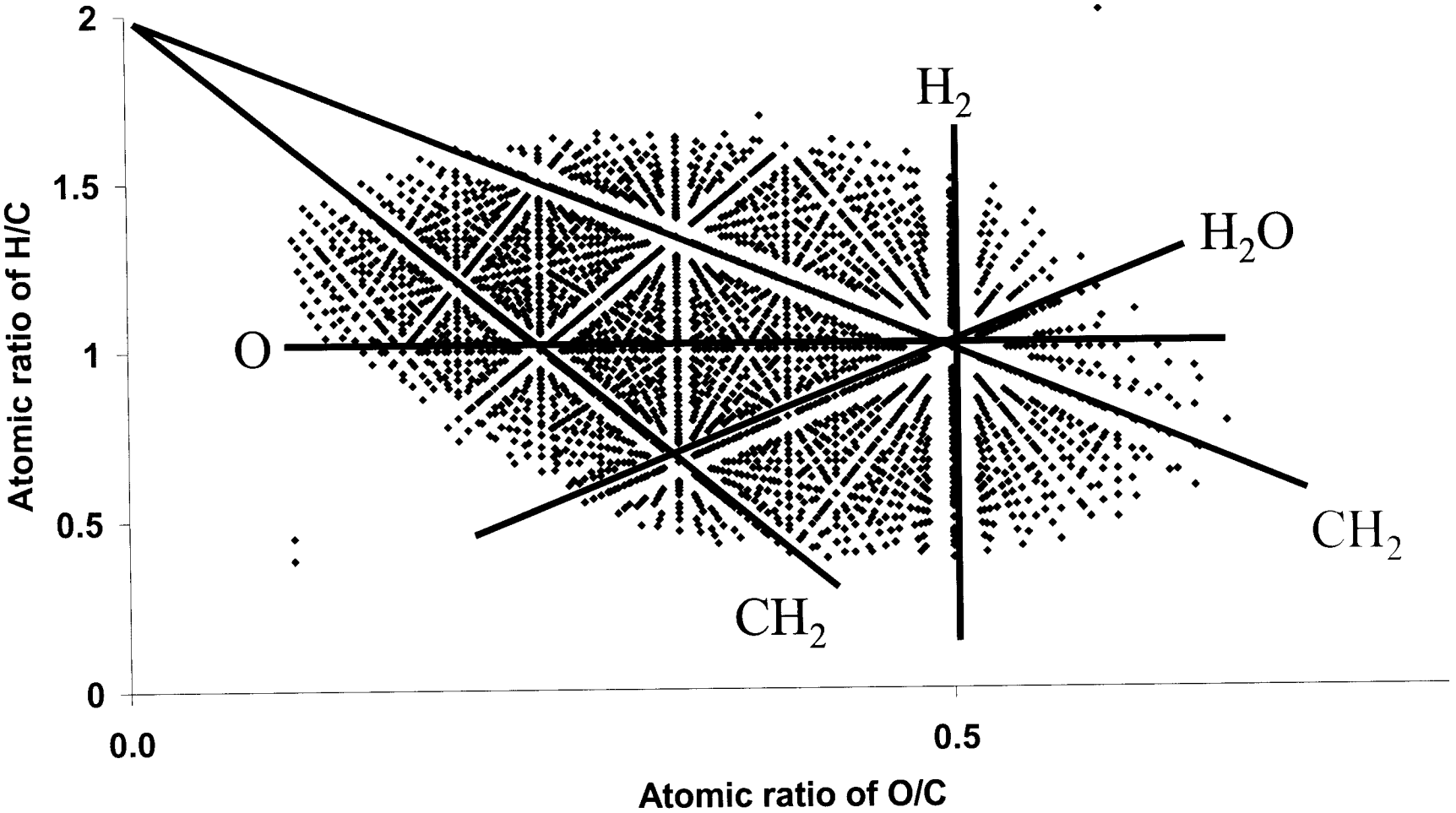


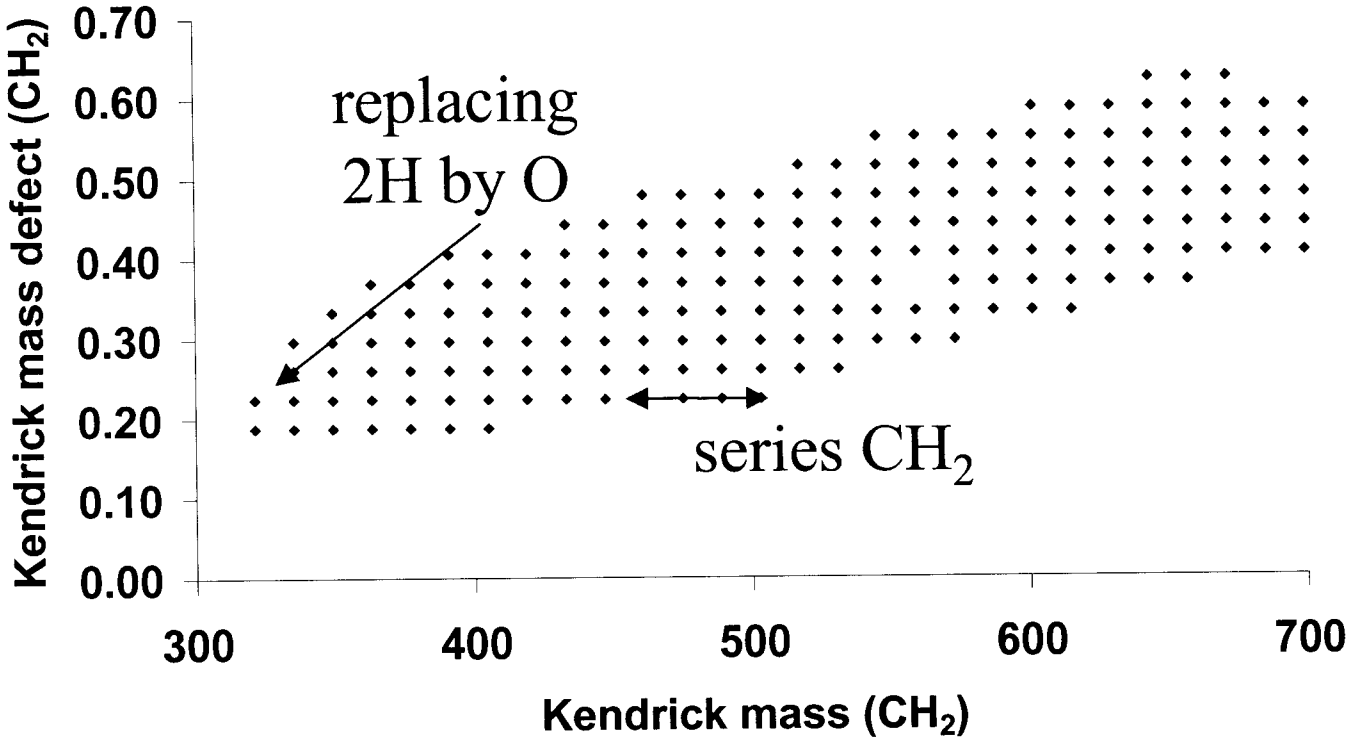
van Krevelen plot as a tool to identify and display series of molecules possibly from various chemical reactions



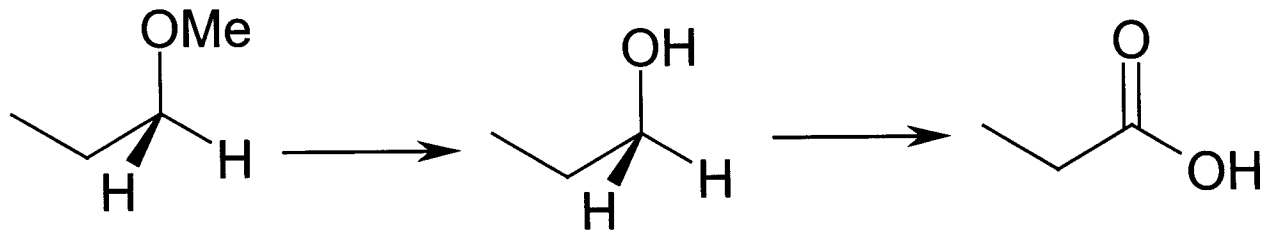
van Krevelen plot as a tool to identify and display series of molecules from various chemical reactions



Kendrick mass defect analysis* on CH_2 series of peaks



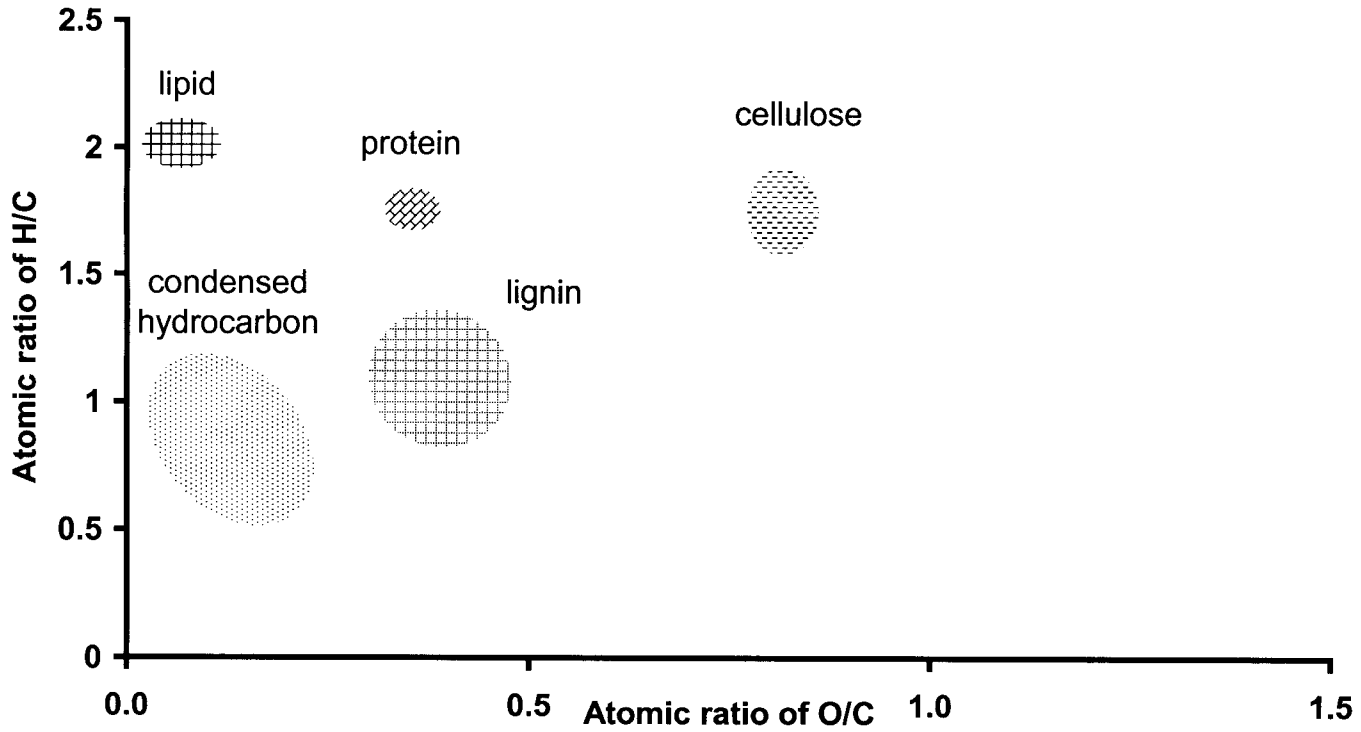
A possible reaction



* Kendrick, E., Anal. Chem , **35**, 2146-2154 (1963)

Bio-markers have their own specific elemental composition

vK plot allows us to do qualitative visual analysis on complicated mass spectrum – analogy to 1D NMR



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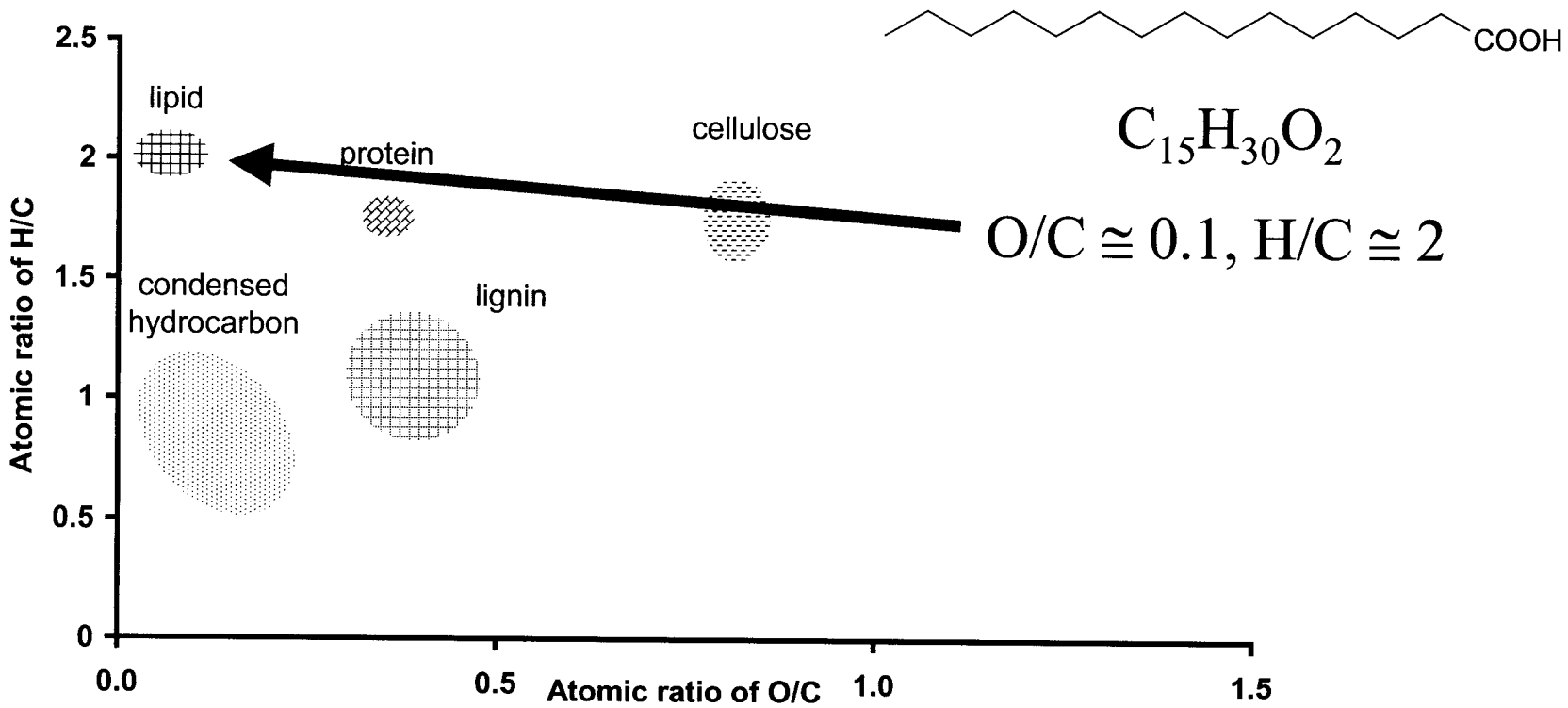

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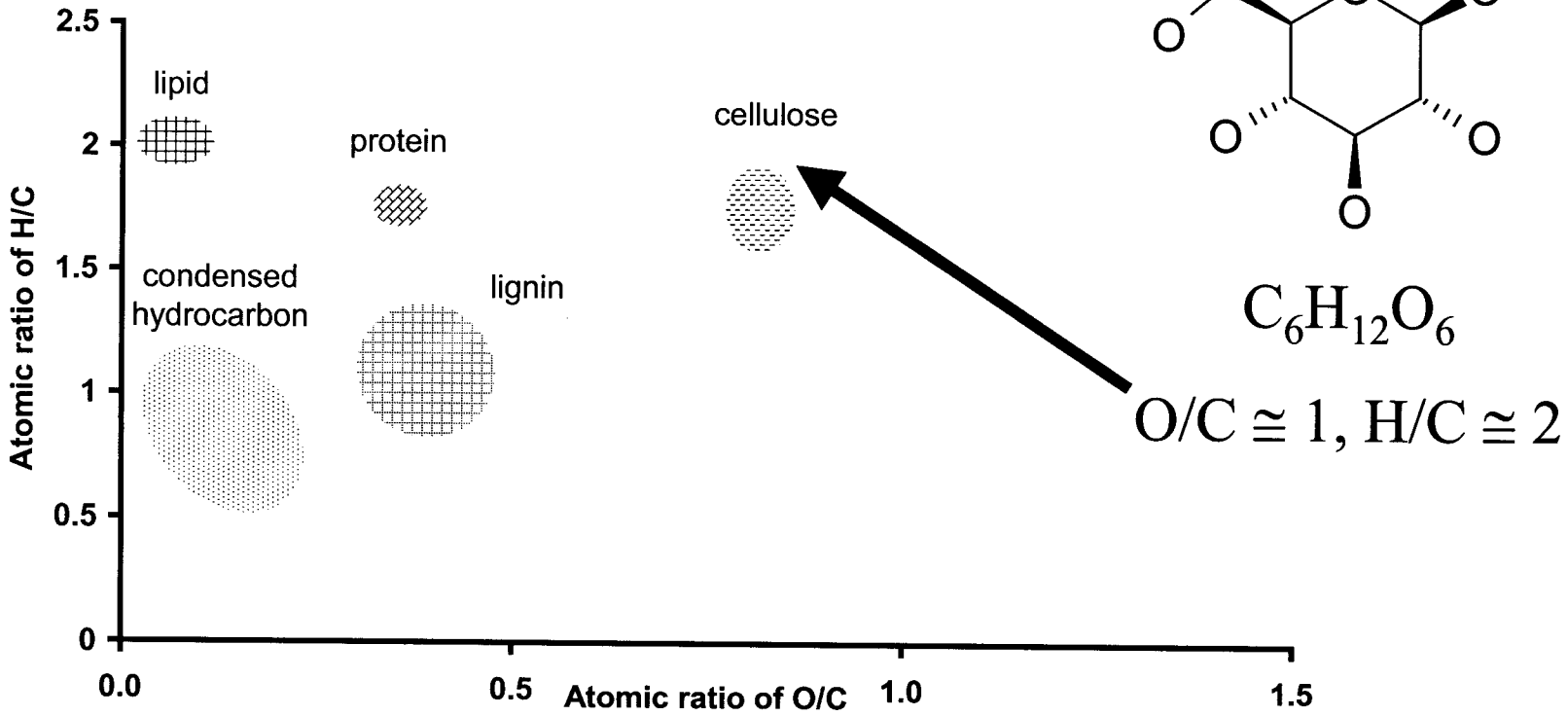

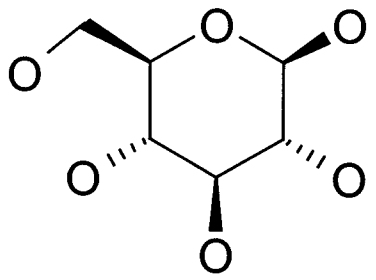

$C_6H_{12}O_6$

O/C ≅ 1, H/C ≅ 2

Bio-markers have their own specific elemental composition

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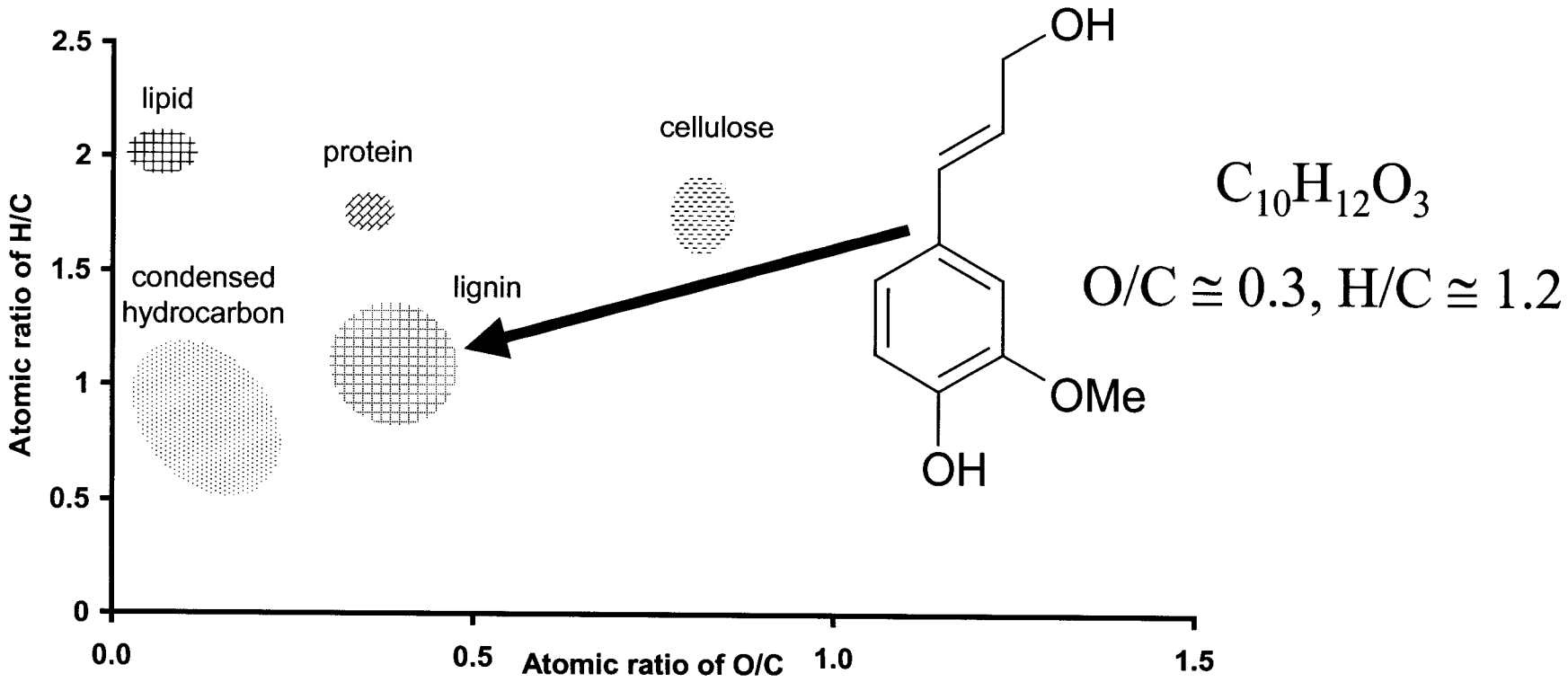
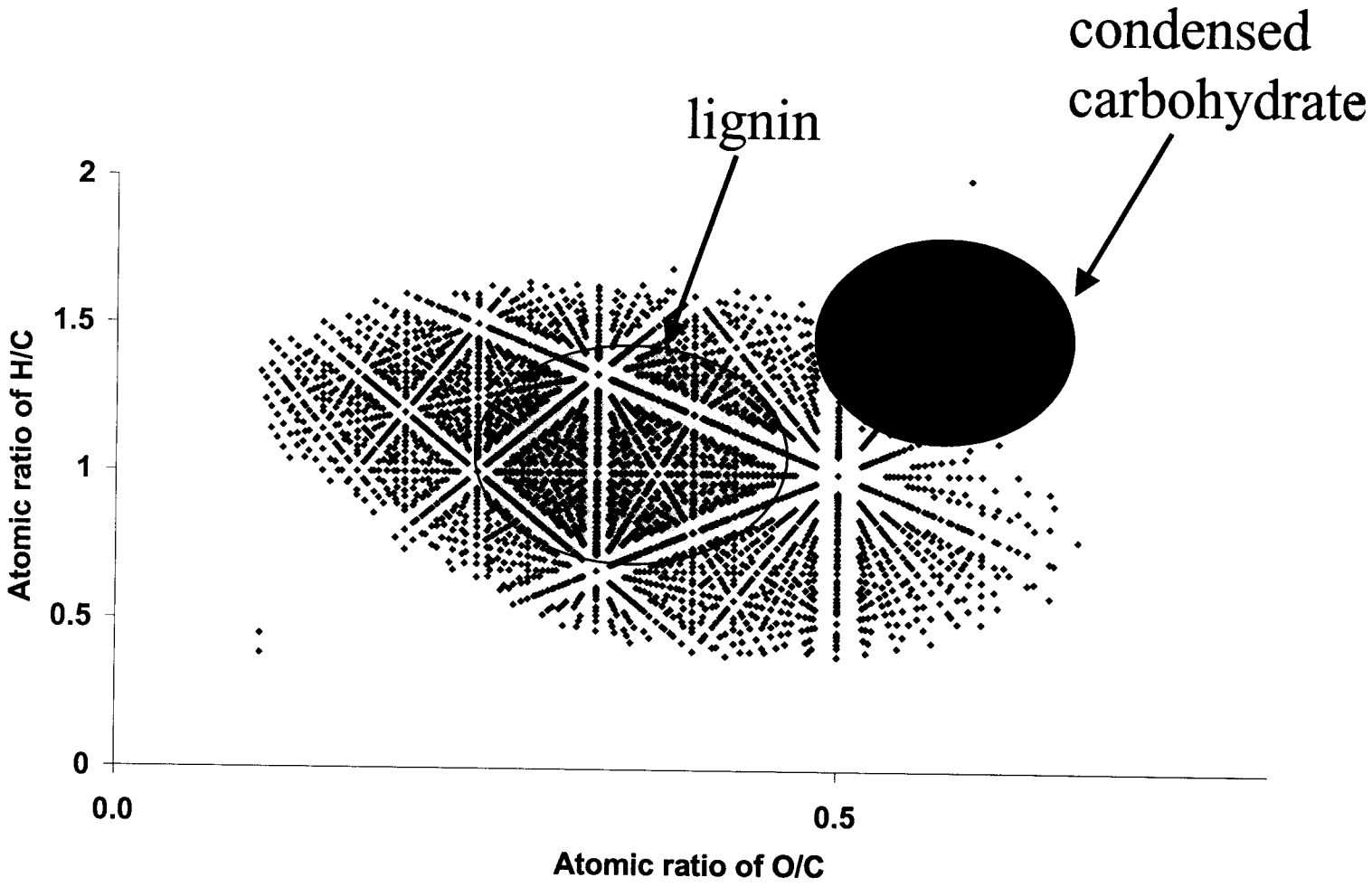
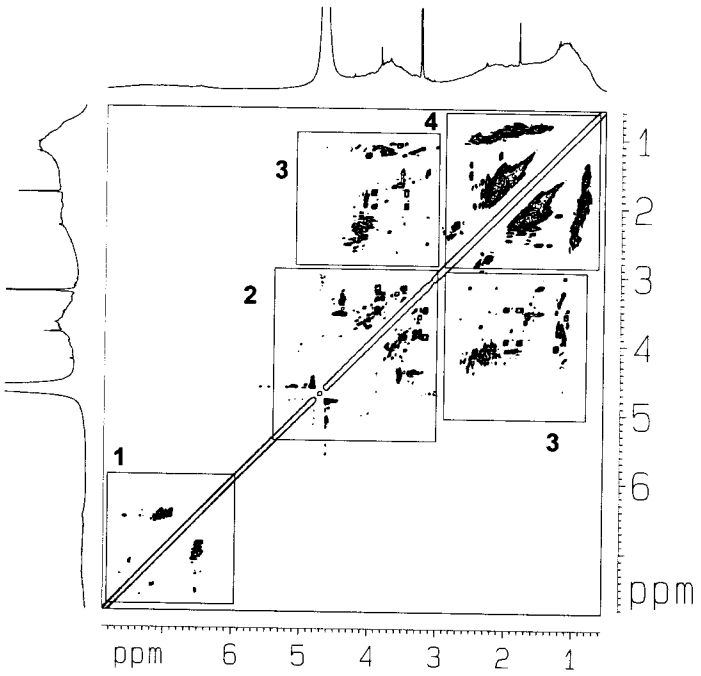



condensed
carbohydrate
lignin
2
1.5
1
0.5
0
Atomic ratio of H/C
0.0
0.5
Atomic ratio of O/C

2D NMR data on DOM

Sample by C_{18} SDE



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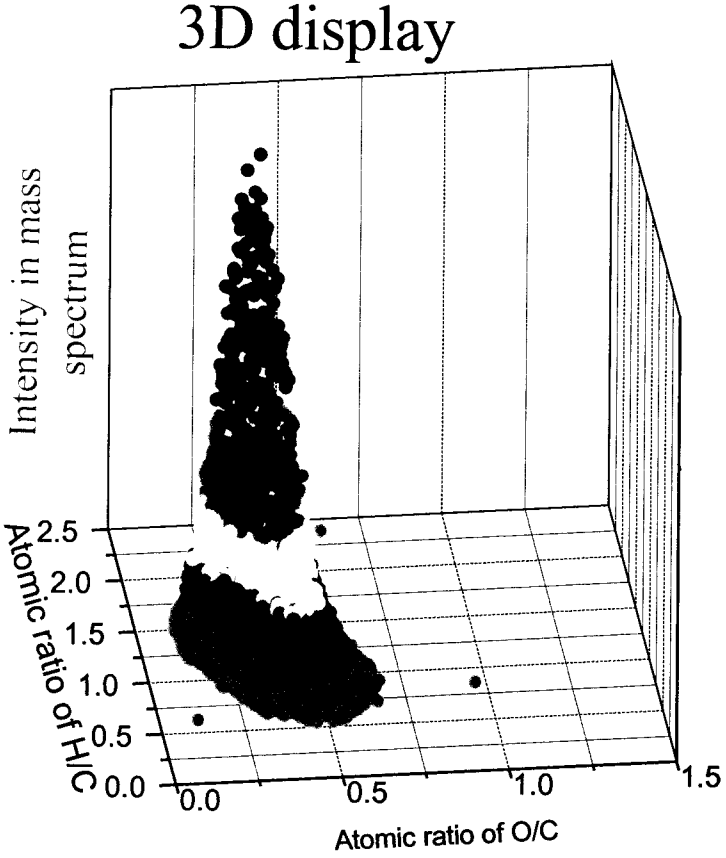
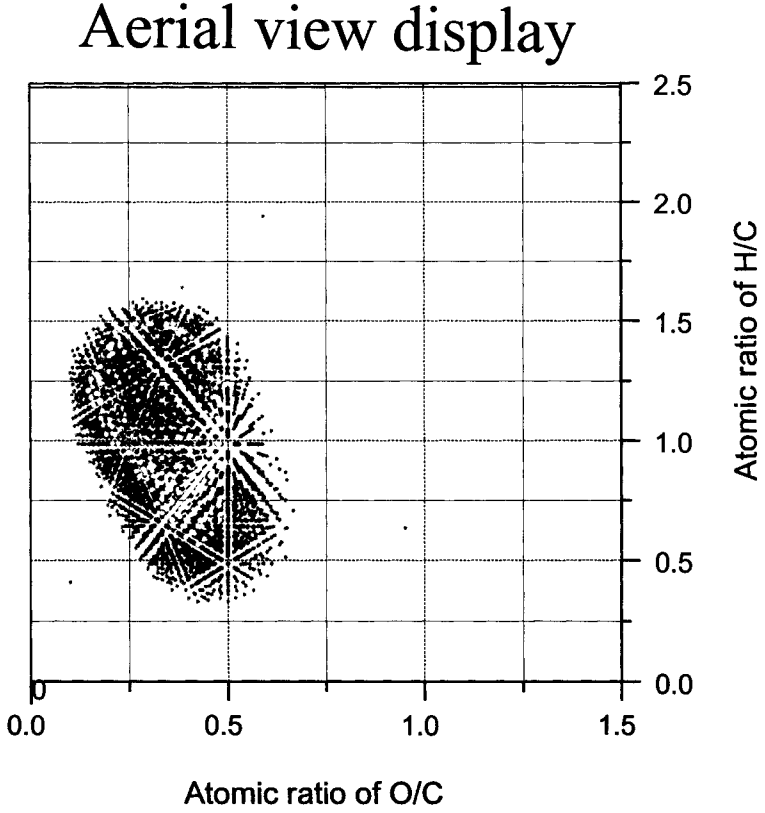
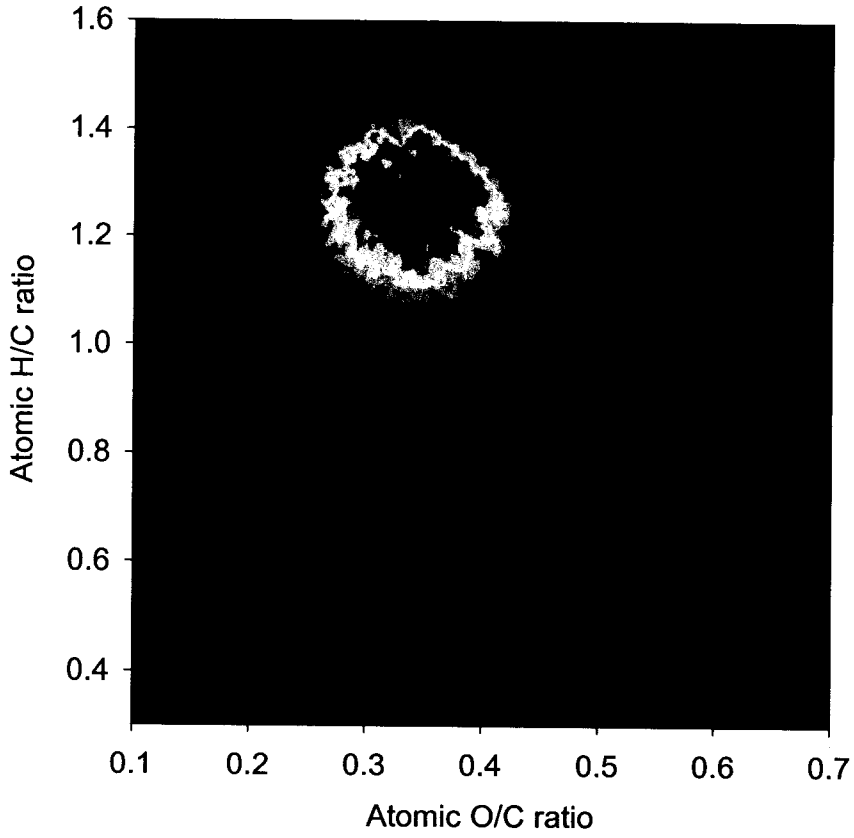
3D vK plot –a visual tool to compare multiple complex spectra





3D vK plot –a visual tool to compare multiple complex spectra

DOM from
McDonalds Branch

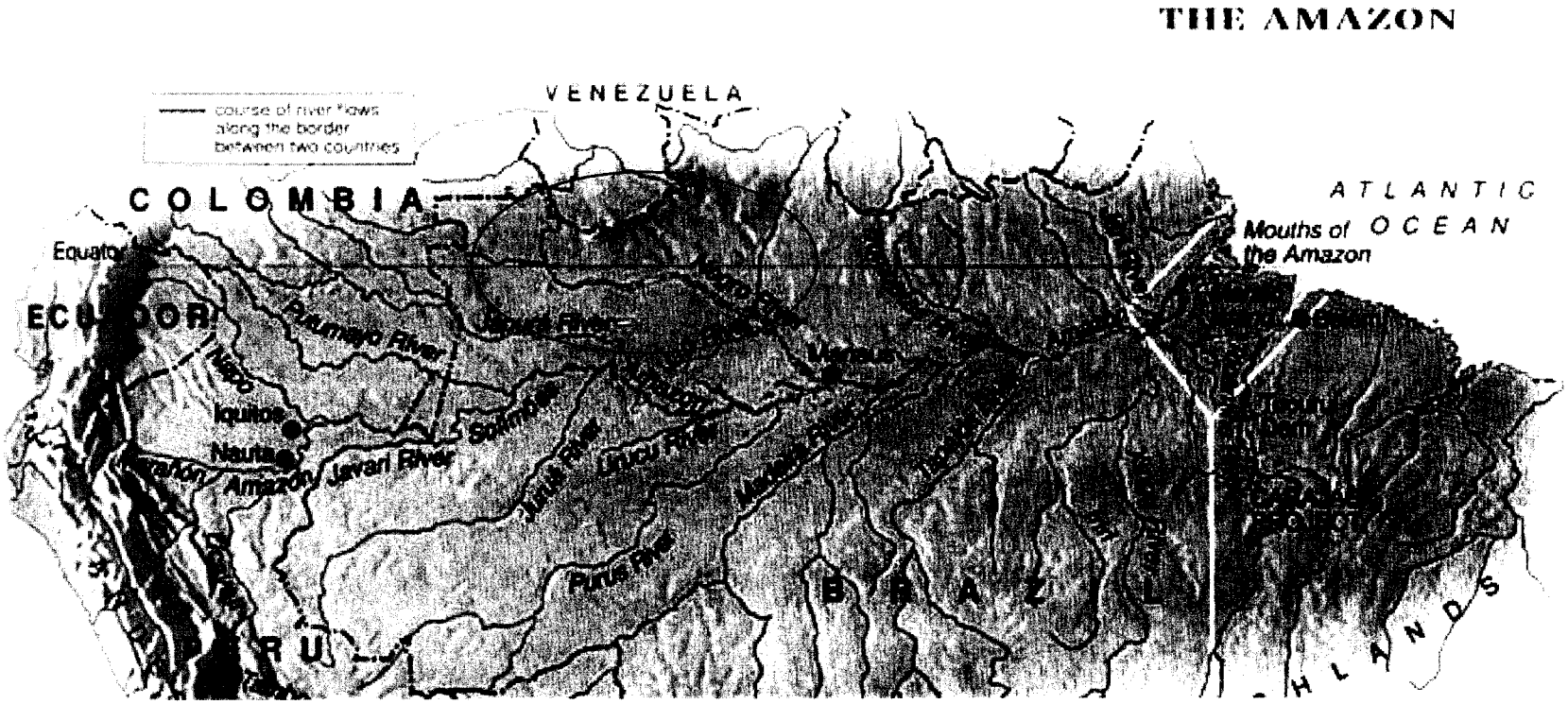


Existence of hydrogen deficient molecules in natural river water samples – an implication for black carbon and black carbon cycle

Black carbon (BC)

- The black carbon (BC) is byproduct of incomplete combustion processes.
- BC has been shown to have discernable influence on biogeochemical cycles, climate change, human health, fertility of soils, and bioavailability of toxins.
- BC is generally accepted to be refractory.

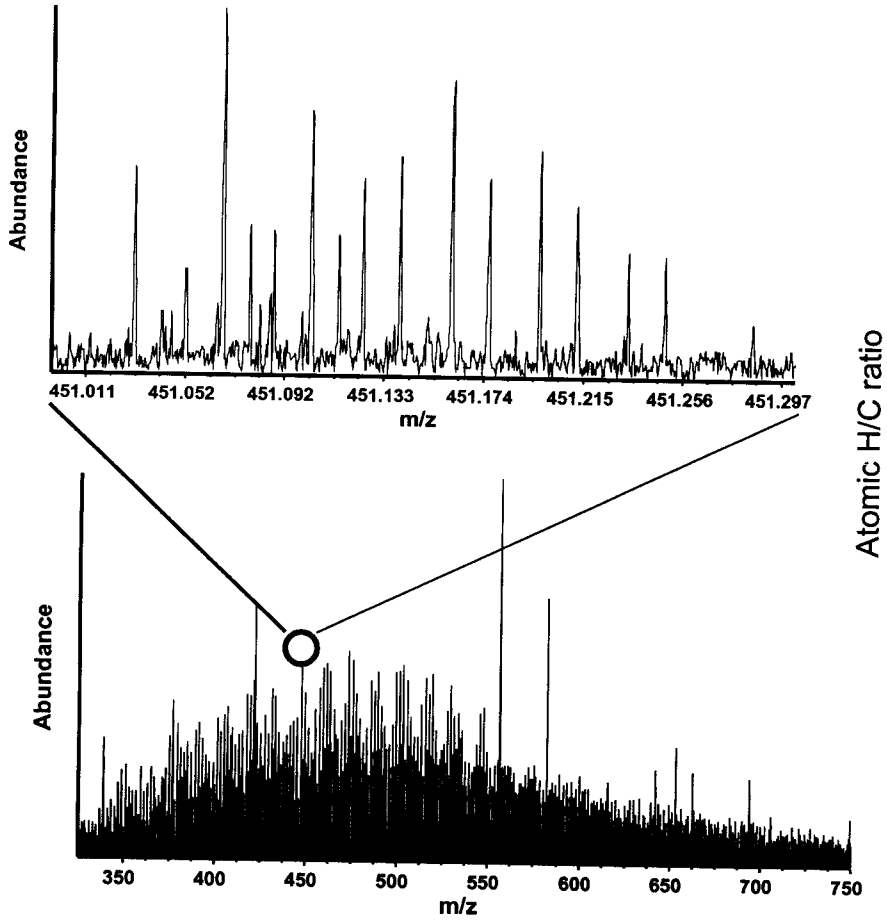
Rio Negro

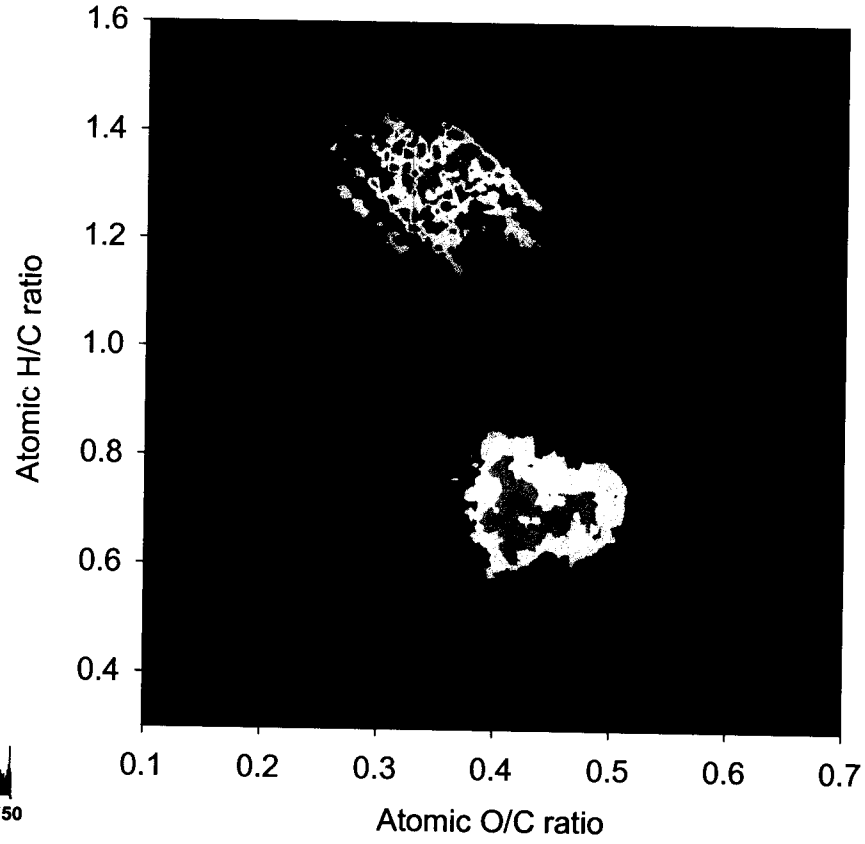


- The Rio Negro is one of the three major tributaries of the Amazon river (accounting for 30 % of Amazon river discharge).

- The Amazon river is the largest river in the world accounting for 20 % of fresh water discharge into the ocean

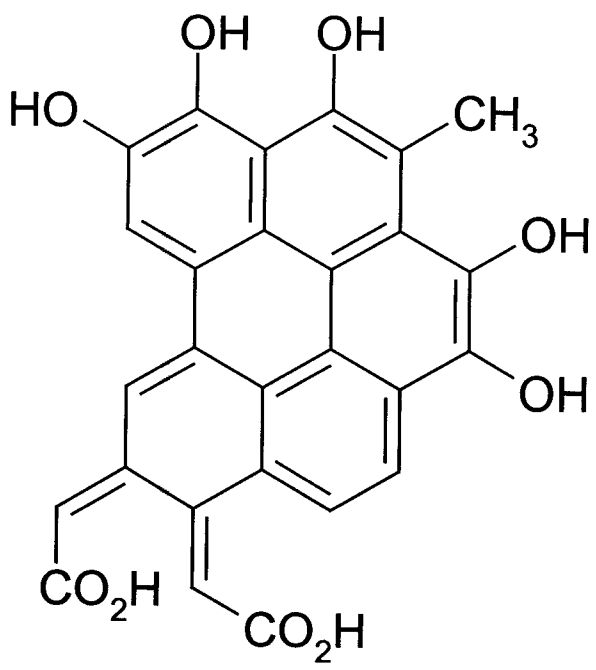
DOM from Rio Negro



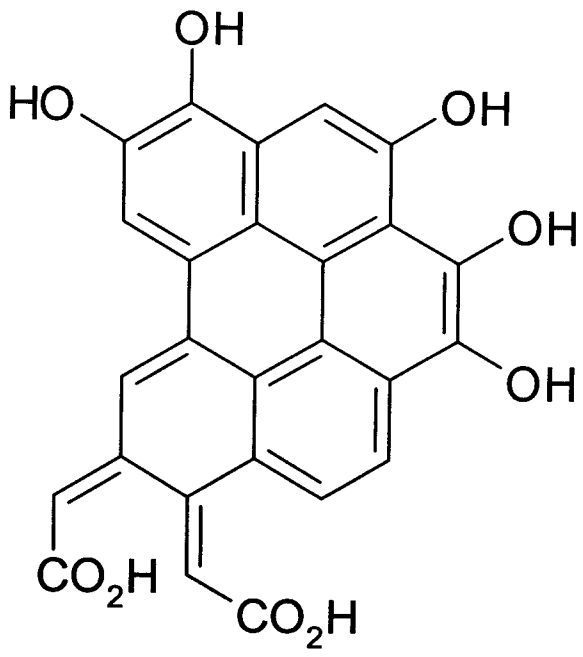


Hydrogen deficient peaks & possible structures

$C_{27}H_{16}O_9$

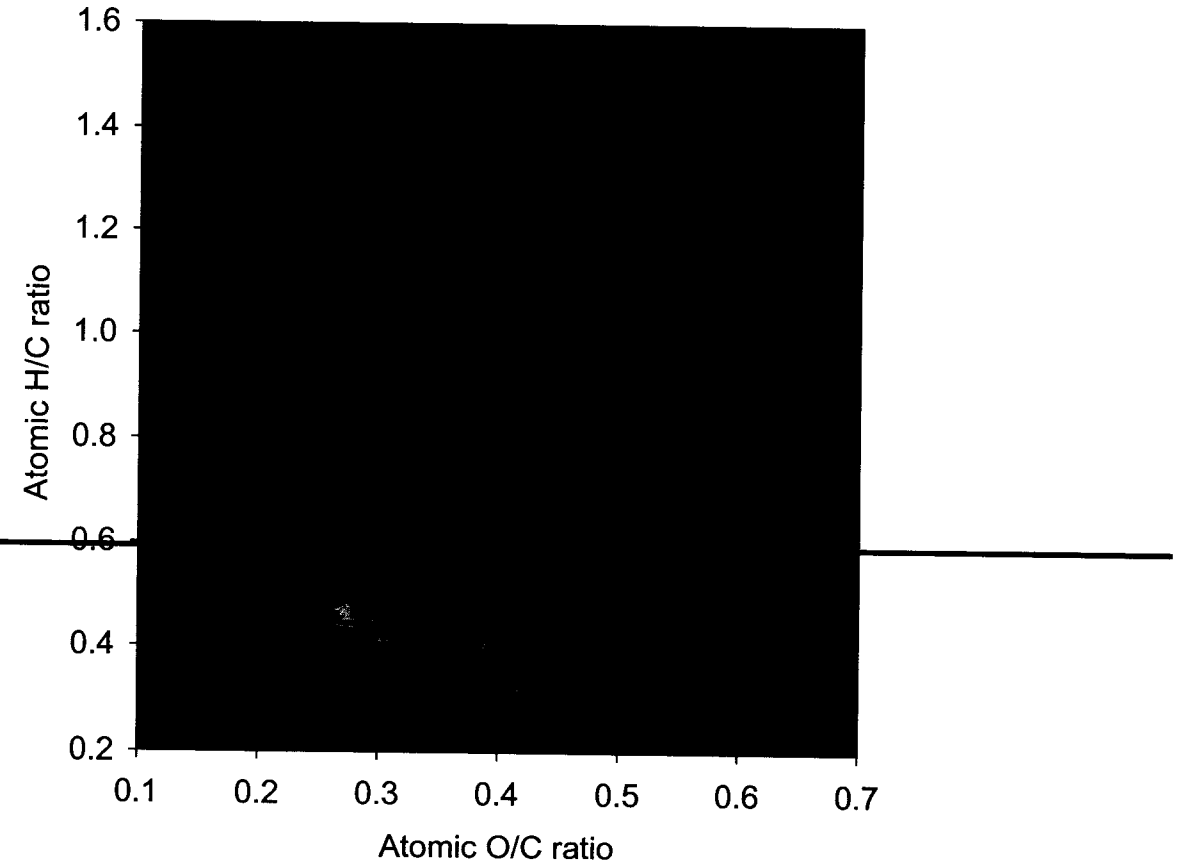


$C_{26}H_{14}O_9$



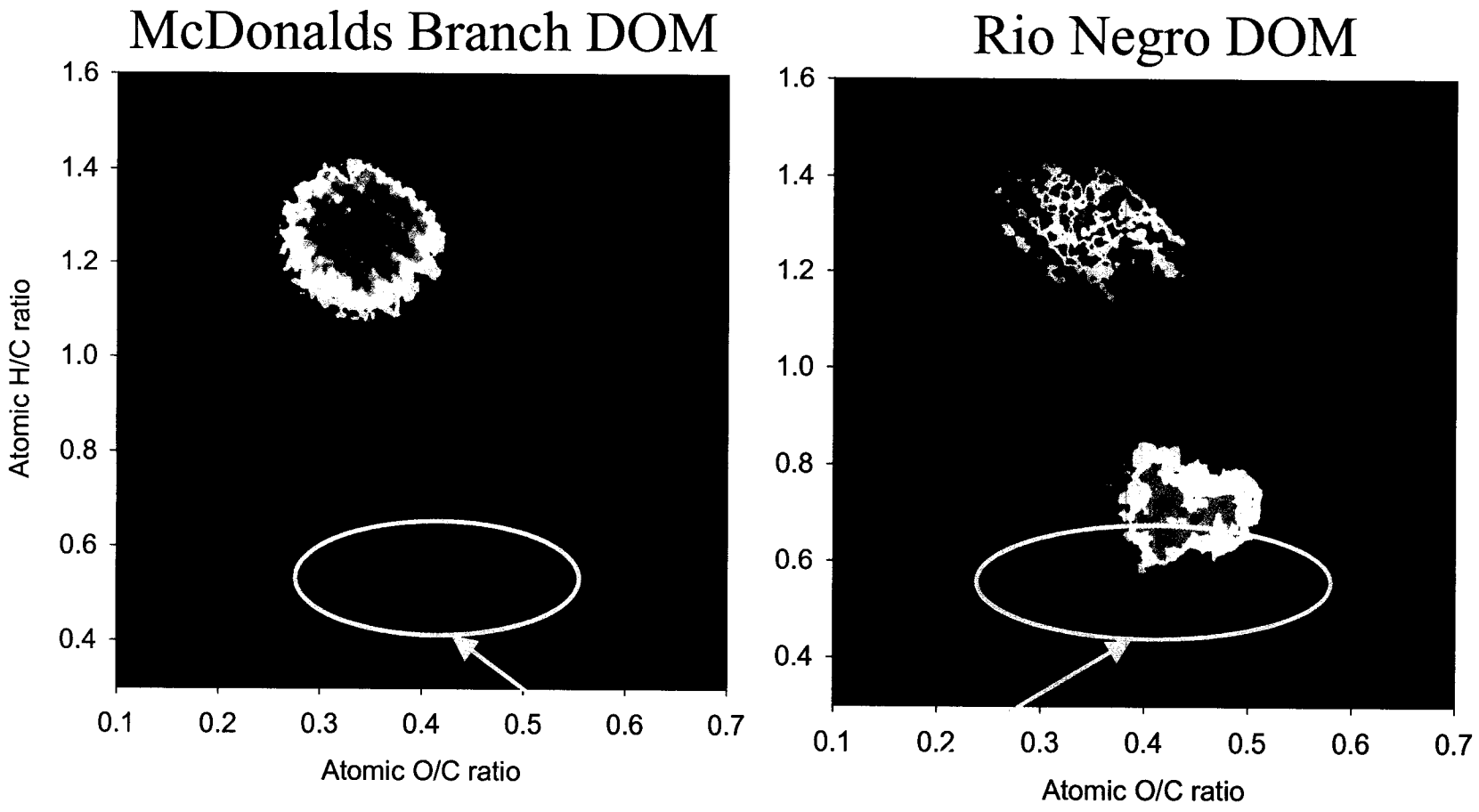
Diluvial humic acid

(volcanic ash soil)



J. A. Baldock, R. J. Smernik, *Org. Geochem.* **33**, 1093-1109 (2002).

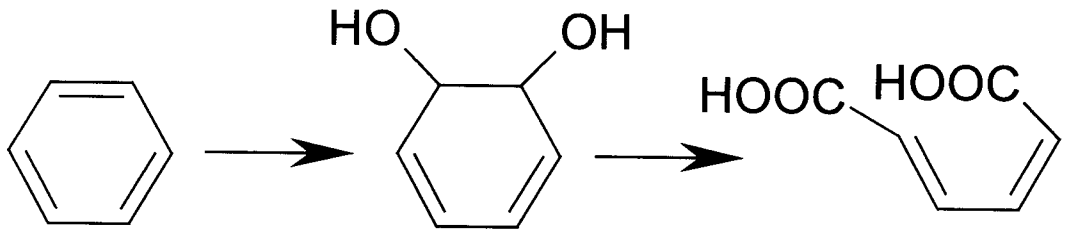
BC in rivers


McDonalds Branch DOM
Rio Negro DOM
Atomic H/C ratio
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.1
0.2
0.3
0.4
0.5
0.6
0.7
Atomic O/C ratio
Atomic O/C ratio
BC

IS BC soluble in water ?

• Oxidation is an important step for microbial degradation of poly-aromatic carbon[1].

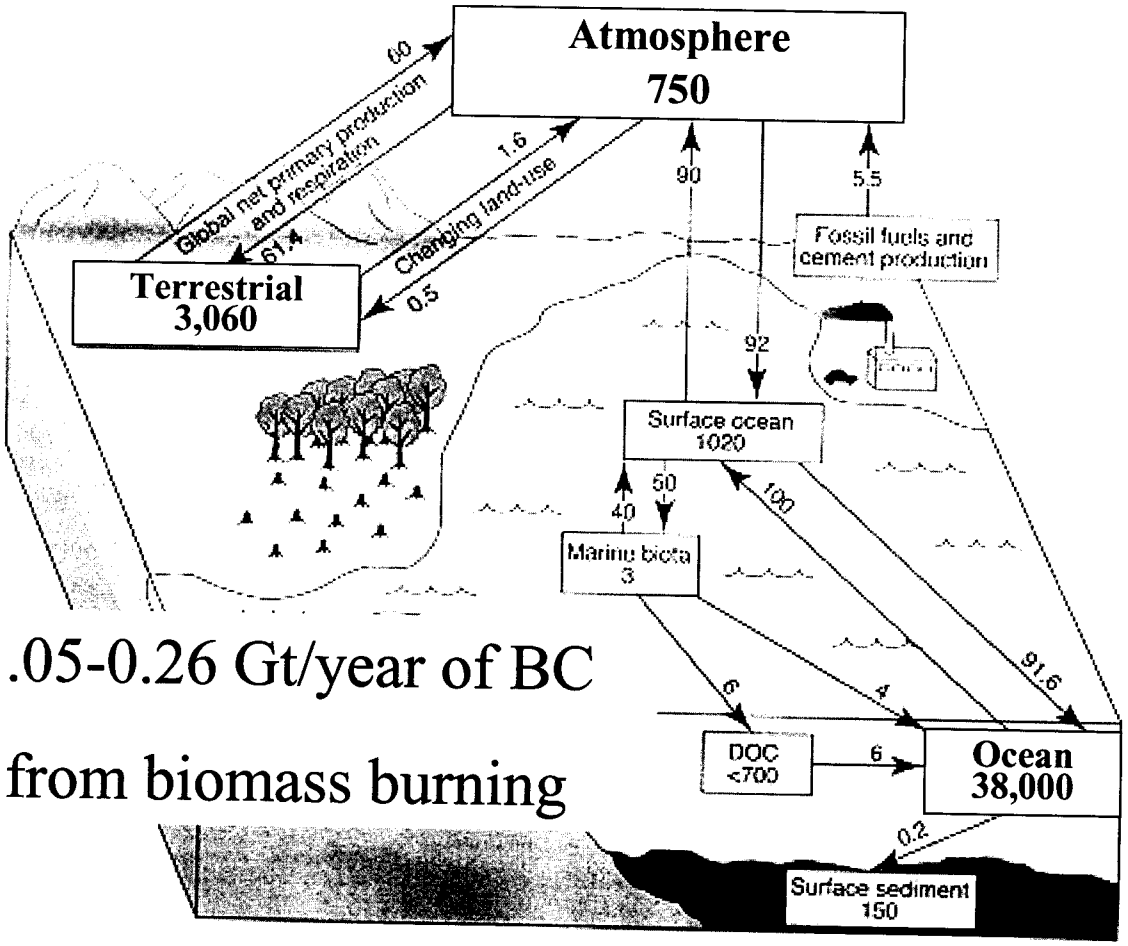
e.g.)



• Microbial decomposition of low rank coal has been reported. However, it is generally known that the degradation process is slow.

1. A. Tschech, *Forum Mikrobiol.* **12**, 251-264 (1989).

Is BC degradable?



.05-0.26 Gt/year of BC

from biomass burning

Global carbon budget

Terrestrial: 3,060 Gt C

Ocean: 40,000 Gt C

\+ Atmosphere: 750 Gt C

Total: 43,810 Gt C

43810/0.05 = 876,200 years

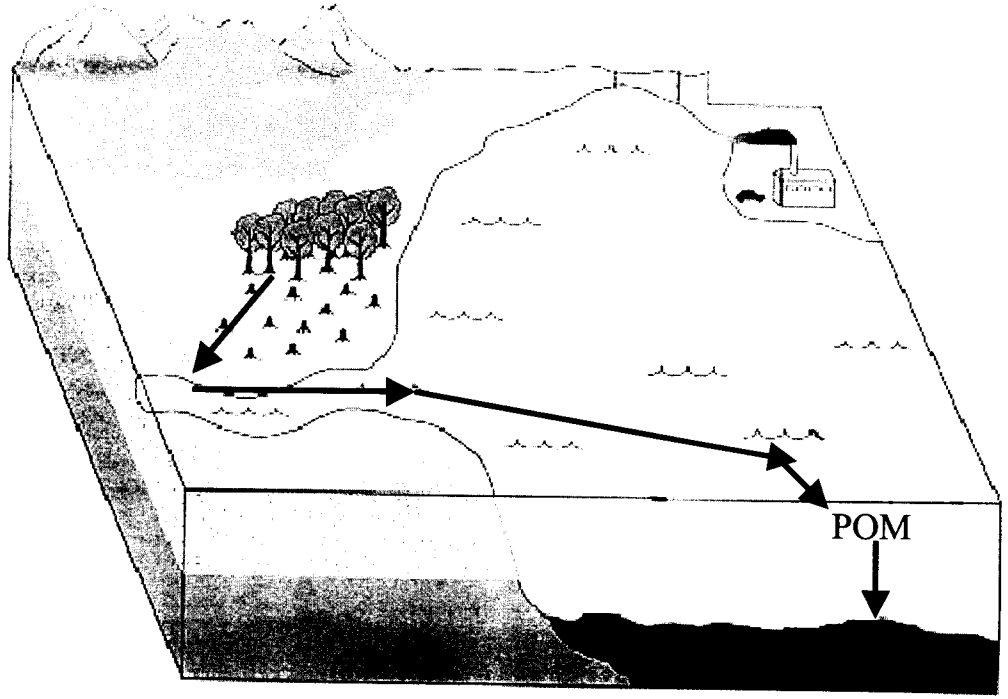
43810/0.26 = 168,500 years

Goldberg

Goldberg, Black carbon in the environment (1985) Wiley, New York

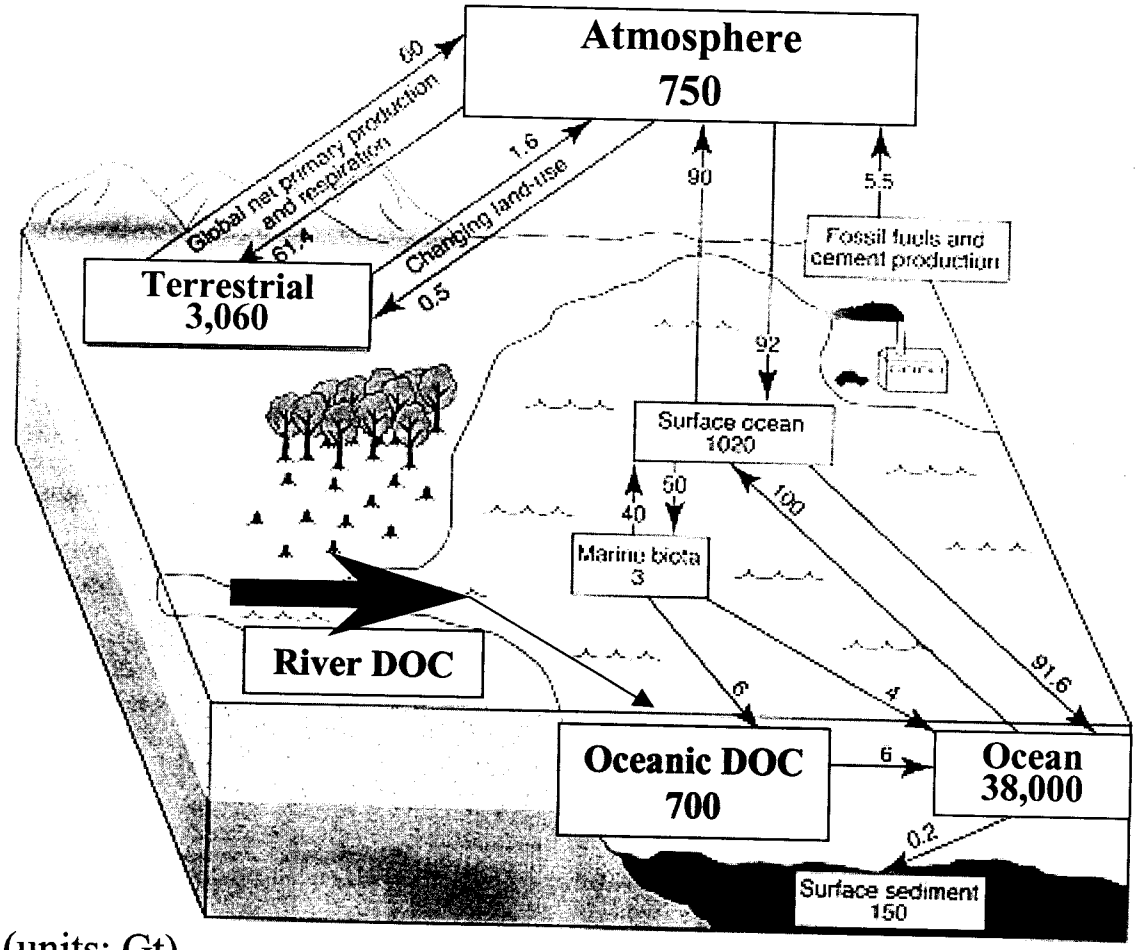
A hypothesis - global black carbon cycle

1. BC is a source of old carbon in the river DOM
2. BC flows into the ocean and is included in oceanic DOM
3. BC flows into the deep ocean
4. BC in DOM is included into particulate organic matter (POM)
5. BC in POM is deposited to ocean sediment



The hypothesis can partly solve the riddle in a global carbon cycle

Selective inclusion of refractory component of river DOC into oceanic DOC pool



(units: Gt)

- "Significant amount of carbon transferred from terrestrial systems to the deep ocean or marine sediments would help balance models of the global carbon cycle."

Schlesinger and Melack, Tellus (1981), 33, 172-187

Adapted from Houghton *et. al.* Climate change 1994 (1995), Cambridge Press, New York