

Phosphorus Release from Eroded Soil in the Aquatic Systems

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May 18, 2018

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Phosphorus cycle

- * Erosion control measures are applied all over the world, in many cases to protect the soil itself, or to reduce off-site impacts
- * Does controlling soil erosion inhibit aquatic eutrophication (rehevöityminen)?
 - The main interest of our study
 - We study the mineralization pathways of Fe, which is coupled to C, S and P cycling.
 - The amount of C, S, aerobic vs anaerobic.

Possible effects of eroded soil on eutrophication

- * (The following summarize applies to estuary (murtovesi), or any SO_4 rich recipient.)
- * If the estuary receives a high input of Fe oxides and a modest level of dissolved P, we may see moderate levels of eutrophication.
- * The settling flux has a low C/Fe ratio and the sediment is mainly in Fe reduction state.
 - As a result the estuary may respond to erosion control because the P concentrations are not maintained by strong P release from the sediment due to coupled cycling of P and Fe.
- * The biotic fauna releases Fe and P from the oxides which then react with O_2 in the aerobic estuary.
 - No P release from sediment to the aquatic system, keeps the "ferrous wheel" spinning.

Possible effects of eroded soil on eutrophication

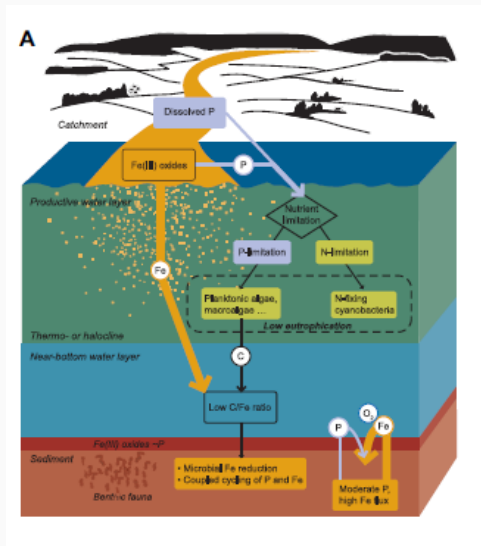


Figure 1: Fe and P cycle in aerobic estuary

Possible effects of eroded soil on eutrophication

- * If erosion control takes place, typically dissolved P increases as we reduce the input of Fe oxides.
- * Increased bioavailable P triggers algal (levä) production, which increases the flux of organic C to the sediment surface → SO_4 reduction becomes important
- * The lowered flux of Fe oxides means higher C/Fe ratio.
- * When SO_4 reduction rates increase, more of the sediment Fe is transformed to non-sorptive Fe sulfides → massive release of Fe-bound P stored in sediments.
- * Now the highly eutrophic estuary can show extensive cyanobacterial booms and benthic fauna may decrease.

Possible effects of eroded soil on eutrophication

- * The Fe and P cycle is affected by hydromorphology and chemistry of the receiving body of water.
 - In deep systems the organic C is largely mineralized, so it does not effect the benthic processes.
 - The depth also affect sediment accumulation areas.
 - The lack of O_2 affect the sediment state by affecting the mineralization and preventing the re-oxidization of Fe(II).
- * The level of SO_4 in the sediment also plays a crucial role.
- * The net effect of soil erosion on eutrophication depends on the balance between labile soil P and the lowering of benthic P release caused by Fe oxides.

Possible effects of eroded soil on eutrophication

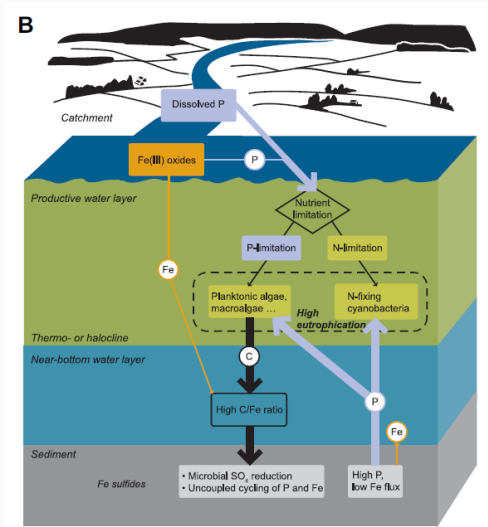


Figure 2: Fe and P cycle in anaerobic estuary

Points of interest

- * The assumptions stated above need to be verified. The sediment processes are not well known.
- * We need to gain information about the changes in mineralization of soil during the processes stated above in the molecular level.

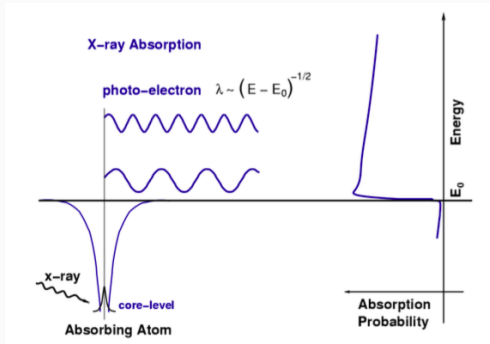
X-ray Absorption Spectroscopy

A small description of XAS

- * X-ray absorption spectroscopy studies how x-rays are absorbed by an atom near and above its core-level binding energies.
- * When an X-ray is absorbed by an atom, core-level (K, L, M) electron is ejected (photoelectron). The atom is left in an excited state with empty electronic level.
- * The excited core-hole is relaxed, a higher level electron fills the empty space and a fluorescence x-ray or auger electron is emitted.
- * When discussing x-ray absorption, we are primarily concerned with the absorption coefficient μ , which gives the probability that x-rays will be absorbed according to Beer's Law:

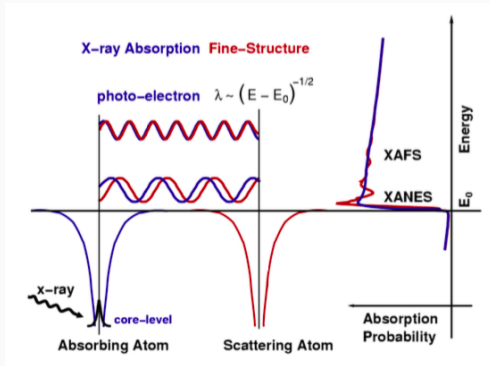
$$I = I_0 e^{-\mu t} \rightarrow \mu(E) = \ln \frac{I_0}{I_t} \quad (1)$$

A small description of XAS



- * An incident x-ray of energy E is absorbed, destroying a core-electron binding energy E_0 , and emitting a photoelectron with kinetic energy $(E - E_0)$. The core state is eventually filled.
- * When the incident x-ray energy is larger than the binding energy, there is a sharp increase in absorption
- * For an isolated atom, $\mu(E)$ has a sharp step at the core-level binding energy and is a smooth function of energy above the edge.

A small description of XAS



- * The ejected photoelectron can scatter from neighbouring atoms. R is related to λ and there is a phase shift associated with the scattering event. Thus outgoing and scattered waves interfere.
- * The scattering photoelectron wave function interferes with itself. $\mu(E)$ depends on the density of states of the absorbing atom.
- * This interference at the absorbing atom will vary with energy, causing the oscillations with $\mu(E)$.

A small description of XAS

- * XAS spectrum is typically divided into two regimes: XANES and EXAFS
 - XANES is strongly sensitive to formal oxidation state and coordination chemistry of the absorbing atom.
 - EXAFS is used to determine the distances, coordination number, and species of the neighbours of the absorbing atom.
- * Some benefits of XAS:
 - Element specific.
 - Many experimental techniques and sample conditions available.

- * In our experiment we are using XAS instrument called HeIXAS, which can be found from the x-ray lab at the second floor.
- * The instrument consists of three main components, x-ray tube, monochromator and detector. These components are motorised and follow the Rowland circle geometry.
- * Each monochromator crystal has a specific crystal orientation, so that we get the wanted wavelength according to Bragg's law:

$$2d_{hkl}\sin\theta = n\lambda \quad (2)$$

- * Energy can be tuned around the edge by changing θ

Measurement preparations

- * The soil is mixed with sea water (from Seili and artificial), and C and S levels are varied.
- * To simulate anaerobic environment, we need an air tight sample environment and preferably a sample rotation to speed up the measurements.
- * The samples in a liquid phase needs to be tested

Some early results

Dry soil samples

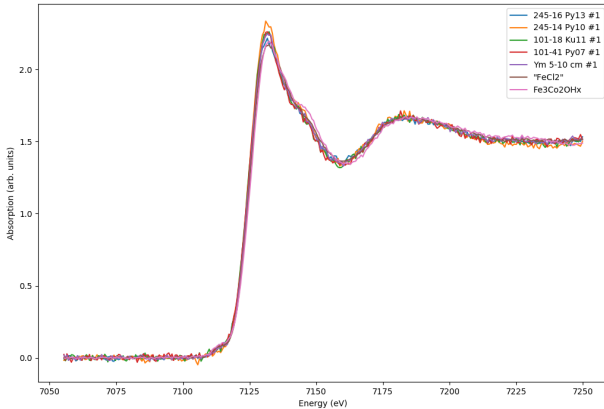


Figure 3: Absorption spectrum of dry soil samples before incubation.

Dry soil samples

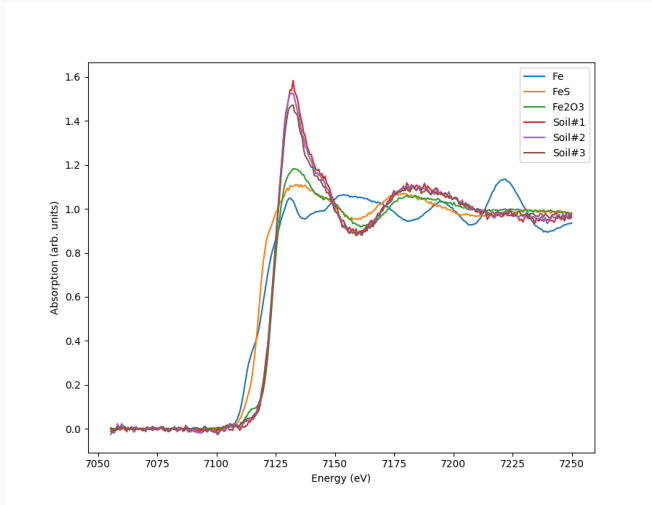






Figure 4: Absorption spectrum of test soil sample and some reference materials.

Wet aerobic soil mixed with sea water

- * X-rays cause water molecules to break and release free O radicals. Water "boils".
- * If sample places in front of the x-ray tube, all the water is gone in less than an hour.
- * New sample environment allows to do measurement in front of the detector → much lower intensity and hopefully less radiation damage.

References

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-  Lehtoranta J., Ekholm P., Wahlström S., Tallberg P., Uusitalo R. *Labile organic carbon regulates phosphorus release from eroded soil transported into anaerobic coastal system*. Ambio 2015, 44(Suppl. 2) 263-273.
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