Water Air Soil Pollut (2020) 231:109
https://doi.org/10.1007/s11270-020-04478-1

Zn/Pb Concentration Ratios Emphasize Spatiotemporal Airborne Metal Dynamics in Soils Under Different Land Use

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Received: 19 June 2019 / Accepted: 18 February 2020

Abstract Zinc (Zn) and lead (Pb) concentrations were measured in 173 samples collected in soils under forest, wetland, and arable land around a Zn smelter plant that stopped activity in the 1960s. The adopted sampling strategy consisted in collecting 0–30-cm-depth samples from all soils, tilled or not, in order to harmonize the analyzed soil volume to that of plowed soils. Airborne deposition was modeled as a function of the distance from the pollution source and of land use. The Zn/Pb concentration ratios in the surface layer remarkably contrasted 3–4, 1.5–2, and ~0.5 for arable, wetland, and forest soils, respectively, independently from the distance to the emission source, while total Zn and Pb concentrations, taken separately, were only slightly discriminant. For metal pollution sites originating from former industrial activity, Zn/Pb concentration ratios determined on relevant soil samples represent a powerful indicator that provides easy and rapid information in real field conditions on time-related input/output dynamics of mobile and less-mobile metal pollutants, and hence, on interactions between pollutants and soils under different land use conditions.

Keywords Airborne metal pollution · Metal mobility · Zn/Pb concentration ratios · Arable land · Wetland · Forest land

1 Introduction

The interpretation of spatial distribution of metal contamination in soils of industrial regions is often difficult, due to the great diversity of anthropogenic activities, leading to heterogeneous patterns of pollutant accumulations. Spatial distribution of metal pollution around a given emission source depends on the history of industrial activity, dominant wind direction, the size and composition of emitted dust, and local geoclimatic conditions, as recently and exhaustively reviewed by Ettler (2016). Mapping of soil heavy metal contamination has been carried out in many countries, using a wide panel of modeling techniques, such as non-linear regression (Godin et al. 1985) and more or less complex geostatistical analyses based on kriging (e.g., van Oort et al. 2002; Ha et al. 2014; Nickel et al. 2015; Borowski and Kwiatkowska-Malina 2017). Such mappings inform about the state of metal accumulation at the time of soil sampling. Once incorporated in soil, the fate of metal pollutants is governed by soil nature and physicochemical conditions induced by land use and cultivation practices (Fernandez et al. 2007, 2010; Chrastný et al. 2012; Baize and van Oort 2014; Nickel et al. 2014). At

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industrials sites sensu stricto, the original soil is often absent or buried due to repeated excavations and backfilling with industrial waste (Thiry et al. 2002). The surrounding land is diversely affected by atmospheric fallout of industrial dust. For instance, with a wind speed of 30 km h^{-1}, most 100-μm particles are deposited within 100 m, but particles smaller than 10 μm may travel for about 1 km (Robert and Juste 1998). Metal nanoparticles (< 100 nm) travel over tenths to hundreds of kilometers, contributing to long-range transboundary air pollution (WHO 2007). The modeling of their atmospheric deposition must consider convective boundary layer theories (Sun 1986; De Wekker and Kossmann 2015).

Dust particles emitted by zinc smelters may contain metals in the form of sulfides, sulfates, silicates, and oxides (Sobanska et al. 1999; Thiry et al. 2002), such as sphalerite, willemite and franklinite. Once deposited on agricultural soils, with nearly neutral to slightly acid soils (pH 5–7), or more acid forest soils (pH 3.5–5), such fine components undergo alternating wet and dry conditions and become unstable. Freed metal elements may be rapidly released in the soil solution (Bataillard et al. 2003), and intercepted by reactive soil constituents, such as organic matter, iron oxides, phyllosilicates, and phosphates (Alloway 2013). They partially migrate to deeper horizons, as reported for different soil contexts and by means of different techniques, such as detailed geochemical analyses in soil profiles, in situ lysimetric monitoring, sequential chemical extractions, or hydrodynamic modeling (Citeau et al. 2003; Labanowski et al. 2008; Chrastný et al. 2012; Mallmann et al. 2012a, b; Rheinheimer dos Santos et al. 2013; Ettler 2016). Metals are not similarly affected by physicochemical changes in soil conditions. Many studies in soils around metal smelters underline the great labile character of Zn and Cd with respect to Pb, often mentioned as a low-mobile element in soils. Zinc is responsive to pH fluctuations (Alloway 2013). In soils of the study region, zinc dominantly occurred in the soil solution as Zn^{2+} ions (Citeau et al. 2003) developing high affinities for negatively charged surfaces, i.e., iron compounds and clay minerals. By contrast, in most soil conditions, Pb is generally little mobile and forms fairly stable complexes with organic matter, Fe and Mn compounds, and phosphates (Alloway 2013). In soils of the study region, only a small proportion of lead was shown to migrate toward depth in colloidal form via the soil solution, preferentially bound to Fe-oxides (Citeau et al. 2003). In an agricultural soil affected by point-source pollution (temporarily paved with residual ore waste), Pb was found to precipitate within iron coatings at great depth (van Oort et al. 2018). Minor migration of lead was reported in acid forest soils (Steinnes and Friedland 2006) or under reduced soil conditions (Charlatchka and Cambier 2000). Due to such diverging cycling dynamics in soils under different physicochemical conditions, the concentration ratio of more-mobile and less-mobile metal elements deriving from industrial fallout deposition will change over time.

Ecosystems around metallurgical complexes represent advantageous sites to study spatial distribution of airborne metal pollution in surface horizons and the incorporation of heavy metals in depth in relation to land use and agricultural practices (Ettler 2016). We assessed the fate of airborne metal fallout in soils under different land use (arable land, wetland, and forest land) covering ~ 4000 ha around a former zinc smelter complex which ceased its activity in the beginning of the 1960s. For about 20 years, this site has been the target of multidisciplinary research, including in situ field survey and monitoring (Thiry et al. 2002; van Oort et al. 2002, 2009; Citeau et al. 2003), pedogeochemistry and modeling of metal transfer at the soil profile scale (Fernandez et al. 2007, 2010; Leguédois et al. 2004; van Oort et al. 2018; Labanowski et al. 2007, 2008; Mallmann et al. 2012a, b; Rheinheimer dos Santos et al. 2013), nanometer-scale chemical speciation (Manceau et al. 2000), impacts on crops (Mench et al. 2009) and soil fauna (Nahmani et al. 2003), and metal extraction by metallophyte species (Dahmani-Muller et al. 2000).

We focused on Zn and Pb, the two dominant airborne pollutants with contrasting cycling dynamics in soils. The spatial distribution of their concentrations in the soil's surface layer was modeled as a function of the distance to the emission source and of land use. In addition, Zn/Pb concentration ratios were calculated to provide rapid and global insight into relative metal movement in the surface horizon of soils during about one century. Although a straightforward comparison of Zn/Pb concentration ratios in soils under different land use may appear simplistic regarding the complex processes and mechanisms that govern metal mobility or immobilization in soils, in our work we considered land use as a parameter that accounts for the complex physicochemistry of metal dynamics in soils of different ecosystems. Such approach basically differs from studies on samples collected in a soil profile that relate metal pollutant mobility to selected major soil characteristics, such as pH, redox conditions, and organic matter. Our work aimed at testing under real field conditions, at the scale of a small region, the validity of extrapolating results obtained by modeling metal mobility on samples under laboratory conditions.

2 Materials and Methods

2.1 The Site

2.1.1 Historical Background

The metallurgical complex of Mortagne-du-Nord included a zinc smelter from 1901 to 1963 and a sulfuric acid plant from 1924 to 1968. An additional lead refining unit also operated for about 10 years. In the mid-1920s, this complex provided 31% of France's zinc production with an annual production of about 25,000 tons, and a total production between 1901 and 1963 estimated at 390×10^4 tons, following the work of Hardy (1970). Moreover, the processed metal ore and the used processing technology did not change consistently during the period of smelter activity. The site was reclaimed in 1989, its waste dump was removed, and it was inventoried as an orphan site in 1996 by the French Ministry of Environment. From 1996 to 2001, its mineralogy and hydrogeochemistry were extensively studied (Thiry et al. 2002; Schmitt et al. 2002).

2.1.2 The Soil Cover

The industrial wasteland, located in the center of the study area, lies close to the confluent of the Scarpe and Escaut rivers and covers about 25 ha (Fig. 1a). The surrounding agricultural soils have mainly developed in Paleocene glauconite-bearing Ostricourt cover sands and were little to moderately differentiated, i.e., Eutric Cambisols and Haplic Luvisols (IUSS-WRB 2006). They were sandy to loamy sand textured (Fig. 1a), moderately acid (pH 5.5–6.5), but their pH temporarily varied due to periodical liming. The organic carbon content varied from 8 to 17 g kg^{-1} in arable soils, and from about 12 to 35 g kg^{-1} in grassland soils (Fernandez et al. 2007, 2010). The cation exchange capacity ranged from about 10 to 20 cmol^{+} kg^{-1}, with a base saturation generally greater than 50%. The mineralogical composition of the soils was dominated by quartz, with minor amounts of feldspars, glauconite, and mica. The clay fraction mainly contained illite and smectite. On the gentle slopes of the Scarpe-Escaut valley, the Ostricourt sands were partially covered by a variable thickness of silty loam-textured Weichselian loess deposits, in which Luvisols have developed. In the north, northwest, and southeast, more sandy textured Eutric Cambisols occurred extensively under agricultural land. Dystric Cambisols and poorly drained podzolic soils were sometimes observed under beech/oak forest. Close to the Belgian border in the north, restricted to pine forest stands on well-drained topographical summit positions, Podzols have developed in coarse-sandy textured Pleistocene alluvial dune reliefs.

2.1.3 Soil Sampling Strategy

Several pedogeochemical survey campaigns have been carried out between 1996 and 2005. Topsoils from agricultural lands were sampled following a 200-m grid, avoiding obvious point pollution sources, such as road maintenance, agricultural embankments, and forest lanes, but also several more unusual sites (temporary storage of industrial waste in the middle of agricultural fields, sporadic use of metallurgical waste for weed-killing, etc.). Additionally, selected soil profiles under specific land use (arable land, grassland, forest land) were studied in more detail, applying a systematic 5-cm-depth increment, as well as characteristic soil horizon sampling schemes. Remarkable differences were revealed for Zn and Pb distributions in the topsoil when comparing the 0–30-cm surface layer, and in the 5-cm increment Zn and Pb concentration profiles (Fernandez et al. 2007, 2010; van Oort et al. 2009). Considering such divergent incorporation of metalliferous atmospheric dust in annually plowed soils, with respect to non-tilled agro- and ecosystems, we adopted a sampling strategy based on a constant plow-layer thickness (Sterckeman et al. 2002) for spatial examination of the fate of Zn and Pb pollution in topsoils. Such approach enhanced the calculation of comparable metal accumulation in soil samples, whatever their land use.

Soil sampling was performed using an iron auger (Eijkelkamp Soil Equipment®, The Netherlands) guaranteed to contain none of the metals studied. Each 0–30-cm bulk sample was an average specimen obtained by mixing 5 auger samples, collected according to a 1-m cross-shape pattern. About 1.5 kg of bulk samples was air dried, homogenized, and carefully quartered; a 200-g

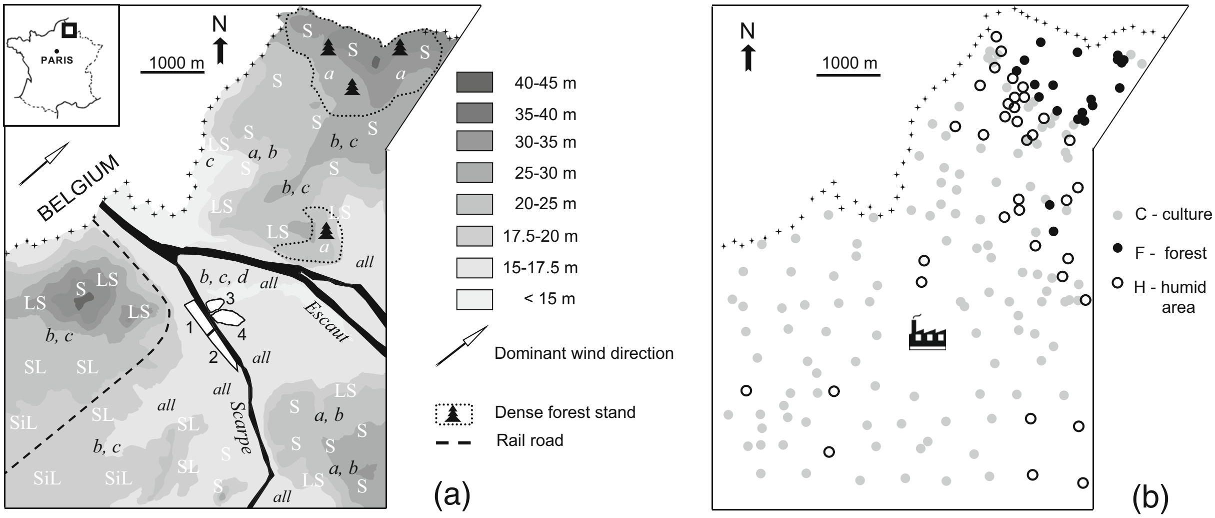

Fig. 1 **a** Schematic topographical map of the study area with location of the former metallurgical site including the zinc smelter complex (1), the sulfuric acid plant (2), extension of the former industrial waste belt (3), and its adjacent metallophyte grassland (4). Main texture of parent materials for soils. all, alluvial deposits including fine sandy to clayey textured materials; SiL, silt loam; SL sandy loam; LS, loamy sand; S, sand. Main classes of soil acidity: *a* pH < 5; *b* 5 < pH < 6.5; *c* 6.5 < pH 7.5; *d* pH > 7.5. ***b*** Sampling location and corresponding soil type

subsample was sieved to < 2 mm and stored prior to chemical analyses. For the present study, 173 surface samples were selected and divided into three groups according to land use (Fig. 1b): cultivated soils (*C*), well-drained forest soils (*F*), and soils from humid areas (*H*). The latter were mostly under grassland and occasionally wet forest stands, and marked by temporary waterlogging due to lower topographical positions.

2.2 Chemical Analyses

Representative sub-samples were totally dissolved using tri-acid digestion HF, HCl, and HNO_3 (NF X 31-147) (AFNOR 2004). Total Zn and Pb concentrations were respectively determined by ICP-AES (NF ISO 22036) and ICP-MS (NF EN ISO 17294-2), at INRA's COFRAC-certified National Laboratory for Soil Analyses (LAS, Arras, France). In addition, for the characterization of soils under different land use, current pedological and physicochemical analyses, such as grain size distribution, pH, organic carbon, C/N ratio, CEC, exchangeable cations, and total and free iron were carried out on surface samples as well as on subsurface horizons from representative soil profiles (van Oort et al. 2002, 2009). These latter data are not further discussed in this paper.

2.3 Modeling Zn and Pb Concentrations in Soils

Basically, Zn and Pb concentrations in soils resulting from industrial airborne fallout were presumed to follow an exponential decrease with increasing distance from the pollutant emitting source (Wu et al. 2011):

$$y = y_0 + \alpha e^{-\beta x} \tag{1}$$

where α represents the apparent contribution at the site of the factory, and β the rate of decrease (in m^{-1}) with distance, x (in m). The term $\alpha e^{-\beta x}$ is thus directly driven by the factory emissions. The factor y_0 corresponds to the local geochemical background, together with the diffuse (remote) atmospheric pollution, which was presumed to have homogeneously affected the area (Fig. 2). First, the contribution from the factory to the total concentration, Z, was isolated by defining $Z = y - y_0$. Geochemical background levels of Zn and Pb, y_0, were estimated from available data (Sterckeman et al. 2002; Fernandez et al. 2007; van Oort et al. 2009), and set at 20 mg kg^{-1} for Zn, and 12 mg kg^{-1} for Pb, in surface horizons of loamy sandy textured soils under arable land (*C*), and at 14 and 8 mg kg^{-1}, for well-drained forest soils (*F*) and humid areas (*H*).

Three models were tested using an analysis of covariance (ANCOVA), which compares groups after controlling the effect of a cofactor. All models hypothesized that Pb and Zn concentrations varied exponentially with the distance from the source (i.e., linearly after ln transformation; Fig. 3). The following analyses were performed separately for Pb and Zn. In model 1 (Fig. 3), for a given distance, metal concentrations were expected to be the same whatever the land use. Once linearized, one obtains:

$$\ln(Z_{i,j}) = \ln(\alpha) - \beta x_{i,j} + \varepsilon_j \quad i = C, H, F \quad j = 1, \ldots, n_i \tag{2}$$

Model 2 considered that slopes were the same (i.e., same distance effect) for the three groups of soils, but that intercepts varied (i.e., depending on land use, metal concentrations were different for the same distance). It can be written as:

$$\ln(Z_{i,j}) = \ln(\alpha_i) - \beta x_{i,j} + \varepsilon_j \quad i = C, H, F \quad j = 1, \ldots, n_i \tag{3}$$

In model 3, both intercepts and slopes varied:

$$\ln(Z_{i,j}) = \ln(\alpha_i) - \beta_i x_{i,j} + \varepsilon_j \quad i = C, H, F \quad j = 1, \ldots, n_i \tag{4}$$

The variable ln(*Z*) was tentatively explained by the combination of a quantitative variable: *x*, the distance to the source, and a categorical variable, featured by three levels: *C* for cultural, *H* for humid, and *F* for forest soils. The evaluation procedure consisted in comparing the linear models with a decreasing degree of complexity, using a sequential ANOVA: model 3 vs model 2, and if the first comparison was not significant, model 2 vs model 1; e.g., Faraway (2005).

3 Results and Discussion

3.1 Zn and Pb Concentrations in Topsoil

Soil surface concentrations varied widely: 29–1285 mg kg^{-1} for Zn, and 16–493 mg kg^{-1} for Pb (Table 1). The spatial distribution maps of total Zn and Pb concentrations in the 0–30-cm surface layers are presented in Fig. 4 a and b. As expected, the highest Zn and Pb concentrations (from 250 to 1285 mg kg^{-1} and 100–493 mg kg^{-1}, respectively) were observed within a 1.5-km radius, centered on the former metallurgical complex. Such concentrations were about ~ 10–60 times higher than the local geochemical background for zinc, and ~ 10–40 times higher for lead. Concentrations then decreased with increasing distance from the former emission source. Nonetheless, some remarkable differences between Pb and Zn distribution patterns were revealed. By comparison to the nearby humid and cultivated soils, the sandy textured soils under forest showed substantially higher Pb concentrations, reaching up to 300 mg kg^{-1} (Fig. 4b), but Zn concentrations in forest soils were always lower. This result was tested more formally using the set of models described above, which do not integrate potential anisotropy, as no prevailing plume transport direction was observed, despite the predominantly southwestern winds.

3.2 Modeling Zn and Pb Concentrations in Soils Under Different Land Use

Model 2 best described the variations in Pb and Zn concentrations (Table 2): metal concentrations decreased at the same rate with increasing distance, whatever the land use, but concentration levels varied according to land use for a given distance (Fig. 5). Different ln(α_i) values were therefore obtained according to the type of land use. These findings cannot be due to variable emissions from the factory. The real emission level remains unknown; industrial dust deposition on soils is variably altered by the vegetation cover and soil physicochemical conditions with time: when ln(α) (or α value) for a given type of soil exceeds the values computed for the other types, that simply means that the input/output balance is more positive, leading to the retention of a greater amount of metals in surface horizon. Several factors can explain this process, each favoring or hindering inputs or outputs. For instance, mobile metals may more easily percolate under acidic soil conditions, favoring outputs from the surface horizon. Other factors, such as metal exportation by harvesting, may also play a major role. As a result, the ln(α) values provide information about the general behavior of metals in soil according to land use. The particular influence of each factor could not be individualized here.

In our work, ln(α) for Pb in forest soils was significantly greater than the values computed for the other types of soils (Fig. 5b). This was ascribed to the presence of the canopy, intercepting more contaminated

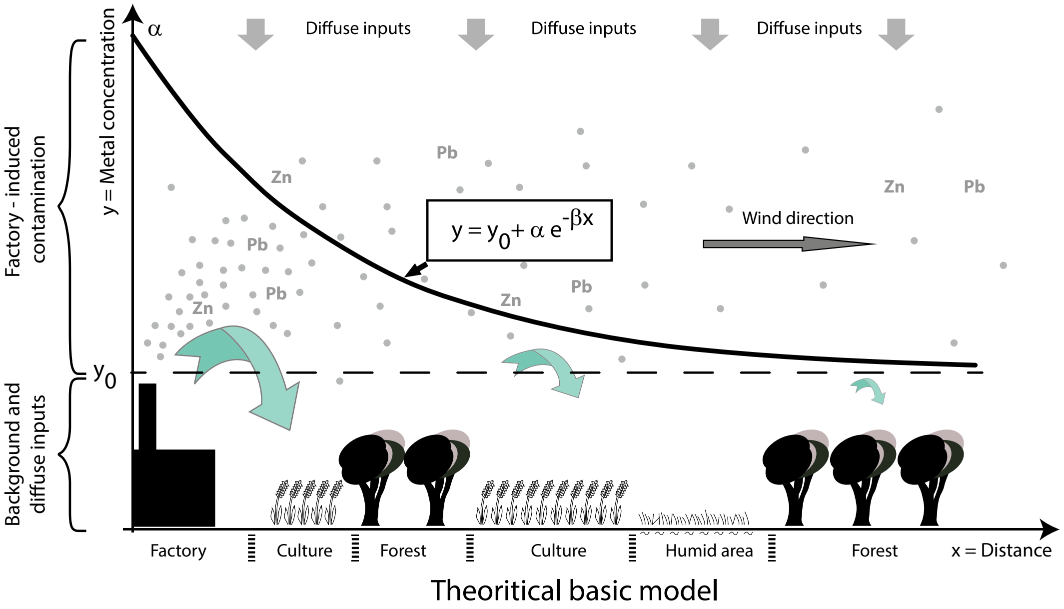

Fig. 2 Concept scheme of exponential decreasing airborne metal deposition from the former zinc smelter complex on soils under cultivated arable land (*C*), humid grassland wet forest soils (*H*), and well-drained forest land (*F*)

dust. Lead finally integrates the litter in autumn, thus increasing metal inputs in surface layers (Baize and van Oort 2014). Although the soil pH in forest soils is often more acid, Pb is known to be only slightly mobile and the balance remains strongly positive with respect to arable and wetland soils, due to amplified metal dust interception. For Zn (Fig. 5a), the greatest ln(α) value was found in arable soils, ascribed to acid-neutralizing treatments in agricultural soils (fertilizers, basic or organic amendments) that tend to immobilize metals in the surface horizons (Fernandez et al. 2007), contrarily to acid forest soil conditions where Zn is depleted. Interestingly, there was no significant difference between the β values estimated separately for Pb and Zn (Fig. 5, Table 2). Such result was coherent with a common origin: both metals are spread over the area via the dispersion of the same dust material. According to model 2, the average distance covered before fallout, calculated as $1/\beta$, was around 1900 m. At ~7 km from the factory, airborne metal input in soils has decreased by more than 97%.

3.3 Zn/Pb Concentration Ratio as an Indicator for Temporal Differential Metal Movement

The Zn/Pb ratios of well-drained arable soils (*C* soils) generally varied between 3 and 4 (1st and 3rd quartiles, cf. Figure 6a). Humid (*H*) soils, including moderately

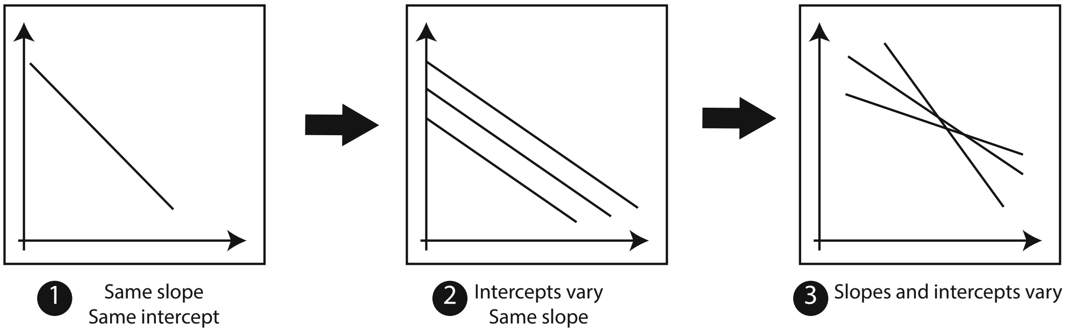

Fig. 3 Modeling hypotheses for airborne metal deposition of Zn and Pb (ln-transformed) in soils as a function of the distance from the emission source, under three different land use. The numbers 1–3 correspond to the models described in the body of the manuscript

Table 1 Summary statistics of Zn and Pb

Variable	Unit	*n*	Mean	Median	Std	Min	Max
Zn	mg kg^{-1}	173	173	130	163	29	1285
Pb	mg kg^{-1}	173	70	50	67	16	493

and poorly drained grassland and wet forest land, predominantly ranged from 1.5 to 2, while the Zn/Pb ratios in acid forest (*F*) soils were always smaller than 1, and outstandingly well-grouped around ca. 0.5. Some overlapping between *C* and *H* soils was observed, probably due to periodical rotation of moderately drained soils from grassland to arable land. Such distinctive Zn/Pb concentration ratios for soils under different land uses were quite remarkable (Fig. 6b), when considering that total Zn and Pb concentrations were found only slightly discriminant. Since the total concentrations of metal pollutants are generally accessible in an early stage of soil contamination studies in the vicinity of industrial sites, and under the condition of little change in metal ore composition, such a "low-mobile/mobile" metal pollutant ratio offers a rapid and easy-to-determine indicator of their cycling dynamics in soils under different land use. The differences in land use account for differences in physicochemical properties (amounts, nature and distribution of organic matter, clay mineralogy, pH, Eh), hydrology (rain event distribution, infiltration, drainage), and biological properties (faunal composition, decomposition of organic matter, aggregation, aeration), impacting the stability of associations between metals and soil constituents. Different behaviors of Zn and Pb deriving from airborne fallout were frequently observed in sandy textured soils, with low reserves of metal-reactive constituents (Sterckeman et al. 2007; van der Grift and Griffioen 2008). However, such a scenario may be different for other soil types, containing more clay and/or oxyhydroxydes, or other types of pollution. In soils amended with sewage sludge or urban waste water, metal pollutants are added concomitantly with large amounts of organic matter but also dissolved salts in the form of phosphates, sulfates and carbonates, thus favoring greater retention of metals in surface horizons (van Oort et al. 2018).

3.4 Relevance of Sampling Strategy in Assessing the Fate of Metal Pollution in Soils

Our 0–30-cm-depth sampling strategy in plowed agricultural and undisturbed ecosystems does not guarantee that all metal pollution is contained in the collected soil

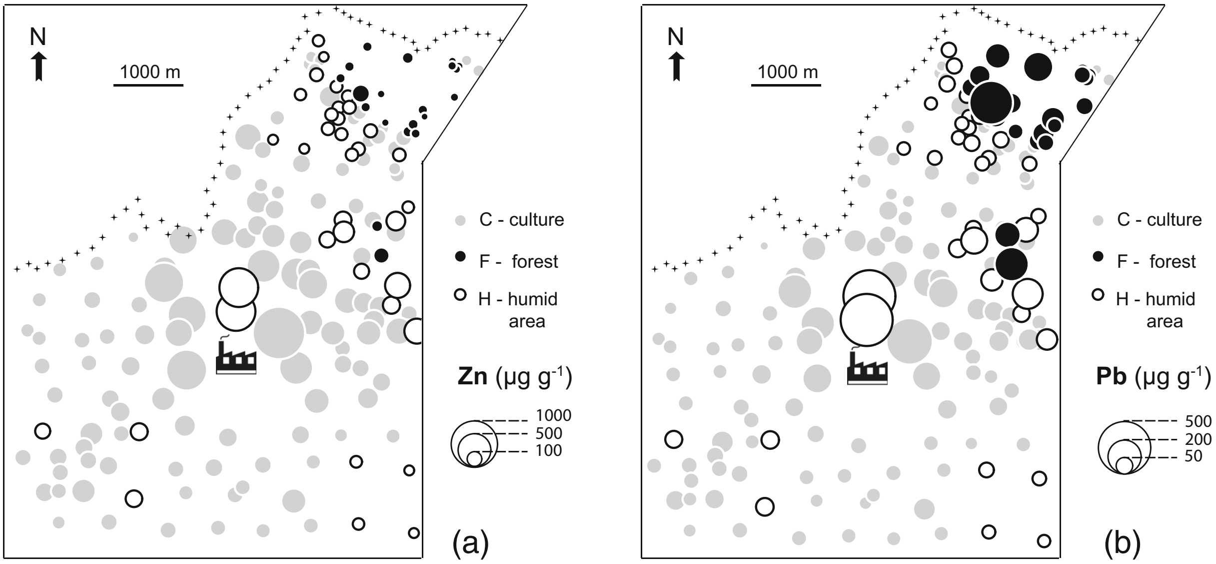

Fig. 4 Spatial distribution maps of total Zn concentrations (*a*) and Pb (*b*) concentrations from 0 to 30-cm surface horizons of soils under agricultural land use and forest stand in a 4000-ha perimeter around a former zinc-smelter complex in northern France. *n* = 173

Table 2 Model settings. Values of the constants used for modeling, models comparison by *F* tests (*F* and *p* values) and estimated parameter values. The average distance corresponds to the mean distance traveled before fallout (= $1/\beta$). The best model is the model 2, whatever the metal considered. It explains more variation than model 1, while, no benefit is obtained by permitting intercepts and the slopes to vary simultaneously (model 3). Linear model assumptions were checked: neither trends nor outliers could be identified using model residuals. *C* for culture, *F* for forest and *H* for humid zone

	Zn (n = 173)	Pb (n = 173)
Constant values	$y_0 = 20$ mg kg^{-1} for C $y_0 = 13$ mg kg^{-1} for F and H	$y_0 = 12$ mg kg^{-1} for C $y_0 = 8$ mg kg^{-1} for F and H
Model #1 vs model #2	F = 6.9; $p = 10^{-3***}$	F = 47.3; $p < 10^{-6***}$
Model #2 vs model #3	F = 2.2; $p = 0.11$	F = 1.9; $p = 0.14$
Best model	Model #2 Adjusted $R^2 = 0.67$ $\beta = 5.4\ 10^{-4}$ ($\pm$ 0.41 10^{-4}) m^{-1} $\ln(\alpha_F) = 5.83$ ($\pm$0.10) $\ln(\alpha_c) = 6.26$ ($\pm$0.10) $\ln(\alpha_H) = 5.99$ ($\pm$0.09) Average distance = 1920 m	Model #2 Adjusted $R^2 = 0.45$ $\beta = 5.13\ 10^{-4}$ ($\pm$0.46 10^{-4}) m^{-1} $\ln(\alpha_F) = 6.40$ ($\pm$0.15) $\ln(\alpha_c) = 4.92$ ($\pm$0.18) $\ln(\alpha_H) = 5.27$ ($\pm$0.10) Average distance = 1950 m

volumes, due to possible plant uptake and/or metal migration to deeper horizons. However, it is surely better than opting for arbitrary sampling depths (i.e., sampling depths of 0–2, 0–5, 0–10, 0–20, 10–20, or 5–15-cm are currently reported in literature (Ettler 2016), but such sampling strategies are seldom explained nor justified), since it takes into account the main way of incorporation and redistribution of airborne metal deposits in agricultural areas: mixing of the surface layer by annual plowing.

However, such strategy with a constant sampling depth must be combined with a complementary, pedological approach that compares metal stocks in pedological horizons and cumulates them over the entire soil profile. In the study area, this was done for two soils under long-term different land use: arable land and permanent grassland (both belonging to the *C* group), and for a forest soil (*F* group), located at similar distances (3.5–4 km), northeast of the former industrial site. The Pb and Zn stocks to 1-m depth were similar in

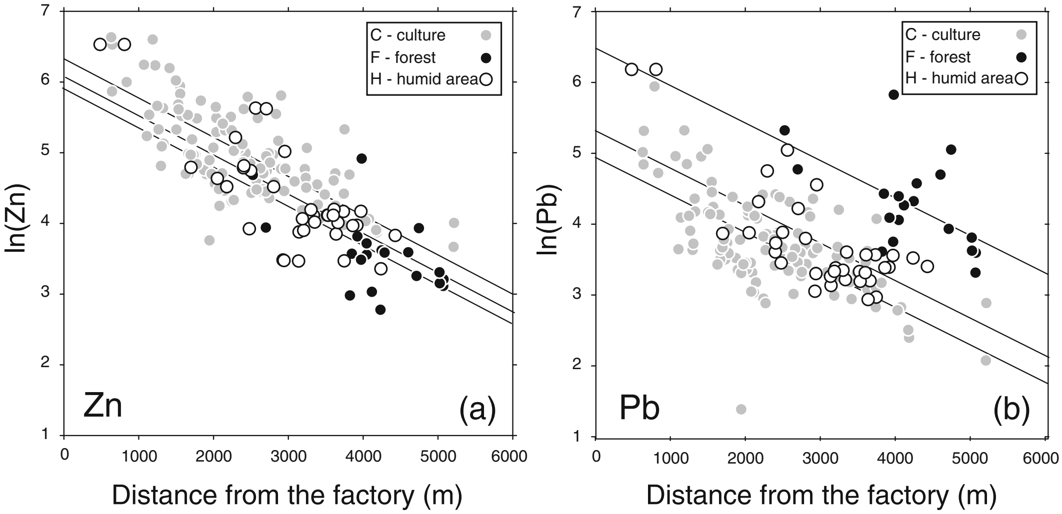

Fig. 5 Modeled Zn concentrations (**a**) and Pb concentrations (**b**) corrected from y_0 with model 2. Metal concentrations decrease at the same rate with increasing distance from the former emission source, whatever the land use, but they differ according to land use at a given distance

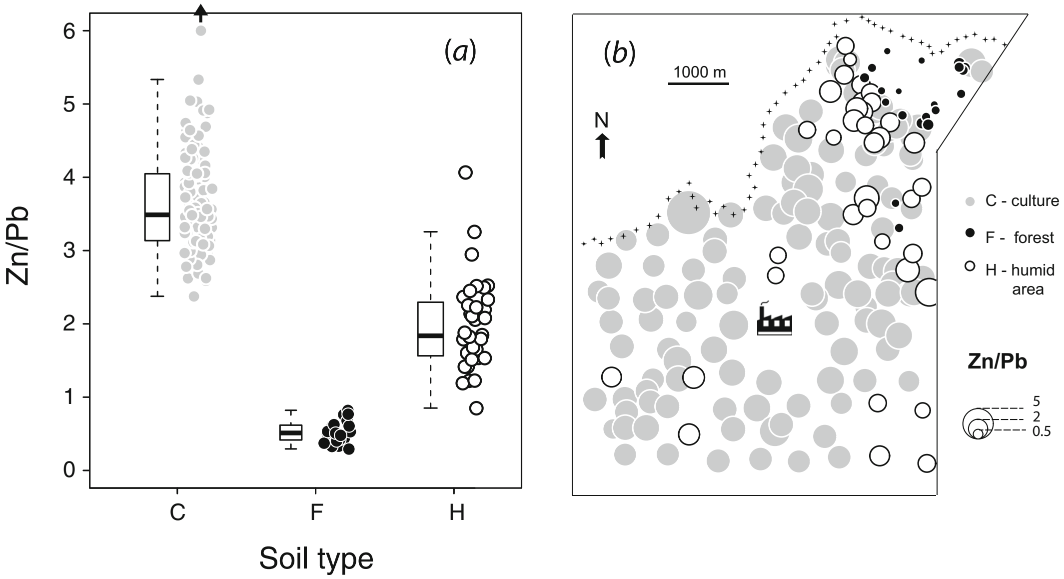

Fig. 6 Zn/Pb concentration ratios (corrected from y_0) for soils under cultivated arable land (C), humid grassland and wet forest land soils (H), and well-drained forest soils (F), (**a**) as boxplot reporting the median, and the 1st and 3rd quartiles, and (**b**) as a map

arable soil and permanent grassland: 32 and 30 g m^{-3} for Pb and 89 and 85 g m^{-3} for Zn (Fernandez et al. 2007), whereas in the acid forest soil (Fig. 1), the Pb stock was higher, 38 g m^{-3}, but the Zn stock was about three times lower, only 30 g m^{-3} (Baize and van Oort 2014). These findings clearly highlighted the filter effect of the canopy, intercepting more atmospheric dust, and the strong leaching of Zn under acid soil conditions (Bergkvist et al. 1989), and were consistent with model 2. To estimate the total amount of Zn deposited on the forest soil, we hypothesized that the original Zn/Pb ratio of airborne deposition could be best approximated with the higher Zn/Pb values observed for arable soils, since metal movement was supposed limited due to recurrent liming and fertilization practices. Using a Zn/Pb value of 4 (Fig. 6a), with a Pb stock of 38 g m^{-3}, the Zn stock should have reached about 160 g m^{-3}, if no Zn downward migration had occurred, instead of the 30 g m^{-3} actually measured. Therefore, more than 80% of Zn has leached out of the uppermost meter of the forest soil. Similar strong metal migration to great depth (3–13 m) has already been reported (van der Grift and Griffioen 2008) for Zn and Cd deriving from metal smelter emissions in acid soils developed in Pleistocene fluvio-eolian cover sands in the Kempen area, at the Dutch-Belgium border.

Selecting the best approach to assess the fate of metal pollutants in soils is dictated by the final research aims. In our work, we aimed to provide spatial distribution maps of total concentrations of mobile and slightly mobile metals derived from industrial fallout and to obtain spatiotemporal insight into their fate in soils under different land uses. We therefore adopted a sampling strategy consisting in collecting 0-30-cm surface samples for all soils, to emphasize metal incorporation by annual plowing practices. With this approach, it is possible to collect a large number of samples covering a great area rapidly. In comparison, the assessment of metal fate in soil profiles, based on cumulating metal stocks in characteristic soil horizons, requires more pedological skills and is more costly and time-consuming. Although complementary and crucial, such detailed study generally remains restricted to some local observations.

4 Conclusion

Soils from agricultural and forest ecosystems surrounding a former metallurgical complex were studied to assess the fate of airborne metal deposition, focusing on a mobile (Zn) and a less-mobile metal pollutant (Pb). We adapted our sampling strategy by collecting 0–30-cm-depth samples from all soils, tilled or not, in order to harmonize the analyzed soil volume to that of the plow layer, where airborne metal loads have been annually mixed. Spatial distribution maps showed general decreasing concentration patterns for both metals, with increasing distance from the source of emission, but substantially higher Pb surface concentrations were found in forest soils. The average depositional distance was the same for both metals, indicating that they have traveled together. Distinct ranges were found for Zn/Pb concentration ratios, independently from the distance to the source: 3–4 for well-drained arable soils, 1.5–2 for grassland and wet forest soils, and ~ 0.5 for well-drained forest soils. Such remarkably different Zn/Pb concentration ratios for soils under different land use were more discriminant indicators of metal fate than total Zn and Pb concentrations taken separately. These findings have several implications. Different Zn/Pb ratios imply that, several decades after industrial activity, a variable fraction of the airborne metal load remains in the surface 0–30-cm sample, depending on land use and induced physicochemical soil conditions. Hence, the produced spatial distribution maps represent the current state of metal dynamics (at the moment of sampling), but they only partially illustrate the overall “metal pollution” of the soils. Notable amounts of metals have been redistributed in the soil profiles by downward migration in the soil solution; biomechanical incorporation by earthworms, especially in grassland soils; or extensive leaching, in acid forest soil conditions. The increased Pb concentrations in forest surface layers clearly underlined the high interception capacity of the canopy for atmospheric dust. It is therefore strongly recommended to take land use into account when assessing airborne pollutant fallout budget through the study of soils. Our approach of studying Zn/Pb concentration ratios on comparable sampling depths for soils under different land use, intends to be integrative, simple to operate, and providing a rapid insight into the temporal evolution of metal pollutants with diverging mobility dynamics in soils. Such approach seems particularly well-adapted in case of historical metal pollution, notably deriving from industrial activity, widespread worldwide during the nineteenth and twentieth century.

Acknowledgments This paper ends more than 20 years of field and laboratory study on soil metal contamination in northern France. Remarkably, although the field survey was one of the first steps of the multidisciplinary research program, this final interpretative work on metal distribution patterns is the last one, taking advantage of the wide range of results provided by laboratory studies. We therefore gratefully acknowledge the contributions of many students and colleagues for field and laboratory assistance. This work was partly granted by the French Ministry of Environment (MATE-SRAE–95.245) and the CNRS ToxNuc-E program (2003–2006).

Author Contributions All authors contributed to the study conception and design. Material preparation, data collection, and analysis were performed by Folkert van Oort, Fabrice Monna, and Stéphane Garnier. The first draft of the manuscript was written by Folkert van Oort, and all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

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