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Effective radium concentration in topsoils contaminated by lead and zinc smelters

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HIGHLIGHTS

- Effective radium concentration (EC_{Ra}) is used to study trace element pollution.
- EC_{Ra} is measured in 186 contaminated topsoils near smelters in the north of France.
- Soil EC_{Ra} values are spatially organized and depend on the geographical units.
- EC_{Ra} helps to identify the natural spatial variability of magnetic susceptibility.
- EC_{Ra} provides a novel index to identify soils able to fix leached components.

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ABSTRACT

Trace elements (TE) are indicative of industrial pollution in soils, but geochemical methods are difficult to implement in contaminated sites with large numbers of samples. Therefore, measurement of soil magnetic susceptibility (MS) has been used to map TE pollutions, albeit with contrasted results in some cases. Effective radium concentration (EC_{Ra}), product of radium concentration by the emanation factor, can be measured in a cost-effective manner in the laboratory, and could then provide a useful addition. We evaluate this possibility using 186 topsoils sampled over about 783 km^2 around two former lead and zinc smelters in Northern France. The EC_{Ra} values, obtained from 319 measurements, range from 0.70 ± 0.06 to 12.53 ± 0.49 $Bq \cdot kg^{-1}$, and are remarkably organized spatially, away from the smelters, in domains corresponding to geographical units. Lead-contaminated soils, with lead concentrations above 100 $mg \cdot kg^{-1}$ <3 km from the smelters, are characterized on average by larger peak EC_{Ra} values and larger dispersion. At large scales, away from the smelters, spatial variations of EC_{Ra} correlate well with spatial variations of MS, thus suggesting that, at distance larger than 5 km, variability of MS contains a significant natural component. Larger EC_{Ra} values are correlated with larger fine fraction and, possibly, mercury concentration. While MS is enhanced in the vicinity of the smelters and is associated with the presence of soft ferrimagnetic minerals such as magnetite, it does not correlate systematically with metal concentrations. When multiple industrial and urban sources are present, EC_{Ra} mapping, thus, can help in identifying at least part of the natural spatial variability of MS. More generally, this study shows that EC_{Ra} mapping provides an independent and reliable assessment of the background spatial structure which underlies the structure of a given contamination. Furthermore, EC_{Ra} may provide a novel index to identify soils potentially able to fix leached components.

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1. Introduction

One of the most important issues for the future of mankind and its living space on Earth is the presence of soil contamination by industrial activities (Osman, 2014). The increase of polluted soils is a topical issue with the growing lack of proper agricultural soils (Banwart, 2011), while the demand is increasing and the amount of pristine soil is shrinking and difficult to assess (Gibbs and Salmon, 2015). Global warming will also increase the release of pollutants to mobile phases, with higher impact on humans (Noyes et al., 2009).

Among the numerous pollutants, trace elements (TE) such as metals are a major concern because of their harmful health (Tong et al., 2000; Abrahams, 2002; Järup, 2003) and disastrous environmental effects (Wood, 1974; Nagajyoti et al., 2010). For already more than two centuries, TE are released/produced massively by various sources: local and well defined sources such as mines (Li et al., 2014) or smelters (Valery and Eugene, 1998; Kabala and Singh, 2001), and more diffuse sources such as traffic and urban emissions (Manta et al., 2002; Lee et al., 2006; Wei and Yang, 2010). While clear signatures of pollution are common in the old industrial Europe (Molina-Villalba et al., 2015) where awareness has increased and exposure has diminished, it is not the case in rapidly advanced countries of Africa (Yabe et al., 2015) and in China (Tong et al., 2000; Li et al., 2015). During the last decade, electronic wastes have been an additional rapidly growing source of TE (Robinson, 2009; Wu et al., 2015).

Numerous analytical techniques exist to measure TE concentration in soils, the most widely used being atomic absorption spectrometry (Soodan et al., 2014). Isotopic methods have also shown a substantial ability to distinguish between sources of pollution (Bollhöfer and Rosman, 2000; Ettler et al., 2004; Cheng and Hu, 2010; Kumar et al., 2013). However, such methods remain costly, time-consuming, and are only systematically applied in concentrated areas of significant TE pollutions, such as around former mines or regions of exceptional activities (Allen-Gil et al., 2003). Thus, alternative methods that can be applied to large numbers of locations disseminated over large regions have been considered to detect TE pollution in soils. The most successful method so far has been the measurement of the magnetic susceptibility (MS) of topsoils. MS has indeed displayed impressive correlation with Hg and Pb concentrations (Hanesch and Sholger, 2002) and is able to efficiently identify and map contaminated areas (Chianese et al., 2006). Nevertheless, in some cases, either the correlation between MS and TE concentrations is only significant for MS larger than 40×10^{-7} m^3 kg^{-1} (Morton-Bermea et al., 2009), or MS appears only correlated with Cu, Ni, and Pb concentrations, but not with Zn and Co concentrations (Canbay et al., 2010). In addition, elevated MS can be measured in the absence of TE pollution (Lu et al., 2008; Cervi et al., 2014; Golden et al., 2015), and when multiple sources for elevated MS and TE are present, their smooth cumulative effect is difficult to disentangle based only on MS (Jordanova et al., 2014). Despite significant advances in our understanding of the origin of the MS signals (Wang, 2013; Ma et al., 2014) and of the magnetic mineralogy (Xia et al., 2014; Jones et al., 2015), attributing unambiguously elevated MS to TE pollution remains difficult in numerous cases.

Effective radium concentration (EC_{Ra}) is the product of radium-226 concentration (C_{Ra}) by the emanation factor (E), which is the probability of the radon-222 atom, radioactive daughter of radium-226, to escape into the pore space (Tanner, 1964). EC_{Ra} is the radon-222 source term to the environment. It is easy to measure in the laboratory with large number of samples (Girault and Perrier, 2012a,b) and is sufficiently representative and reliable to be used, in the case of rocks, for geological studies (Girault et al., 2012), and, in the case of soils, for pedological studies (Girault et al., 2011a). In essence, EC_{Ra}, which reflects the concentration of a particular TE, radium, could provide an immediate first-order proxy for the soil ability to fix metals. Furthermore, some interesting patterns were observed with MS in topsoils (Girault et al., 2011b), as radium has a strong affinity with some oxides and oxy-hydroxides (e.g., Flexser et al., 1993), thus leading to an increase of MS.

In this paper, we investigate in what way EC_{Ra} can be a useful additional parameter in TE pollution studies. For this purpose, we selected a site in the former coal-mining region of Northern France characterized by large TE pollution (Frangi and Richard, 1997; Douay et al., 2008, 2009), in the absence of uranium mining or processing activity, and where a systematic bank of 186 soil samples was available with known MS (Clozel-Leloup and Théveniaut, 2001; Hammade et al., 2004).

2. Methods

2.1. Site and samples

The studied region (Fig. 1) is located around the former Metaleurop Nord (ME) lead and zinc smelter in the town of Noyelles-Godault (north of France), which was operated for over a century until its closure in 2003 (Douay et al., 2008; Lopareva-Pohu et al., 2011). Another zinc smelter (Nyrstar; NY) was also operated in Auby, 5 km to the east of ME. Extensive contamination by TE was characterized in details during the last decade over several targets, including agricultural soils (Sterckeman et al., 2000, 2002), woody habitats soils (Douay et al., 2009), trees (Migeon et al., 2009), and streams (Superville et al., 2015). The smelters have released large quantities of dust, especially before 1970 (4 to 5 tons per day as an assumption; Hammade et al., 2004), containing mainly Pb and Zn, but also Cd, Cu, Sb, and Bi. Lead concentrations (C_{Pb}) larger than 100 $\mathrm{mg \cdot kg^{-1}}$ are observed in topsoils over an area of 106 km^2 around the two smelters (Fig. 1). C_{Pb} is the highest (>2000 $\mathrm{mg \cdot kg^{-1}}$) in the vicinity of ME (Fig. 2), remains always larger than 100 $\mathrm{mg \cdot kg^{-1}}$ within 3 km of ME, and then decreases with increasing distance from ME, with a few exceptions to this trend around the NY plant (Douay et al., 2008). These contaminations are essentially explained by atmospheric deposits, but ore and industrial processes residues were also dumped in some agricultural or urban lands, making this area one of the most polluted zones in France. From 1994 onwards, extensive programs have been continuously implemented to protect the population, including phytoremediation studies (Migeon et al., 2009; Pourrut et al., 2011).

The region extends over four geological and geographical units (Fig. 1). To the north, the Pévèle unit, with a basement of Tertiary sands and clays, emerges from the rather flat landscape with an altitude varying from 30 m to 105 m. To the south, the Gohelle unit, with Cretaceous chalk substratum covered by several meters of Quaternary loess deposits, shows lower altitudes. In between the Pévèle and the Gohelle units, the Deûle Canal flows from the Scarpe Plain to the north-west into the Deûle Valley. This alluvial plain is filled with Holocene deposits (Deschodt et al., 2012). The organo-mineral horizons of soils present a dominant silt fraction, but highly variable clay and sand contents (Sterckeman et al., 2002).

The studied area is subject to an oceanic temperate climate with continental influence. Mean temperature is 10.8 °C over the last 30 years, with rare periods below −5 °C. Dominating winds come from south-west (Fig. 1) with an annual moderate rainfall of 744 mm per year on average, well spread over the year, with about 175 days with rain per year. The area is highly urbanized, with <45% of agricultural land, and is crossed by numerous roads, highways, and railways. Population exceeds 55,000 inhabitants around ME in the central zone from Oignies to Douai (Fig. 1).

In this study, we used three sets of well documented reference samples (Clozel-Leloup and Théveniaut, 2001; Hammade et al., 2004). The N samples ($n = 115$) are topsoils sampled during a systematic campaign, carried out in 2002, which included also in-situ measurement of MS. Most samples ($n = 100$) were taken from ploughed cultivated lands; the others were taken from non-ploughed lands ($n = 6$), small woods ($n = 3$), grazing lands ($n = 3$), mining heaps ($n = 2$), and a ditch ($n = 1$). The N samples display a regular grid with a spacing of about 2 km (Fig. 1). The sampling was performed over a depth 0 to about