

Experimental Report - Proposal A16-1-814

Impact of wildfires on nickel contamination at ultramafic drinking water catchment sites : A model study in New Caledonia

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Proposal Summary

Wildfires represent a growing environmental forcing on continental ecosystems. An underestimated impact is trace metal dispersion toward freshwater systems after soil heating. In New Caledonia where Ni-rich ultramafic soils are widespread, such a dispersion is suspected to contribute to nickel exposition of the inhabitants through consumption of impacted freshwater. The aim of **Proposal A16-1-814** was to address this issue by assessing nickel speciation at a model site representative of the most fire-sensitive drinking water catchment sites of this French overseas territory.

Experimental report

Ni K-edge XAS data were collected on soil and sediment samples collected at two drinking water catchments at *Ile des Pins* (Figure 1) that showed high dissolved nickel concentration (up to 6,000 µg/L compared to the WHO drinking water quality guideline of 70 µg/L).

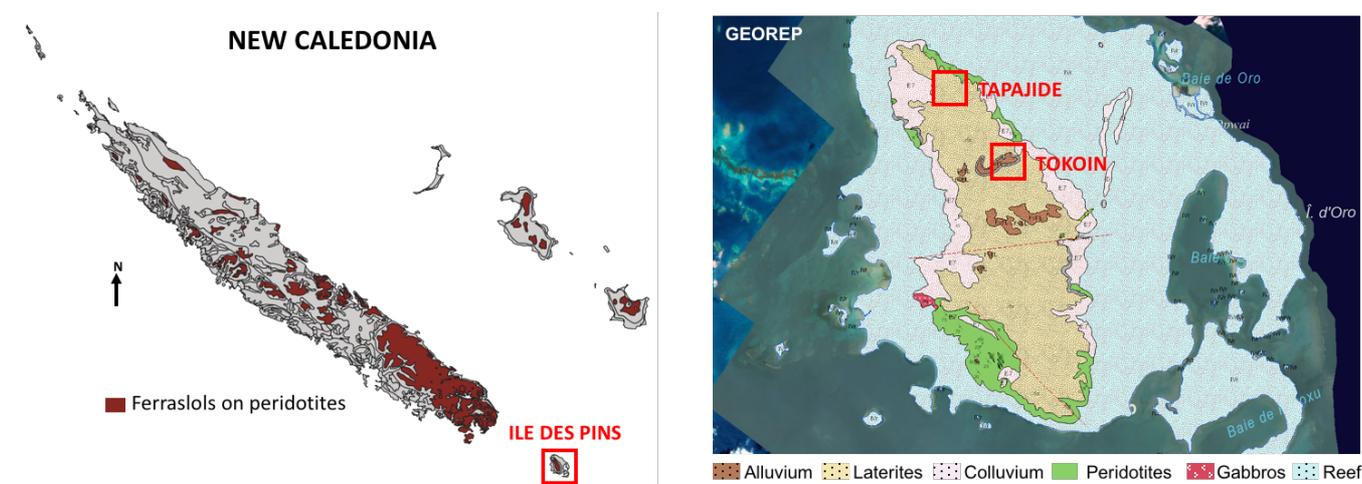


Figure 1. Maps showing (left) the location of Ferrasols on ultramafic rocks and (right) the geological setting of Ile des Pins. The brown-colored areas on the geological map of Ile des Pins figure the ponds that can serve as a source for some drinking water catchments.

The first drinking water catchment (Tokoin, Figure 1) is supplied by an upstream pond where dissolved nickel concentration have been measured up to 300,000 µg/L and where preliminary mineralogical analyses

(XRD, SEM and TEM) revealed nickel hosting by both oxidized (sulfate, oxides, clays) and reduced (sulfides) mineral species in the sediments. Since this first context is quite unusual, a second drinking water catchment (Tapajide, [Figure 1](#)) located at the outlet of a small watershed was also sampled to serve as a model site more representative of the local context. Both sites are located on Ferralsols developed on ultramafic rocks and covered with pine forest (*Pinus caribea*) that was partly burnt by several fires those last 5 years ([Figure 1](#)).

During the experimental session, 22 soil and sediment samples collected at both sites were analyzed by HERFD-XAS spectroscopy at the Ni K-edge. Preliminary investigations on these soil and sediment samples indicated nickel concentration ranging from 800 to 5,000 mg/kg. In addition, a synthetic sample of Ni-bearing magnesium sulfate was also analyzed because preliminary XRD analyses revealed the occurrence of this Ni species in the pond sediments from the first site (Tokoin).

At the first site (Tokoin), a quick overview on the nickel concentration in the $< 0.2 \mu\text{m}$ fraction of water collected in the three ponds averaged on three sampling campaigns indicates an increasing trend from the pond 3 to the pond 1 ([Figure 2](#)). This trend might be related to the influence of burned pine forest that surrounds ponds 1 and 2 and is only partly present around pond 3.

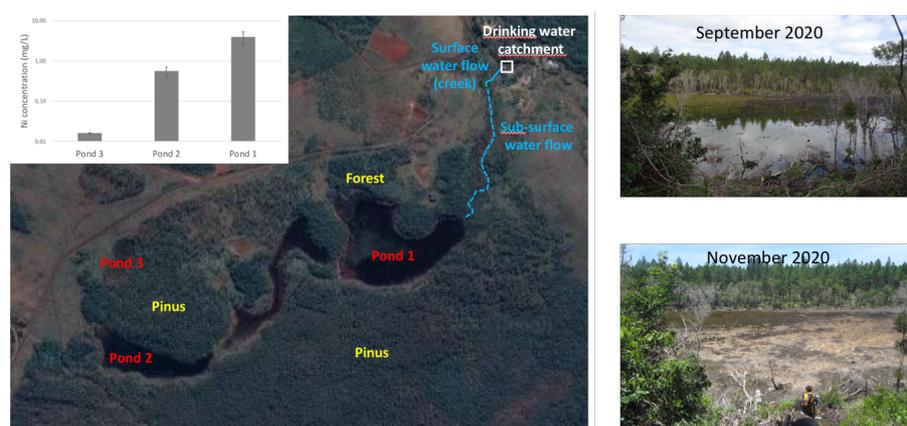


Figure 2. Situation map of the Tokoin catchment site showing the location of the three ponds and the two types of soils around. The histograms in the upper left show the averaged nickel concentration in the $< 0.2 \mu\text{m}$ fraction of the water collected in the three ponds over three sampling campaigns. The two pictures on the right illustrate the wet and dry sampling conditions at pond 1.

Although the first derivative of Ni K-edge XANES spectra collected on the pine and forest soils and on the sediments sampled in pond 1 after a dry period appear quite similar, significant variations can be observed in the $k= 6-9 \text{ \AA}^{-1}$ region of EXAFS spectra ([Figure 3](#)). Comparison with relevant model compounds ([Figure 4](#)) suggests that Ni speciation may be dominated by goethite and Ni-hexahydrate.

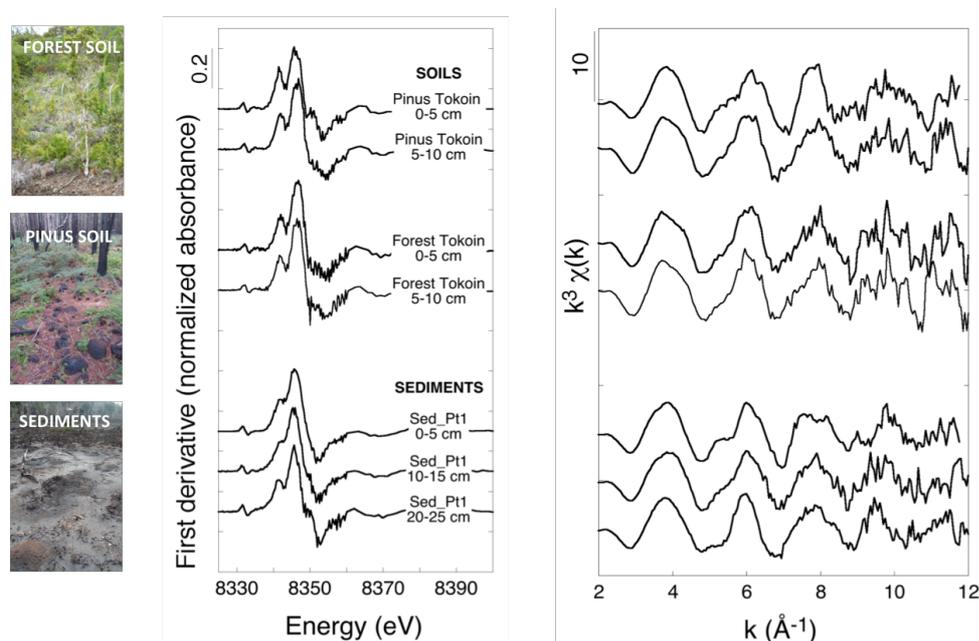


Figure 3. Pictures (left), first-derivative of normalized Ni K-edge XANES spectra (center) and Ni K-edge EXAFS spectra (right) of the forest and pines soils and sediments (pond 1) collected at the Tokoin catchment site after a dry period.

Owing to the very high solubility of this latter phase, and considering its previous XRD detection in the surface horizons of the sediments, Ni-hexahydrite might have a major control on nickel mobility at the drinking water catchment site of Tokoin.

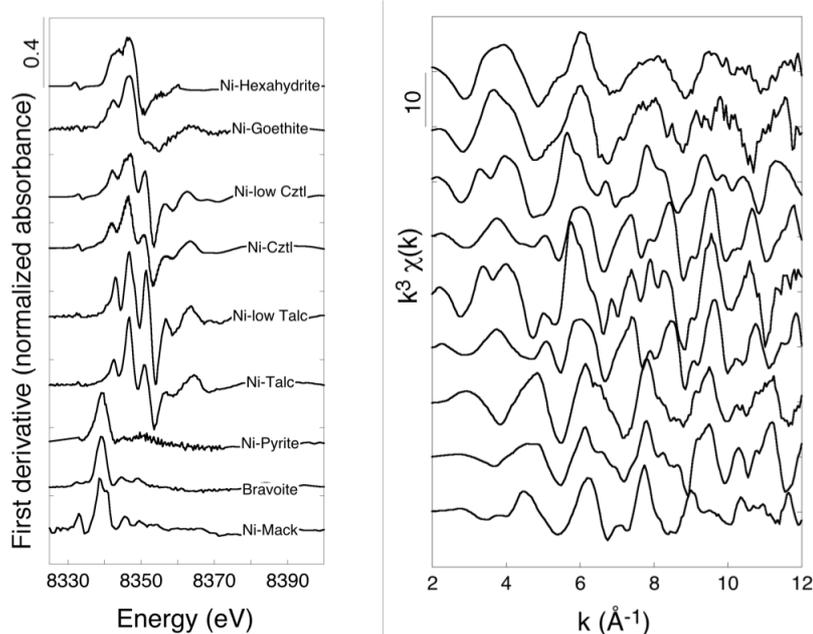


Figure 4. First-derivative of normalized Ni K-edge XANES spectra (left) and Ni K-edge EXAFS spectra (right) of relevant model compounds for the least-square fitting procedure that will be applied to the experimental data collected during Proposal A16-1-814.

However, comparison of the Ni K-edge XAS data collected on the sediments from the pond 1 sampled after a dry period (Figure 3) with those collected on the sediments from ponds 1, 2 and 3 sampled after a wet period (Figure 5) emphasizes the additional occurrence of Ni-sulfides in the wet period-sediments (especially in ponds 1 and 2). This latter phase might thus also contribute to nickel cycling at the sediment-water interface in the wet season.

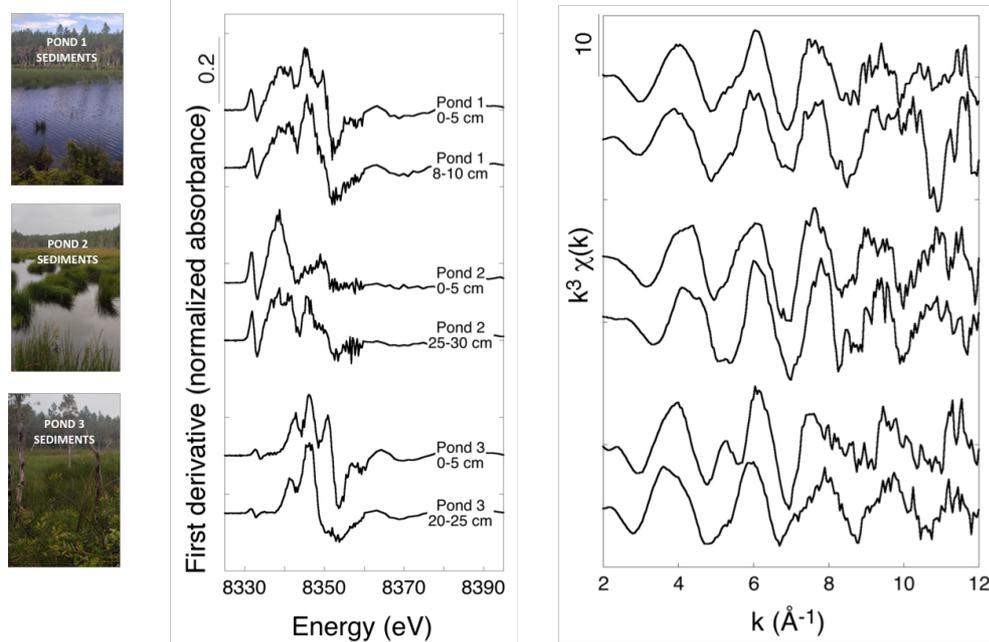


Figure 5. Pictures (left), first-derivative of normalized Ni K-edge XANES spectra (center) and Ni K-edge EXAFS spectra (right) of the sediments collected in ponds 1, 2 and 3 at the Tokoin catchment site after a wet period.

At the second site (Tapajide), Ni K-edge data collected on the pine soils surrounding the drinking water catchment, as well as on the sediments in the creek feeding the catchment, are significantly different to support the hypothesis of a contrasted nickel speciation at both systems (Figure 3).



Figure 5. Picture of the Tapajide catchment site showing the location of the Pinus forest, the sediments and the water precipitates sampled.

In addition, Ni K-edge XAS data collected on water precipitates are also significantly different from those collected on the sediments (Figure 3). This latter result suggests that a secondary biogeochemical process might at least partially drive nickel speciation at the sediment/water interface at the drinking water catchment site of Tapajide.

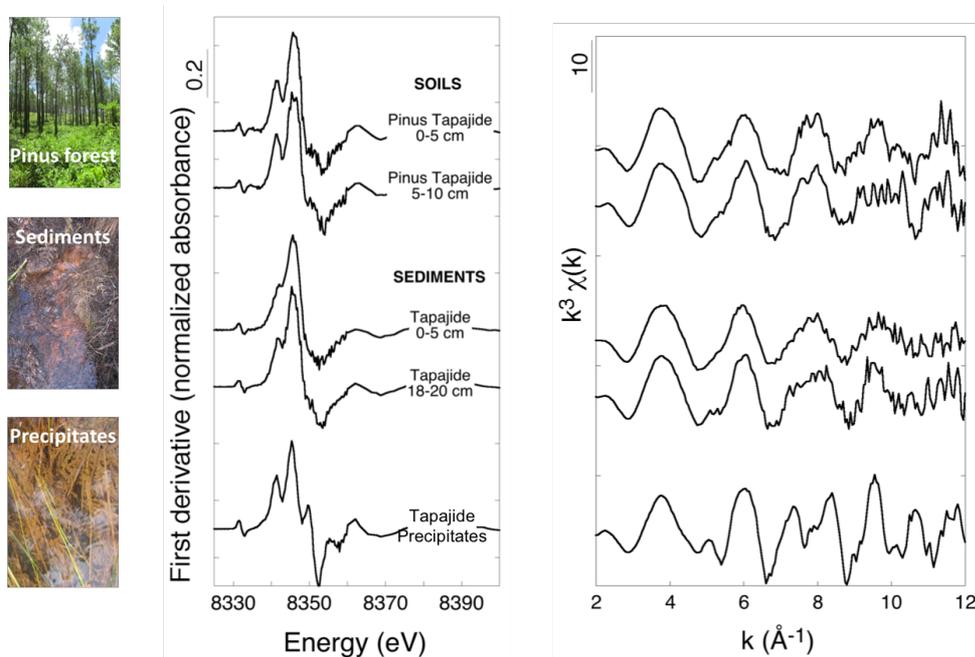


Figure 6. Pictures (left), first-derivative of normalized Ni K-edge XANES spectra (center) and Ni K-edge EXAFS spectra (right) of the soils and sediments collected at the Tapajide catchment site.

Perspectives

All the Ni K-edge XAS data collected on soils and pond sediments on Proposal A16-1-814 will be further analyzed by Linear Combination Fitting using relevant model compounds, like Ni-goethite, Ni-phyllosilicates, Ni-sulfides and Ni-hexahydrate (Figure 4). The molecular-level information thus revealed will be compared to the results of leaching experiments with a 10^{-2} M CaCl_2 solution that evidenced a larger nickel mobility in pond sediments compared to soils, but also at burned areas compared to non-burned ones, to better understand how wildfires can impact drinking water quality at ultramafic catchments in New Caledonia.

Beyond the single case of New Caledonia, the results on nickel speciation gained on Proposal A16-1-814 will serve as a model study for South America, Central and South Africa, South East Asia and Australia where mafic and ultramafic rocks significantly contribute to the geological setting and which are among the most exposed continental surfaces to wildfires (https://earthobservatory.nasa.gov/global-maps/MOD14A1_M_FIRE).