Lecture 22
Nutrients and Particles in Fresh Waters

Last time

1. estuaries - Fresh-salt water mixing interactions; Particle-Aqueous Solute Interactions revisited.

Today

2. estuaries - Case Studies from Estuarine and near Shore Marine Environments.

Recall from last time….Fe behavior in estuary mixing zones

Flocculation of Fe in the mixing zone of estuaries is a very important process for governing the distribution of other heavy metals between water and sediment.

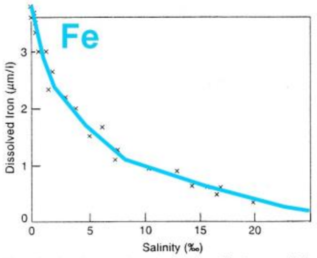


Figure 7.4. Total dissolved iron (μm/l = micromoles per liter) versus salinity in the Merrimack Estuary., Massachusetts. Data points in order of increasing salinity fall on a concave-up (iron removal) curve. (Modified from E. A. Boyle, R. Collier, A. T. Dengler, J. M. Edmond, A. C. Ng, and R. F. Stallard, "On the Chemical Mass Balance in Estuaries," *Geochimica et Cosmochimica Acta*, 38, p. 1722 Copyright © 1974 by Pergamon Press, reprinted by permission of the publisher.)

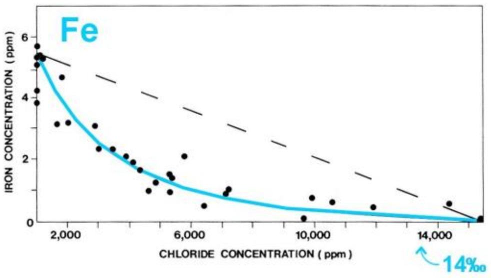
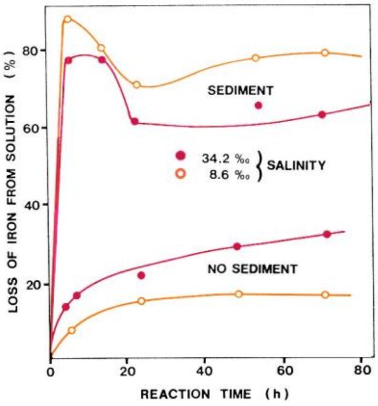


Fig. 63. Nonconservative behavior of dissolved iron in the freshwater/seawater mixing zone of Mullica River/Great Bay, New Jersey (Coonley et al., Geochim. Cosmochim. Acta, *35*, 1971. Reproduced with permission of Pergamon Press, Oxford)

Fe is found in a number of forms in river water:
(a) free ion, (b) as Fe-oxide/hydroxide colloids, (c) chelated by DOC and (d) sorbed by colloidal POC.
of these, the free ion is typically the lowest.

Laboratory determinations of Fe precipitation from estuarine waters show it is enhanced in the presence of other active surfaces (i.e., other sediments) due to sorption of Fe on sediment surfaces and more effective colloid destabilization of in saltier waters.



Fe Flocculation

(1) sed > no sed
(2) more salt > less salt when sed is absent
(3) sed not as effective in salty water

Fig. 62. Influence of suspended particles on the precipitation of iron compounds in the freshwater/seawater mixing zone (after Aston and Chester, 1973)

Without sediments, Fe loss from solution is enhanced in more saline by destabilization of Fe colloids, Fe-DOC complexes and Fe-POC colloids.

Note that sediment is not as effective in saline waters as in fresher water because there is more “competition” between Fe and other ions for active sorption sites on the sediment in saltier water.

Other metals "act like Fe" in sorption behavior to colloids (including Fe-colloids themselves).

As Fe-bearing colloids are desolvated in the estuary, many other metals are brought down to the sediments in the process.

But some metals are flocculated more or less efficiently than Fe, so we can not to assume that Fe-flocculation is the only controls on metal flocculation in general.

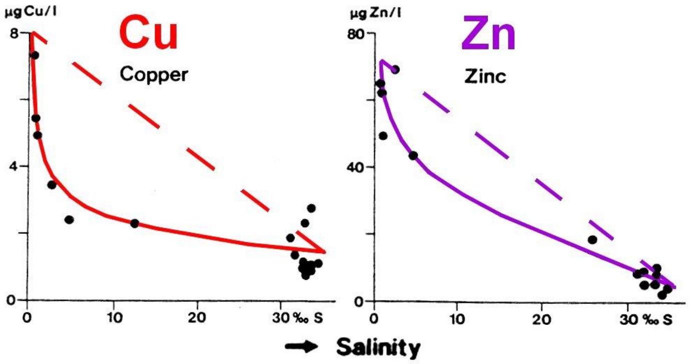


Fig. 64. Nonconservative effects for dissolved copper and zinc (values in µg/l) in the Rhine Estuary (Duinker and Nolting, 1977, Marine Pollution Bulletin *8* (3) p. 70. Reproduced with permission of Pergamon Press, Oxford)

Cu has a steeper “draw-down” curve than Zn, indicating that Cu flocculates more readily in this estuary. Part of its flocculation must be due to removal of a phase that is less stable in the presence of salt water than the dominant Zn-carrying phase.

Cu is strongly chelated by organic colloids such that there is almost no free Cu ion concentration in waters with DOC/POC. POC colloids are even-more salinity sensitive that Fe colloids and thus flocculated more efficiently in estuarine mixing.

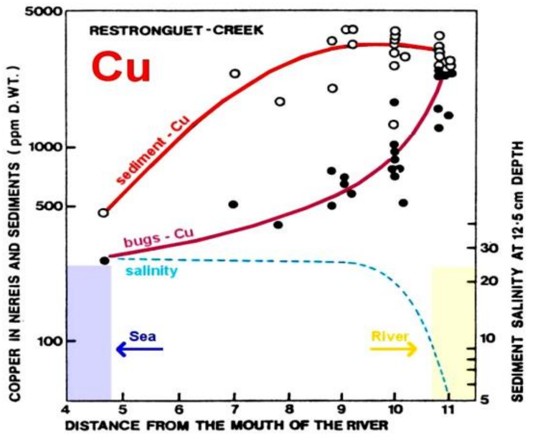


Fig. 80. Correlation of sediment salinity (in per mille) and copper concentrations in sediments to copper in *Nereis diversicolor* at different points of Restronguet Creek, Southwest England. *Solid line, Nereis diversicolor; light line,* sediment; *broken line,* salinity (Bryan and Hummerstone, 1971, J. Mar. Biol. Assoc. U. K. *51*, p. 850. Reproduced with permission of Cambridge University Press, London)

In this example, Cu is associated with labile (reactive) particulate organic matter in newly flocculated sediment that forms (and is removed) far from the estuary mouth. Copper concentration is also high in organisms in the sediment (e.g., Nereis, a polychaete worm).

Cu removed farther downriver is associated with less-labile material and is not incorporated as effectively by organisms.

Pb is also commonly flocculated more quickly than Zn (and Fe) due to partial association with organic matter

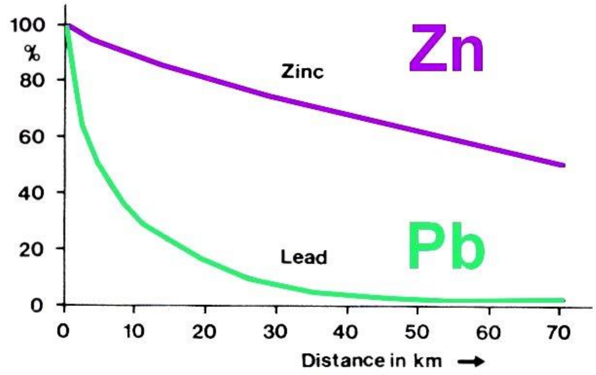
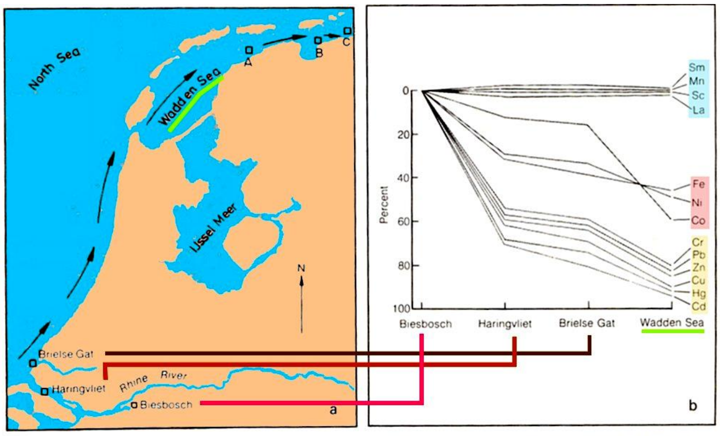


Fig. 55. Immobilization of lead and zinc from artificially induced lead and zinc solution in a section of the Ruhr River catchment area (from Koppe, 1973)

We would thus also find high Pb content in sediments further upstream than the concentration peak of Fe and Zn in many river-estuary systems.

Other floccable heavy metals.

Some metals are removed more efficiently than others along a water flow path through the Rhine estuary and along the coast to the Wadden sea.



These can be grouped in to:

a. “Fe-like group”

b. “more floccable than Fe group”

c. a “not flocced group”

Fig. 52. a Direction of movement of sediments in the Rhine estuary, North Sea, and Wadden Sea. **b** Mobilization of metals in the Rhine Estuary, North Sea, and Wadden Sea, expressed as a percentage of the original contents. (Both parts after de Groot et al., 1971, 1973)

This demonstrates that the rate of dispersal of metals to the ocean is highly dependent on dissolved-particulate equilibria in the estuarine and near-shore environment.

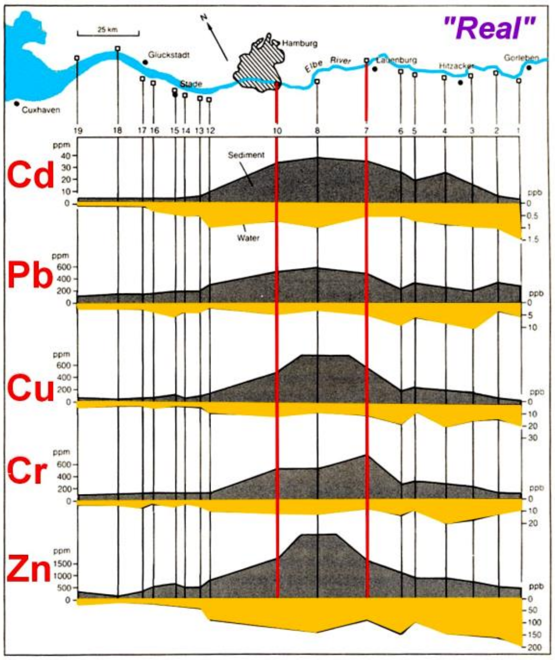


Fig. 53. Distribution of heavy metals in sediments (pelitic fraction) and water from the estuarine mixing zone of the Elbe (Müller and Förstner, 1975)

Förstner and Wittman, Metal Pollution in the Aquatic Environment

In the Elbe River estuary, there are broad peaks in sediment metal concentration (gray) in the zone between stations 7 and 10, corresponding to the maximum point of infiltration of seawater through tidal action.

Yellow here indicates element concentration in the water. Note the huge enrichments in the sediments (from ppb levels in the water to many ppm in the sediments).

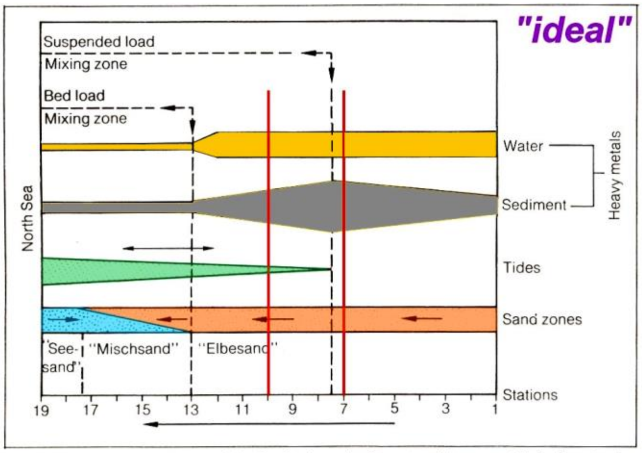


Fig. 54. Schematic presentation of the distribution of sediments and heavy metals in the estuarine mixing zone of the Elbe (Müller and Förstner, 1975, based on investigations of Simon, 1953)

Förstner and Wittman, Metal Pollution in the Aquatic Environment

Sediment distribution patterns indicate that the sediment being deposited where metal deposition is greatest are riverine ("Elbesand").

Marine particulate matter ("Seesand") is not involved in the metal draw-down process.

Heavy Metals in Polluted Estuaries

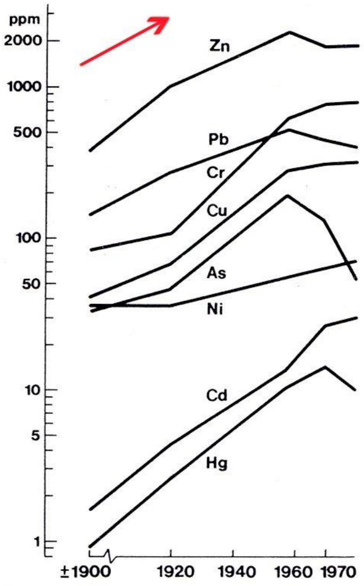


Fig. 101. History of trace metals in Rhine sediments (after Salomons and De Groot, 1978)

Dissolved and colloidally suspended materials in a *polluted* river are subject to the same processes as pristine river waters during mixing in estuaries.

Flocculation will affect pollutant as well as naturally-occurring organic carbon and heavy metals in the incoming river water

The sediments of the Rhine river show increased concentration of many heavy metals since the start of the 20th century presumably due to flocculation from increasingly metal-concentrated river water over the years.

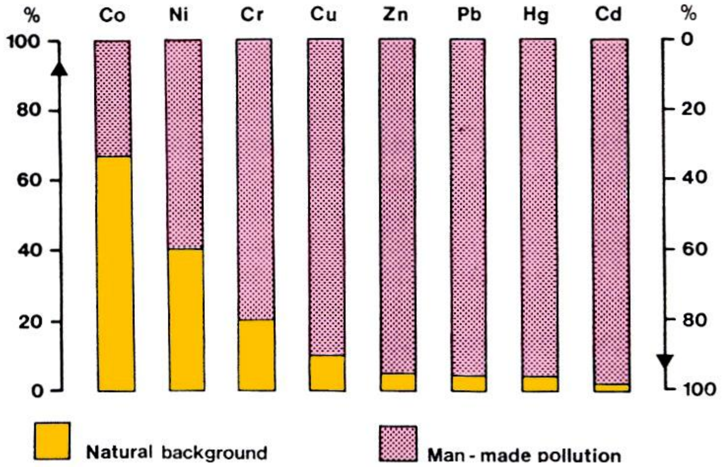


Fig. 100. Sources of heavy metals in pelitic sediment from the lower Rhine River

Mass balances for various input sources suggest that most of the metal load of the Rhine is from human activities (except for Co, for which only 40% of the contamination is human-derived).

Salinity Effects on Heavy Metals

We must also consider the effect of **high** salinity on elemental **speciation**, which results in enhanced competition for sorption sites on solids in contact with high TDS waters.

There are important speciation differences in fresh and salt water systems for a number of important pollutant metals.

Estuarine and harbors sediments, which can be washed out to sea during storms, and sewage outfall plumes to near-shore marine environments both desorb many metals in the process.

Note the strong desorption of almost all of these metals in seawater relative to fresh water.

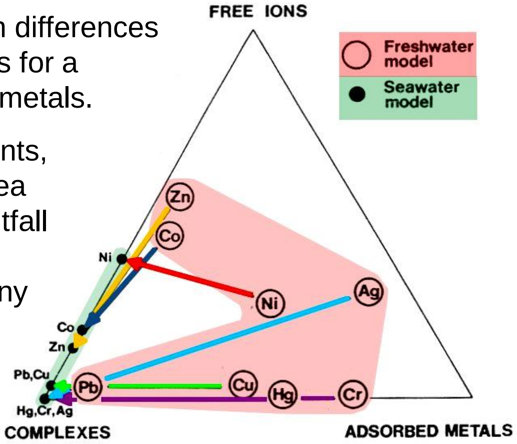


Fig. 19. Evaluation of the changes in chemical species of selected trace elements from a seawater/freshwater model (data from Sibley and Morgan, 1977)

As you might infer, when polluted solids are introduced into the ocean in near shore environments, large fluxes of metals to the dissolved state can occur.

Table 72. Release of trace metals from contaminated particles after contact with seawater (experiments by Rohatgi and Chen, 1975)

	Sewage Primary/secondary effluent dilution with seawater 1:5		**Urban River Water** Los Angeles River, dry weather flow dilution with seawater 1:2	
	initial conc.	% release 4 wks	initial conc.	% release 4 wks
Iron	0.50%	0%	1.22%	0%
Manganese	51 ppm	0%	498 ppm	0%
Chromium	3,296 ppm	0%	452 ppm	0%
Zinc	1,481 ppm	38%	905 ppm	60%
Lead	140 ppm	58%	516 ppm	17%
Nickel	896 ppm	63%	407 ppm	72%
Copper	2,182 ppm	69%	1,063 ppm	66%
Cadmium	87 ppm	93%	–	–

Data for Los Angeles River water and treated sewage effluent show that desorption occurs upon contact of contaminated particles with seawater.

This desorption in turn often results in high metal concentrations in near-shore marine organisms, many of which are food sources for humans, birds and other organisms higher up on the food chain.

At sewage outfalls into the ocean, introduced solid human wastes might mix up through the water column to the base of the thermocline and desorb many of its bound metals.

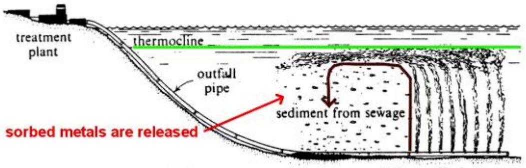


Figure 7.4. Settling of solids from an ocean-floor sewage effluent discharge.

Manahan, "Environmental Chemistry"

An example from a sewage outfall offshore of Los Angeles demonstrates that the concentrations of dissolved Zn, Cu and Pb are highest at the depth where the outfall plume is most concentrated (as measured by turbidity of the water).

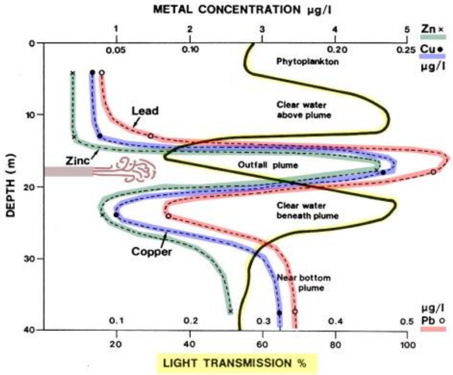


Fig. 24. Depth distribution of light transmission (*solid line*) and concentrations of zinc (*crosses*), copper (*closed circles*) and lead (*open circles*) in a water column near Los Angeles County waste-water outfall (after Martin et al., 1976. In: *Marine Pollution Transfer*. Lexington Books, D.C. Heath and Co., Mass.)

Spatial/Temporal variability in estuarine conditions

Tides, river flow and sediment load vary over a range of time scales, making it difficult to get a complete picture of an estuary from a single set of water measurements.

Estuarine **sediments** give us an idea of present and past conditions **integrated** over longer time periods.

Colloid flocculation and "normal" sedimentation result in a rapid and continual buildup of sediments rich in the products of:

- ♦ terrestrial weathering
- ♦ photosynthesis/respiration in rivers and lakes
- ♦ various chemical inputs of human society.

Estuarine sediments

Recall that rapid E_H changes with depth in high organic matter sediments causes the redox ladder series of chemical changes.

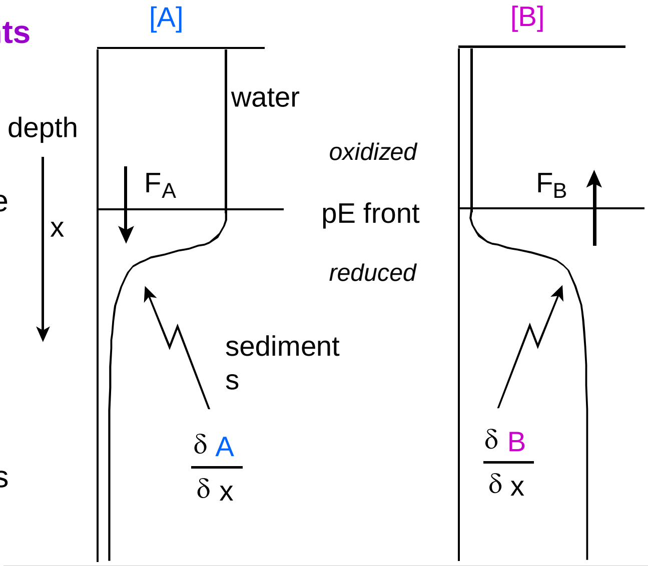
Most estuarine **sediments are anoxic within 2-10 cm** of their interface with the overlying water, creating a "chemical front" between oxidized and reduced sediment pore waters.

The E_H front is from dissolved O_2 consumption in pore waters and microbially-mediated breakdown of DOC/POC.

Estuarine sediments

E_H changes result in dramatic shifts in chemical form of some materials in the sediment stack.

Materials that are removed from solution by reactions under reducing conditions will show concentration profiles like “A”. Materials that are produced in the sediment will exhibit profiles like “B”.



“Fick’s Law”

Flux(diff) = -D(δc/δx)

the flux of component "c" across a chemical front per unit time is proportional to the size of the concentration contrast and a constant of proportionality (the diffusion constant - D)

Examples of "A" are elements that like the oxic conditions of the water but become insoluble when reduced (U, Cr, Re) or are otherwise consumed in the sediments (O_2).

Examples of "B" are elements that are more soluble when reduced (Fe, Mn) or are produced in the sediments (DIP, DIN).

[X]	oxidized		reduced	
Mn	Mn^{+4} as MnO_2	*insoluble*	Mn^{+2}	*soluble*
Fe	Fe^{+3} (many forms)	*insoluble*	Fe^{+2}	*soluble*
U	U^{+6} as $UO_2(CO_3)_2$	*soluble*	U^{+4} as $UO_2(s)$	*insoluble*
Cr	Cr^{+6} as $Cr_2O_7^{2-}$	*soluble*	Cr^{+3} as Cr_2O_3	*insoluble*
Re	Re^{+7} as ReO_4^-	*soluble*	Re^{+4} as ReO_2	*insoluble*

Other chemical species that are soluble in *both* reduced and oxidized forms (e.g., sulfur as SO_4^{2-} and H_2S) show diffusion gradients near the particular redox boundary that causes their transformation from one form to another.

Turbulent water flow in high-porosity sediments may "smooth out" the diffusion profile and make the shape less ideal. Nevertheless, it's important to recognize a concentration gradient at least partially controlled by diffusion.

Sediments of the Feldsee estuary display a large particulate Fe and Mn enrichment just above a drop in measured E_H,. These elements diffused upward as soluble reduced metals from the low E_H region and then precipitated as solids.

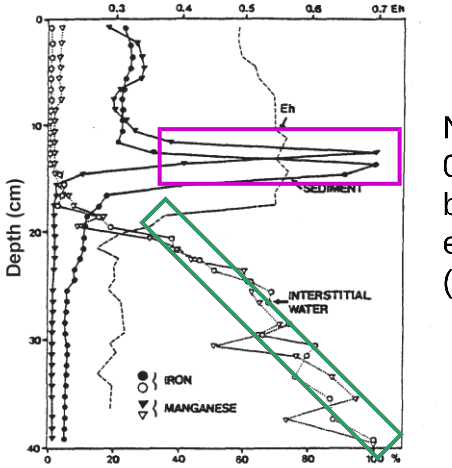


Fig. 68 Redistribution of iron and manganese in recent sediments from the Feldsee (West Germany) as functions of Eh and pH conditions (Tessenow and Baynes, 1975, Naturwissenschaften 62, p.342)

Notice that the E_H jump is from ~ 0.55V to 0.3V, which is well below the E_H of waters in equilibrium with the atmosphere (E_H = 1.22 for H_2O - O_2).

Estuarine sediments

Sediments are not static stacks of stata. They accumulate over time, so chemical fronts also move location with time.

Conditions will ***migrate up*** through the sediment stack as sediments accumulate, eventually isolating deeper strata from activity near the sediment/water interface, due to the low rate of water flow in the sediments.

However, a ***sudden change*** in conditions of the system, such as dredging of the sediments or an unusually large storm event can cause the system to equilibrate to the new conditions quickly.

This can set the stage for rapid oxidation of many chemicals (which may instigate their release back into the oxic waters above).

Estuarine sediments

A case study of estuarine processes from sediment pore water profiles: the White Oak River Estuary (North Carolina). We look at data from 4 stations (F, P, S and C) moving in from the coast, along a gradient of salinity and pH in the estuary.

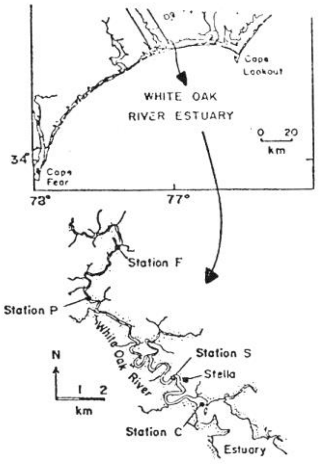
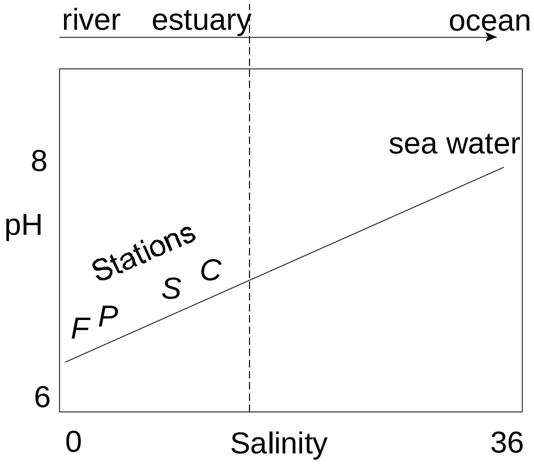


Fig. 1. White Oak River Estuary study site. Individual station locations indicated on expanded scale sketch.

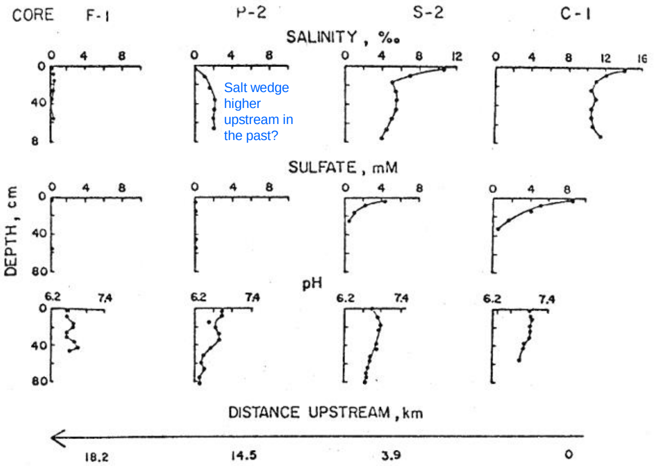


✶ salinity decreases in upstream cores. The increase with depth at station P likely reflects a time when saline bottom water penetrated further up the estuary.

✶ Sulfate in surface waters decreases upstream. Sulfate in sediment pore waters is used up by sulfate reducing bacteria, causing a concentration gradient with depth.

✶ pH of surface waters decreases upstream.

✶ General pH decrease with depth as H^+ is liberated during digestion of organic matter and dissolution of the resulting CO_2 (g).



Salt wedge higher upstream in the past?

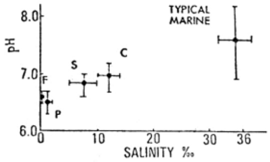


Fig. 7. pH range vs. salinity range observed in interstitial waters at each station. pH range commonly observed in marine sediments plotted for comparison.

Fig. 2. Variations in salinity, dissolved sulfate, and pH depth distributions in interstitial waters with distance upriver. Data points for salinity and sulfate represent midpoint of 5 to 10 cm of squeezed core sections.

✺ Total organic carbon decreases downstream (and somewhat down core) but DOC increases downstream (and in some down core cases).

✺ Reduced sulfur increases from sulfate reduction. Since SO_4^{2} concentrations increase downstream, these sites show bigger increase with depth of reduced sulfur, leading to more **"sulfidic"** conditions in sediments where S is present.

✺ Reduced sulfur decreases at depth may be due to pyrite formation

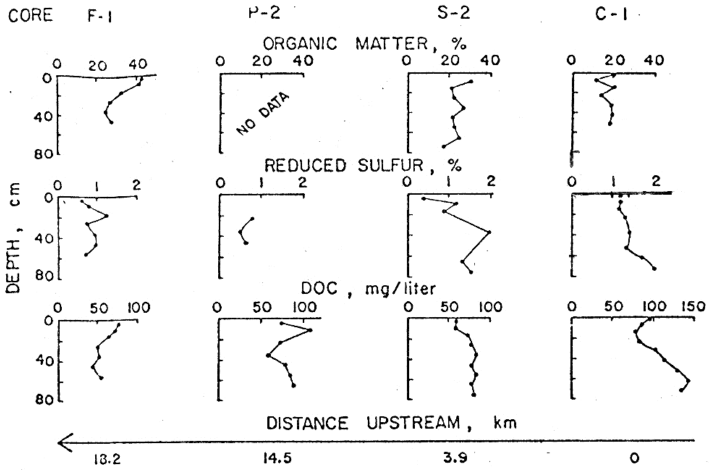
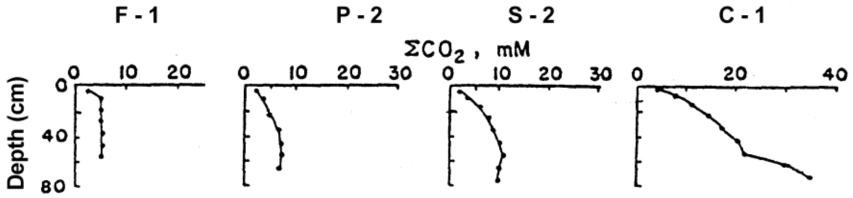


Fig. 6. Variations in depth distributions of percent sedimentary organic matter and reduced sulfur, and dissolved organic carbon with distance upriver.

✷Higher DOC in downstream cores reflects both input of marine DOC and are more flocculation in the more saline waters. This is reflected in higher $\Sigma CO_2(aq)$ in more oceanward cores due to microbial consumption of DOC



✷ Higher DOC means higher rate of consumption of O_2 and therefore shallower level of EH front in the sediments.

✷ DIN (as ammonia) increase at a greater rate from DOC consumption in downstream cores (because marine humics have greater N content than fresh water humics.

✷ Once O_2 is gone, Mn and Fe are utilized quickly as oxidizing agents followed by SO_4^{2-} (if present) and HCO_3^-. Fe^{2+} and PO_4^{3-} increase with depth as this occurs. Fe and P diffuse away from the depth of the transition but can also be affected by ($Fe^{2+} \leftrightarrow FeS_2$ and some P adsorption onto clays)

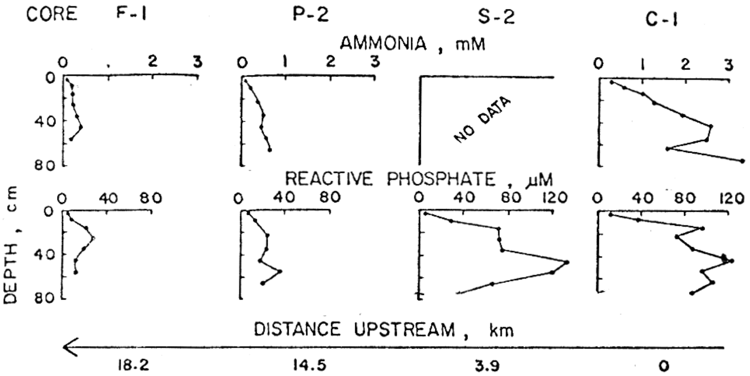


Fig. 5. Variations in depth distributions of dissolved ammonia, reactive phosphate, and reactive silica in interstitial waters with distance upriver.

Estuarine sediments

Such variations in sediment pore water chemistry (both at estuaries and elsewhere) as a function of:

a. E_H/pH conditions

b. the composition of the overlying waters

has led to a number of environmental classification schemes based on the presence of absence or "marker" materials (either in the pore waters or as solid phases in the sediments).

The "Berner Scheme" is one such classification.

The "Berner Scheme" uses *authigenic* phases (as opposed to *detrital* ones) as a measure of conditions in which the sediment formed. It allows one to make generalizations about waters that no longer exist (using the geologic record), using:

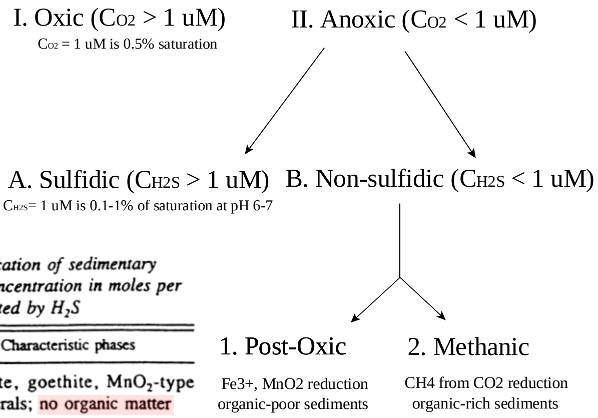
✺ the *mineralogical* differences between oxic and anoxic sediments and the organisms that mediate these changes.

✺ the solubility differences for reduced Fe and Mn depending upon the relative abundances of HCO_3^- and H_2S.

✺ oxic and anoxic conditions defined from practical limits of microbial activity, rather than specific conditions of pE/pH.

Oxic conditions :	**Anoxic conditions**
Aerobic organisms (die at $[O_2]<10^{-6}$ M, which = ~0.5% saturation; can not tolerate traces of H_2S). Oxidized minerals (unstable at low pe)	Anaerobic bacteria (can not tolerate traces of O_2). Reduced minerals (unstable at high pe)

Characteristic minerals for each environment at the boundary conditions specified:



I. Oxic (C_{O2} > 1 uM)

C_{O2} = 1 uM is 0.5% saturation

II. Anoxic (C_{O2} < 1 uM)

A. Sulfidic (C_{H2S} > 1 uM)

C_{H2S}= 1 uM is 0.1-1% of saturation at pH 6-7

B. Non-sulfidic (C_{H2S} < 1 uM)

1. Post-Oxic

Fe3+, MnO2 reduction
organic-poor sediments

2. Methanic

CH4 from CO2 reduction
organic-rich sediments

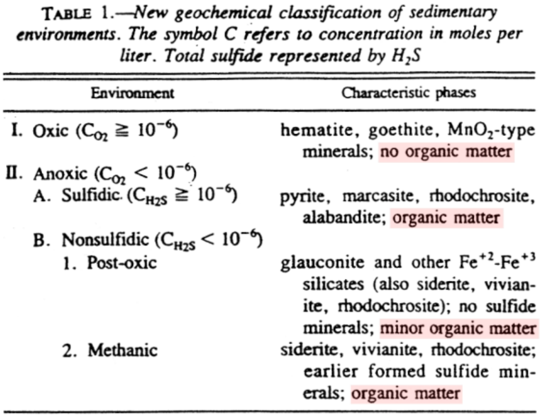


TABLE 1.—*New geochemical classification of sedimentary environments. The symbol C refers to concentration in moles per liter. Total sulfide represented by H_2S*

Environment	Characteristic phases
I. Oxic ($C_{O_2} \geqq 10^{-6}$)	hematite, goethite, MnO_2-type minerals; no organic matter
II. Anoxic ($C_{O_2} < 10^{-6}$)	
A. Sulfidic ($C_{H_2S} \geqq 10^{-6}$)	pyrite, marcasite, rhodochrosite, alabandite; organic matter
B. Nonsulfidic ($C_{H_2S} < 10^{-6}$)	
1. Post-oxic	glauconite and other Fe^{+2}-Fe^{+3} silicates (also siderite, vivianite, rhodochrosite); no sulfide minerals; minor organic matter
2. Methanic	siderite, vivianite, rhodochrosite; earlier formed sulfide minerals; organic matter

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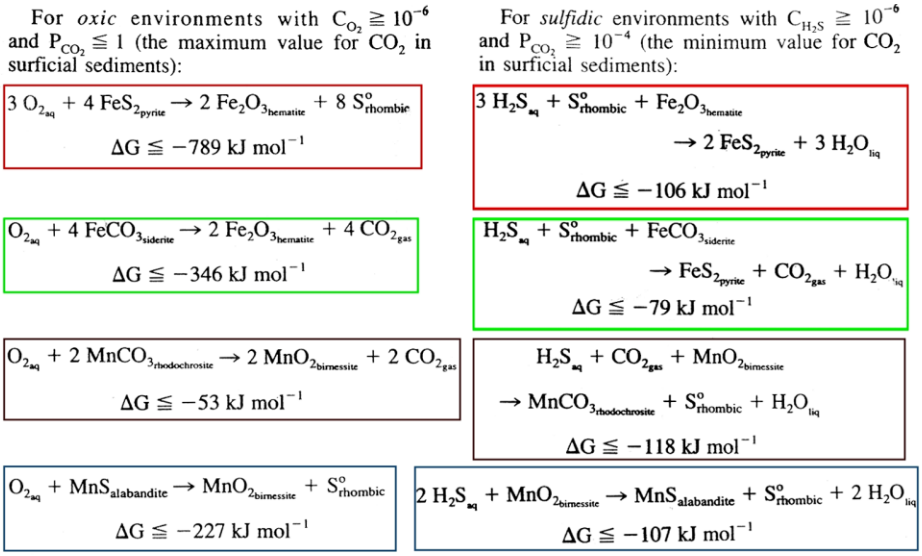
ΔG_f values for mineral transformations at the boundary conditions specified.



For *oxic* environments with $C_{O_2} \geqq 10^{-6}$ and $P_{CO_2} \leqq 1$ (the maximum value for CO_2 in surficial sediments):

$$3\,O_{2_{aq}} + 4\,FeS_{2_{pyrite}} \rightarrow 2\,Fe_2O_{3_{hematite}} + 8\,S^o_{rhombic}$$
$$\Delta G \leqq -789 \text{ kJ mol}^{-1}$$

$$O_{2_{aq}} + 4\,FeCO_{3_{siderite}} \rightarrow 2\,Fe_2O_{3_{hematite}} + 4\,CO_{2_{gas}}$$
$$\Delta G \leqq -346 \text{ kJ mol}^{-1}$$

$$O_{2_{aq}} + 2\,MnCO_{3_{rhodochrosite}} \rightarrow 2\,MnO_{2_{birnessite}} + 2\,CO_{2_{gas}}$$
$$\Delta G \leqq -53 \text{ kJ mol}^{-1}$$

$$O_{2_{aq}} + MnS_{alabandite} \rightarrow MnO_{2_{birnessite}} + S^o_{rhombic}$$
$$\Delta G \leqq -227 \text{ kJ mol}^{-1}$$

For *sulfidic* environments with $C_{H_2S} \geqq 10^{-6}$ and $P_{CO_2} \geqq 10^{-4}$ (the minimum value for CO_2 in surficial sediments):

$$3\,H_2S_{aq} + S^o_{rhombic} + Fe_2O_{3_{hematite}} \rightarrow 2\,FeS_{2_{pyrite}} + 3\,H_2O_{liq}$$
$$\Delta G \leqq -106 \text{ kJ mol}^{-1}$$

$$H_2S_{aq} + S^o_{rhombic} + FeCO_{3_{siderite}} \rightarrow FeS_{2_{pyrite}} + CO_{2_{gas}} + H_2O_{liq}$$
$$\Delta G \leqq -79 \text{ kJ mol}^{-1}$$

$$H_2S_{aq} + CO_{2_{gas}} + MnO_{2_{birnessite}} \rightarrow MnCO_{3_{rhodochrosite}} + S^o_{rhombic} + H_2O_{liq}$$
$$\Delta G \leqq -118 \text{ kJ mol}^{-1}$$

$$2\,H_2S_{aq} + MnO_{2_{birnessite}} \rightarrow MnS_{alabandite} + S^o_{rhombic} + 2\,H_2O_{liq}$$
$$\Delta G \leqq -107 \text{ kJ mol}^{-1}$$

Other points about the Berner Scheme:

✺ Salinity of overlying waters not a factor but presence of SO_4^{2-} (from especially marine waters is)

✺ there must be Fe and Mn present in the system to make Mn- and Fe-bearing minerals.

✺ Alabandite (MnS) is not a good tracer of sulfidic conditions because rhodochrosite ($MnCO_3$) is more stable except at very high ΣH_2S.

✺ FeS_2, although stable to fairly low H_2S, is sometimes slow to form and sometimes metastable minerals such as Mackinawite ($Fe_{1+x}S$) and Greigite (Fe_3S_4) can be found.

✺ $Mn^{4+} \Rightarrow Mn^{2+}$ transition corresponds almost exactly to O_2 dropping below 0.5% saturation, whereas $Fe^{3+} \Rightarrow Fe^{2+}$ occurs at lower pe (more reducing conditions). We can therefore find sediment horizons where Fe^{3+} and Mn^{2+} minerals can coexist in "anoxic" settings.

✺ In theory, the Berner scheme could be extended to include other tracer minerals based upon other ions too.