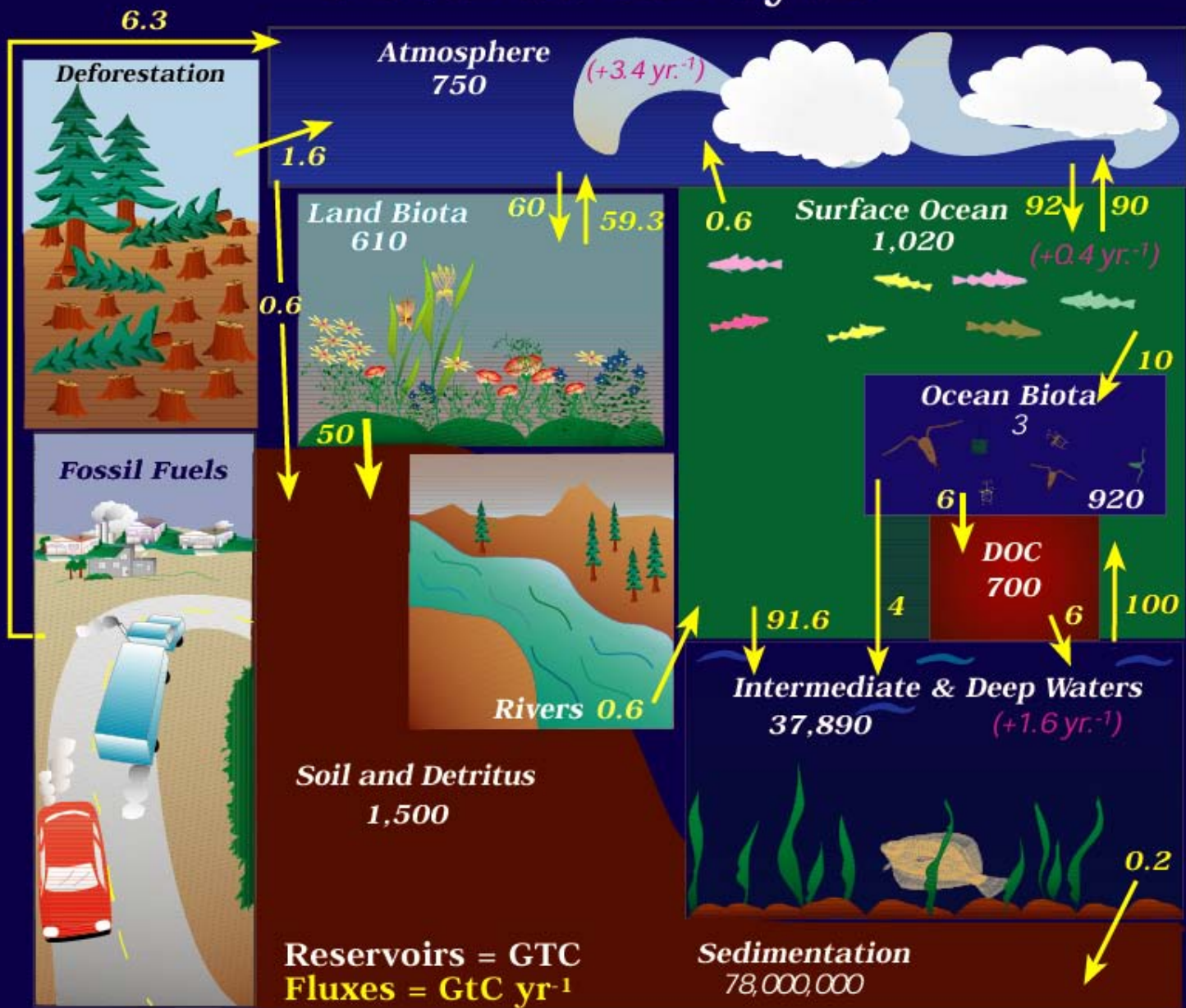


1. Carbon Cycle
2. Analytical techniques in chemical oceanography

12.097 Lecture
January 18, 2006

Global Carbon Cycle



The Marine C Cycle

Image removed due to copyright considerations.
Please see: Valiela, 1994. (See readings.)

DOC distribution

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Please see: Williams 2000. (See readings.)

Summary depth profile of DOC in
open ocean, separated into low and
high molecular weight components.

Sources of DOC to surface ocean

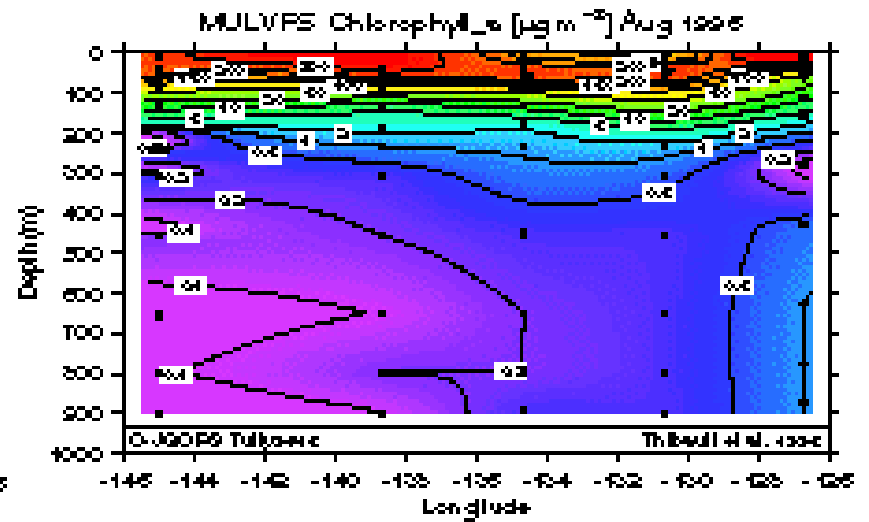
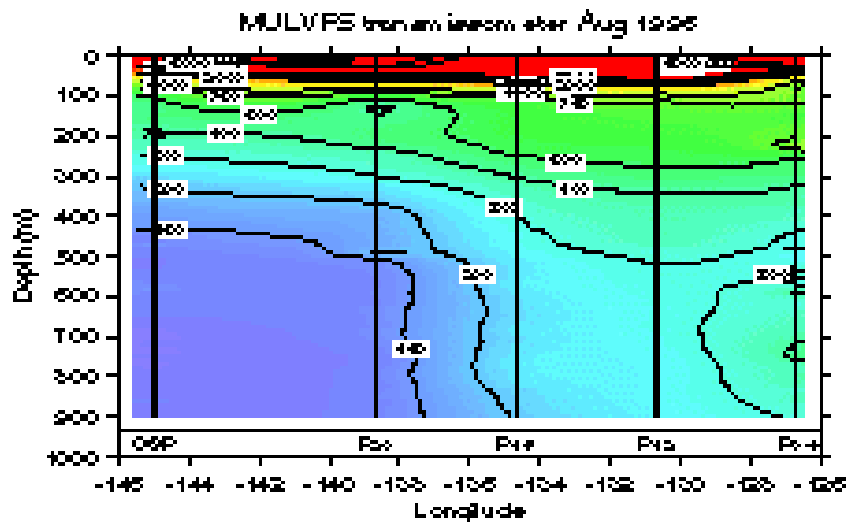
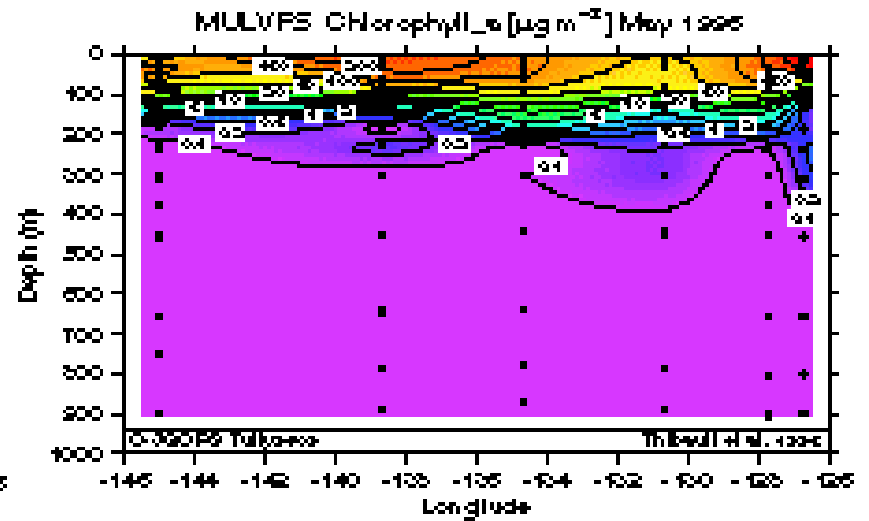
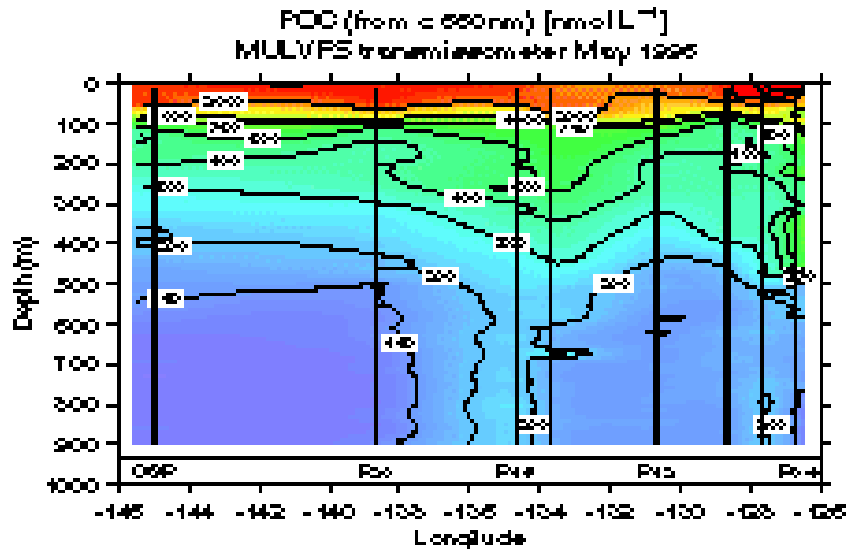
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Please see: Nagata, 2000. (See readings.)

What is DOC?

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Please see: Williams, 2000. (See readings.)

POC distribution



Particulate Organic Carbon (POC)

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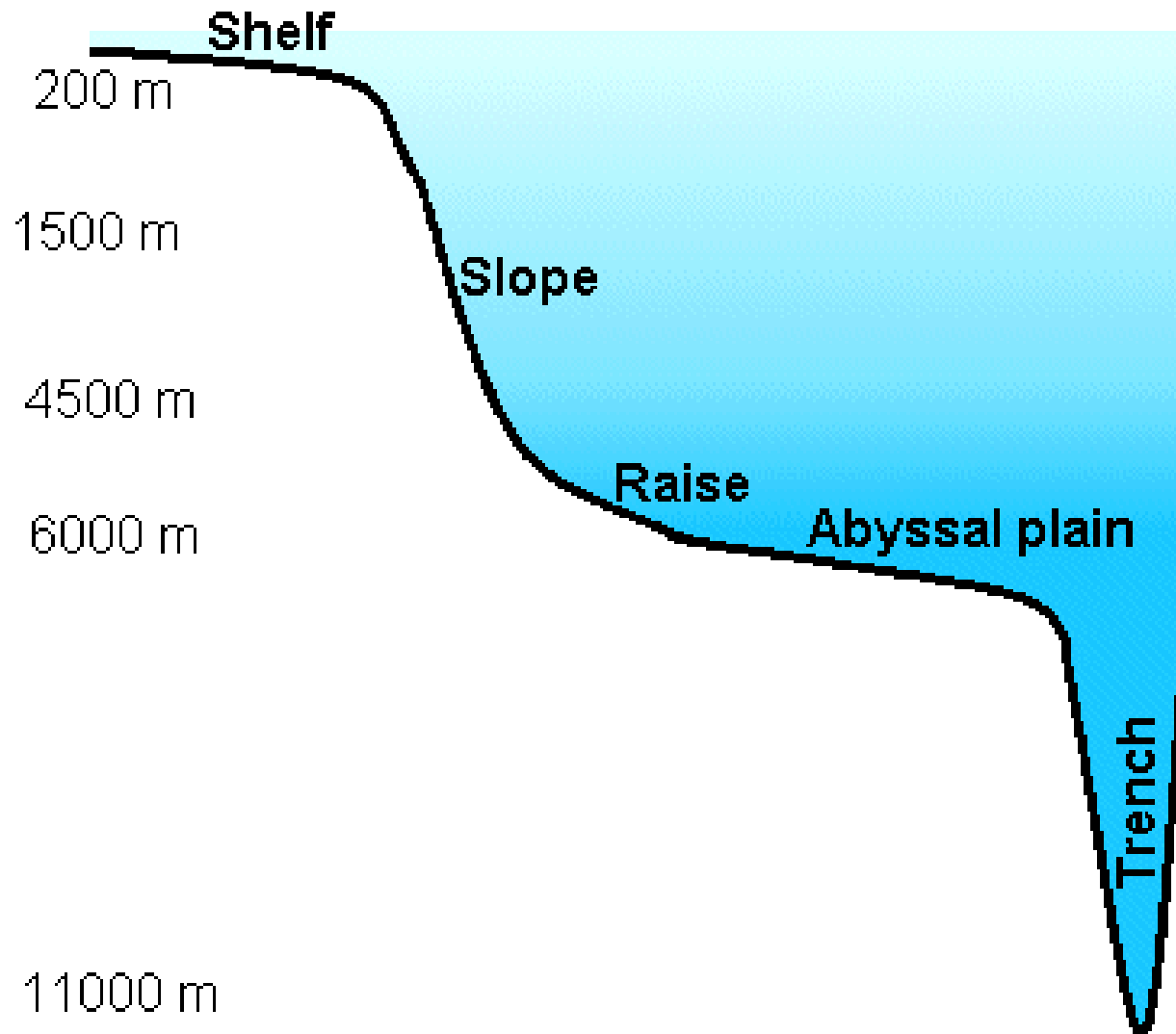
Please see: S. Wakeham (www.skio.peachnet.edu/research/biogeochemlab/)

- POC falls in episodic “clumps”
- Cannot be sampled adequately by Niskin bottles – must use (semi-)permanently moored sediment traps
- Flux: 1-100 mgC / m² / d
- Varies seasonally
- Labile organic matter is transported quickly to ocean floor.

Carbon cycle rates

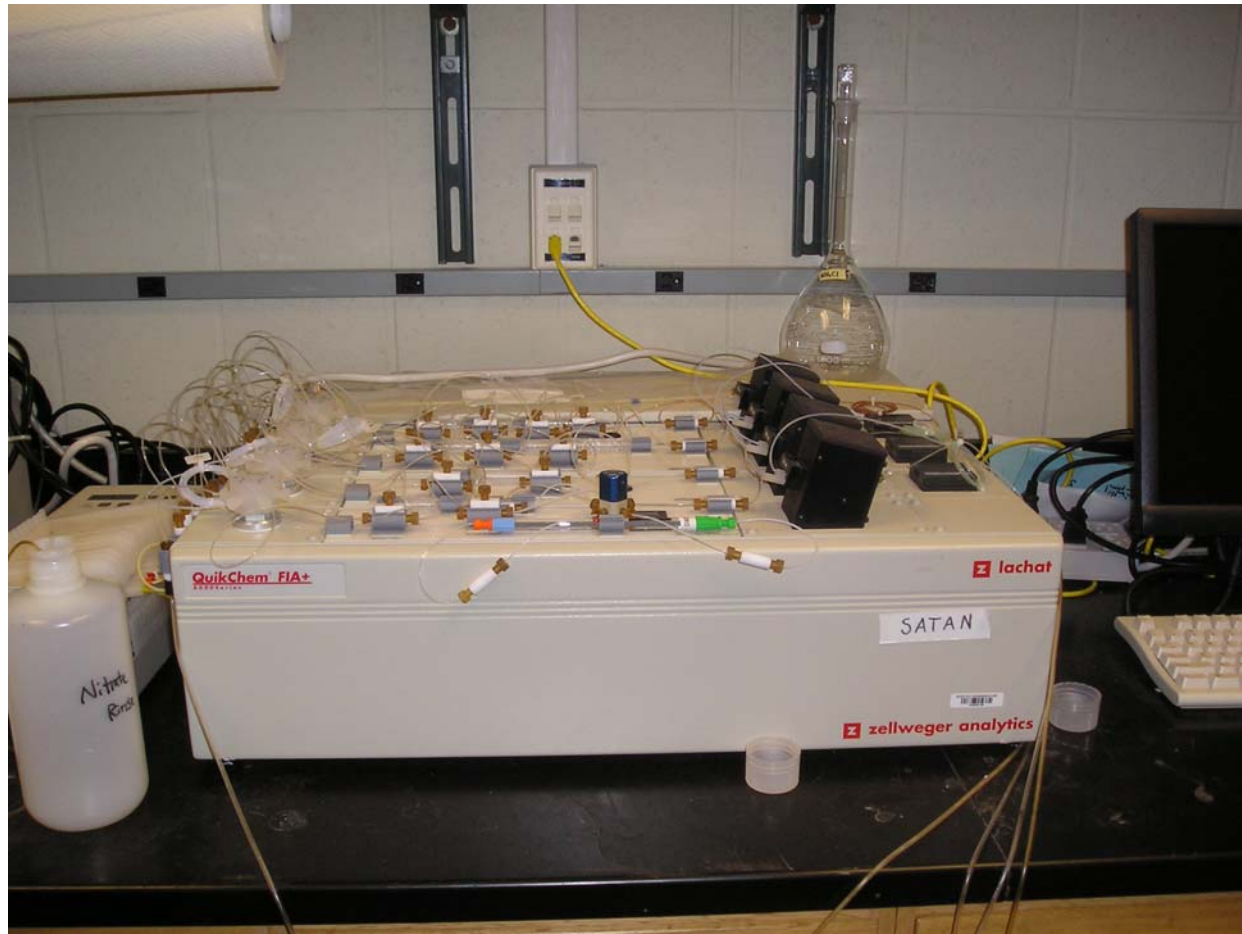
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Please see: Williams, 2000. (See readings.)

Analytical techniques in chemical oceanography



Nutrient analyzer


Matt Charette's lab in Marine Chemistry dept at WHOI



- Lachat nutrient auto-analyzer: measures total dissolved nitrogen (TDN), ammonia, nitrate, nitrite, phosphate, silicate
- Based on standard spectrophotometric techniques

Metals: ICP-MS

1 H																2 He	
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89 Ac	104 Rf	105 Ha	106 Sg	107 Ns	108 Hs	109 Mt	110	111	112	(113)	(114)	(115)	(116)	(117)	(118)
(119)	(120)	(121)	(154)	(155)	(156)	(157)	(158)	(159)	(160)	(161)	(162)	(163)	(164)	(165)	(166)	(167)	(168)

 Multicollector ICP-MS

Lanthanides	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
-------------	----------	----------	----------	----------	----------	----------	----------	----------	----------	----------	----------	----------	----------	----------

Actinides	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr
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Super-Actinides	(122)	(123)	(124)	(125)	(126)							(153)
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Figure by MIT OCW.

Metals: ICP-MS

Image removed due to copyright considerations.
Please see: Thermo-Finnigan NEPTUNE/TRITON brochure

Organic Carbon Analyses 1

- Bulk analyses:
 - Elemental analysis
 - Amt of C, H, or N in solid sample
 - Used on particulate material or freeze-dried “dissolved” material
 - Carbon combustion
 - Amt of C in sample after removal of CO₂
 - High-temperature combustion (>800°C)
 - Used for aqueous samples only.

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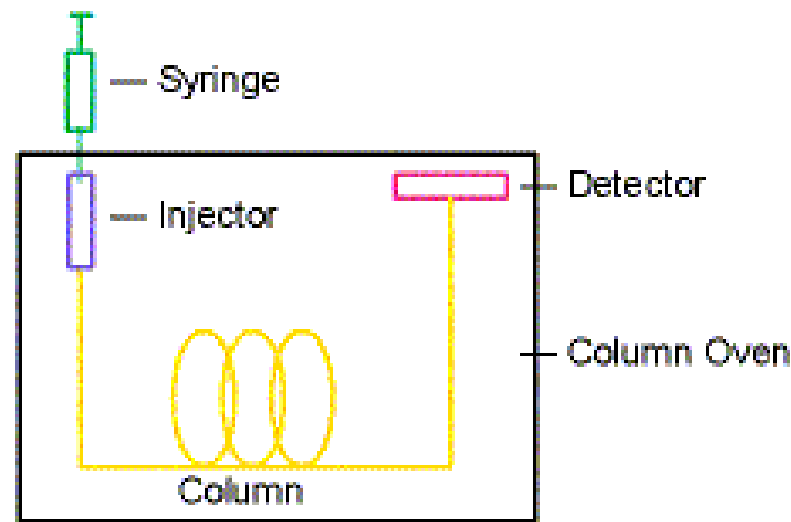
Please see: http://www.uark.edu/ua/isotope/about/elemental_analyzer.jpg

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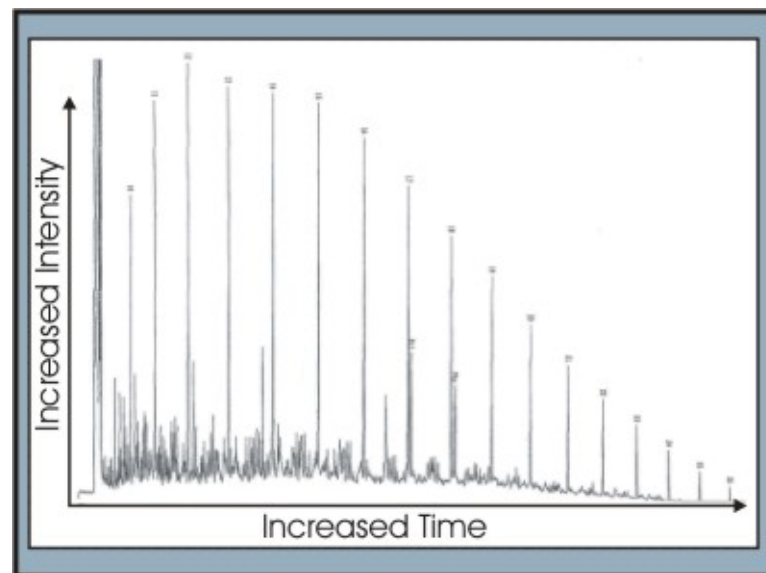
Please see: L. Guo(<http://denali.frontier.iarc.uaf.edu/>)

Organic Carbon Analyses 2

- Compound-specific analyses require (relatively) large amounts of a single compound: need to concentrate initial sample!
- Polar compounds: remove water
 - Analysis by HPLC
- Nonpolar compounds: extract with organic solvent or solid organic matrix (SPE)
 - Analysis by GC
- Semi-polar compounds
 - Change pH of solution to make compound neutral (non-ionic)
 - Derivatize polar component with non-polar functional group
- Mass spectrometry
 - Used to characterize structure and/or composition of individual molecules



Schematic of a gas chromatograph



Organic Carbon: Isotopes Overview

- There are 3 isotopes of carbon:
 - ^{12}C : 6 neutrons, 6 protons, stable, 98.89% of all carbon
 - ^{13}C : 7 neutrons, 6 protons, stable, 1.11% of all carbon
 - ^{14}C : 8 neutrons, 6 protons, radioactive, $10^{-10}\%$
- Dominant process for determining $^{13}\text{C}/^{12}\text{C}$: fractionation
 - The small mass difference (approx 1 Da) creates a small (but significant) in energy requirements for bonds between ^{13}C and the more abundant ^{12}C atoms.
 - Thus, biological systems will preferentially use ^{12}C over ^{13}C , resulting in a decreased $^{13}\text{C}/^{12}\text{C}$ in biological material and an increased $^{13}\text{C}/^{12}\text{C}$ in the reservoir.

- Reported values: $\delta^{13}\text{C}$

$$\delta^{13}\text{C} = \left[\frac{\left(\frac{^{13}\text{C}}{^{12}\text{C}} \right)_{\text{sample}} - \left(\frac{^{13}\text{C}}{^{12}\text{C}} \right)_{\text{std}}}{\left(\frac{^{13}\text{C}}{^{12}\text{C}} \right)_{\text{std}}} \right] * 1000$$

$\delta^{13}\text{C}$ ratios in environment

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Please see: http://basinisotopes.org/basin/tutorial/gifs_2/irms_diagram.html

Image removed due to copyright considerations.

Please see: http://www.geosc.psu.edu/~dbice/DaveSTELLA/Carbon/c_isotope_models.htm

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Please see: <http://www.eva.mpg.de/evolution/images/isotope.jpg>