

Lecture 21

Nutrients and Particles in Fresh Waters

Reading for today: BB Ch7

Today

1. reactions on particle surface.
2. estuaries - Fresh-salt water mixing interactions and Particle-Aqueous Solute Interactions in action.

Next time

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

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Particles in the aqueous environment

- The behaviors of sparingly and insoluble elements and compounds in aqueous environments are **largely affected by interactions with particles**.
- The transport and fate of particles is thus a key parameter for describing such environments
- **Chemical reactions** on particle surfaces cause numerous **predictable effects**, such as:
 - ☞ charge transfer
 - ☞ chemical exchanges
- **Colloids are extremely small particles** that do not settle effectively, and are very important agents of transport in the environment.

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Size relationship of aqueous dissolved and suspended materials

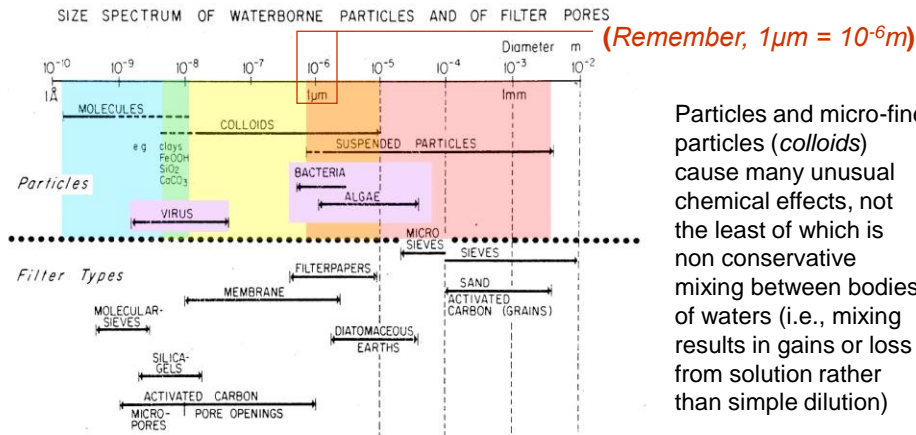


Figure 10.16 Suspended particles in natural and wastewaters vary in diameter from 0.005 to about $100\ \mu\text{m}$ (5×10^{-9} to 10^{-4} m). For particles smaller than $10\ \mu\text{m}$, terminal gravitational settling will be less than about $10^{-2}\ \text{cm sec}^{-1}$. Filter pores of sand filters, on the other hand, are typically larger than $500\ \mu\text{m}$. The smaller particles (colloids) can become separated either by settling if they aggregate or by filtration if they attach to filter grains. Particle separation is of importance in the following processes: aggregation of suspended particles (clays, hydrous oxides, phytoplankton, biological debris) in natural waters; coagulation (and flocculation) in water supply and wastewater treatment; bioflocculation (aggregation of bacteria and other suspended solids) in biological treatment processes; sludge conditioning (dewatering, filtration); filtration, ground water infiltration, removal of precipitates. [From W. Stumm, *Environ. Sci. Technol.*, 11, 1066 (1977).]

Strumm and Morgan, *Aquatic Chemistry*

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Properties of sub μm particles in water:

Particles less than about $1\ \mu\text{m}$ ($= 0.001\ \text{mm}$) do not settle very effectively, forming colloids in aqueous solution.

Colloids form because **electronic forces** (also known as **solvation forces**) acting upon their surfaces are stronger than gravitational forces that cause particles to settle.

Particles become charged by interaction with water.

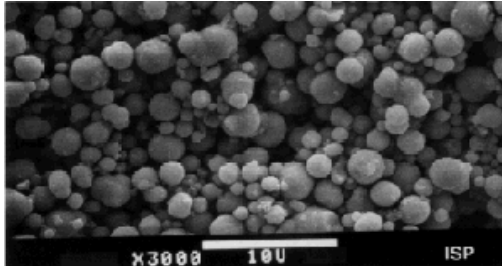
Just like true solutes, small particles that carry some sort of chargeable or polar component are solubilized by water to form colloids.

The more charge a particle acquires from interactions with water, the more easily it forms colloids.

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- * **Colloids** form a very important part of the interaction between the aqueous phase and solids.
- * **Colloids** are extremely small particles with generally very high surface area to mass ratios.
- * **Colloids** are so small and well-dispersed that they behave almost as if they were part of the dissolved load (TDS), even though they are technically part of the particulate load.

Spectroscopic Image of Spherical FeO Colloids



FeO colloids are commercially available in a range of sizes for water treatment applications.

<http://www.pnl.gov/agg/technologies/ironcolloid.stm>

The bar at the bottom of represents 10 micrometers.

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Chemical interactions between **colloids** and **dissolved solutes** play a major role in the overall chemistry of natural waters.

Chemical elements associated (e.g., chelated, sorbed) **with colloids** can be removed from the water when the latter are removed from solution.

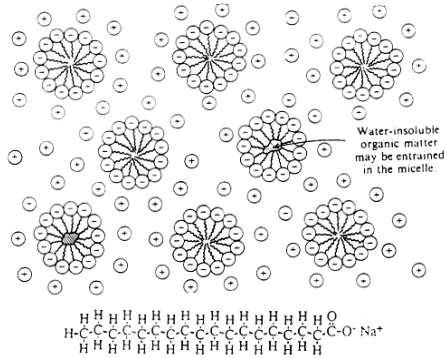
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- * **Colloids** can form from agglomeration of even finer particles kept in solution by electronic forces acting on their surfaces.
- * **Colloids** are composed of H_2O -solvated particles called **sols**. These often organize into structures known as **micelles**.
- * Removing non-bound H_2O from colloid particles forms a **gel** (a reversible process). Drying a gel further makes a solid.
- * **Colloids** are only stable at certain conditions of pH and TDS

When one or more of these conditions change sufficiently, colloids become unstable.

Destabilized colloids flocculate (the particles aggregate) and the **flocs** are removed from solution, settling to the sediment (i.e., the true particulate) component of a natural or manmade aqueous system.

Figure 5.4. Representation of colloidal soap micelle particles.



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Solute-Solids interactions – review from lecture 12

clays and oxide particles obtain charge in natural waters

The sign of the charge is a function of pH and the density of charge is a function of the structure

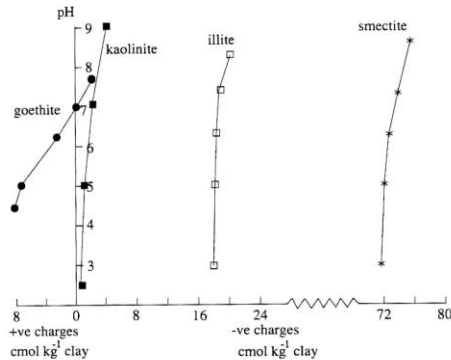
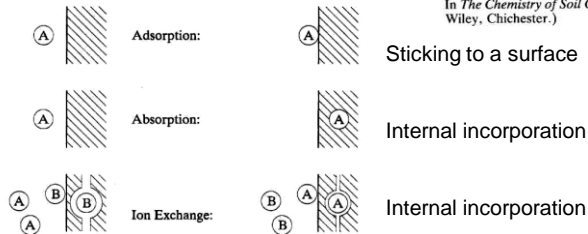


Figure 4.1 Positive and negative charges on three clay silicates: smectite, illite and kaolinite, and on goethite. (From Greenland, D.J. and Mott, C.J.B., 1978. In *The Chemistry of Soil Constituents* (eds. D.J. Greenland and M.H.B. Hayes). Wiley, Chichester.)
From Wild, 1993, *Soils and the Environment*

3 mechanisms of compositional “exchange” with water operate.

FIGURE 4-25 Processes of adsorption, absorption, and ion exchange.



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Solute-Solids interactions – review from lecture 12

Particle Surface Charge is acquired by:

- ⊗ acid-base (primary mechanism)
- ⊗ ion exchange reactions.
- ⊗ charge transfer (e.g., ligand/donor, sorption)

Colloids can be made from non-dissolved organic or inorganic particulates.

Each compound has specific properties that dictate how and when a colloid will form, and at what conditions it can stay in "solution".

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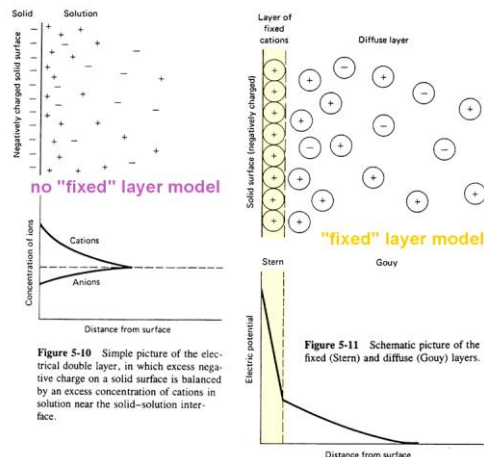
Recall How charge is distributed around colloids:

The size and charge density of ion clouds around surfaces *are the solvation forces* for colloids.

❖ These clouds expand and collapse depending on solution properties (e.g., pH, concentration and types of free ions in solution).

❖ the interaction of one colloid's ion cloud with that of another can affect aqueous solution composition. For instance:

❖ in an open body of water, too much ion-cloud interaction could destabilize colloids and cause them to be desolvated, pulling solutes with them.



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Removal of colloids from solution:

- Small, surface-charged particles charges tend to repel one another if the sign is the same, preventing the close physical interaction necessary to form large particles.
- **Flocculation**, **agglomeration** and **coagulation** are all terms that refer to the collapse of sols and the removal of colloids as clumps of solid particles. (We will use the terms interchangeably)
- **Flocculation** occurs when electrical and physical forces keeping colloids in solution are exceeded by other electronic and physical forces.
- As flocculation removes colloids of DOC, clays, metal oxides etc.. from solution, **ions attached to these colloids** may also be removed to the sediments of that body of water.

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Four common causes for flocculation are:

- ❖ change of flow field in the body of water.
- ❖ change of ionic strength of the solution (ionic strength is a measure of the total dissolved charge in solution - ionic strength corresponds to large amounts of dissolved ions.)
- ❖ evaporation of H₂O (which changes ionic strength).
- ❖ introduction of a (chemical) colloid destabilizing agent.

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Relationship of flow field, particle size/concentration and ionic strength:

The water flow field controls the size and concentration of particles in suspension, and the number of collisions among colloids (which can lead to agglomeration).

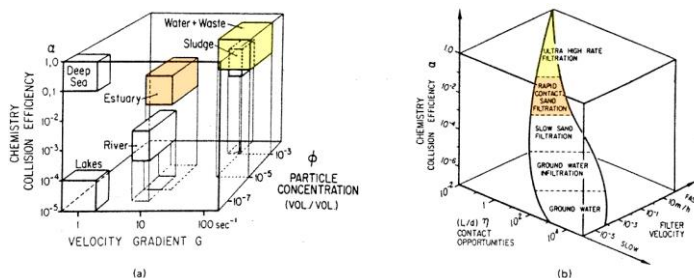


Figure 10.23 Variables that typically determine the efficiency of coagulation in natural waters and in water and waste treatment systems. (a) How the variables determine the coagulation efficiency. (b) Marked increase in filtration rate can be achieved by counterbalancing a reduction in contact opportunities by chemically improving the contact efficiency, with similar efficiency in particle removal. (Compare with Table 10.12.) [From W. Stumm, *Environ. Sci. Technol.*, 11, 1065 (1977) *Strumm and Morgan, Aquatic Chemistry*

Ionic strength and ionic composition affects the shape and size of the electric layers around colloid particles and their stability in solution. In general, when the ionic strength gets too high, colloids are destabilized and flocculate.

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Simple Ionic Strength experiments:

Here and on the next slides are results of various laboratory simulations of the conditions that prevail when low TDS water (river) meets high TDS water (sea water) in estuaries.

For instance, the rate and extent of kaolinite (clay) flocculation increases as increasing ionic strength increases.

Recall that ionic strength is related to the molality of charge in solution

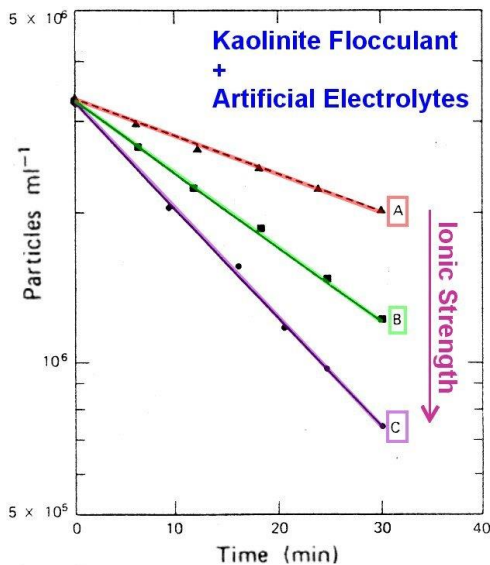


Figure 10.24 Rates of coagulation of kaolinite in synthetic solutions simulating estuarine waters of different salinities. Ionic strengths, uncorrected for ion pairing, were: A, 0.036; B, 0.087; C, 0.343. (From Edzwald et al. [65].)

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Many metals are associated with particles surfaces.

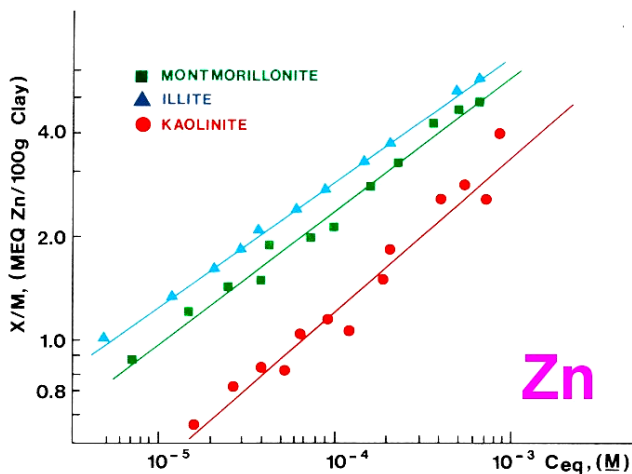


Fig. 59. Adsorption isotherms of zinc on different clay minerals. (Bourg and Filby, 1974. Proc. Int. Conf. *Transport of Persistent Chemicals in Aquatic Ecosystems*, Ottawa)
 Förstner and Wittman, *Metal Pollution in the Aquatic Environment*

This is an example of Zn sorption to clay surfaces in proportion to its dissolved concentration.

Flocculation of such particles leads to non-conservative behavior of many metals in estuaries.

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Another laboratory experiment examined how electrolytes cause flocculation of inorganic ions and DOC of river waters in the mixing zone of estuaries, using **Artificial** and **Real (seawater)** electrolytes.

Artificial electrolytes:

* flocculent effectiveness:
 $\text{NaCl} < \text{MgCl}_2 < \text{CaCl}_2$.

* **NaCl-MgCl₂** difference:
 there are two equivalents of Mg^{2+} per mole of MgCl_2 versus only one equivalent per mole of NaCl . Mole for mole, MgCl_2 increases the ionic strength more than does NaCl .

* **CaCl₂-MgCl₂** difference:
 Ca^{2+} ions are larger than Mg^{2+} ions, making them better at destabilizing Fe, Al and humic acid colloids.

Artificial Electrolytes with "Real" Flocculants

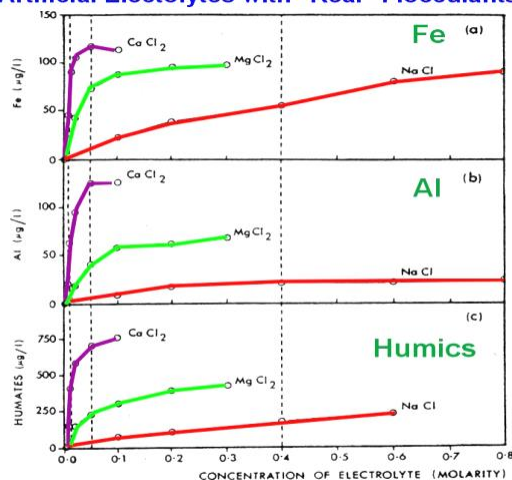


Fig. 1. The flocculation of (a) Fe (b) Al (c) humates from Scottish river water by added electrolytes! The amounts of flocculated species are expressed as μg per liter of river water. The vertical broken lines indicate the molarities of the salts present in sea water: CaCl_2 , 0.01 M; MgCl_2 , 0.05 M; NaCl , 0.4 M ($S \cong 35\text{‰}$).

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Real electrolyte (seawater)

- * Flocculation is fast for all major river borne ions.
- * Fe and Humic Acids (HA) flocculate more efficiently with seawater than with pure artificial electrolytes, but most other elements behave similarly with both.

"Real" Electrolyte (sea water) with "Real" Flocculants

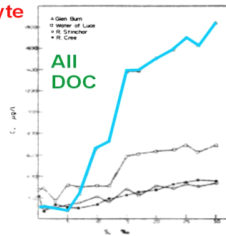


Fig. 1. **All DOC** flocculation vs salinity. Flocculant concentrations are given in µg Fe/l of river water. Only 1 hr flocculants were collected on Whatman GF F filters.

Sholkovitz (1976) *Geochim. Cosmochim. Acta*, Vol 40, p831-845

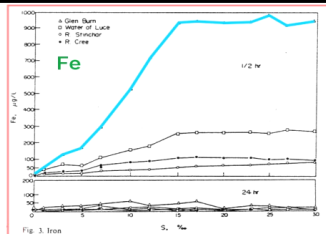


Fig. 3. **Iron** flocculation vs salinity for the four river waters. Flocculant concentrations, both 1 hr and 24 hr after mixing with sea water, are given in µg Fe/l of river water.

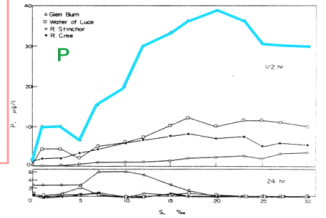


Fig. 4. **Phosphorus** flocculation vs salinity for the four river waters. Flocculant concentrations, both 1 hr and 24 hr after mixing with sea water, are given in µg P/l of river water. Points below abscissa indicate concentrations below detection.

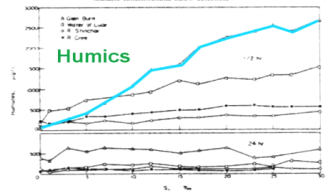


Fig. 7. **Humics** flocculation vs salinity for the four river waters. Flocculant concentrations, both 1 hr and 24 hr after mixing with sea water, are given in µg humics/l of river water.

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Estuaries

Estuaries are semi-enclosed coastal water bodies connected to the sea and into which one or more rivers or streams flow

Mixing of fresh and salt water in estuaries create unique chemical and biological characteristics whose effects outweigh their small volumetric proportion of the hydrologic cycle.





 Estuaries are an excellent locale to study the role that particles play in the hydrospheric.

 Estuaries are also a gradient in the hydrosphere between non-marine and marine waters.



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The chemical composition of estuarine waters reflects mixing between rivers of locale-specific chemistry water and sea water, for which major ion chemistry show little geographical variance.

Physical attributes pertinent to the way the mixing occurs:

-  river flow rate
-  river suspended load
-  estuary shape
-  local tidal fluctuations

Geochemical attributes pertinent to the effects of mixing:

	pH	TDS (salinity)	Chlorinity	Sediment Load
 seawater	8.0-8.2	35‰	19‰	low
 river	<4 to >6	<5-10‰	~0‰	High

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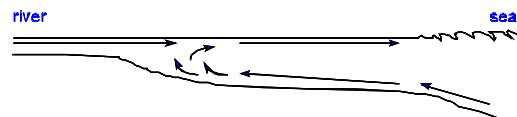
Physical features of estuaries:

Water circulation in most estuaries arises from river versus tidal flows and density differences between water masses. Density differences are largely due to salinity rather than temperature.

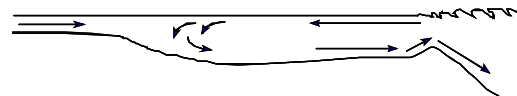
Two general circulation types (but variations exist):

* **Estuarine Circulation:** the "standard" type, where low density river water overlays higher density sea water. Mixing is accomplished by upward entrainment of deeper waters into the surface zone. It is driven mostly by water flow.

Estuarine Circulation

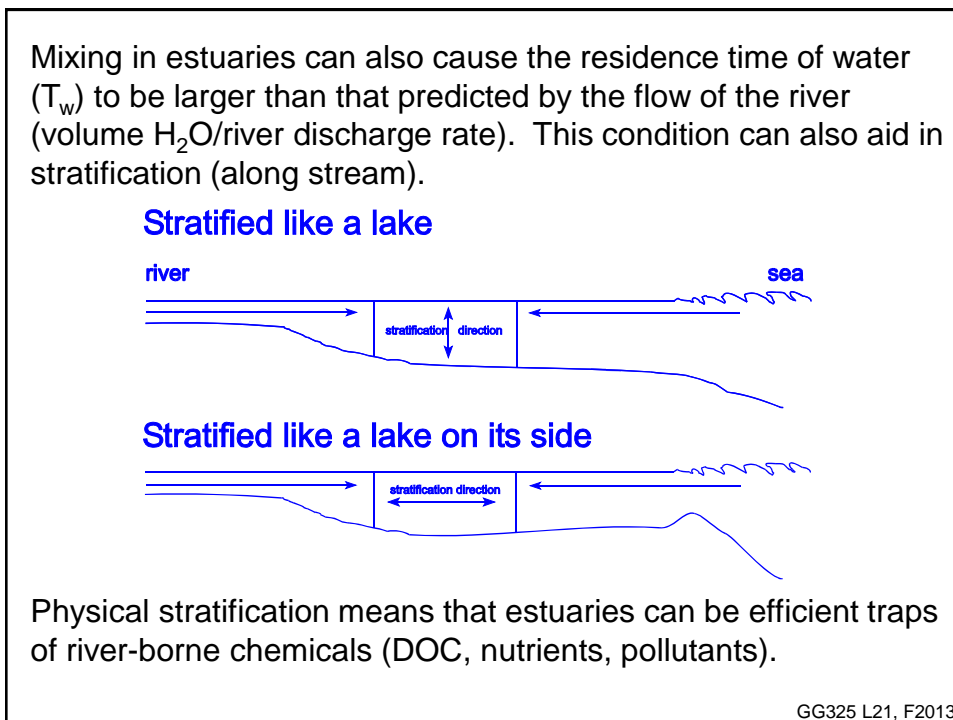
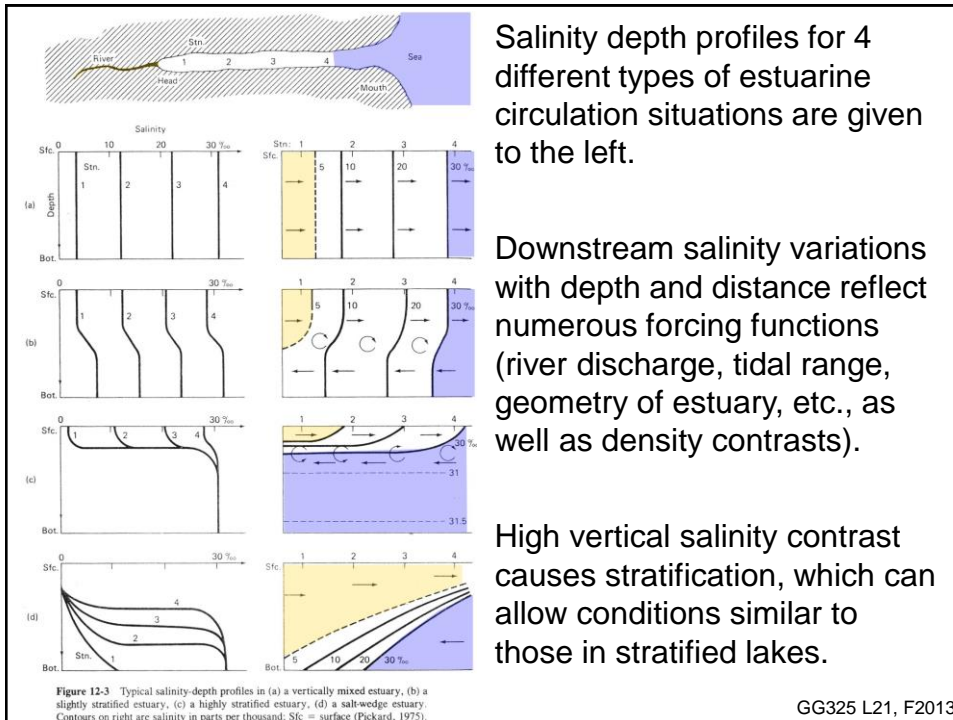


Anti-Estuarine Circulation



* **Anti-Estuarine Circulation:** less common. It occurs at low river flow + high surface evaporation. Mixing is driven by density gradients.

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Chemical features of estuaries:

Estuaries are chemical fronts in the hydrosphere where a number of compositional changes take place.

For instance....

Rivers usually have more Fe, Al, P, N, Si and DOC.

Sea water has more Ca, Mg, Na, K, Cl, SO₄

These differences are from:

- a. **conservative mixing** in estuaries
- b. **chemical processes** within estuaries (export of some elements to sediments rather than to the sea, or addition of some elements from sediments to estuarine water)
- c. **chemical processes** within the oceans (post-estuarine); these are a topic for later this semester.

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Chemical reactions involving particles in estuaries are very important for:

1. the composition of the oceans, because they limit the extent to which some river-borne solutes enter the sea.
2. the composition of estuarine sediments; some chemicals are found in high concentrations in the particles that settle out to form estuarine sediments.

During non-conservative mixing, particles control

- Ion “loss” from solution by **solute sorption + sedimentation**
- Ion “gain” from solution by **solute desorption**

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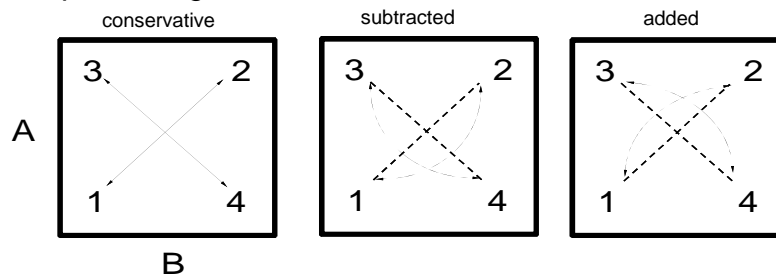
Estuaries, provide an excellent natural laboratory for studying the effects of solution composition and fluid flow changes on particle suspension.

- Rivers carry huge particle burdens (~80% of the “chemical burden” of rivers is carried in the suspended load).
- Seawater carries a much larger dissolved load, so there is a large contrast in salt content between river water and seawater.
- The fate of the suspended particle burden influences pollutant and contaminant transport to the ocean.

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In most estuaries, mixing of river water and seawater produces chemical gradients between the two types of water. Dissolved compounds and ions exhibit one of two behaviors.

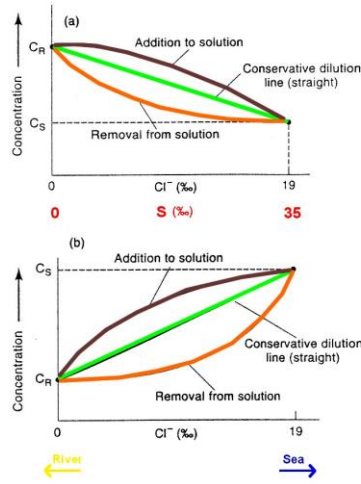
- * **Conservative mixing:** simple dilution.
- * **Non-conservative mixing:** elements can be subtracted from or added to the water mass at amounts greater than expected for simple mixing.



We use either Salinity or Chlorinity as a conservative mixing reference material ("B") in the figures above.

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Non conservative mixing occurs in other parts of the hydrosphere, but it is particularly pronounced in estuaries.



The non conservative mixing profiles shown here result from interactions between **solutes** and **particles**.

Particle sedimentation in estuaries dramatically changes the composition of waters there and is a primary reason for the large compositional differences between fresh waters and seawater.

Figure 7.3. Idealized plots for estuarine water of the concentration of dissolved components versus chloride (which serves as conservative measure of the degree of mixing between fresh water and seawater). C_R = concentration in river water; C_S = concentration in seawater. (a) Component whose concentration in fresh water is greater than it is in seawater (for example, P, N, Si). (b) Component whose concentration in fresh water is less than it is in seawater (for example, Ca, Mg, K). (Modified from P. S. Liss, "Conservative and Non-Conservative Behavior of Dissolved Constituents During Estuarine Mixing," in *Estuarine Chemistry*, ed. J. D. Burton and P. S. Liss, p. 95. ©1976 by Academic Press, reprinted by permission of the publisher.)

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The fate of heavy metals in estuaries are closely linked to the behavior of Fe.

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.

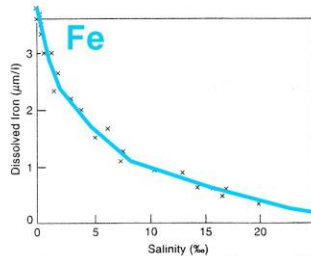


Figure 7.4. Total dissolved iron (µM/l = micromoles per liter) versus salinity in the Merrimack Estuary, Massachusetts. Data points in order of increasing salinity fall on a concave-up (iron removal) curve. (Modified from E. A. Boyle, R. Collier, A. T. Dengler, J. M. Edmond, A. C. Ng, and R. F. Stallard, "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.)

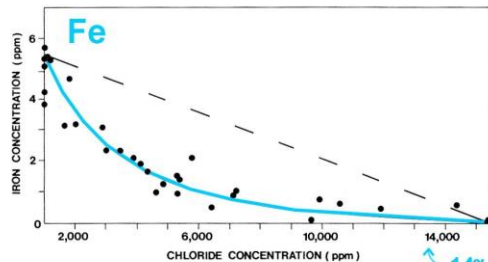


Fig. 6.3. Nonconservative behavior of dissolved iron in the freshwater/seawater mixing zone of Mullica River/Great Bay, New Jersey (Cooney et al., *Geochim. Cosmochim. Acta*, 35, 1971. Reproduced with permission of Pergamon Press, Oxford)

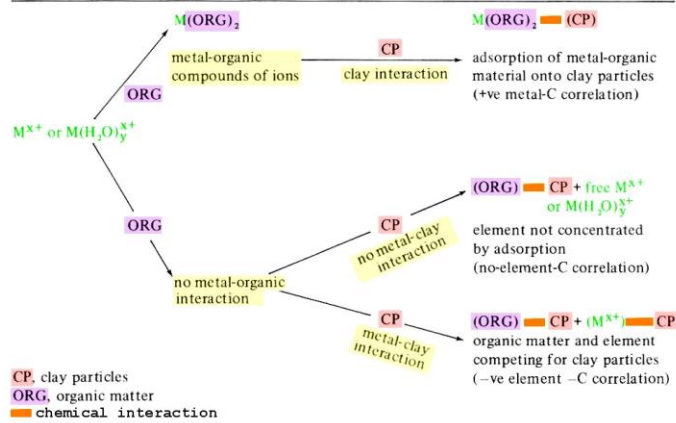
Flocculation of Fe in the mixing zone of estuaries is a very important process for governing the distribution of other heavy metals between water and sediment.

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Metal Flocculation in estuaries:

Metals bound to clays and/or organic mater in the particulate load of a river will be flocculated in estuaries, as indicated schematically here.

Table 62. Generalized metal-organic-solid reaction scheme as proposed by Curtis (1966)



Modified from Förstner and Wittman, *Metal Pollution in the Aquatic Environment*

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