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Contaminated soils salinity, a threat for phytoextraction?

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HIGHLIGHTS

- ▶ Contaminated soils salinity should also be considered for phytoremediation.
- ▶ Nitrate and to a less extent sulfate inhibit *Noccaea caerulescens* establishment.
- ▶ Plants sensitivity to organics limits co-phytoremediation.

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ABSTRACT

Phytoremediation, given the right choice of plant, may be theoretically applicable to multi-contamination. Laboratory and some field trials have proven successful, but this ideal technique is in all cases dependent on plant growth ability on (generally) low-fertility soil or media. While contaminant concentration has often been proposed as an explanation for plant growth limitation, other factors, commonly occurring in industrial soils, such as salinity, should be considered. The present work highlights the fact that besides contaminants (trace elements and PAH), soil salinity may strongly affect germination and growth of the hyperaccumulator *Noccaea caerulescens*. Elevated concentrations of nitrate proved highly toxic for seed germination. At the growth stage the salt effect (sulfate) seemed less significant and the limited biomass production observed could be attributed mostly to organic contamination.

1. Introduction

In Europe, potentially polluting activities are estimated to concern nearly 3 million sites (EEA, 2007). Soil contamination can be localized, resulting from intensive industrial activities or waste disposal, or more diffuse, covering large areas (EEA, 2010). Trace elements and mineral oils are the most frequent soil contaminants at investigated sites in respectively 37.3% and 33.7% of cases, followed by polycyclic aromatic hydrocarbons (PAH) in 13.3% (EEA, 2007). Among pollutants, PAH given their ubiquity, toxicity and persistence in the environment, and Cd given its significant toxicity to humans, are of particular concern.

Organic and/or metal-contaminated soils can be remediated by physical, chemical, or biological techniques (Khan et al., 2004). In recent years, phytotechnologies have attracted attention due to their low cost of implementation and environmental benefits. Many of them are at the demonstration level, but relatively few have been applied in practice on large sites and may prove successful at market level (Marmiroli and McCutcheon, 2003; Vangronsveld et al., 2009; Mench et al., 2010). Phytoremediation technologies encompass several techniques including phytoextraction, phytomining, phytovolatilization, phytofiltration or rhizodegradation (Sterckeman et al., 2012). In the case of organic contamination, rhizodegradation mostly relies on the increased microbial activity of the rhizosphere for pollutant degradation, while direct plant uptake is marginal (Harvey et al., 2002; Susarla et al., 2002). Most of the plants used are crops or weeds selected by agronomical practices on the basis of dense root system establishment and tolerance to pollutants (Henner et al., 1999; Merkl et al., 2004). For trace elements, phytoextraction is based on the use of accumulating plants that uptake pollutant from soil and concentrate them in their harvestable parts. Thus, given the right choice of plant, phytoremediation may theoretically be suitable for the treatment of co-contaminated sites with organic and metal pollutants, but these multiple pollution situations have seldom been studied (Sandrin and Maier, 2003; Lin et al., 2008; Schröder et al., 2009). In multi-contaminated soils, trace elements may modify root growth and thus affect the root enhanced dissipation, or exert direct effects on microorganisms and thus affect pollutant

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degradation. Lin et al. (2008) investigated the influence of co-contamination of Cu and pyrene on the growth of *Zea mays* L. and the fate of pollutants in plants and soil. They observed that the dissipation of soil pyrene was enhanced in the presence of plants. However, high Cu level was unbeneficial to the dissipation of pyrene, thus suggesting a change in either the microbial composition and microbial activity or in the modified root physiology under Cu stress. Schröder et al. (2009) also presented evidence that pollution with trace elements may interfere with both the oxidative stress defense in plants and their ability to conjugate organic xenobiotics. Consequently, the presence of trace elements, like Cd, may impede rhizodegradation of organic compounds.

For the co-remediation of organics and trace elements, plants must be able to cope with multiple pollution situations and those plants with higher trace element tolerance, such as hyperaccumulators, should have an obvious advantage. Indeed, a field experiment focusing on Cd and Zn extraction by the hyperaccumulator *Noccaea caerulescens* (formerly *Thlaspi caerulescens*), conducted on a soil co-contaminated by metals and organic compounds proved successful (Schwartz et al., 2003). However, no diagnosis was made for the organic contamination. Moreover, other stress factors (e.g., pollutant toxicity, physical soil properties, salinity) can limit the effective implementation of phytotechnologies at field level (Mench et al., 2010). Indeed, besides containing pollutants, contaminated soils are often Technosols (IUSS Working Group WRB, 2006), i.e. soil materials strongly impacted by human activities, and presenting only moderate to low fertility. These may result from artifact addition (e.g. concrete, tiles, glass) or industrial waste and by-products or simply from earth-work.

In 2005, a long-term field experiment was set up on the experimental site of the French Scientific Interest Group – Industrial Wasteland (GISFI) (http://www/gisfi.fr), Homécourt (49°21367N, 5°99608E), North-eastern France. The aim was to assess the fate of multi-contaminated soil (high in organic contamination and moderate in metallic contamination), under various management practices including phytoextraction with *N. caerulescens*. However, the attempt at co-remediation with the hyperaccumulating species *N. caerulescens* proved impossible due to some unidentified phytotoxicity factor that inhibited plant germination and the development of juvenile plants (Ouvrard et al., 2011). The aim of this work was to investigate the salinity as a possible limiting factor to *N. caerulescens* establishment.

2. Materials and methods

2.1. Soil material and physico-chemical properties

The contaminated soil was sampled in October 2004 on a former industrial site with coking and metallurgical activities located in Neuves-Maisons, North-eastern France. The soil (NM) was homogenized, air dried and sieved at 2 cm. Its main properties are presented in Table 1. Moreover, the specific electrical conductivity (SEC) of the material evaluated using the normalized protocol (NF ISO 11265) was 2.6 mS cm^{-1}.

To remove excessive salt, the NM soil was lixiviated with deionized water in a column system (NM-LIX). Briefly, a glass column was filled with 750 g of dry NM and lixiviated at 2.5 mL min^{-1} with deionized water. The elution was performed until reaching a liquid/solid ratio (L/S) of 150 L kg^{-1} dry material, which corresponded to a sulfate concentration below 200 mg L^{-1} in the leaching water. The leaching water was analyzed to follow salt concentrations (sulfate, nitrate) and pollutants (PAH). Remaining concentrations of pollutants and salts in NM-LIX were estimated with a mass balance. The post-treatment SEC value was 2.0 mS cm^{-1}.

An inert quartz sand supplied by SIKA (Silice Kaolin SA, Hostun) referenced as S30, was used as a substrate dilution medium for germination and growth tests. Its SiO_2 purity was above 99.0% and granulometric distribution between 0.3 and 1.25 mm.

2.2. Water analyses

Major anions in the leachates were analyzed by ionic chromatography using a Dionex® system DX320 (AG11-HC and AS11-HC columns; flow rate: 1 ml min^{-1}; isocratic eluent: 30 mM KOH; self-regenerating suppressor ASRS Ultra II 4 mm at 100 mA).

PAH in solution were extracted by solid phase extraction using Tenax® beads. Two grams of Tenax were added to a 1 L solution and agitated for 2 h. This was repeated once and both charged Tenax samples (4 g) were gathered and extracted twice with 25 mL hexane/acetone 50:50 for 1 h by sonication. The hexane/acetone solvent was exchanged for acetonitrile prior to HPLC analysis using a Varian system. All 16 EPA-PAH were separated on a C18 Prosphere column (Alltech) with a water/acetonitrile gradient and detected by fluorescence (Prostar 363, Varian) (except for acenaphtylene detected by UV, PDA Detector 330, Varian).

2.3. Experimental design

The adverse effects of soil salinity on plant germination and growth were assessed by diluting the NM soil. Dry soil was sieved (<2 mm) and mixed with quartz sand to give a final concentration of 0%, 3%, 6%, 12%, 25%, 50%, and 100% (dry weight/dry weight) of contaminated soil. These materials had SEC values of respectively 0.34, 0.98, 1.6, 2.0, 2.3, 2.5 and 2.6 mS cm^{-1}. In the case of the NM-LIX soil, only the 100% concentration was tested. As soil salinity in the contaminated soil was mainly explained by sulfate and nitrate concentrations, both salts were tested on the quartz sand. Stock solutions of high grade $MgSO_4$ $7H_2O$ and $Mg(NO_3)_2$ $6H_2O$ were prepared at a concentration of 20 g L^{-1} equivalent to SO_4 and NO_3. For the germination test, the stock solutions were then diluted with deionized water to reach the following salt

Table 1
Contaminated soil main properties.

Particle size distribution (g kg^{-1})					
Clay (<2 μm)	Fine silt (2–20 μm)	Coarse silt (20–50 μm)	Fine sand (50–200 μm)	Coarse sand (200–2000 μm)	
123	148	75	83	571	
Agronomic parameters (g kg^{-1})					
pH	Organic C	Total N	Olsen P_2O_5	$CaCO_3$	Total S
7.0	62.0	2.7	0.050	19.2	33.1
Pollutants (mg kg^{-1})					
16 PAH[a]	Zn	Cd	Pb	Ni	
1924	2086	2.66	482	97.3	

[a] 16 PAH: priority polycyclic aromatic hydrocarbon listed by the US EPA.