

# Assessing the origin and fate of Cr, Ni, Cu, Zn, Pb, and V in an industrial polluted soil by combined micro-spectroscopic techniques and bulk extraction methods

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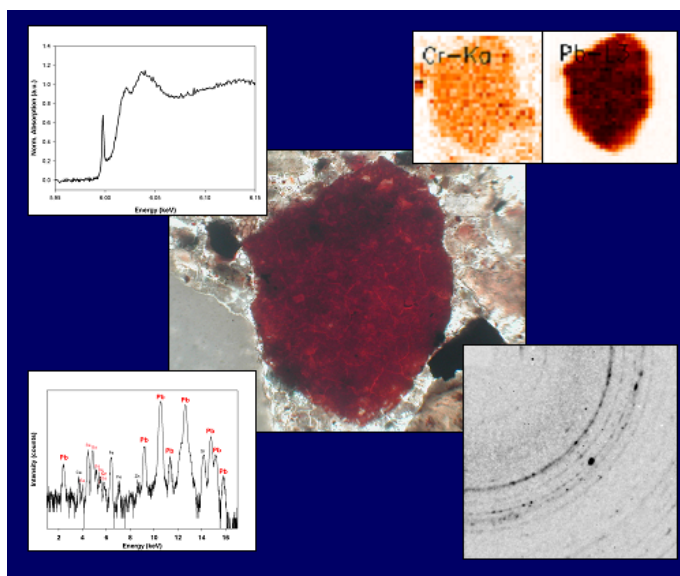
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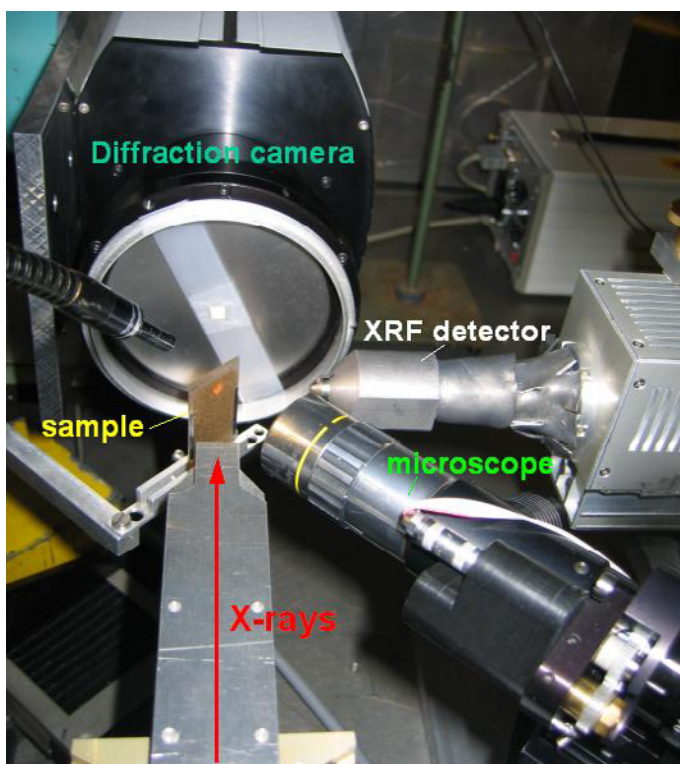


*It is commonly recognized that soil is the major sink for heavy metal (HM) contaminants released into the environment by human activities and that the mobility, bioavailability and toxicity of metals strongly depend on their solubility and therefore on their geochemical forms. Soil contaminated with HM can cause serious risks to human health, e.g. if vegetables cultivated on contaminated soil are consumed. The correct identification of HM chemical forms in soil is therefore of paramount relevance for a proper risk assessment and for the formulation of effective remediation strategies.*

*The major geochemical forms of Cr, Ni, Cu, Zn, Pb, and V in a soil from an industrial polluted site in the South of Italy were determined by means of synchrotron X-ray micro-analytical techniques. Based on the identified geochemical forms, among others, two major former industrial activities were tentatively ascribed as being responsible of the observed major pollution: PVC and cement-asbestos productions.*

In recent years, the development of new analytical methods exploiting high energy and high intensity synchrotron X-rays has provided soil scientists with new powerful tools for shedding light on HM speciation in soil [1-3]. In particular, given the large number of different phases in soils and their complex and heterogeneous distribution, the use of synchrotron X-ray microbeam techniques can resolve the metal bearing phases at the micrometer (or sub-micrometer) level thus allowing a more selective and direct approach to HM speciation. These techniques have also the advantage of reducing analytical artefacts caused by extensive sample manipulations.

In this study, we used a combination of micro-analytical techniques exploiting synchrotron X-rays as well as different bulk extraction methods to assess the geochemical forms and chemical behaviour of various HM pollutants [Cr, V, Pb, Ni, Cu, and Zn] in a soil from an industrial polluted site in the South of Italy. Micro X-ray fluorescence ( $\mu$ -XRF) was used to localize metals in soil thin sections and to find correlations among different elements. Simultaneously, micro X-



**Figure 1.** Experimental set-up adopted for combined  $\mu$ -XRF/ $\mu$ -XRD at Beamline L.

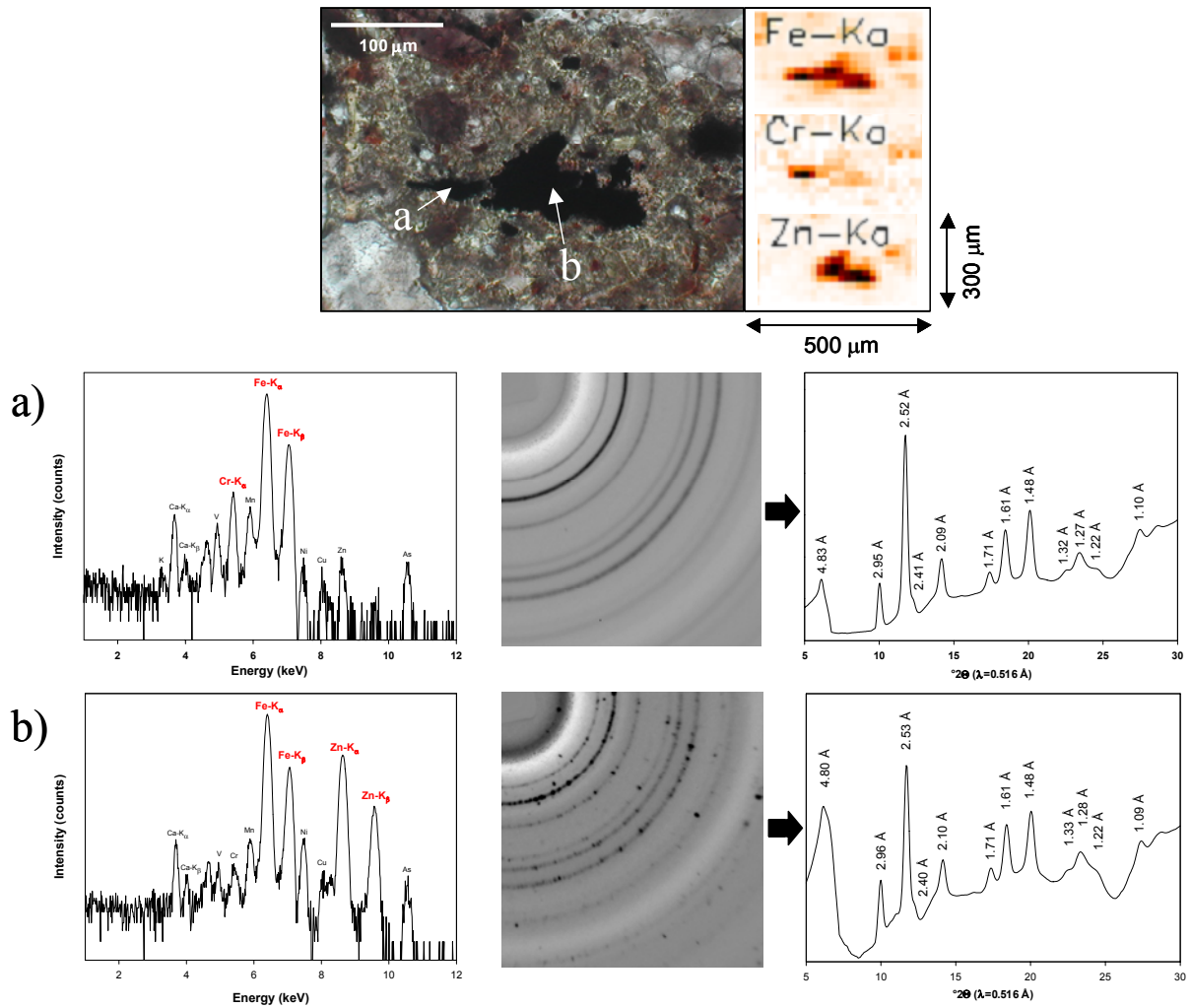
ray diffraction ( $\mu$ -XRD) patterns were collected to get information about the minerals HM were associated to. The simultaneous acquisition of  $\mu$ -XRF and  $\mu$ -XRD data was possible by collecting XRD patterns in transmission mode rather than in reflection mode [4]. In addition,  $\mu$ -XANES spectroscopy point analyses were performed to determine the oxidation state of pollutants such as Cr and V and to better define the association of various other metals with minerals by comparison with selected mineral standards. The information revealed by these synchrotron X-ray analyses allowed HM speciation at the microscopic level.

All the results emerging from both the “microscopic” (x-ray based) and the “macroscopic” (bulk extraction based) investigations were combined and employed to identify the possible former sources of metal pollution and to predict the fate of these elements in soil.

The experimental set-up adopted for the combined micro-analytical investigation at Beamline L (HASYLAB) is shown in Figure 1: The X-ray beam from DORIS, focused at 10-20  $\mu$ m, hits the sample in a microscopic point (yellow spot) which is also in the focus of an optical microscope, essential to see which part of the sample is being analysed. The sample is mounted at an angle of 45° to the incident beam. A silicon-drift detector, which is mounted at an angle of 90° to the incident beam, measures the fluorescence of the sample, while a large-area CCD-detector, which is mounted behind the sample, measures the X-ray diffraction pattern. Since both detectors can operate simultaneously, fluorescence and diffraction are measured on the same spot of the sample at the same time.

Several micro-areas on different soil thin sections were analysed by means of combined synchrotron radiation  $\mu$ -XRF/ $\mu$ -XRD (Figure 2). In addition, for selected points of interest, metal speciation was more clearly assessed by  $\mu$ -XANES (Figure 3). For  $\mu$ -XANES analyses, it was necessary to slightly modify the set-up by changing the broadband multilayer to a tuneable Si(111) double crystal monochromator and by inserting a different (polycapillary) lens to produce a 20  $\mu$ m analyzing X-ray beam.

Using this approach, various mineral phases were microscopically identified for the different metals, as reported in Table 1.



**Figure 2.** (top) Micrograph with the corresponding  $\mu$ -XRF distribution-maps (for Fe, Cr, and Zn) of a microscopic area on a soil thin section analysed by combined  $\mu$ -XRF/ $\mu$ -XRD. Darker pixels correspond to relative higher concentrations of the element. (bottom)  $\mu$ -XRF spectra and  $\mu$ -XRD images (also converted into 1D diffraction patterns) were collected in points *a* and *b* (indicated by the arrows in the micrograph). The d-spacing values corresponding to the diffraction peaks are also shown in the 1D diffractogram. The reported d-spacings are characteristic of spinel-type minerals: a) Chromite and/or Magnetite, b) Franklinite and/or Magnetite.

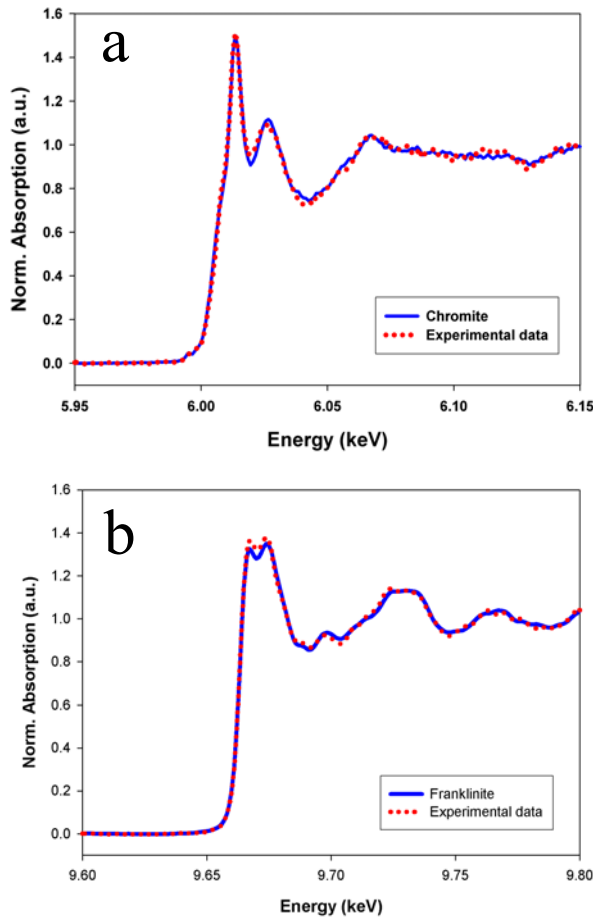
**Table 1:** Soil chemical composition for major and trace elements and microscopically identified metal geochemical forms.

Major elements (%)	Trace elements ( $\mu\text{g/g}$ )	Microscopically identified phases
$\text{SiO}_2^\dagger$ 40.1	$\text{Cr}_{\text{tot}}^*$ 352 $\pm$ 37	Chromite, Zincochromite, sorbed on Hematite
$\text{TiO}_2^\dagger$ 0.6	$\text{Cr(VI)}_{\text{alk}}^*$ 5.1 $\pm$ 0.9	Crocoite
$\text{Al}_2\text{O}_3^\dagger$ 9.8	$\text{Cr(VI)}_{\text{ac}}^*$ 12 $\pm$ 2	
$\text{Fe}_2\text{O}_3^\dagger$ 16.4	$\text{Zn}^*$ 1196 $\pm$ 53	Franklinite, Zincochromite, sorbed on Hematite
$\text{MnO}^\dagger$ 0.3	$\text{Ni}^*$ 394 $\pm$ 17	Trevorite, sorbed on hematite
$\text{MgO}^\dagger$ 1.4	$\text{Cu}^*$ 449 $\pm$ 8	Cuprospinel, Volborthite, sorbed on Hematite
$\text{CaO}^\dagger$ 18.1	$\text{Pb}^*$ 1080 $\pm$ 150	Minium, Lanarkite, Crocoite
$\text{Na}_2\text{O}^\dagger$ 0.6	$\text{V}^*$ 1688 $\pm$ 24	Volborthite, V(V) sorbed on Hematite
$\text{K}_2\text{O}^\dagger$ 1.1	$\text{Ba}^*$ 445 $\pm$ 12	Barite
L.O.I. 11.6		

$^\dagger$  Determined by XRF      alk: alkaline extraction

$^*$  Determined by ICP-AES      ac: acidic extraction

Cr, Ni, Zn and Cu were found in spinel-type geochemical forms (chromite, trevorite, franklinite, zincochromite, cuprospinel) and often in association with magnetite and hematite. V was mainly present as V(V) associated to Fe-oxides or in the form of volborthite  $[\text{Cu}_3(\text{OH})_2\text{V}_2\text{O}_7 \cdot 2\text{H}_2\text{O}]$ . Pb was speciated as minium ( $\text{Pb}_3\text{O}_4$ ), lanarkite  $[\text{Pb}_2\text{O}(\text{SO}_4)]$  and, in association with Cr(VI), as crocoite ( $\text{PbCrO}_4$ ).



**Figure 3.** a) Cr  $\mu$ -XANES spectrum collected in point a of Figure 1. b) Zn  $\mu$ -XANES spectrum collected in point b of Figure 1. The experimental spectra are shown overlapped with the spectra of selected Cr and Zn standards (chromite and franklinite, respectively).

The main limit of such micro-analytical method is represented by the difficulty to reliably extrapolate the obtained results to a higher length scale. Therefore, to analyze larger amounts of soil samples, various extraction procedures have been also adopted, including single or sequential extraction steps. Most of the results obtained at the microscopic level have been confirmed by the extraction procedures. However, batch extractions failed to identify correctly some HM chemical species (in particular for Pb). Therefore, for the analysed soil samples, an extrapolation of the results obtained by using micro-spectroscopic techniques to the macroscopic level seems to be applicable even if most of the well-known limitations of the extraction procedures are confirmed [5].

From all the data presented in this research, despite a high total concentration, most of the HMs appear to be speciated in rather insoluble geochemical forms. Therefore, the environmental danger connected to their presence in the investigated soil is estimated to be much lower than expected. However, particular attention should be still paid to Zn, Cu, V, and Pb that show non-negligible mobilisable fractions, as evidenced by EDTA extractions.

Finally, the detailed HM speciation determined by micro-spectroscopic techniques has been compared with the geochemical characteristics of the site under investigation and the possible sources of anthropogenic impact have been determined.

In particular, two major former industrial activities were tentatively ascribed as responsible of the observed major pollution: PVC and cement-asbestos productions. These plants were operating on this site during the 1960s-1980s and they extended over an area of ca. 1000 ha. Beside the metals, which were the objective of this research, a diffuse mercury contamination is also visible in the same area, as well as pollution from various toxic organic compounds.

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