

Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office via the User Portal:

<https://www.esrf.fr/misapps/SMISWebClient/protected/welcome.do>

Reports supporting requests for additional beam time

Reports can be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.



	Experiment title: Co-localization and chemical speciation of size-fractionated phosphorus in leachate from Swedish agricultural soils.	Experiment number: EV-324
Beamline: ID 21	Date of experiment: from: 29 June 2018 at 08:00 to: 02 July 2018 at 08:00	Date of report:
Shifts: 9	Local contact(s): PRADAS DEL REAL Ana Elena	<i>Received at ESRF:</i>

Names and affiliations of applicants (* indicates experimentalists):

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Report:

Abstract

Colloids and nanoparticles are important nutrient-bearing materials known to facilitate eutrophication of natural waters through phosphorus (P) leaching. However, the chemical nature of colloidal and nanoparticulate P in leachates that drains through agricultural soils is not fully understood. Such knowledge is crucial to the mitigation of nutrient loss and prevention of groundwater contamination. We were awarded 9 shifts on ID21 - X-ray microscopy beamline to reveal the chemical nature of colloids and nanoparticles in leachates that drain through Swedish agricultural soils situated in the drainage basins of the North and Baltic Seas. Our experiment led to the successful acquisition of multi-elemental XRF images and micro-focused sulphur (S) & P K-edge XANES spectroscopic data in colloids and nanoparticles collected from four agricultural sites.

Experimental and Results

Leachates from experimental fields were collected from drain pipes and fractionated into two different size ranges using membrane filtration and ultrafiltration with nominal cut-offs of 0.45 µm and 10 kDa, respectively. The fractions are henceforth referred to as ‘colloids’ (~2,000–450 nm) and ‘nanoparticles’ (450-1 nm). The fractions were deposited on Ultralene® thin film allowed to dry at 25 °C and subjected to high-resolution XRF mapping from 1 to 8 keV in vacuum. The result (example from the Krusenbergs site, ‘KRUS’) shows that both fractions contained multiple elements, including macronutrients such as P and S and potential metal

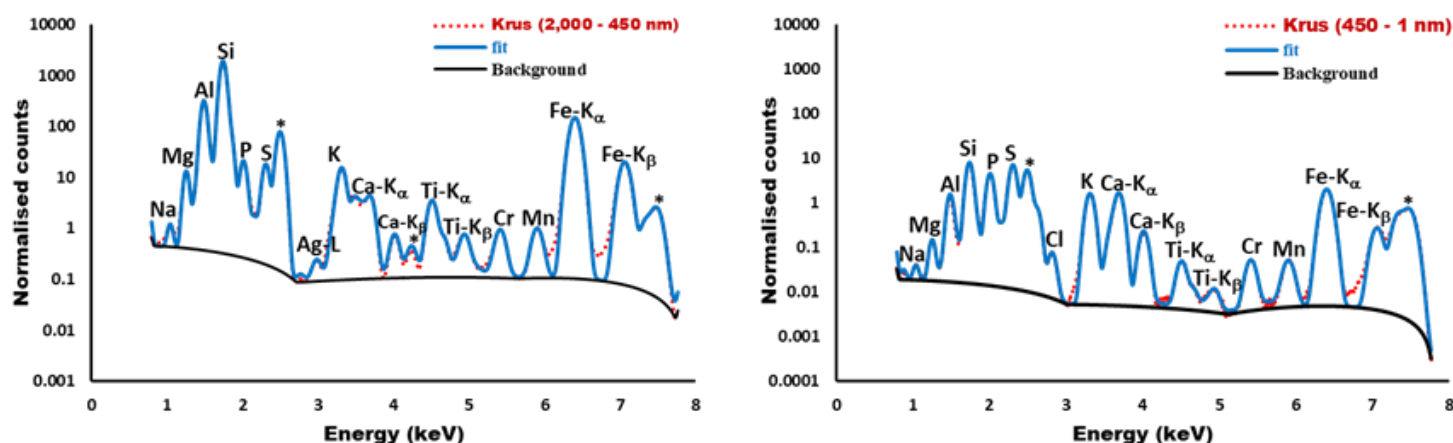


Figure 1: XRF spectra of detected elements in colloids and nanoparticles of leachates at KRUS. * are scatter peaks.

contaminants such as chromium (Cr) (Figure 1). However, the intensity of aluminium (Al) & silicon (Si)

appeared to be higher in the colloidal fraction. The latter is expected for a fraction likely to be dominated by aluminosilicate clay minerals. The intensity of P appeared to be similar regardless of particle size.

The co-localisation of P with other elements, especially Al, S, calcium (Ca) and iron (Fe), which are known to influence P speciation, was investigated by principal component analysis (PCA). The result suggests co-localisation of P with S in both size fractions (Figure 2).

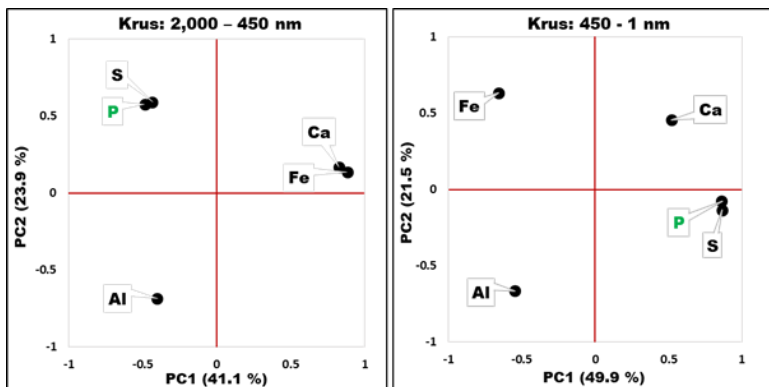


Figure 2: Loadings of PCA revealing co-localisation of P with elements known to influence its chemical speciation

The XRF map of the P and S distribution confirms almost identical features in their spatial distribution (Figure 3). This significant co-localisation of S with P made further examination of the chemical speciation of S necessary in order to establish the extent to which the S co-localized with P was inorganic. We therefore acquired S K-edge XANES data from up to six S hot spots in our samples.

The result shows distinctive peaks at 2473.8 eV in all size fractions showing the presence of reduced organic S (Figure 4).

Moreover, P K-edge XANES spectra were acquired from up to 10 spots in our samples in order to establish the spatial variability of

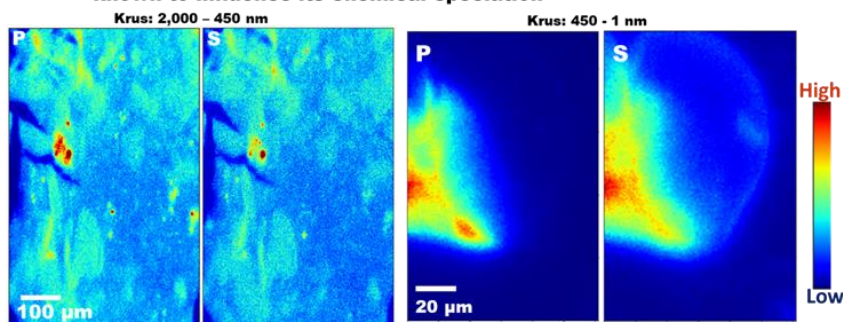


Figure 3: Spatial distribution of P and S in colloids and nanoparticles

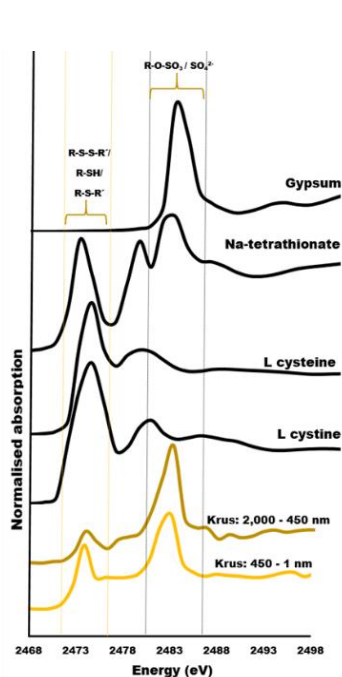


Figure 4: Merged S XANES collected from 5 unique S hot spots in colloids/nanoparticles and S XANES of reference compounds depicting organic disulphide (cystine), organic thiols (cysteine), inorganic polythionate (Na-tetrathionate) and sulphate (gypsum) functional groups.

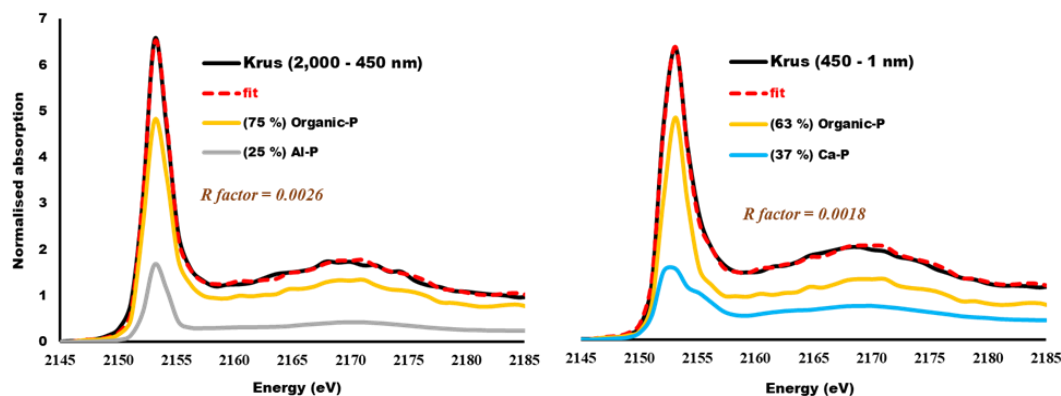


Figure 5: Linear combination fittings of P XANES spectra of size-fractionated (2,000 - 450 nm & 450 - 1 nm) particulate phosphorus in KRUS natural leachate. The dotted red line shows measured data and the black line is the linear combination fit. The XANES spectra below the fits are reference standards with the most significant contributions to the fit.

chemical P in the samples. P speciation in KRUS showed only little spatial variation. The XANES data were treated in Athena, in which the 8-10 P-XANES scans collected from each spot were merged into a single spectrum and compared to selected reference compounds using linear combination fitting.

The results show that P existed predominantly (70 (\pm 7) %) as organic P regardless of the particle size (Figure 5). The only difference in P speciation with regard to particle sizes was in the 30(\pm 7) % inorganic P fraction, which appeared to be dominated by Al-bound P in the colloids and by Ca-bound P in the nanoparticles.

Conclusions

The results of elemental co-localisation and S & P K-edge XANES spectroscopy revealed organic P as the dominant leached particulate P phase in our experimental sites. This calls for further research into the mechanism of the translocation of organic particles through the soil profile. Unlike the high-level uncertainties associated with P speciation studies using bulk P-XANES, our results in which the spatial co-localisation of elements was revealed by XRF mapping in combination with size-specific molecular speciation analysis of P-XANES is to our knowledge the most accurate characterisation of particulate P in natural leachates to this date.