Standard Experimental Report
(All fields are mandatory)

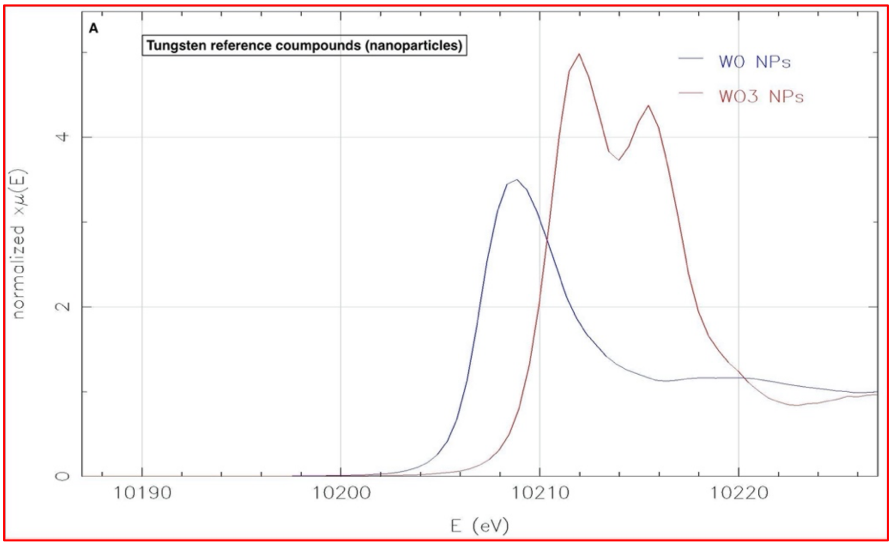
Proposal title: (Bio)transformation of W particles released in the environment in case of Tokamak Lost of Vacuum Accident
Proposal number: 20180191
Beamline: FAME-UHD
Shifts: 18
Date(s) of experiment: from: 14/06/202 to: 20/06/2022
Date of report: 14/07/2022

- Objective & expected results (less than 10 lines):

Our project focused on the characterization of the environemental exposure and impacts of W particles that can be produced in thermonuclear fusion reactors (ITER type). It is known that particles ranged from 50 to 300 nm can be released in the environment even after high efficiency filtration. To assess their behavior, fate and impacts in the environment, such submicron W particles were synthesized in the lab by plasma production to simulate ITER-like particles potentially released. Indoor aquatic mesocosms were used to simulate the contamination of a pond ecosystem to these W particles. The beamtime on FAME-UHD aimed at deciphering the mechanisms and kinetics of (bio)transformation of submicronic W particles in diluted environmental samples (sediment, macrophyte, and aquatic snails). HERFD-XAS appears as one of the more suitable technique to perform such structural investigation on diluted elements.

- Results and the conclusions of the study (main part):

Due to the limited litterature available regarding the W speciation using HERFD-XAS, we started this session by analysing W reference compounds at the W L_3-edge (10.21 KeV) and at an emission energy og 8.39 KeV. The selection of the standard reference compounds was based on different oxidation state of W (0, IV, VI), different degree of polymerisation (e.g. monotungstate and polytungstate), and different particle sizes (<20 nm, ~300 nm, > 1µm) (see figure 1, A and B). We also prepared pellets with mixtures of the 3 oxidation states of W using different percentages of (0), (IV), and (VI) species : 20% W(0) / 40% W(IV) / 40% W(IV) ; 20% W(0) /50% W(IV) / 30% W(IV) ; 20% W(0) /30% W(IV) / 50% W(IV). This was done in order to assess the ability of quantifying the percentage of mixed valence states in our mesocosm and microcosm samples (see figure 1C).



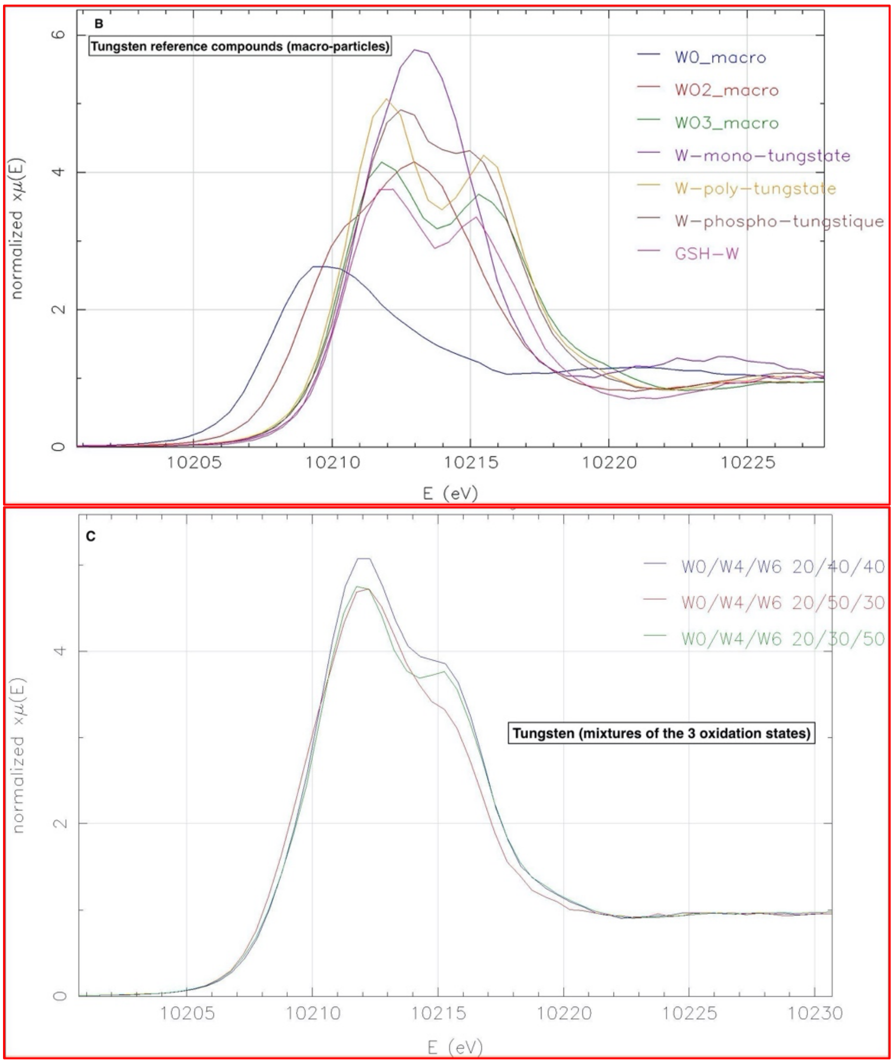


Figure 1. (A) W L_3-edge of nanoparticles used in micro and mesocosm experiments, (B) W L_3-edge standard reference compounds. (C) Experimental mixture standard reference compounds of different W oxidation states (0, IV, and VI).

To understand the mechanisms of (bio)transformation of W species in freshwater ecosytems, we first assessed the speciation of W(0) nanoparticles, WO_3 nanoparticles, sodium monotungstate and sodium polytungstate in freshwater microcosms. These microcosms were made of 750 mL of volvic water, 3 cm of sediment, 10 g (dry weight) of characea and 5 physa exposed during 7 days. The exposure concentrations of macrophytes and snails in the microcosms were higher (13 to 130 times) than the ones used in the mesocosms to ensure about the detection and limit the noise on the XANES/EXAFS spectra. A total of 12 samples were analysed (Figure 2). We first observed a similar speciation of W in the characea whatever the initial W speciation. Interestingly, we also observed differences with regard to the initial speciation of the W dosed in the microcosm in the snail but not in the sediments where they feed. The internalisation in the snail likely occurred via ingestion of the benthic biofilm, and the enzymatic activities involved during the digestion could explain such differences. A carefuly analysis of the W speciation using linear combination fit using standard reference compounds previously analyzed will help us to better understand these mechanisms of biotranformation.

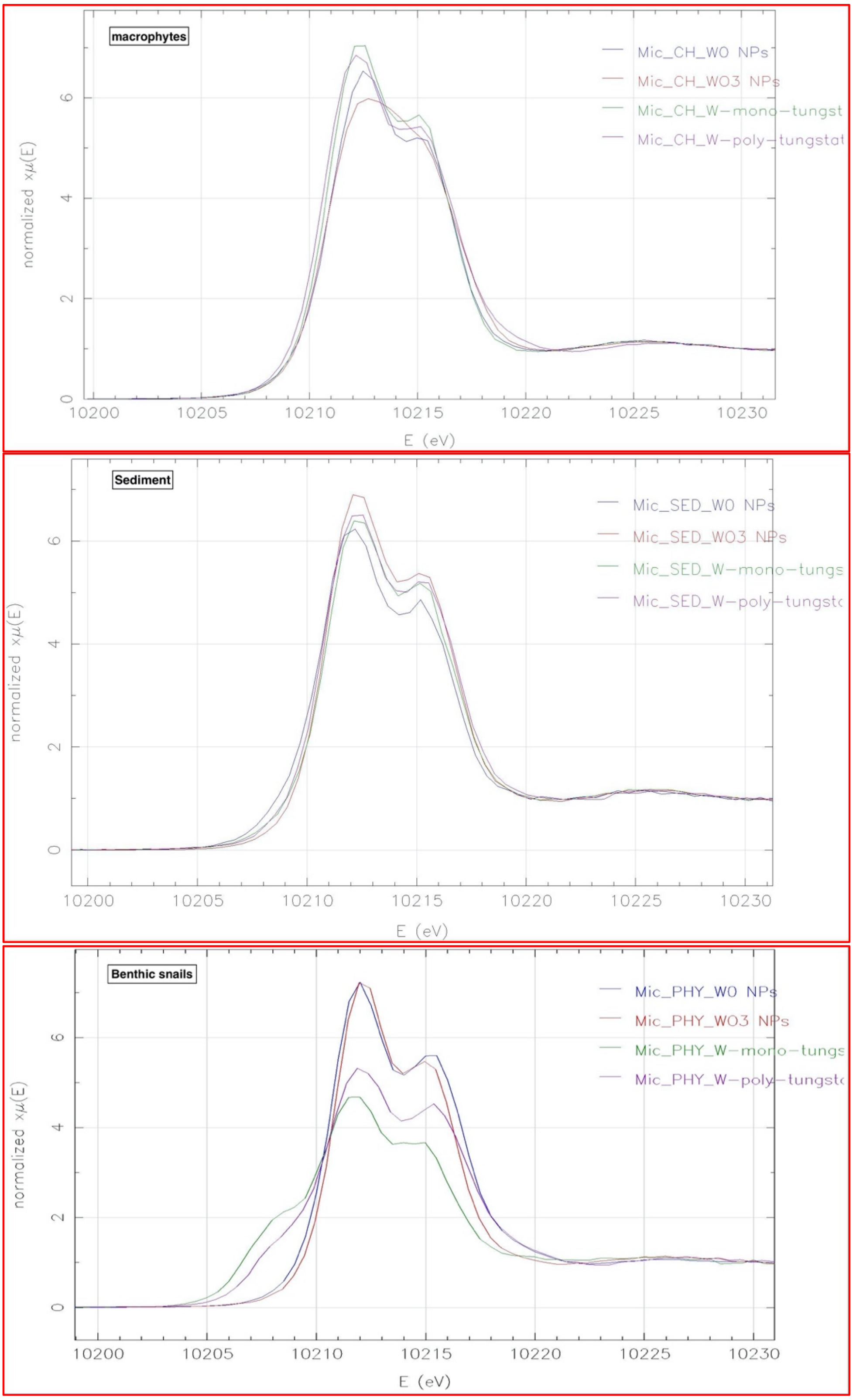


Figure 2. HERFD-XAS spectra at the W L_3-edge of macrophytes, sediment and benthic snails exposed during 7 days to nanoW, nanoWO$_3$, monotungstate, and polytungstate in microcosms.

Finally, macrophytes and sediment exposed in mesocosms to the W(0) nanoparticles and WO_3 nanoparticles during 21 days were analyzed (Figure 3 and 4). The high quality of FAME-UHD, the very low signal/noise ratio level, allowed us to analyze samples with W concentrations down to few ppm. Such a low detection limit was necessary because of the low W concentrations in our environmental matrices initially exposed to 75 to 750 $\mu g.L^{-1}$ in the water column of the mesocosms. At such concentration, a special attention had been paid to the beam-induced transformation during acquisition. To limit these effects, we used a helium cryostat and change the position on the pellets between each spectrum using the automatic procedure proposed on the FAME-UHD. By taking these precautions, we did not observe any transformation under the beam.

The results reveal an effect of aquatic plants (*Ranunculus aquatilis* (RNCL) and *Chara vulgaris* (CH)) on the tungsten speciation in the mesocosms after 21 days of exposure. Moreover, we observed that the speciation of tungsten nanoparticles mainly depends on the localization on/in the plant (branchlet or stem). Contrary to the branchlets of *Chara vulgaris*, where no change of speciation occured, we noticed an evolution of the tungsten speciation towards states more oxidized on/in the branchlets of *Ranunculus aquatilis* and the stems of both plants. This localized effect can be attributed to specific pH, redox conditions or the presence of organic acids.

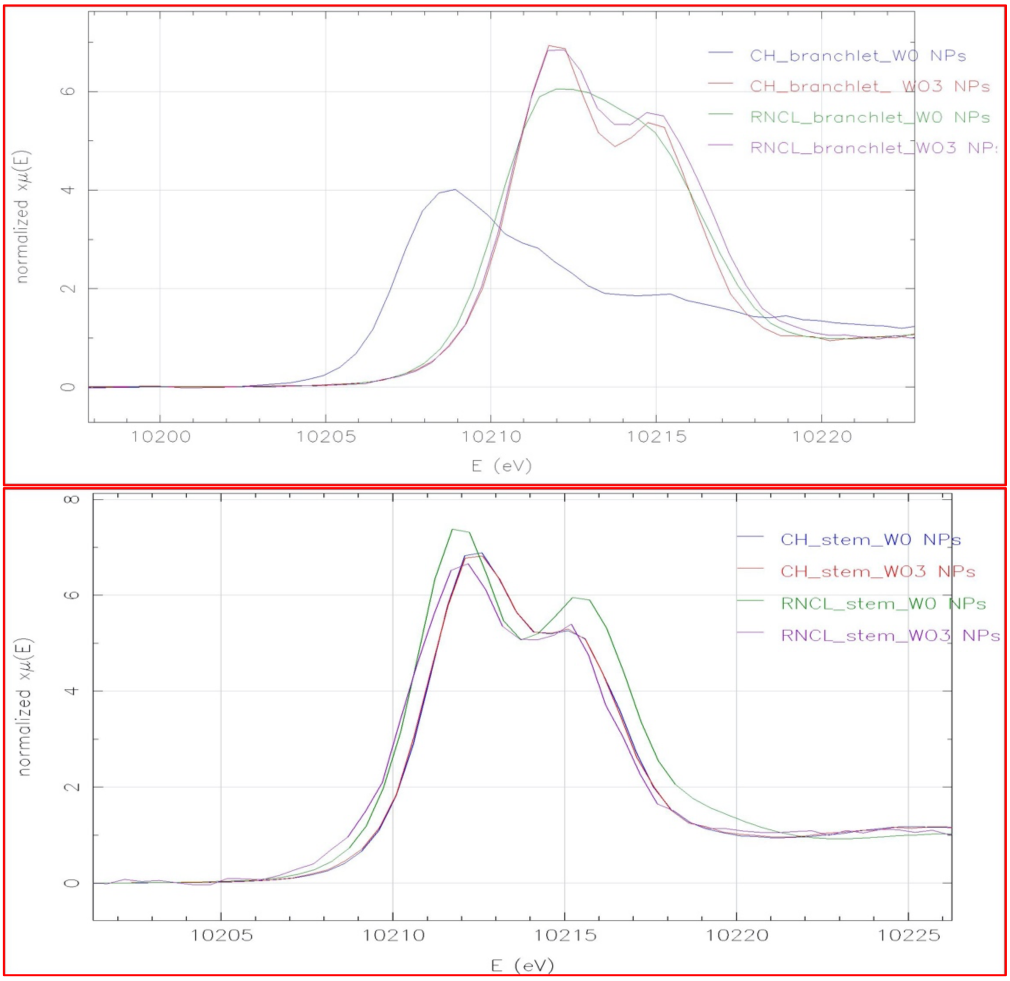


Figure 3. HERFD-XAS spectra at the W L_3-edge of branchlets and stems exposed during 21 days to nanoW and nanoWO_3 in *Ranunculus aquatilis* and *Chara vulgaris* mesocosms.

Regarding the sediment in both modalities of mesocosm (RNCL and CH), we observed changes in the initial speciation of metal tungsten nanoparticles W(0). The root exudates via the rhizoidal system of plants or the biofilm at the surface of the sediment can induce such changes in the speciation of tungsten.

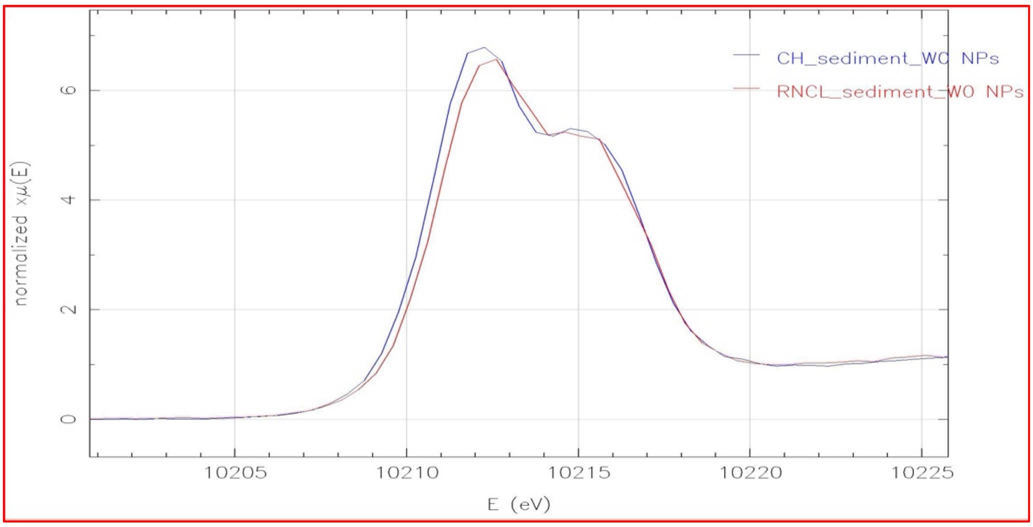


Figure 4. HERFD-XAS spectra at the W L_3-edge of sediment during 21 days to nanoW and nanoWO_3 in *Ranunculus aquatilis* and *Chara vulgaris*.

<u>- Justification and comments about the use of beam time</u> <u>(5 lines max.): -</u>

Analyses were performed on all the initially envisaged samples and even more due to the very low detection limit of W on the FAME UHD beamline. Those results combined with biodistribution and toxicity data will allow us to go deeper on the behavior and fate of W particles in a freshwater environment. All the samples were taken back to our labs after analysis.