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ESRF	**Experiment title:** Colloidal arsenic transport and speciation in soil surface runoff from contaminated mine sediments in natural systems	**Experiment number**: EV 41
Beamline: BM25A	**Date of experiment**: from: 13/12/2013 at 08:00 to 17/12/2013 at 08:00	**Date of report**: 07/09/2017
Shifts: 12	**Local contact(s)**: Dr. Eduardo Salas	*Received at ESRF:*

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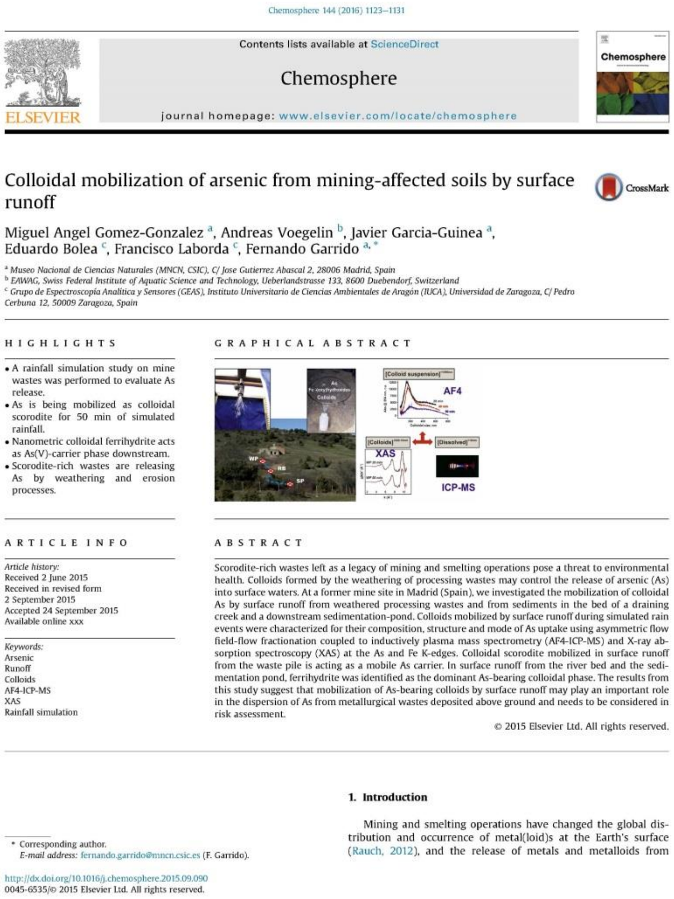
Report:

Wastes rich in scorodite and arsenopyrite left as a legacy of past mining and smelting operations pose a threat to environmental health. Colloids formed by the weathering of mining and processing wastes may control the release of hazardous elements such as arsenic (As) into surface waters and may contribute to long-distance contaminant transport and dispersion. The nature of colloidal As determines its impact on As mobility and bioavailability and needs to be considered for the mitigation of As release from weathered mine wastes. In this study, we investigated the importance and mode of colloidal As mobilization from weathered processing wastes and from sediments from the draining river bed and a more distant sedimentation pond. Colloids in the surface runoff were collected during simulated rain events and were characterized for their composition, structure and mode of As uptake using a combination of flow field-flow fractionation coupled to plasma mass spectrometry (AF4-ICP-MS) and X-ray absorption spectroscopy (XAS) at the As and Fe K-edges. Colloidal As mobilized from weathered processing wastes was identified as scorodite, whereas ferrihydrite was the dominant colloidal As carrier in the sedimentation-pond. Considering that surface runoff effectively mobilizes colloidal As from the weathered wastes, measures should be taken to remove the waste material or to cover the material to eliminate further dispersion of colloidal As.



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Colloidal mobilization of arsenic from mining-affected soils by surface runoff

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HIGHLIGHTS

- A rainfall simulation study on mine wastes was performed to evaluate As release.
- As is being mobilized as colloidal scorodite for 50 min of simulated rainfall.
- Nanometric colloidal ferrihydrite acts as As(V)-carrier phase downstream.
- Scorodite-rich wastes are releasing As by weathering and erosion processes.

GRAPHICAL ABSTRACT

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ABSTRACT

Scorodite-rich wastes left as a legacy of mining and smelting operations pose a threat to environmental health. Colloids formed by the weathering of processing wastes may control the release of arsenic (As) into surface waters. At a former mine site in Madrid (Spain), we investigated the mobilization of colloidal As by surface runoff from weathered processing wastes and from sediments in the bed of a draining creek and a downstream sedimentation-pond. Colloids mobilized by surface runoff during simulated rain events were characterized for their composition, structure and mode of As uptake using asymmetric flow field-flow fractionation coupled to inductively plasma mass spectrometry (AF4-ICP-MS) and X-ray absorption spectroscopy (XAS) at the As and Fe K-edges. Colloidal scorodite mobilized in surface runoff from the waste pile is acting as a mobile As carrier. In surface runoff from the river bed and the sedimentation pond, ferrihydrite was identified as the dominant As-bearing colloidal phase. The results from this study suggest that mobilization of As-bearing colloids by surface runoff may play an important role in the dispersion of As from metallurgical wastes deposited above ground and needs to be considered in risk assessment.

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1. Introduction

Mining and smelting operations have changed the global distribution and occurrence of metal(loid)s at the Earth's surface (Rauch, 2012), and the release of metals and metalloids from

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Table 4
Linear combination fit results for As and Fe K-edge EXAFS or XANES spectra.

As EXAFS/XANES [a]						
Sample	Scorodite [b]		As sorbed to ferrihydrite [b]		R Factor [e]	Red χ^2 [f]
	% [c]	ΔeV [d]	%	ΔeV		
WP 20 min [g]	94.2	–	5.7	–	0.0249	0.8562
WP 50 min [g]	91.3	–	8.7	–	0.0199	0.6527
SP 20 min [h]			99.7	−0.3	0.0116	0.0062
SP 50 min [h]			99.6	−0.4	0.0125	0.0068

Fe EXAFS/XANES [a]												
Sample	Scorodite[b]		Nontronite[b]		Hematite[b]		Smectite[b]		Schwert-mannite[b]		R Factor	Red χ^2
	%	ΔeV	%	ΔeV	%	ΔeV	%	ΔeV	%	ΔeV		
WP 20 min [i]	91.1	–	8.6	–							0.0517	0.665
WP 50 min [i]	95.7	–			4.2	–					0.0505	0.619
SP 20 min [j]			27.1	0.1			50.3	−0.1	23.3	0.2	0.0003	0.0001
SP 50 min [j]			20.9	0.3			50.4	−0.1	29.3	−0.1	0.0003	0.0001

[a] EXAFS spectra of waste-pile (WP) colloids and XANES spectra of sedimentation-pond (SP) colloids were analyzed by LCF analyses.
[b] Characteristics and procedence of reference spectra are shown in the Supplementary Material.
[c] Fittings were not constrained to sum 100%.
[d] Fitting variations of XANES LCF given by the software Athena (Ravel and Newville 2005).
[e] Normalized sum of the squared residuals of the fit [$R = \sum(\text{data-fit})^2/\sum \text{data}^2$)].
[f] Goodness-of-fit was assessed by the χ^2 statistic [= (F factor)/(no. of points − no. of variables)].
[g] LCF EXAFS range: 2–11 Å, spectra measured at ESRF (Grenoble, France).
[h] LCF XANES range: 11 855–11,935 eV, spectra measured at ALBA (Barcelona, Spain).
[i] LCF EXAFS range: 2–9 Å, spectra measured at ESRF (Grenoble, France).
[j] LCF XANES range: 7105–7185 eV, spectra measured at ESRF (Grenoble, France).

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Appendix. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.chemosphere.2015.09.090.

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