

Effect of temperature, gas phase composition, pH and microbial activity on As, Zn, Pb and Cd mobility in selected soils in the Ebro and Meuse Basins in the context of global change

A.V.P. Joubert ^{a,*}, L. Lucas ^b, F. Garrido ^b, C. Joulian ^b, M. Jauzein ^a

^a *Laboratoire des Interactions Micro-organismes, Minéraux et Matières organiques dans les Sols (LIMOS) UMR 7137, Nancy University, CNRS, BP 239, 54506 Vandœuvre-les-Nancy cedex, France*

^b *Bureau de Recherches Géologiques et Minières (BRGM), Service Environnement et Procédés Innovants-Unité Ecotechnologie (EPI/ECO), 3 Avenue Claude Guillemin, BP 6009, 45060 Orléans cedex 2, France*

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An experimental method applicable for different soil systems enables the determination of the effect of environmental parameters, potentially affected by global change, on the mobilization of inorganic pollutants.

Abstract

This study estimates the effect of environmental parameters on the mobility of four inorganic contaminants (As, Zn, Pb and Cd) in soils from three areas in the Ebro and Meuse River basins, within the context of global change. An experimental method, applicable to various soil systems, is used to measure the effect of four global-change-sensitive parameters (temperature, gas phase composition, pH and microbial activity). The aqueous phase of batch incubations was sampled regularly to monitor toxic element concentrations in water. Statistical processing enabled discrimination of the most relevant variations in dissolved concentrations measured at different incubation times and under different experimental conditions. Gas phase composition was identified as the most sensitive parameter for toxic element solubilization. This study confirms that total soil concentrations of inorganic pollutants are irrelevant when assessing the hazard for ecosystems or water resource quality.

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1. Introduction

Pollution induced by trace elements in soils is a major environmental problem because, compared to atmospheric and water pollution, the soil environment is much less resilient. The main sources of soil pollution are improper waste dumping, abandoned industrial activities, incidental accumulation, atmospheric fallout and agricultural chemicals (Alloway, 1994). Among known pollutants, trace elements are widely recognized as being potentially toxic to living organisms.

The total content of a trace element in the soil is a poor indicator of environmental risk. Mobility and bioavailability must be assessed to elucidate trace elements' behaviour in soils and prevent potential toxic hazards (Sauvé et al., 2000; Yin et al., 2002; Banat et al., 2005; Wu et al., 2006; Navarro et al., 2006; Margui et al., 2007). The mobility of inorganic pollutants (such as As, Zn, Pb and Cd) depends on physical, chemical, and biological processes, including microbial activities (Deneux-Mustin et al., 2003). The soil solution speciation of trace elements is critical for assessing their bioavailability and potential threat to the environment (Sauvé et al., 1997). The effect of microorganisms on the fate of contaminants in soils can be direct or indirect. Microbial activity changes the physical and chemical characteristics of the environment and

* Corresponding author. Tel: +33 3 83 68 42 94; fax: +33 3 83 68 42 84.

E-mail addresses: antoine.joubert@limos.uhp-nancy.fr (A.V.P. Joubert), f.garrido@brgm.fr (F. Garrido).

may, therefore, indirectly affect contaminant speciation and mobility. Microbial activity in soils is, in turn, strongly affected by physical and chemical soil characteristics (acidity, redox potential, nutrient availability, pore space, etc.). Biogeochemical processes in soils influence the fate of trace elements, i.e. their speciation, mobility and, therefore, their bioavailability and toxicity (Deneux-Mustin et al., 2003).

Changes in climatic conditions and land-use practices associated with soil and sediment pollution can have large-scale adverse impacts on water quantity and quality. The current knowledge in river basin management is not adequate to deal with these impacts. The functioning of the river–sediment–soil–groundwater system is linked to key biogeochemical processes that determine the filtering, buffering and transformation capacity of soils and sediments. Global changes such as increased temperatures and CO₂ fertilization are likely to affect soil biogeochemistry (Van Ittersum et al., 2003). Both are expected to stimulate soil microbial activity and thus influence soil pH and redox conditions (Karnosky, 2003). Indeed, an increase in soil microbial activity would increase soil solution CO₂ saturation, O₂ consumption and nitrogen compound transformation, modifying pH and redox conditions. Changes in the temporal and spatial distribution of rainfall accompanied by an increased risk of both heavy rainfall events and droughts (IPCC, 2001; Eckhardt and Ulbrich, 2003) would modify the hydric regimes and thus O₂ availability and related redox conditions.

The Ebro and Meuse River basins are characterized by different soil nature, land use, climate and pollution (organic/inorganic, diffuse/local). Along the Meuse River, several groundwater and sediment contamination problems are linked to past industrial activities. There is increasing evidence of the devastating ecological effects of high metal levels near point sources such as smelters. Long-range atmospheric transport of metals has led to the contamination of soil and water worldwide (Watmough et al., 2005). In the last century, large amounts of trace elements have accumulated in the embanked river flood plain areas of the Dutch part of the Meuse River system (Schroder et al., 2005) where many groundwater catchment areas are located. The Ebro River is a typical Mediterranean river characterized by seasonal low flow and extreme floods. Substantial agricultural and industrial activity has caused contamination anomalies such as historical Hg pollution (coming from plants manufacturing solvents and pesticides) and widespread accumulation of pesticides (Lacorte et al., 2006; Terrado et al., 2006).

The aim of this work was to develop an experimental approach to test the sensitivity to the effect of four global-change-sensitive parameters (temperature, gas phase composition, pH and microbial activity) on the mobility of four inorganic pollutants (As, Zn, Cd and Pb) in soil or subsoil samples. Applied to soil samples from three sites in the Meuse and Ebro Basins, statistical processing enabled us to discriminate the most relevant variations in dissolved concentrations measured after various incubation times and under various experimental conditions. Focusing on predominantly observed effects, the potential use of the proposed method for other

soil environments can be assessed, in view of deriving parameter values for transfer modelling. This study showed that total soil concentrations of inorganic pollutants are not indicative of the hazard for ecosystems or water resources quality.

2. Materials and methods

2.1. Site description and sample collection

2.1.1. The Dommel site

The Dommel River is a tributary of the Meuse that flows through an old zinc-producing industrial area. During the last hundred years, these activities have led to diffuse atmospheric deposition of zinc and cadmium on land and localized areas with residual industrial contamination (former waste deposits for instance). The experimental site is located in the “De Plateaux-Hag-even” nature reserve on the Dutch side of the Belgian–Dutch border. This location was formerly used as a cinder bank by local industries (zinc foundries). The natural soils in this area are podzolized soils developed on alluvial sands. Birches and grass constitute the vegetation on the site. Three sampling points are located along a 20-m line (Fig. 1a), each corresponding to an area of several square meters. Zone 1 is located on the edge of the source of contamination (former zinc foundry cinder bank), while zones 2 and 3 are located along the assumed direction of groundwater flow. Soil pits (70 × 40 cm across and 70 cm deep) were dug at each sampling point and the nature and thickness of each horizon were recorded (not presented). Soil samples of the A horizon at each sampling point (D01, latitude 51°27′3.7″N and longitude 5°40′53.3″E; D02, latitude 51°27′6.2″N and longitude 5°40′52.6″E and D03, latitude 51°27′10.8″N and longitude 5°40′51.3″E) were taken with a sterile metal cylinder.

2.1.2. The Gallego site

The Gallego River, a tributary of the Ebro, flows into the Ebro's alluvial plain. The lower alluvial zone covers about 125 km². The Gallego is affected mainly by agricultural activities. A gravity irrigation system, taking its source near Ontinar, supplies river water to alfalfa, corn and wheat fields along the banks of the Gallego (Fig. 1b). The irrigation canal ends near Juslibol on the Ebro River, slightly upstream from Zaragoza. The natural soils surrounding the fluvisols of the alluvial plain are gypsic xerosols and gleyic cambisols. Soil pits (70 × 40 cm across and 70 cm deep) were dug on irrigated corn and alfalfa fields, and the nature and thickness of each horizon were recorded (not presented). Thirteen soil samples were collected using a sterile metal cylinder, four of which (0–20 cm depth) were selected for this study as a function of their location along the gravity irrigation system (G01, latitude 41°45′3.5″N and longitude 0°49′23.4″W; G02, latitude 41°56′3.2″N and longitude 0°46′45.2″W; G03, latitude 41°59′26.5″N and longitude 0°46′40.5″W and G04, latitude 41°41′27.3″N and longitude 0°56′28.8″W).

2.1.3. The Flémalle site

The site of the former Flémalle coke plant is a brownfield with a surface area of 0.073 km², located on the left bank of the Meuse River, 10–15 m from the river, upstream from Liège. Various activities related to coking processes were carried out here between 1922 and 1984. Nowadays, all industrial substructures have been removed. Former activities greatly contaminated the soil, subsoil and groundwater with inorganic (such as trace elements) and organic pollutants. Birch trees and grass subsist in spite of the heavy contamination. Two types of soil samples were collected in nine trenches with a small sterile shovel and stored in sterile glass bottles: fill (1–3 m) and sandy to clayey alluvial silt (3–5 m). Sixteen soil samples were collected, four of which were selected by PCA (results not shown) as being the most representative of the pollution's spatial heterogeneity (Fig. 1c): F01 (fill) and F02 (silt) (latitude 50°36′22.2″N and longitude 5°29′16.3″E), F03 (fill) (latitude 50°36′20.4″N and longitude 5°29′16.5″E) and F04 (fill) (latitude 50°36′18.5″N and longitude 5°29′10.7″E).

Soil samples were preserved in ice chests during the sampling campaigns and at 4 °C in the dark until use.

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