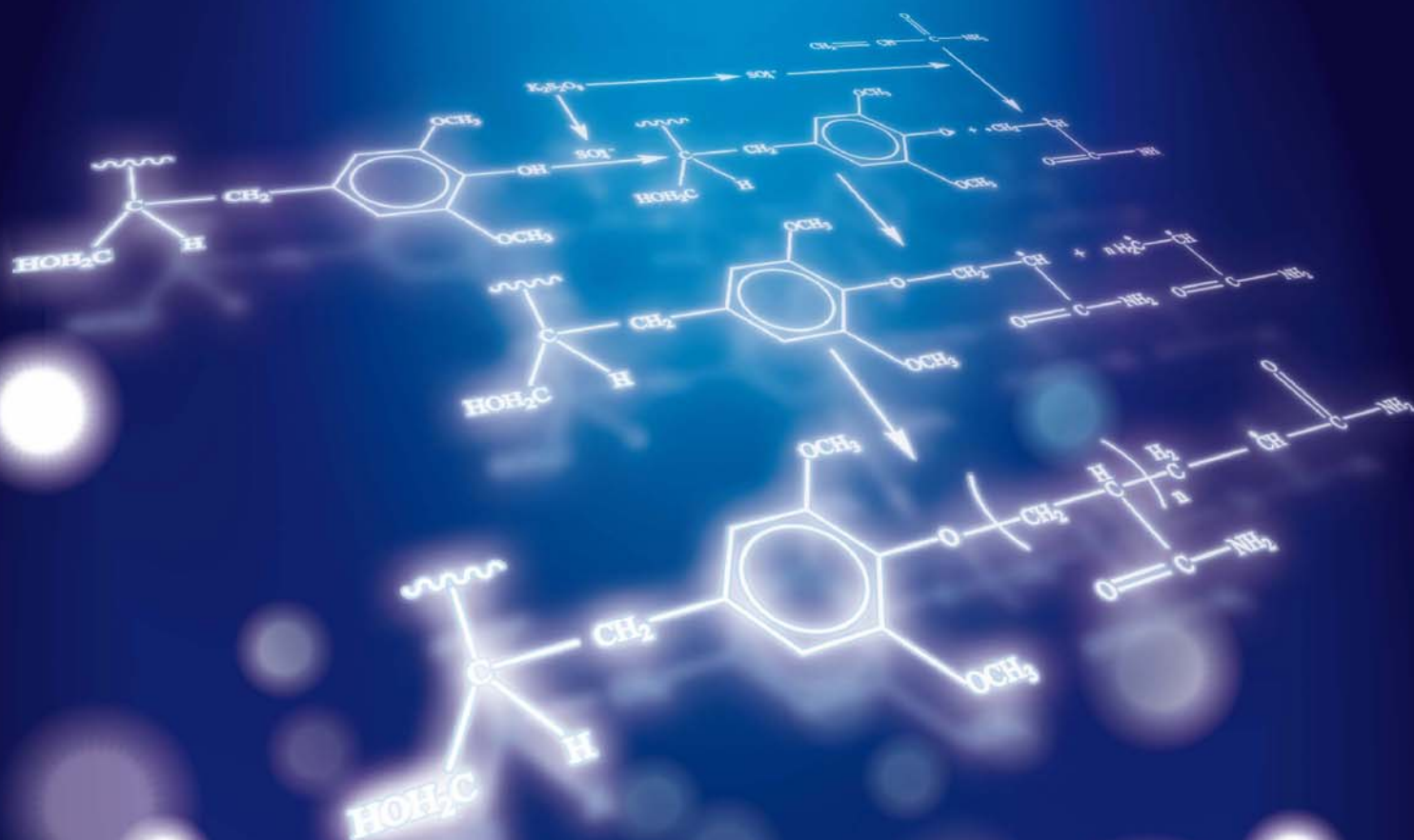


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Water extraction kinetics of metals, arsenic and dissolved organic carbon from industrial contaminated poplar leaves

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Abstract

In industrial areas, tree leaves contaminated by metals and metalloids could constitute a secondary source of pollutants. In the present study, water extraction kinetics of inorganic elements (IE: Pb, Zn, Cd, As, Fe and Mn), dissolved organic carbon, pH and biological activity were studied for industrial contaminated poplar leaves. Moreover, the distribution of the IE through the size fractions of the associated top soil was measured. High quantities of Mn, Zn and As and polysaccharides were released in the solution from the strongly contaminated leaves. The kinetic of release varied with time and metal type. The solution pH decreased while dissolved organic contents increased with time after 30 days. Therefore, these contaminated leaves could constitute a source of more available organic metals and metalloids than the initial inorganic process particles. However, the distribution of the IE through the size fractions of the top soil suggested that a great part of the released IE was adsorbed, reducing in consequence their transfers and bioavailability. It's concluded that mobility/bioavailability and speciation of metals and metalloids released from the decomposition of polluted tree leaves depends on soil characteristics, pollutant type and litter composition, with consequences for environmental risk assessment.

Key words: metals and metalloids; dissolved organic carbon; litter decomposition kinetics; speciation; water extraction

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Introduction

Soil pollution with potentially toxic metals has become a serious environmental dilemma and poses a great threat to the ecological environment and human health (Uzu et al., 2011; Schreck et al., 2011; Guo et al., 2012). Heavy metals are encountered ubiquitously in the environment owing to their release in substantial amounts by various natural and anthropogenic sources (Arshad et al., 2008; Shahid et al., 2012b, 2013). Industrial activities are particularly considered the major source of polluting the environment (Uzu et al., 2010; Zhang et al., 2011; Shahid et al., 2012a). Heavy metals emitted from industrial smelters are transported up to several kilometres away from their sources by wet or dry deposition (Douay et al., 2009; Bing et al., 2011). The forest canopy serves as an efficient filter of atmospheric heavy metals emissions (Chrastný et al., 2012). The fall of plant litter and their subsequent decomposition in soil refers to a number of processes involved in decomposing

litter to its elemental chemical constituents (Carrillo et al., 2012; Riutta et al., 2012). Plant litter decomposition is not only a key process in carbon and nutrient cycling but also in metals dynamic, accumulation and speciation in organic matter and soils (Park et al., 2011; Bengtsson et al., 2012). When the contaminated tree leaves breakdown, metals could be progressively released as the organic matter decays (bioactivity or hydrolysis). Depending on their speciation, metals released from decomposing leaf litter may be leached into the soil, become sorbed by the soil organic matter or taken up by living organisms (Chrastný et al., 2012).

In forest soils, tree leaves decay is a major origin of soil organic matter. Soil organic matter has large sorption capacities for metals and plays a key role in governing the metal mobility/bioavailability in soil (Park et al., 2011; Shahid et al., 2012c). Generally, the solid phase soil organic matter is implicated in retention, decreased mobility and reduced bioavailability of trace metals by sorption (Chrastný et al., 2012) while DOC increases the mobility

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and bioavailability of metals (Chrastný et al., 2012). Soil organic matter strongly reacts with metals, but it is subject to long-term transformations and thus may have only a transient effect in the fixation of metals (Martínez et al., 2003). In addition, the applied/natural levels of soil organic matter and their distribution in soil fractions affect the plant uptake of heavy metals (Godet et al., 2011; Shahid et al., 2012c).

Considering contaminated tree leaves as precursors of natural organo-metallic complexes, their study could give pertinent information about biogeochemical behaviour of released metals in soil. The contaminated tree leaves could constitute a secondary source of metals with different characteristics in terms of speciation and bioavailability compared to the primary inorganic atmospheric source (Dabkowska-Naskret, 2003). The tree leaves therefore have been used to monitor atmospheric trace metal deposition/contamination in large-scale surveys (Serbula et al., 2012). The contaminated tree leaves represents a reliable and easy way to monitor the air and soil quality on large areas with the concepts of time and spatial variability (Serbula et al., 2012).

Tolerant to high metal concentrations, poplar trees can absorb large amounts of metals and are often used to stabilise polluted soils and improve the landscape of industrial sites (Gamalero et al., 2012). The main objectives of the present work were: (1) to evaluate the behaviour of metals present in industrial contaminated poplar leaves during organic matter decomposition under water leaching experiments; and (2) to discuss the results in terms of metal speciation and fate in the soil: transfer of pollutants from leaves to soil water and superficial waters. Compartmentation and speciation of inorganic pollutants both in contaminated poplar leaves and the corresponding top soil was therefore studied; their interactions with organic carbon were more particularly investigated.

1 Materials and methods

1.1 Leaves and top soil sampling and preparation

Active for more than 100 years (1884–2004) and located near Evin-Malmaison (North of France), Metaleurop was one of the largest European smelter plant. Dust particles with high contents of Pb, Zn, Cd and As have contaminated the nearby agricultural field throughout a 40 km² area surrounding the central smelter. According to Sobanska et al. (1999) they consist mainly of sulphide and oxide metal ions. The studied undisrupted (50 years) poplar grove is located 500 m North-East from the smelter. The highly contaminated pseudogley brown leached soil develops over quaternary clays (0.6–1.5 m) covering the Ostrincourt sand in which the water table is 1 m below ground level (Dumat et al., 2001).

Four kilograms of preserved leaves were collected in autumn 2011 during litter fall and five kg of the corre-

sponding top soil sample (0–3 cm) were also collected just below. After drying at room temperature, leaves were rinsed 10 min with MQ water, dried again and crushed. Before water extraction, the leaf material was homogenised and characterised.

After mixing, the top soil sample was air dried, sieved at 2 mm and homogenised. An initial physical dispersion of the soil samples was performed by end-to-end shaking overnight in pure de-ionized water before particle size fractionation. The suspensions were then sieved through a series of grids (AFNOR French reference) with decreasing mesh size (2000, 1000, 500, 200 and 50 µm). Then the fractions (20 µm < size < 50 µm), (2 µm < size < 20 µm) and < 2 µm were obtained by sedimentation. All the recovered particles were air dried at 60°C, weighed, ground (200 µm) and homogenized. Particle size fractionation resulted in the recovery of (98 ± 0.5)% of the initial soil sample mass. Metals, As, C and N concentrations were measured in all the various size fractions.

1.2 Batch water extraction experiments from contaminated leaves

Batch water extractions experiments were realised in triplicates with various times of reaction (from 1 to 70 days) in polypropylene centrifuge tubes. A known amount of rinsed leaves was put in contact with a known volume of MQ water. The solid/liquid ratio was chosen after preliminary experiments in order to take into account the heterogeneity of the leaves sample, the metals and organic carbon detection limits and the extraction efficiency. The 2 g of leaf material were mixed with 25 mL of MQ water and the mixture was shaken with an end-over-end apparatus. The solid-liquid were separated by centrifuge (i.e., 30 min at 30000 ×g in a Avanti J301, Beckman, UK). Then, the pH of the supernatant was measured after filtering at 0.22 µm on a Sartorius cellulose acetate filter, previously rinsed with 20 mL of MQ water. The soluble fraction is therefore operationally defined as the fraction passing through the 0.22 µm membrane.

1.3 Chemical analysis methods used for leaves and soil samples

The solutions were finally acidified with HNO₃ to a pH < 2 and stored at 4°C, before analysis realised within 2 weeks maximum. Total inorganic elements (IE) concentrations in supernatants were measured by inductively coupled plasma optical emission spectrometry (ICP-OES) on a JY 238 apparatus (Jobin Yvon, Longjumeau, France). The ICP-OES technique was also used for the solid soil samples after tri-acid (HF, HCl and HNO₃) digestion. Supernatant analysis was assured through the use of reference standard water on replicates; the % RSD was < 10%. The detection limits were 0.23, 0.47, 0.12, 0.11, 0.17 and 0.13 mg/L for Pb, Zn, Cd, As, Fe and Mn respectively. Measurement accuracies were controlled using standard references:

home made leaf sample and GRX2 soil. The DOC was analysed with a total organic carbon analyser, Shimadzu TOC-5000 apparatus. Analytical quality was addressed by the systematic use of blanks and replicates. At 680°C, the carbon was measured as CO₂ by an infrared detector (Shimadzu). Organic carbon and nitrogen contents of the soil samples were determined by dry combustion in a NA 1500 CHN elemental analyser, Carlo Erba, France.

1.4 Study of the micro organism activity on metals and DOC release

Kinetics of IE and DOC release was followed with or without NaN₃ addition (300 mg/L). NaN₃ induces the death of micro organisms (Szabados et al., 2004) and therefore differentiates the influence on IE and DOC release of strictly chemical processes from biological ones. The chosen times for these experiments were 8, 18 and 22 days of water extraction.

1.5 Statistical analysis

Analysis of variance (ANOVA 1 factor) and the least significant difference (LSD) test were used to determine the significance of the differences between treatments. The software used for this purpose was Statistica Edition'98 (StatSoft Inc., Tulsa, OK, USA). For each experiment, mean values with different letters are significantly different ($p < 0.05$) as measured by LSD Fisher test.

2 Results

2.1 Contaminated top soil

The bulk topsoil presents an acidic pH (5.5) and a cation exchange capacity of 22.6 meq(+)/100 g. Concentrations of Fe, Mn, Al, Si and P are respectively: 27246 ± 763 mg/kg, 498 ± 15 mg/kg, 41900 ± 1676 mg/kg, 33420 ± 1002 mg/kg and 330 ± 11.2 mg/kg. The size repartition of the loamy clayed top soil is presented in the **Table 1**, with the results of elemental analysis. The relative standard deviation of all the measured values never exceeded 7%. The (1000–500 µm) coarse fraction exhibits the highest organic carbon concentration (17.1%), then organic carbon concentration decreases with size fraction, except for the clay fraction. The C/N ratio decreases from the coarse

to the clay fractions. The values of the bulk top soil, for Pb (2914 mg/kg), Zn (2003 mg/kg) and Cd (43 mg/kg) concentrations are higher than the legal French limit (100 mg/kg, 300 mg/kg and 2 mg/kg for Pb, Zn and Cd respectively). High IE concentrations, all above the legal French limit were measured for the coarser fractions (size > 50 µm), with potentially large plant organic debris and also the clay-sized fraction (< 2 µm).

2.2 Kinetics of the inorganic elements release from leaves by water extraction

Total concentrations of IE (mg/kg dw, mean ± SD, $n = 5$) in leaves are Pb 1245 ± 134, Zn 2071 ± 289, Cd 45.5 ± 6, As 15 ± 2, Fe 410 ± 55, Mn 40.7 ± 0.55, and organic C 428400 ± 21420. Except for Zn and Cd, the others IE occur in higher concentrations in the bulk top soil than in the leaves. **Figure 1** shows the results of IE concentrations released in solution during 70 days water extraction with the corresponding statistical analysis. A high quantity of all the inorganic elements is released during the first three weeks of extraction. Three types of comportment regarding the kinetic release of IE have been observed. First the released quantity of Pb (15 mg/kg maximum) and Fe (30 mg/kg maximum) slowly increases. Secondly the released quantities of Zn, As and Mn increase with a quite linear way during 3–4 weeks, then a plateau is reached: 500 mg/kg at 30 days for Zn, 2 mg/kg at 20 days for As and 30 mg/kg at 20 days for Mn. And thirdly, Cd presents a particular design: its released quantity increases during 30 days and then decreases perhaps in relation with a modification of the physicochemical characteristics of the medium.

The ratios between the IE concentrations in solution and the initial total concentrations in the leaves were calculated as a function of time. The observed trends are different when compared with the total IE quantities measured: Mn (80%), Zn (25%) and As (15%) are the most easily water extracted IE after 70 days. The following water extraction sequence was observed: Mn > Zn > As > Fe and Cd > Pb.

2.3 Kinetics of the dissolved organic carbon release and pH evolution during water extraction

Evolutions of DOC and pH in function of extraction time are represented on **Fig. 2** with corresponding statistical

Table 1 Total IE, organic C and nitrogen for the different topsoil fractions

Top soil (0–3 cm)	Bulk	1000–500 µm	500–200 µm	200–50 µm	50–20 µm	20–2 µm	< 2 µm
Size distribution (%)	8.7	22	29.5	10.6	6.8	4.9	16.5
C (%)	6.9±0.4	17.1±1.35	15.3±0.6	13.2±0.8	nd	7.2±0.3	12.2±0.2
N (%)	4.1±0.3	0.89±0.15	0.85±0.15	0.76±0.13	nd	0.45±0.09	0.85±0.04
C/N ratio	16.8	19.2	18	17.4	nd	16	14.3
Pb (mg/kg)	2914±153	3088±132	3501±167	3457±184	1458±86	2565±142	6702±253
Zn (mg/kg)	2003±122	2611±78	3014±95	2972±69	947±51	1606±82	5013±286
Cd (mg/kg)	43±4.9	69±4.2	62±3.5	57.3±3.8	21±2.7	32±2	70.3±5.5
As (mg/kg)	37±1.8	35±3	34±2	36±2.7	16.7±1.4	52.8±2.3	89.4±4.3

Values are means of five replicates. nd: not detected.

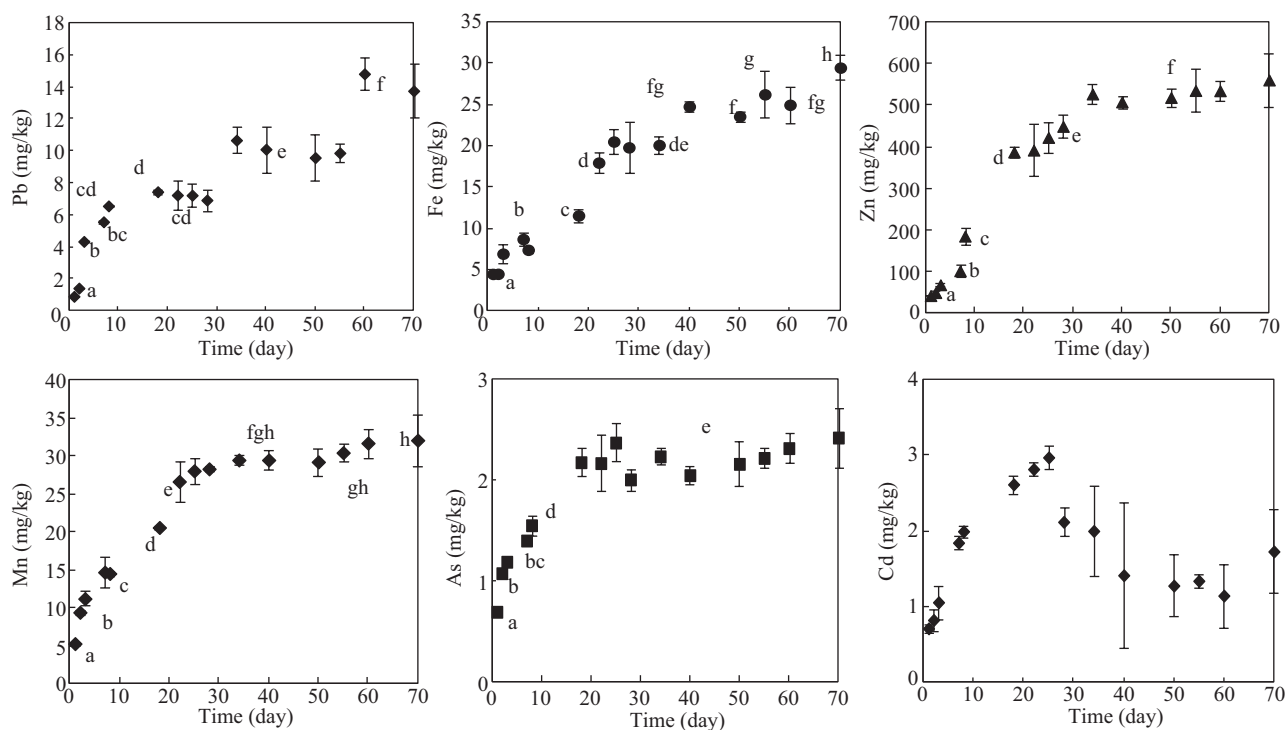


Fig. 1 Inorganic element (Pb, Zn, Cd, As, Fe and Mn) concentrations released in solution (mg IE by kg of leaves dry weight) from water extraction during 70 days. Values are means of five replicates. Significant differences at $P < 0.05$ are indicated with small letters.

analysis.

Like for Zn, As and Mn, the kinetics of organic carbon release shows a plateau, reached around 25 days of water extraction: the DOC stays around the maximum value 20,000 mg/kg (concentration = 1600 mg/L), i.e., 5% of the total initial organic carbon. The pH decreases during three weeks with a quite linear way from 7.5 to 5.5. Then a plateau was reached and no significant variations were observed between 20 and 70 days of water extraction.

2.4 Characterisation of the residual OM and of the water extracted OM

Figure 3 shows the ^{13}C CPMAS, NMR and FT-IR spectra and chromatograms of the pyrolyse produce.

In agreement with the study of Lorenz (2000) and Kogel-Knabner (1992), the following ^{13}C NMR signals

were observed: (i) at 0–50 ppm, aliphatic carbon of lipids, cutin or proteins. The 30 ppm peak corresponds to the $(\text{CH}_2)_n$ chains; (ii) at 50–110 ppm, O-alkyl of carbohydrates (polysaccharides). The signal at 56 ppm corresponds to O-CH₃ groups of lignin, along with the signals at 122 and 152 ppm. C–O bonds of carbohydrates are characterised by signals between 20 and 200 ppm, with a maximum at 72 ppm and a thick signal at 105 ppm; (iii) at 110–160 ppm, unsaturated C (aromatic or not) of lignins; (iv) at 160–220 ppm, carboxyl, carbonyl or amide groups. C=O of esters and carboxylic acids from hemicelluloses were characterised by a signal at 170 ppm (with its spinning side bands at 130 and 210 ppm). The FT-IR spectrum is quite similar to that obtain by Senesi and Sposito (1989) for organic matter from litters: (i) a broad band at 3415 cm^{-1} corresponding to OH groups; (ii) two signals at 2950

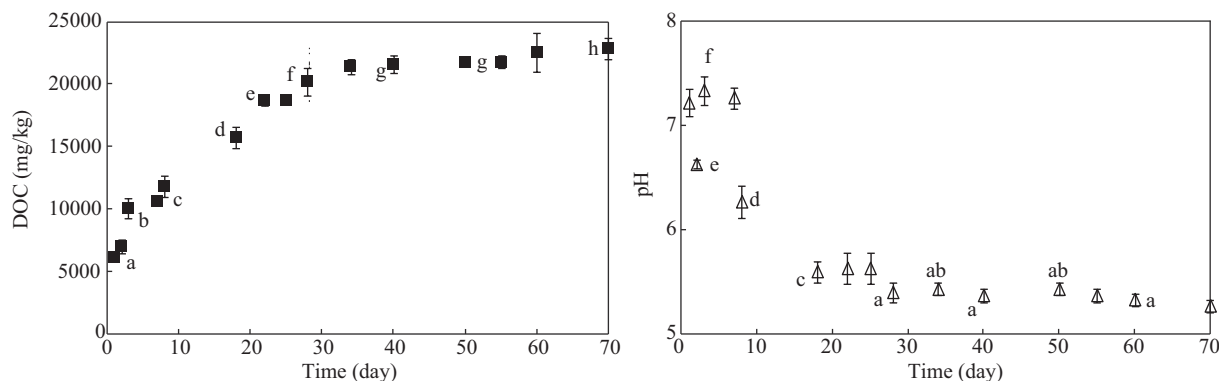


Fig. 2 Evolution of DOC and solution pH in function of time extraction. Values are means of five replicates.

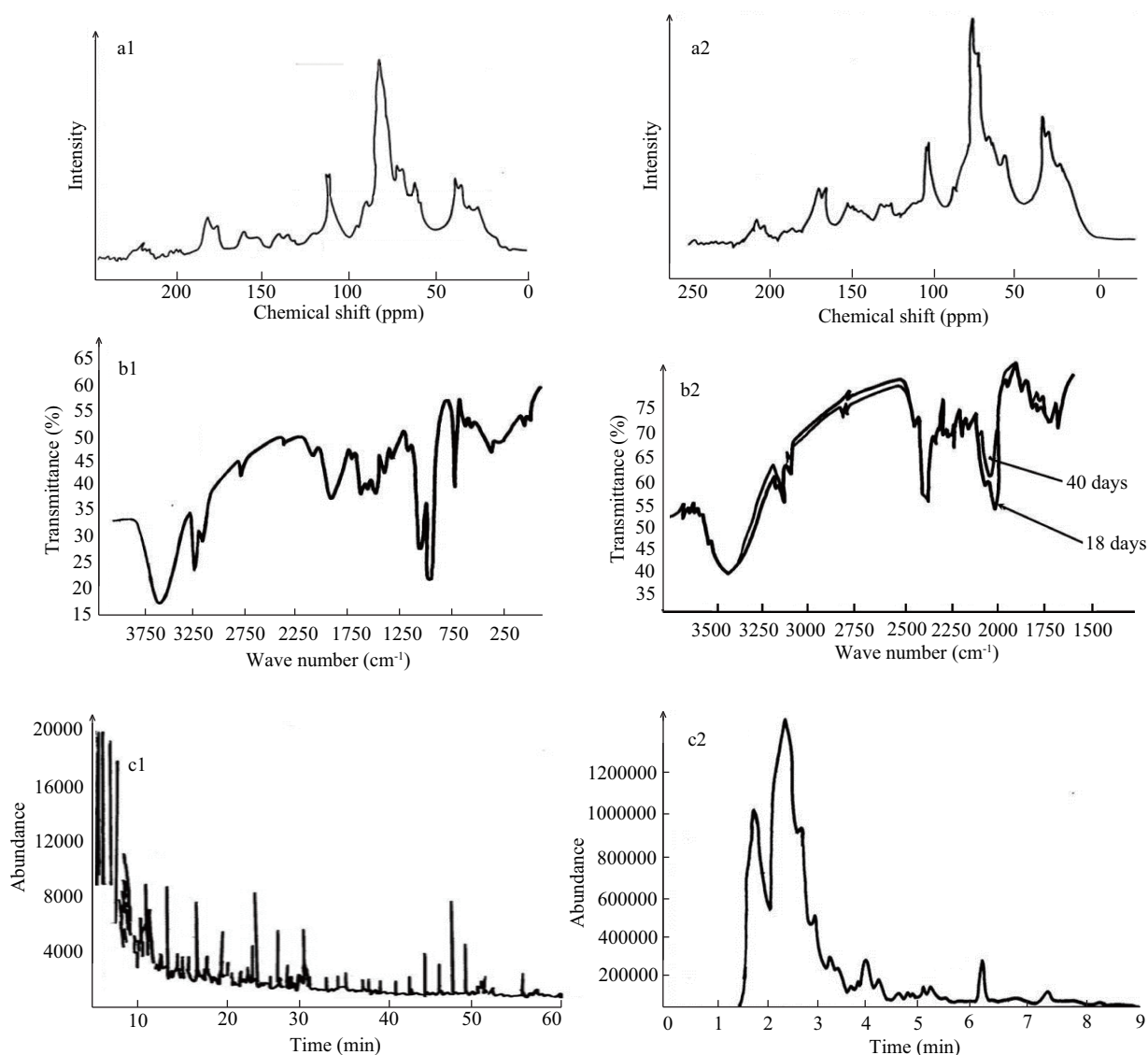


Fig. 3 ^{13}C CPMAS NMR spectra (a), FT-IR spectra (b), and chromatograms (c) of the pyrolyse produce: (a1) reference leaves and (a2) leaves after 40 days of water extraction; (b1) reference leaves and (b2) leaves after 18 and 40 days of water extraction; (c1) reference leaves and (c2) DOC after 40 days of water extraction.

cm^{-1} and 1450 cm^{-1} characteristics of aliphatic groups (CH_2 and CH_3); (iii) a broad band at 1635 cm^{-1} for the $\text{C}=\text{O}$ groups of amide or for $\text{C}=\text{C}$; (iv) two intense bands at 1090 and 1050 cm^{-1} correspond to $\text{C}-\text{O}$ bonds characteristic of polysaccharides; (v) a band at 881 cm^{-1} could indicate the presence of calcium oxalate (CaC_2O_4) identified by XRD: main signals I/I_0 : 3.65 (1), 5.93 (1), 2.97 (1). The Py-GC trace confirms in particular the presence of: aliphatic chains (*n*-alkanes and *n*-alkenes from 13 to 31 carbons), furans (benzofuran), proteins (indole) and phenols. The 3-methyl-phenol, 4-methyl-phenol, 3-methoxy-phenol, 2,4-dimethyl-phenol and 2-ethyl-phenol were identified using a selective detection of ions with mass/charge ratio of 94, 108, 122 and 124.

Leaves after 18 and/or 40 days of water extraction and DOC after 40 days of water extraction (**Fig. 3**). The 881 cm^{-1} FT-IR band disappeared after 18 days of

water extraction (**Fig. 3b2**), suggesting that M-oxalate was extracted, while no significant difference between the residual OM and the initial leaves material was observed: (i) by ^{13}C NMR, probably because the oxalate represents a very low proportion of the total carbon and (ii) by Py-GC-MS, probably because these technique is not adjusted to study polar and volatile compounds like oxalate. After 40 days of water extraction, the ^{13}C NMR polysaccharide signal (at 72 ppm) and the FT-IR polysaccharide signals (at 1090 and 1050 cm^{-1}) of the residual OM (**Fig. 3a2, b2**) are significantly lower in comparison with the reference initial signals of leaves before water extraction.

2.5 Influence of the micro organisms on the IE and DOC release

Figure 4 gives the comparison of the results obtained with and without the addition of poison (NaN_3) for each IE

at 8, 18 and 22 days of water extraction. For these three durations, the released Pb, Zn, Cd and As quantities with and without poison are quite similar. On the opposite, the Mn and Fe release are significantly influenced by the activity of microorganisms. The kinetics of organic carbon release is similar with and without biological activity, it means with and without poison (data not presented).

3 Discussion

3.1 Inorganic elements and organic matter released from polluted leaves in relation to IE nature and bio-physicochemical conditions

The release/extraction of metals from contaminated leaves into solution correlates with DOC release. After that the DOC plateau was reached (around 30 days), we observed a significant increase of the IE quantity released for Fe and Pb, but not for Zn, As and Mn. These results suggest that initially the IE could be variously associated with the leaves components: adsorbed at the surface of the leaves, absorbed or complexed by polysaccharides or others compounds. In plant cell, the phytochelutins, metallothioneins and glutathione are the best characterized metal-binding ligands (Pourrut et al., 2011). The binding of heavy metals by these ligands is via formation of mercaptide bonds between them (Maestri et al., 2010). Depending on the energy of binding and on the solubility of their carrying phases, the IE could be released alone or as organic complexes. In the solid phase, only the IE strongly associated with poor water soluble OM will be staying. The comparison

of the kinetics of DOC and IE, suggests the release of IE from two different pools: (1) in a first time (0–30 days), IE linked with soluble OM; (2) in a second time (30–70 days), IE (mainly Fe and Pb) strongly bond by low water soluble OM. The particular design of Cd could be explained by the modification of the physicochemical characteristics of the medium.

No effect of biological activity was observed on release of DOC and heavy metals except for Fe and Mn. It shows that the release of Pb, Zn, As, Cd and DOC is not due to biodegradation but depends mainly on chemical processes. The activity of microorganisms is decreased by high metal concentrations (Park et al., 2011) and several studies showed a decrease of organic matter decay on highly metal contaminated sites (Quenea et al., 2009). At the opposite, the Mn and Fe release is influenced by the activity of microorganisms. This suggests that redox phenomena could be involved, because in our reduce media, anaerobic bacteria could use Fe and Mn oxidation as energy source (Javanaud et al., 2011).

Value of pH is widely considered to be one of the most important factors affecting metal mobility and bioavailability (Kunhikrishnan et al., 2012; Shahid et al., 2012d). During the first three weeks, the pH decreases from 7.5 to 5.5. In natural media, except for As, a low pH increases the solubility of the IE (Shahid et al., 2012d). At the opposite, a low pH decreases the solubility of the OM. Therefore, in our study, the presence and the nature of DOC could be the main factors for IE fate. Moreover, the solubility of Pb, Zn, Cd and As could be influenced in particular by the presence of Fe and Mn in solution. As the dissolution of IE from

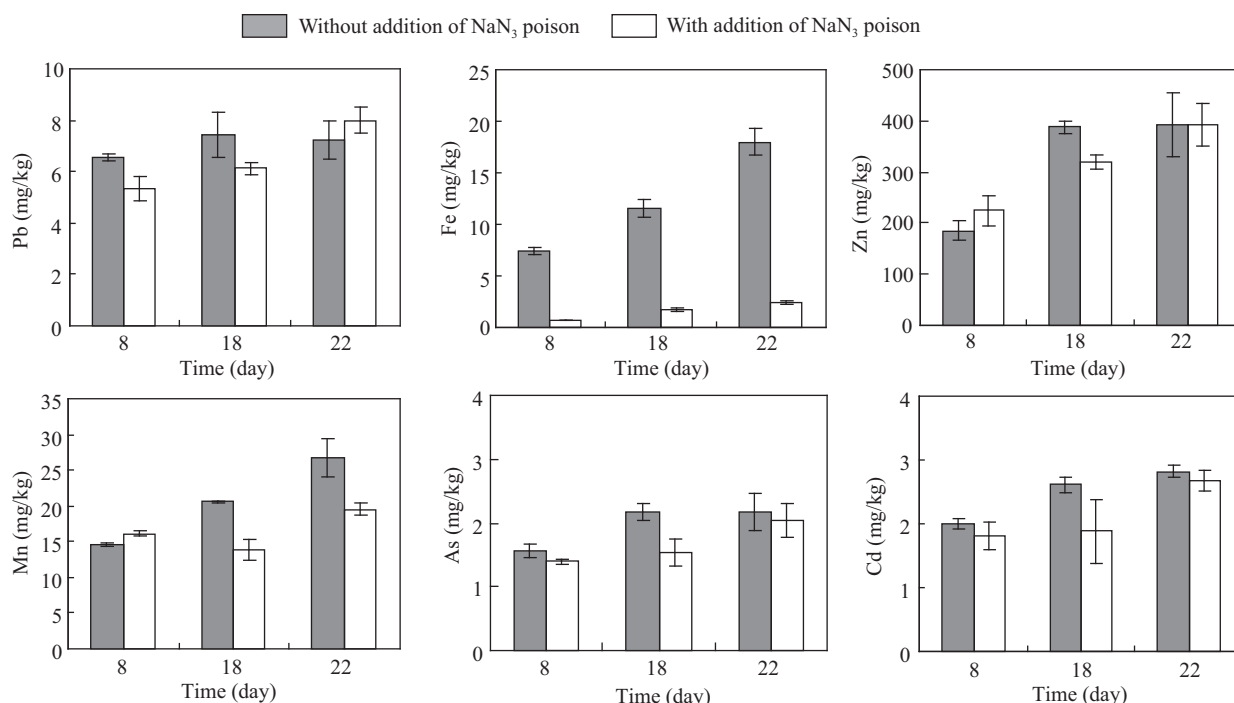


Fig. 4 Comparison of the results obtained with and without addition of NaN₃ poison, for each IE (Pb, Zn, Cd, As, Fe and Mn) at 8, 18 and 22 water extraction days. Values are means of five replicates.

solid to solution phase favours their bioavailability these results indicate therefore a potentially higher availability for Mn, Zn and As in comparison with Cd and Pb.

3.2 Influence of the dissolved organic carbon on IE fate

The water extraction induces a separation between labile (DOC) and less labile organic matter. From the spectroscopic analysis we can conclude that polysaccharides and oxalate were the most labile organic compounds, released by water extraction during the 70 days of experiment. These compounds could be associated with metals and As and play an important role in their fate into the environment. Due to pH conditions and weight characteristics, fulvic acids would be mainly present in the DOC fraction of leaves in comparison with HA and humin (Wu et al., 2002).

In few weeks after the fall of leaves, great amounts of potentially toxic IE could be released in the soil solution, under organic and more available forms than the initial inorganic forms (Fotovát and Naidu, 1998). DOC is involved in many soil processes which may affect heavy metal speciation by changing soil pH, CEC, redox status, buffering capacity, fixation/aging and competing ion concentration which in turn modify metal mobility, bioavailability and toxicity (Shahid et al., 2012d). However, inconsistency exists in the literature on the role of DOC towards heavy metal bioavailability (Zeng et al., 2010; Shahid et al., 2011). Results range from a lower than expected decrease in heavy metal bioavailability (Shahid et al., 2012d) to an increased bioavailability in the presence of DOC (Zeng et al., 2010; Shahid et al., 2012d). Farrell et al. (2010) observed that soil solution concentrations of Cu, Pb, and Zn decreased in an acidic, heavy metal contaminated soil after the DOC (as compost) application. Zeng et al. (2010) described a positive correlation between DOC contents and EDTA-extractable Cr, Cu, Fe, Mn, Pb and Zn contents in a heavy metal contaminated soil.

3.3 Behaviour of IE in the topsoil in relation to organic carbon and leaves fallouts

The calculated IE stocks and organic carbon in the contaminated top soil, as function of the size fraction suggest an important role both of the clay fraction and of the coarse plant fragments ($> 50 \mu\text{m}$) in the retention of IE and organic carbon. A thick litter was observed in the field inducing a large amount of plant fragments (coarse particles) and a high organic carbon concentration. Our results suggested that organic matter mainly accumulates in (1000–500 μm) coarse soil fraction. Pan et al. (2008) also reported that soil organic carbon preferentially accumulates in the 2–0.25 mm and 0.25–0.02 mm size fractions. Generally the “young” carbon is most often associated with the coarse micro-aggregates (0.25–0.02 mm) (Bossuyt et al., 2002). In contrast and according to Uzu et al. (2009) and Schreck et al. (2012), metals and As mainly accumulated in fine soil

fractions ($< 2 \mu\text{m}$).

The C/N ratio decreases with the size fractions (Table 1) and this trend is in agreement with a change in chemical nature of SOM throughout the biodegradation process. Size decreases leading to higher specific surfaces, biochemical composition shifting towards more hemicelluloses and lignin (Besnard et al., 2001). We can therefore hypothesize that the IE-SOM interaction depends on two different ways for the two type of reactive size particles (fraction $> 50 \mu\text{m}$ and fraction $< 2 \mu\text{m}$). After the fall of contaminated leaves, a selective degradation takes place depending on their metal contents and of the soil characteristics (pH, texture and structure). The leaves debris with low metals concentrations decay more quickly than the high contaminated debris: the organo metallic complexes are more stable and resistant to the biodegradation (Shahid et al., 2012d). Therefore an accumulation of coarse leaves debris highly contaminated results. However, the particulate organic matter: coarse sized fraction composed by recently accumulated organic rest, is poorly associated with the soil mineral matrix and has a relative rapid turn-over in comparison with the others SOM (Fuente et al., 2011). Metals present in these coarse fractions are progressively released during the decay of particulate organic matter. Then a part of these IE is sorbed by the reactive colloid organic matter of the clay fraction (Cecchi et al., 2008) with a potential long term stabilisation effect.

The biogeochemical behaviour of IE in soils is particularly influenced by pH, SOM and microbial activity. Soil pH influences desorption/dissolution of IE, soil microbial activity and in consequence the metal bioavailability. According to Saratale et al. (2011), the microorganisms can increase metal mobility and bioavailability by lowering the rhizosphere pH and releasing certain metal-chelating compounds. Soil organic matters are characterized by numerous chemical compositions, sizes and reactivity and they exist both in the solid and solution phases. Different interactions with IE are therefore developed (Dumat et al., 2001) and contrasted influences can be observed on availability and mobility of inorganic pollutants in soils.

4 Conclusions

We observed a high contamination of the poplar leaves in particular for Pb and Zn. As relatively high quantities of As, Mn, Zn and polysaccharides were released by water extraction, these contaminated leaves constitute a significant secondary source of available organic form metals and metalloids. Poplar trees are tolerant to the metal contamination and improve the visual impact of the site, but they could actually induce progressively a transformation of inorganic metal components into more available organic metal components. As a consequence of our results, the replacement of contaminated leaves by uncontaminated organic matter could be advised in these

types of polluted sites. In the field, high IE concentrations characterise the clay fractions of the contaminated top soil. We can suppose that the IE released from the decay of leaves are mainly adsorbed or complexed by the reactive soil components of the size clay fraction.

Metal speciation controls the biogeochemical behaviour of metals. The speciation of metals and metalloids released from the decomposition of polluted tree leaves may vary with plant leaves composition, metal type and bio-physico-chemical soil characteristics. Therefore, it is necessary to evaluate the speciation and kinetic of release of metals and metalloids from litter decomposition in the context of risk assessment and remediation studies to control the transfer toward soil solution and superficial water.

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