Chemosphere 172 (2017) 80–88

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Radial metal concentration profiles in trees growing on highly contaminated soils

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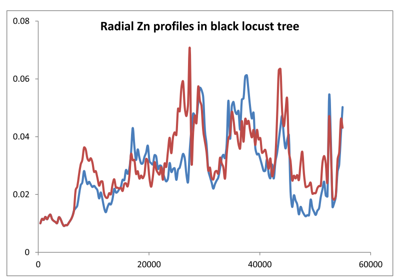
HIGHLIGHTS

- White willow was the best accumulating tree for Zn and Cd.
- The more mobile the metal in the soil, the higher its concentration in the trunk.
- Laser ablation ICPMS visualizes radial metal concentration profiles.
- Radial profiles were mostly periodical for Pb and decreasing for Cu.
- Radial Cd and Zn profiles were related to their soil mobility.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 12 August 2016
Received in revised form
23 December 2016
Accepted 28 December 2016
Available online 31 December 2016

Handling Editor: X. Cao

Keywords:
Metals
Trees
Soil
Amendment
Laser ablation
Concentration profiles

ABSTRACT

The soil around Metaleurop, a big smelter, is heavily contaminated by Zn, Pb, Cd and Cu. In order to compare the impact of different soil amendments on the metal availability to trees, the polluted soil section was divided in a reference parcel and two others with either sulfo-calcic or silico-aluminous ash amendments. Five different tree species were planted on the parcels and the uptake of heavy metals in these trees was studied. Total and labile metal fractions were assessed in each of the 3 parcels. The mobility and assimilation of the metals was highest in the non-amended, reference soil parcel which had the lowest pH, organic matter and carbonate content. In all soils, pH decreased while organic matter content and mobility of the metals increased over time.

Highest bulk concentrations of trace metals were found in white willow trees (*Salix alba* L.). Laser ablation-ICPMS was used to study changes in metal accumulation over a period of 10 years after planting the trees. The radial metal profiles in the trunk core samples varied between elements and tree species, however, in all willow trees the radial Cd and Zn profiles were significantly correlated.

Radial pollutant concentration patterns are discussed in terms of seasonal effects, health status, tree species and metal mobility in the soil. For Cd and Zn, the profiles were influenced by their mobility in the soils. In general, periodical patterns were observed for Pb. Cu concentration profiles were decreasing over time, with the strongest decrease in the initial growth period.

1. Introduction

Metaleurop in Noyelles Godault, Pas de Calais (France) was one of the biggest smelters in the world. Founded in 1894, it was closed down in 2003. Typical production values of Pb and Zn were respectively 150,000 and 100,000 tons per year (Magnier et al.,

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http://dx.doi.org/10.1016/j.chemosphere.2016.12.142
0045-6535/

2011). High amounts of these metals, but also of Cd, Cu or Hg, were released in the environment with, for example, in 2002, 32 tons/y of Zn, 17 tons/y of Pb and 1 ton/y of Cd (Lopareva-Pohu et al., 2011). In the Deûle Canal, Metaleurop directly discharged wastewater containing high concentrations of several metals but transport of ores to the factory also contributed to the pollution of the Canal. In sediments of the Deûle, Pb values ranged between 500 and 6000 mg/kg, and in the soil around the smelter (an area of about 45 km^2), the average Pb concentration amounted to 200 mg/kg. However, values could be much higher locally (Sterckeman et al., 2000, 2002).

Since the closing down of the smelter, several studies were performed to establish an inventory of the environmental damage caused by the smelter's activity (Lesven et al., 2010; Lourino-Cabana et al., 2010; Lopareva-Pohu et al., 2011; Magnier et al., 2011). After the factory was completely destroyed, an eco-project aiming at the recycling and/or vaporization of the industrial wastes was developed and managed by Suez Environment (Sita Agora) on the former industrial site of about 0.5 km^2.

But outside and especially downwind of the production site, large areas of soils are still heavily contaminated. Unfortunately, the contaminated area is too large to be remediated in an economically relevant way by currently applied remediation techniques (dig and dump of soil). Moreover, in order to find new income sources for local farmers, a sustainable management of these polluted soils is crucial. In this context, the PHYTENER project (Rapport Phytener, 2014) aimed to study phytostabilisation in combination with energy crop production and eventually soil de-pollution. An approximately 1 ha experimental site was set up in 1999 on a former agricultural field, 600 m north and downwind of the former smelter. Trees were planted on the entire surface, following regional practices for restoring brownfield land, with about 1800 trees.

The wood crop project focused on the capacity of trees to stabilize the soil and to remove metals from it. In addition, the long-term effect (10 years) of soil amendments on the metal profiles in the trees and on the soil stability was studied. For this purpose, the polluted soil section was divided in three sub parcels: one called "T", the reference parcel without any soil amendment, one called "C", a parcel where ash from the thermal power plant in Carling was used as soil amendment, and a third parcel "G", where ash from the thermal power plant in Gardannes was used as soil amendment.

The goals of this study were (1) to assess the effect of the modification of the soil characteristics on the mobility of the metals in the amended and non-amended soils; (2) to compare the metal assimilation behaviour of the different tree types in each of the sub-parcels and (3) to determine assimilation behaviour changes through the growth time of the trees and afterwards. General parameters and metal concentrations in the soils in the 3 parcels (total and labile concentrations) were measured in 2001, 2008 and 2011. To study the metal assimilation by the trees, core samples from the bark of the tree trunk towards its center (5 mm in radius) were collected in 2011 and radial profiles of Cd, Cu, Pb, Zn and C (the latter element to account for instrumental variations) were determined along the sample's section length using Laser Ablation Inductively Coupled Mass Spectrometry (LA-ICP-MS). Some studies have used LA-ICPMS to determine element concentration profiles in wood samples, but use of this method is limited (Prohaska et al., 1998; Hoffmann et al., 2000; Kyser et al., 2003; Witte et al., 2004; Bukata and Kyser, 2008; Monticelli et al., 2009; Novak et al., 2010). Moreover, these studies generally focused on the relation between changes in metal accumulation by one tree species in response to a significant change in soil chemistry during the growth of the trees, which did not happen in this study. In addition, these studies studied trees over a much larger time span (>60 years) than this study.

2. Methods and materials

2.1. Study area

Details about the sampling site can be found in Lopareva-Pohu et al. (2011). Briefly, the sampling site was set up on a former agricultural field in 1999. This site is located at Evin-Malmaison, 600 m north and downwind of the former Metaleurop Nord smelter, France. The sampling site is approximately 10,000 m^2 in area. In 2000, it was separated into three parcels, each of about 3000 m^2. In two of those parcels, ashes were added to the soil while the third parcel, which did not receive any addition, served as a reference (parcel T). The first ashes, called Carling and spread out on parcel C, correspond to silico-aluminium ash issuing from combustion of hard coal sludge. Gardanne ashes, consisting of sulfo-calcic ash issuing from the combustion of 90% lignite from the Provence and 10% of sludge from the Gard (France), were spread out on parcel G (the composition of the ashes is shown in Table S1 Suppl. Inform.). For each of the ashes, the supply to the soil was equal to 6% (mass/mass) considering a homogenized depth of 30 cm. In fall 2000, 1800 trees of 5 species were planted: black locust (*Robinia pseudoacacia* L.), black alder (*Alnus glutinosa* L.), pedunculate oak (*Quercus robur* L.), sycamore maple (*Acer pseudoplatanus* L.) and white willow (*Salix alba* L.).

Due to a very dry spring in 2001, a high mortality of the trees was observed in this year, especially in the black locust (between 25 and 44%) and oak trees (between 24 and 38%). In the 3 remaining species the mortality ranged from 2 to 7% depending on species and parcel. In December 2001, each dead tree was replaced by a tree of the same species originating from the same garden center. In 2004, 80% of the black alder, sycamore maple and white willow trees, planted or replanted, were still alive in each parcel. Only oak trees still showed a high level of mortality. Between 2001 and 2004, most of the trees showed several signs of stress, such as leaves turning yellow, fading and wilting, abnormal defoliation, deformations and abundant fructification for certain species, but those signs gradually disappeared. Results indicate that the soil amendments had no effect on the growth of the trees, neither the height nor the diameter of the trunk were different between parcels.

2.2. Trunk core samples

Horizontal cores were sampled in 2011 from the bark to the center of the trunk at a height of 1.5 m using a 5 mm stainless steel increment borer. The cores were washed with ethanol and abundantly rinsed with distilled deionized water. Tree cores were then air-dried and stored in sealed plastic bags until analysis with LA-ICPMS. A total of 9 cores were analysed: T1S1, T1S2 and T1S3 (3 white willows (S) from the non-amended soil parcel), T1A1, T1R1 and T1E1 (black alder (A), black locust (R) and sycamore maple (E) from the non-amended soil parcel), G2S1 (the white willow in soil parcel G) and C2S2 and C2S3 (white willow trees in soil parcel C). This made it possible to compare different species in the same soil parcel (non-amended T) to investigate inter-species variability and to study the effect of soil amendment (comparison between the same tree species in soil parcels T, G and C).

To assess the growth rhythm of the trees, trunk core samples were treated with increasingly fine sandpaper at the University of Arras until individual growth rings became visible.

2.3. LA-ICPMS analyses of trunk core samples

Element concentration profiles in the tree cores were determined along the growth axis using LA-ICPMS with a UP193FX laser (New Wave Research) coupled to a quadrupole-based ICP–MS