CHEMICAL PATH OF FIELD SOIL: FROM FIELD TO BOTTOM SEDIMENT WITH K-EDGE XANES

Antti-Jussi Kallio[a], Petri Ekholm[b], Jouni Lehtoranta[b], Simo Huotari[a]

[a] Department of Physics, University of Helsinki, Finland [b] Finnish Environmental Institute

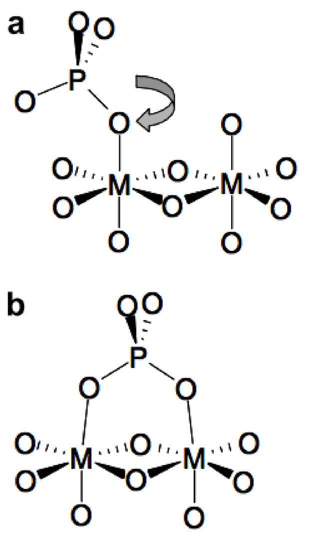
ABSTRACT

Eutrophication (*rehevöityminen*) is a global challenge, where chemical processes in bottom sediments play a key role. Yet, eutrophication science lacks understanding of the role of terrestrial matter on the processes that mobilize or immobilize phosphorus, a central algal nutrient, in sediments. During burial the sediment microbial processes change the redox-conditions which affect the chemistry of settled soil.

Here, methods were developed to follow the evolution of the chemical state of soil during burial with iron K-edge X-ray absorption near edge spectroscopy, with a novel home laboratory-based spectrometer. The chemical state of the sediment, and especially the chemistry of iron is linked to the release and binding of phosphorus in the bottom sediments.

SOIL EROSION AFFECTS EUTROPHICATION: CHEMISTRY OF IRON IS LINKED TO THE RELEASE AND BINDING OF PHOSPHORUS IN BOTTOM SEDIMENTS

- Eroded soil is transported to the water bodies
- Eroded soil is rich in Fe, C, Mn, P
- Soil will ultimately end up in bottom sediment, and will face various conditions
- The chemical path of these elements will affect the health of the ecosystem

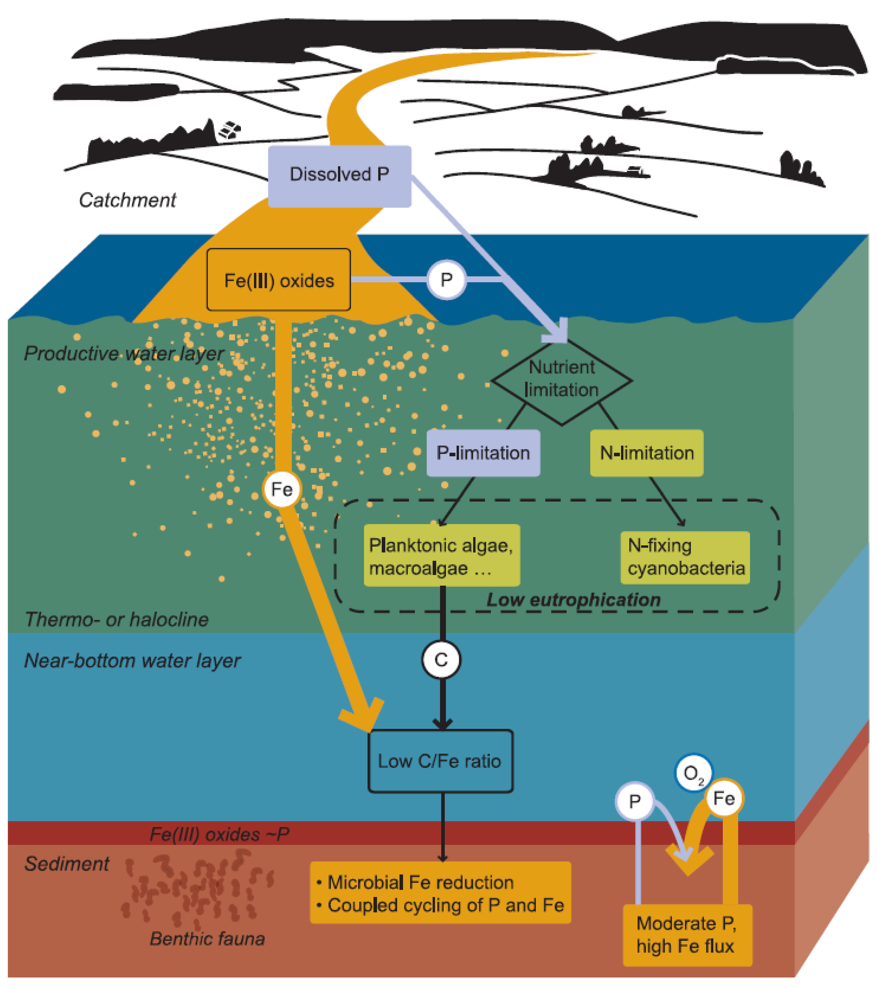


In sediments Fe oxides are mineralized by two mechanisms:

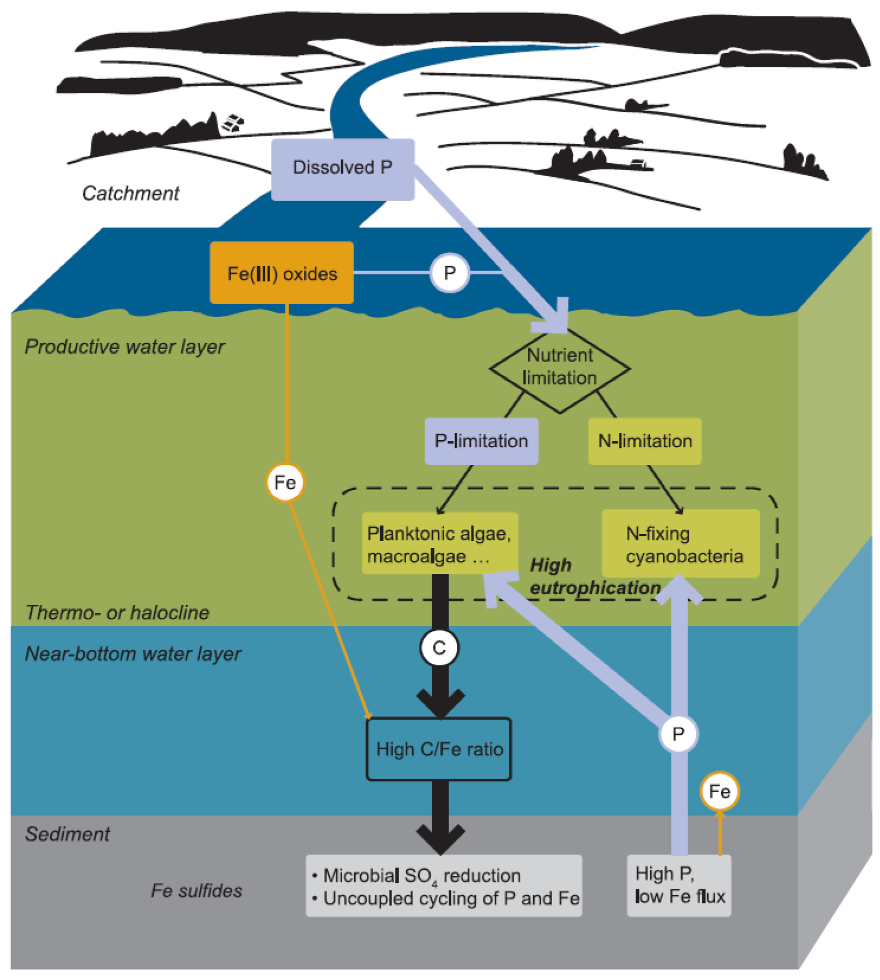
(1) Microbial Fe reduction, P is bound by Fe oxides

(2) Microbial SO_4 reduction, resulting in FeS production and release of P to the surrounding water → **increase of eutrophication**

The erosion control measures affect the incoming flux Fe and P, and the following outline is the basis of our research:



- With high flux of Fe oxides the Fe reduction dominates and P is buried in sediments

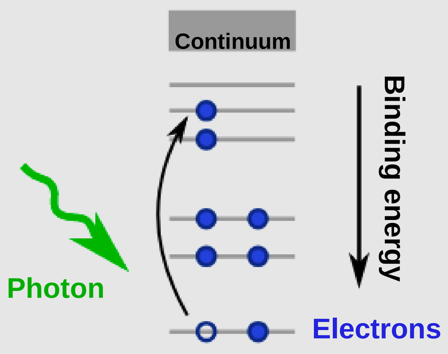


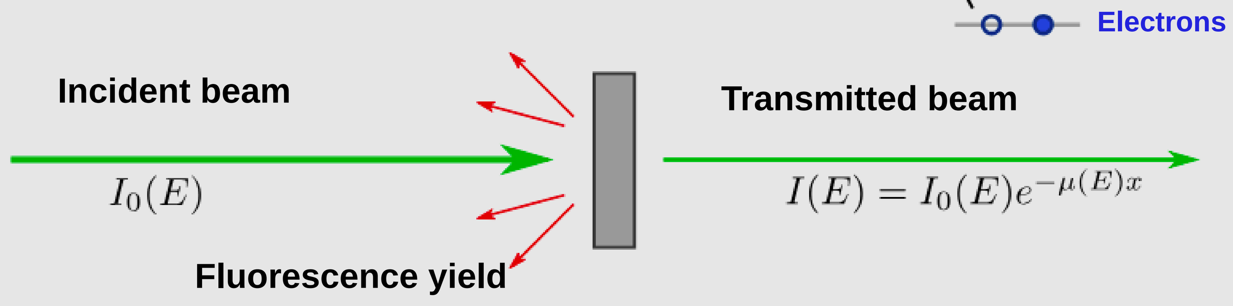
- When erosion control measures take place, flux of Fe oxides is lower, and SO_4 reduction starts to dominate, resulting in release of P

X-RAY ABSORPTION NEAR EDGE SPECTROSCOPY: TOOL TO FOLLOW THE EVOLUTION OF CHEMICAL STATE

X-ray Absorption Spectroscopy

- Measuring the absorption coefficient µ at core electron binding energies
- Gives access to element-specific local environment (e.g. coordination numbers, bond lengths) and chemical information (erg. oxidation state)





$$I_f(E) \propto \mu(E) I_0(E) \quad \text{for} \quad \mu(E)x \ll 1$$

- XANES portion essentially a chemical fingerprint of a specific element

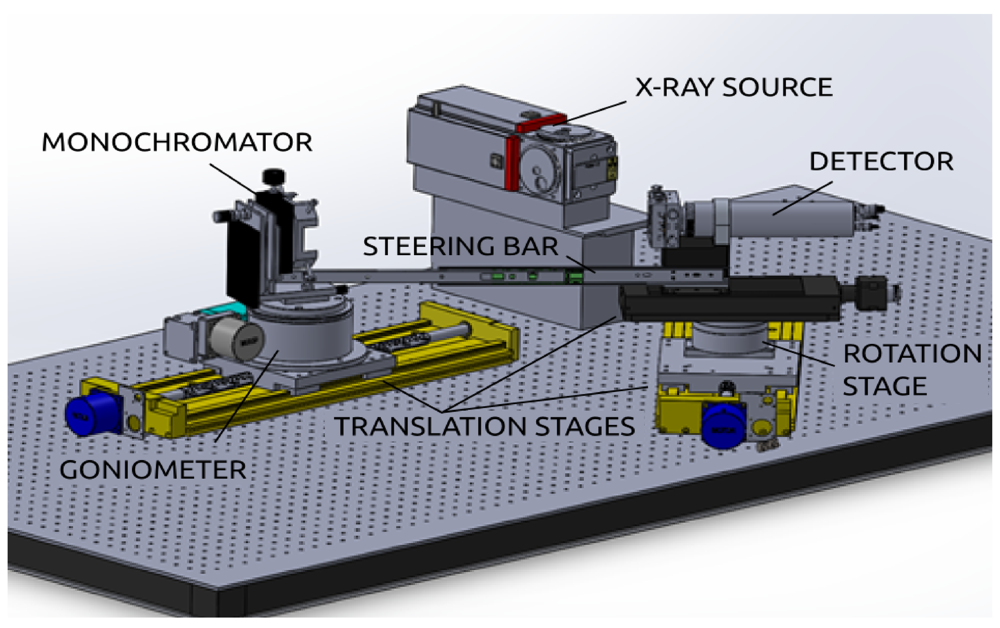
Spectrometer

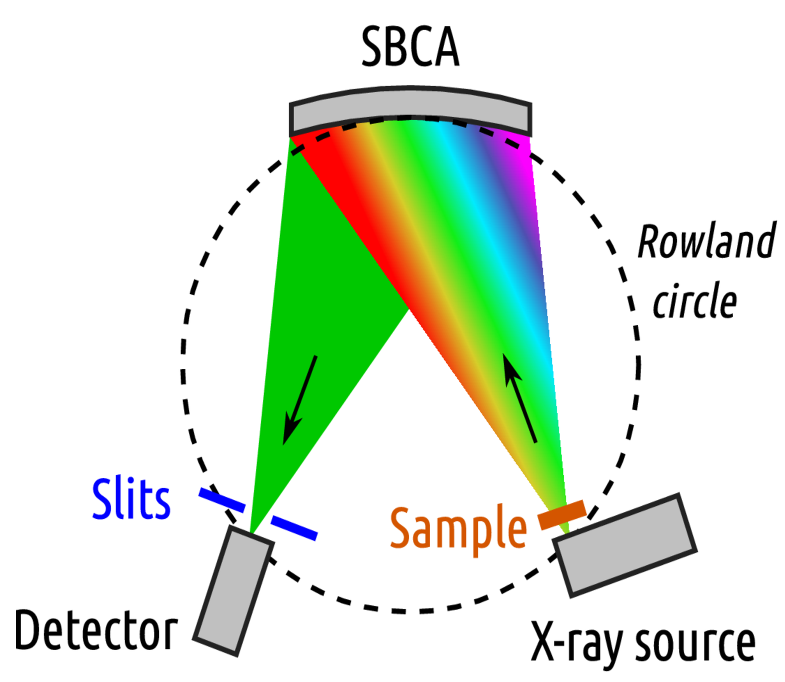
A novel laboratory scale X-ray absorption spectrometer found in X-ray Laboratory of University of Helsinki.

Suitable for K-edge *3d* transition metals, L edge of *5d* transition metals and actinides.

Allows complex sample conditions and easy to upgrade.

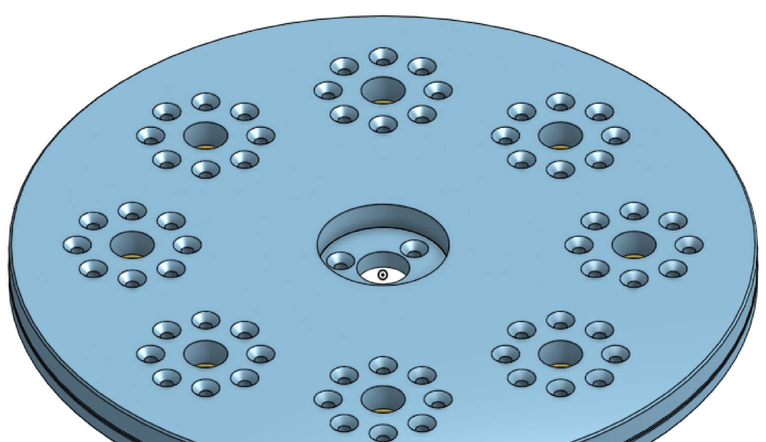
Transmission, fluorescence and imaging modes.





Sample preparation

- New sample environment for anaerobic samples
- New method to make a gel out of soil-water mixes with agar
  - Uniform and homogeneous samples required in XAS
  - Was also done in anaerobic conditions
- A set of reference Fe compounds was measured
  - Used to quantify the changes in chemical state
- The evolution of chemical state was simulated with anaerobic chemical incubations of 5 soils
  - Soil mixed with sea water and C and/or SO_4



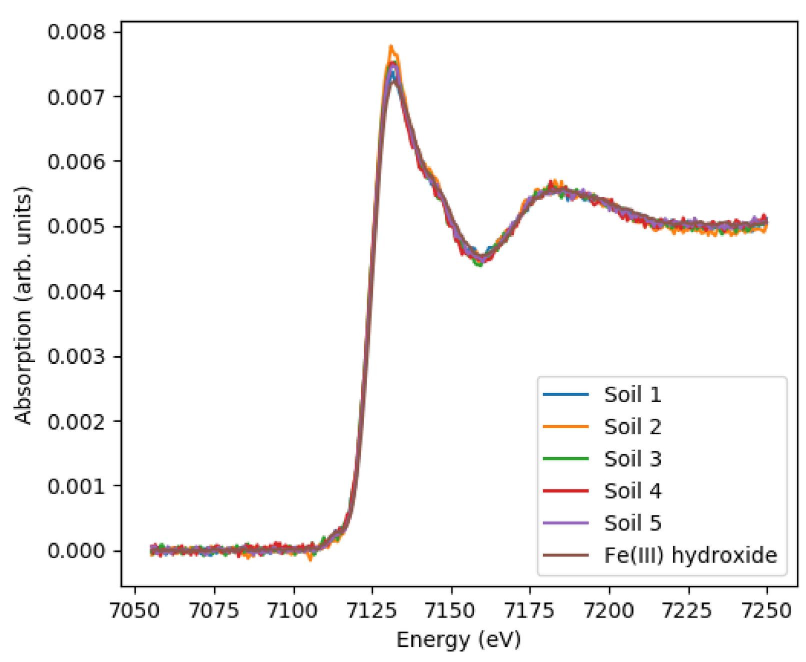
RESULTS AND DISCUSSION: THE RELEASE OF PHOSPHORUS WAS HIGHER WITH HIGH C/Fe RATIO

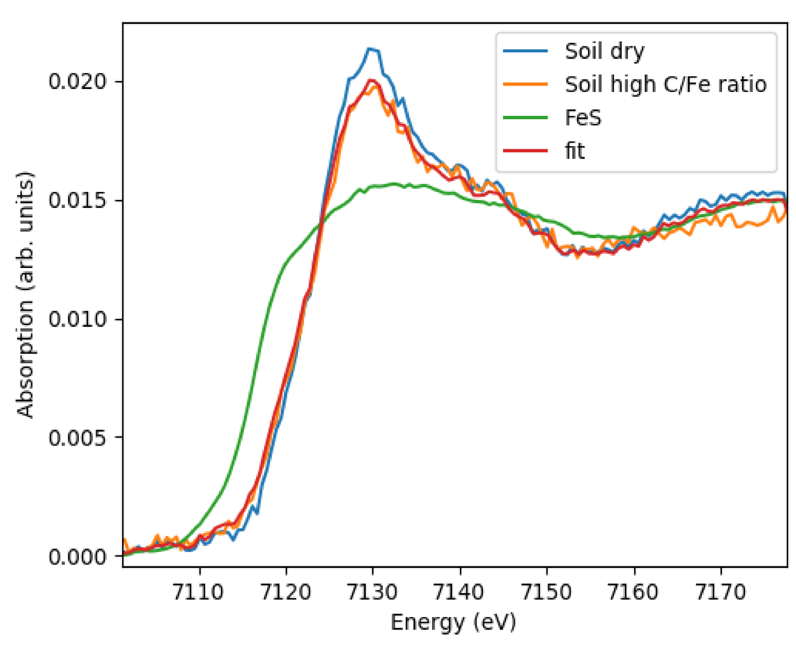
Dry soils:

- Fe in dry soils is mostly present as Fe(III) hydroxides
- Almost no variation between samples
- As expected, since the samples had similar geological age
- Soils should be suitable for mineralization

24 hours of incubation:

- No changes in chemical state, as expected





After two months of incubation:

- In anaerobic conditions low C/Fe ratio resulted in production of iron phosphates
- High C/Fe ratio resulted in production of iron sulphates
- In line with the outline discussed above
- Some unknown compounds might be present

Discussion

The results shed light on iron chemistry in anoxic sediments, which can be used in management of eutrophication. The measurement method can also be used to measure much larger set of various soils in many different water types to form even better picture of chemical processes in bottom sediments.

References:

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[3] A.-P. Honkanen, LABORATORY-SCALE X-RAY ABSORPTION SPECTROMETER WITH VERSATILE DETECTION MODES, presentation at Physics Days 2019