EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

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://wwws.esrf.fr/misapps/SMISWebClient/protected/welcome.do*

Deadlines for submission of Experimental Reports

Experimental reports must be submitted within the period of 3 months after the end of the experiment.

Experiment Report supporting a new proposal ("relevant report")

If you are submitting a proposal for a new project, or to continue a project for which you have previously been allocated beam time, you must submit a report on each of your previous measurement(s):

- even on those carried out close to the proposal submission deadline (it can be a *"preliminary report")*,

- even for experiments whose scientific area is different form the scientific area of the new proposal,

- carried out on CRG beamlines.

You must then register the report(s) as "relevant report(s)" in the new application form for beam time.

Deadlines for submitting a report supporting a new proposal

- 1st March Proposal Round - **5th March**
- 10th September Proposal Round - **13th September**

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.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report in English.
- include the experiment number 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.

ESRF	**Experiment title:** Dynamics of selenium speciation and reservoir in seleniferous soil of Punjab, India, and potentiality of biochar as a soil amendment to reduce selenium bioavailability in soil	**Experiment number**: EV-460
Beamline: BM16	**Date of experiment**: from: 23 June 2022 to: 30 June 2022	**Date of report**: 10 September 2022
Shifts: 18	**Local contact(s)**: Dr. Olivier Proux	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Ashis Biswas*, Subhashree Dalai*, Mohd Amir Husain*

Department of Earth and Environmental Sciences, Indian Institute of Science Education and Research (IISER) Bhopal, Bhopal Bypass Road, Bhauri 462066, Bhopal, Madhya Pradesh, India

Report:

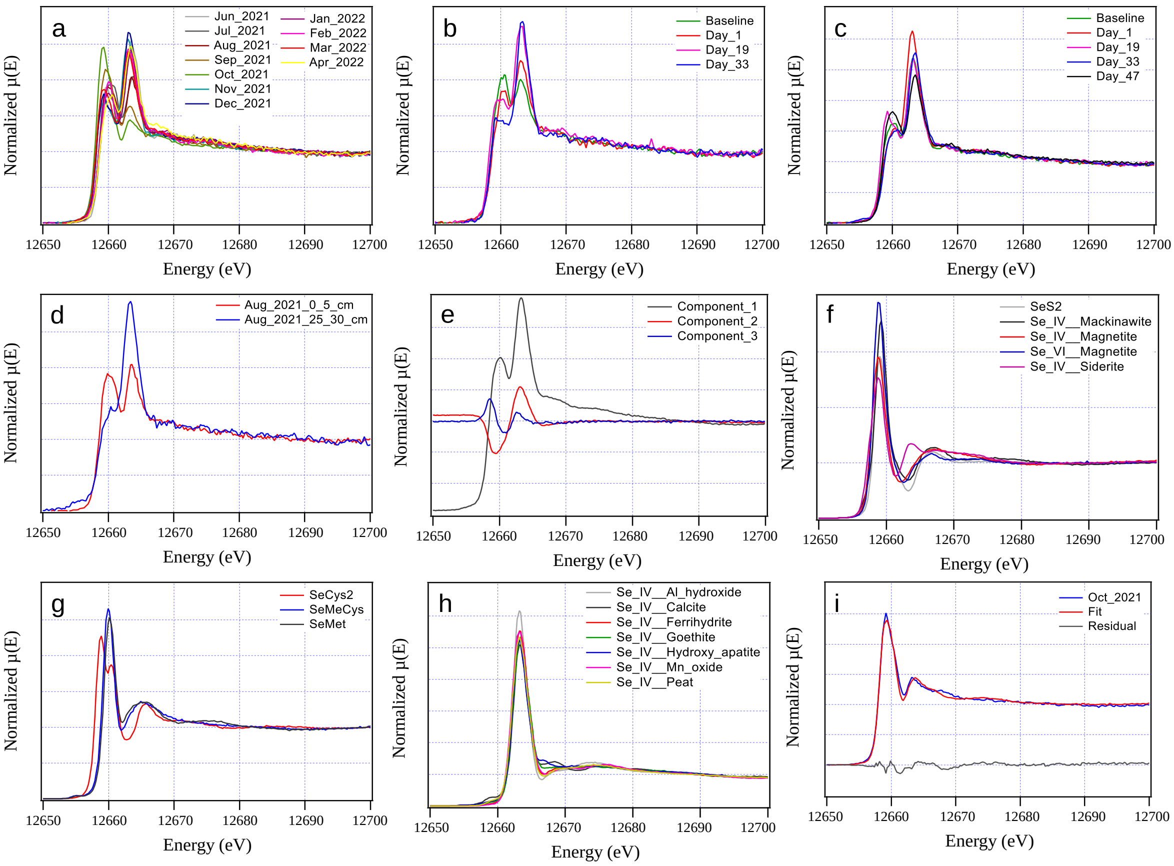

Fig. 1: XANES spectra of a) monthly top soils (0 to 5 cm) from the plot with the longest history (4 years) of crop residue incorporation, b and c) top soils at different times from the control plot, where no burning of crop residue was conducted, and from a plot, where crop residue was burnt, respectively d) comparison of the XANES spectra of topsoil and soil collected at the deeper depth (25 to 30 cm), e) three components identified by PCA, f-h) XANES spectra of references, representative of Se(0), organic Se, and exchangeable and coprecipitated Se pool, respectively, and i) LCF of a representative sample with three components.

Background of the experiment: The goal of the experiment was to determine the dynamics of selenium (Se) speciation in the seleniferous soil of Punjab, India, in relation to different agricultural activities performed on the land. The specific research questions to investigate were i) the influence of the rice-wheat crop rotation on the temporal dynamics of Se speciation in the soil, ii) the effect of the crop residue incorporation into the soil on the Se speciation, iii) the effect of the crop residue burning on the soil Se speciation, and iv) the mechanism of Se species interactions with biochar. As detailed in the experiment proposal, soil core samples were collected every two weeks (more frequently during the crop residue burning experiment) over an entire season of the rice-wheat crop rotation (11 months: June 2021 to April 2022) for this investigation from the depth range of 0 to 45 cm from three seleniferous agricultural plots with different histories of crop residue incorporation into the soil. In the in-house laboratories, soil cores were sectioned to a thickness of 5 cm, dried under an inert atmosphere, and processed for different biogeochemical analyses.

Experiment at the beamline: With the allocated beamtime of 18 shifts at the BM16 beamline, we could collect Se K-edge XANES data for twenty-nine Se reference standards, which could be a possible Se reservoir in this soil and thirty-three soil samples. The analysed soil samples represent monthly topsoil (0 to 5 cm) samples collected over the entire monitoring period from the plot with the longest history (4 years) of crop residue incorporation into the soil, topsoil samples collected at different times after the burning of the crop residue, and a few samples to determine the variation in Se speciation with depths in the soil. Therefore, among the research questions mentioned above, the first and third questions were investigated thoroughly, the second question partly, and the fourth question left entirely to be investigated in the future if an additional beamtime is allocated.

Data processing: The energy calibrated, merged, and normalized representative sample spectra are displayed in Fig. 1a to d, grouped according to the specific question to be addressed. Two peaks dominated the XANES spectra of samples: one in the energy position of zero-valent Se (Se(0)) (~12658 eV) to organic Se (~12660 eV) and the other in the position of selenite (Se(IV)) (~12663 eV). The principal component analysis (PCA) with these sample spectra suggested that three components (Fig. 1e) are required to account for the variability in these samples; these three components cumulatively explain 99.3% of the variability in the data. Target transform analysis of the Se reference standards using these three components provided an excellent SPOIL value (≤1.5) for fifteen of the twenty-nine analysed references, suggesting that these fifteen references can be fitted to the sample spectra. A close inspection of these references revealed that according to the white line peak position, they could be broadly grouped into three categories, representative of the Se(0), organic Se, and exchangeable and coprecipitated selenite (Fig. 1f to h). Since differences between the spectrum of individual references were in the level of noise associated with the sample spectra, it is concluded that further refinement of the identification of references for fitting the sample spectra would be an overinterpretation of the data. Therefore, data interpretation was limited to determining the sample-to-sample variability in these three reservoirs of Se. To determine this variability, a reference with the lowest SPOIL value in each of the three categories was selected for the linear combination fitting (LCF) of the sample spectra (Fig. 1i).

Results obtained so far: Results showed that in the agricultural plot with a history of four years of crop residue incorporation, Se speciation was dominated by organic Se (average of 54% ± std. dev. of 12%), followed by an equal share of Se(0) (25% ± 11%) and exchangeable and coprecipitated Se (24% ± 8%). The temporal change in Se speciation was closely linked to the rice-wheat crop rotation, especially to the irrigation pattern practiced for their cultivation. From the beginning of rice cultivation (June 2021) to the end of the panicle formation stage (October 2021), when the paddy soil was under constant submerged conditions, the exchangeable and coprecipitated pool of Se decreased gradually over the period with a concomitant increase of the Se(0) pool. When the land was dried up for grain ripening, the Se(0) content started to decrease immediately and decreased continuously over almost the entire duration of the wheat cultivation, when irrigation was intermittent only. At the end of the wheat cultivation, the Se(0) content in the soil decreased to the level of the pre-rice cultivation time. The decrease of the Se(0) content was accompanied by an immediate increase in the exchangeable and coprecipitated Se pool during the ripening of rice grains, and that level of the exchangeable and coprecipitated Se pool was broadly stable over the entire duration of the wheat cultivation. The organic pool of Se decreased steadily from the beginning to the end of the rice cultivation and remained stable during the month of transition from rice to wheat cultivation. In the early stage of wheat cultivation, the organic Se content in the soil increased within a short duration of one month and remained broadly stable over the rest of the wheat cultivation. Although compared to the baseline, an ~10% increase in the exchangeable and coprecipitated Se pool was observed within 24 h of the crop residue burning at two plots, the effect of burning on soil Se speciation was inconclusive because a similar increase of the exchangeable and coprecipitated pool over the same period was also observed in the control plot, where no burning was conducted. Analysis of a few samples indicated that Se speciation could be significantly different at the deeper depths (25 to 30 cm) compared to the topsoil (0 to 5 cm). On average, the exchangeable and coprecipitated Se content increased by 26%, and organic Se content decreased by 28% in the analysed samples collected from the deeper depth compared to the topsoil. However, analysis of more samples is required to make any definite conclusion on the variation of Se speciation with depths.