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.

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 km² 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·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·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; Járup, 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 (Sooban 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 soils. 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 m3 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., 2009). Moreover, elevated MS can be measured in the absence of TE pollution studies (Tanner, 1964). In addition, elevated MS can be measured in the absence of TE pollution data (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 (ECR) is the product of radium-226 concentration (CRa) 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). ECRa is the radon-222 source term to the environment. It is easy to measure in the laboratory with large numbers 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,b). In essence, ECRa, 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., Flexer et al., 1993), thus leading to an increase of MS.

In this paper, we investigate in what way ECRa 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 Metaluipment 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 mg·kg−1 are observed in topsoils over an area of 106 km2 around the two smelters (Fig. 1). C Pb is the highest (>2000 mg·kg−1) in the vicinity of ME (Fig. 2), remains always larger than 100 mg·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 (Deschot 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...
25 cm with a spade. Each soil sample was dried at ambient temperature under ventilated hood to avoid chemical changes, and then crushed gently. One half was kept (bulk) and the other half separated and machine crushed to pass through a 2 mm sieve. We used these two subsample sets (bulk and <2 mm fraction).

The N set was preceded by the T set (n = 100), obtained during an initial campaign in 2001. A total of 59 of these T samples were available for this study. These are mostly topsoils from ploughed cultivated lands (n = 40), but include also soils from lawns (n = 7), planted trees (n = 7), and grazing lands (n = 2), and other soils mixed with mining residues (n = 3). The T sampling sites are separated by about 500 m and are located within 5 km of ME or NY smelter. These samples were complemented by 6 reference samples located outside the studied area. The T and reference samples were machine crushed to pass through a 2 mm sieve (Clozel-Leloup and Théveniaut, 2001).

Finally, the original sample bank (N and T sets) was complemented in 2011–2012 by 12 additional topsoil samples (D set). The D samples were taken in various locations, at different distances from the ME smelter, in order to perform additional chemical analyses more specifically dedicated to the interpretation of \( EC_{Ra} \) in the context of TE contamination. These samples were not sieved.

2.2. Effective radium concentration (\( EC_{Ra} \))

We consider only, from the uranium–238 decay chain, the isotopes radium-226 (half-life 1600 years) and radon-222 (half-life 3.82 days). The method to measure \( EC_{Ra} \) has already been described in detail (Girault et al., 2011a; Girault and Perrier, 2012a) and is only briefly recalled here. Radon emanation from natural samples results from its radium concentration and the probability (emanation factor \( E \)) that the radon atom can freely propagate in the pore space and then to the outside (Tanner, 1964; Sakoda et al., 2011). The product \( EC_{Ra} \)
consequently the relevant radon source term (Stolous et al., 2004), can be measured in the laboratory using accumulation experiments.

A sample of mass $m$ is installed in a sealed container of known volume. At radioactive equilibrium, the radon concentration $C_r$ in the free air volume is homogeneous. In the absence of leakage and when diffusion effects of radon-222 can be ignored, we have (Girault and Perrier, 2012a):

$$C_r = \frac{m}{V} E_{Ca},$$  

(1)

where $V_a$ is the total air volume available in the container, including the sample connected pore space. Various methods can be used to measure the radon concentration in the container air (Stolous et al., 2003). To measure large numbers of samples in a reliable manner (Girault and Perrier, 2012a), it turned out that the best method is to use scintillation flasks, which provide experimental uncertainties varying from 10% for $E_{Ca} = 1$ Bq·kg$^{-1}$ to smaller than 6% for $E_{Ca} > 10$ Bq·kg$^{-1}$. The method is consequently particularly well suited for soils, for which $E_{Ca}$ values range typically from 5 to 20 Bq·kg$^{-1}$ (Girault and Perrier, 2012b).

We followed the protocol detailed in previous studies (Girault et al., 2011a,b; Girault and Perrier, 2012a,b) with two types of accumulation containers: glass bottles with volume 262 mL with sample mass of about 50 g for the T set and 100 g for the D set and a portion of the N set, and glass bottles with volume 518 mL with a sample mass of about 200 g for most of the N set. The bottle was left open so that the air concentration dropped to the ambient laboratory concentration about 50 g for the T set and 100 g for the D set and a portion of the N set domains of several kilometers size (Fig. 5). Lower values of $E_{Ca}$ for the <2 mm subsamples (Fig. 3). The two values agreed remarkably well over the whole measurement range within the experimental uncertainties, with a small, but statistically significant, excess of $E_{Ca}$ for the <2 mm subsample set (Supp. mat., Fig. S1). These experimental uncertainties are adequate for our purpose, given the large $E_{Ca}$ variation.

2.3. Magnetic parameters

The ratio of the induced magnetization by the inducing magnetic field defines the MS, which is a dimensionless parameter. Dividing MS by the density of the sample gives the low-field magnetic susceptibility, $\chi_m$, expressed in m$^3$·kg$^{-1}$ (Evans and Heller, 2003). This quantity $\chi_m$ is the combined magnetic response of all the minerals present in the bulk sample.

In the field, apparent MS was measured at all N sample locations using a hand-held field magnetic susceptibility meter (KT-9 Kappameter, Exploranium, Canada) equipped with an inductive coil and operating at a frequency of 10 kHz (Hammade et al., 2004). All measurements were well above the detection level of the instrument.

In the laboratory, samples for magnetic measurements have been dried in a stove at 40 °C, crushed into powder, and conditioned into 8 cm$^3$ plastic cube (both in IPGP, Paris, and BRGM, Orléans). In 2001 and 2002 for the T and N sets, respectively, $\chi_m$ measurements were conducted in BRGM (Clozel-Leloup and Théveniaut, 2001; Hammade et al., 2004) on a KLY3™ Kappabridge (AGICO Inc., Czech Republic), operating at 875 Hz with a field intensity of 300 A·m$^{-1}$. In 2013 in IPGP, we used a KLY2™ Kappabridge (AGICO Inc., Czech Republic), operating at 920 Hz with a field intensity of 300 A·m$^{-1}$. Experimental $\chi_m$ values are expressed in 10$^{-7}$ m$^3$·kg$^{-1}$. Experimental uncertainty is of the order of 1%. In BRGM, the Isothermal Remanent Magnetization (IRM) was induced with an electro-magnet (IM10-30, ASC Scientifìc©, USA) and measured with a JRS rotary inductometer (AGICO Inc., Czech Republic). In IPGP, IRM experiments were conducted with a vibrating sample magnetometer (VSM), a MicroMag™ model 3900 with 4-inch laboratory electromagnet (Princeton Measurements Corporation, USA). For the VSM experiments, the samples were conditioned in small gel caps. The VSM was also used to determine hysteresis parameters: saturation magnetization $M_s$, saturation remanence $M_{rs}$, coercivity $H_c$, and coercivity of remanence $H_{cr}$. The use of a VSM in IPGP is generally user-friendly, more productive, and more accurate than the use of the combination of the two others instruments used in BRGM. Finally, in 2014, thermo-magnetic experiments in weak field were performed with a KLY3™ Kappabridge in IPGP.

2.4. TE concentrations and additional chemical analyses

Lead concentration ($C_{Pb}$) was determined in the field and in the laboratory by X-ray fluorescence (Soodan et al., 2014) for the N and T sets. A subset was used to validate these measurements by comparing with results obtained using inductively-coupled argon plasma atomic emission spectrometry (ICP-AES). For the D set, $C_{Pb}$ and other metallic elements concentrations were determined by inductively-coupled argon plasma mass spectrometry (ICP-MS). Granulometric analysis and organic matter content were determined as in Douay et al. (2009). $C_{Pb}$ measured in the laboratory are given with an uncertainty of 5%.

3. Results

In this paper, the experimental uncertainties of all the measured quantities are given within one standard deviation that corresponds to a confidence level of 68%.

3.1. Effective radium concentration ($E_{Ca}$)

A total of 319 measurements of $E_{Ca}$ were carried out, representing a total of 957 radon accumulation experiments. This is the most extensive set of radon emanation data reported so far on a single site of this scale. For the N set, we compared the $E_{Ca}$ values obtained independently for the bulk and for the <2 mm subsamples (Fig. 3). The two values agreed remarkably well over the whole measurement range within the experimental uncertainties, with a small, but statistically significant, excess of $E_{Ca}$ for the <2 mm subsample set (Supp. mat., Fig. S2). This systematic test, carried out here for the first time with a large number of samples ($n = 113$), provides a unique test of the reliability of our approach, and validates the inter-comparison and aggregation of all the three sets of samples with different grain-size. For each N sample, the two values were then combined to provide a single $E_{Ca}$ value, with an experimental uncertainty of about 5% over the whole measurement range, while experimental uncertainty was of the order of 6% to 7% for the D samples. For the T samples, because of the smaller mass available, the uncertainty was of about 8% for $E_{Ca} < 5$ Bq·kg$^{-1}$, and up to 10% for $E_{Ca} < 5$ Bq·kg$^{-1}$ (Supp. mat., Fig. S1). These experimental uncertainties are adequate for our purpose, given the large $E_{Ca}$ variation.

The $E_{Ca}$ values (Table 1) range from 0.70 ± 0.06 Bq·kg$^{-1}$ to 12.53 ± 0.49 Bq·kg$^{-1}$ with an arithmetic average of 7.55 ± 0.15 Bq·kg$^{-1}$, with 90% of the data between 5 Bq·kg$^{-1}$ and 10 Bq·kg$^{-1}$ (Fig. 4a). $E_{Ca} < 5$ Bq·kg$^{-1}$ correspond to the smelter processing waste piles and one woody topsoil. The distribution of $E_{Ca}$ for this site is narrower than the large range observed over all our other soil samples measured in France so far (Fig. 4b), but has a similar average. The $E_{Ca}$ of the studied zone can therefore be considered as typical for the context of sedimentary conditions in France. By contrast, $E_{Ca} > 20$ Bq·kg$^{-1}$, which were commonly observed in lacustrine sediments and tops soils of the Kathmandu Valley, Nepal (Girault et al., 2011a), were not observed in the present case (Fig. 4a, c).

The $E_{Ca}$ dispersion in Fig. 4a is caused by significant spatial variations (Fig. 5). Indeed, similar $E_{Ca}$ are grouped in conspicuous spatial domains of several kilometers size (Fig. 5). Lower values ($E_{Ca} < 6$ Bq·kg$^{-1}$, blue in Fig. 5) are mainly found in the Scarpe Plain and at the southern edge of the Pèvèle. $E_{Ca}$ between 7 and 8 Bq·kg$^{-1}$
The kriging algorithm (Grid_3D from VisualNumerics) is used to account for the irregular spacing of the samples, based on a smooth spline function for spatial averaging. No constraints are imposed on the boundaries of the mapped domain. It is the first time that sufficient data are available to produce an EC\textsubscript{Ra} map for topsoils. The predictability of this map is discussed in the Supp. mat. (Fig. S3). The main structures, that the center of industrialized and most populated zone around the Gohelle to the south-west shows a south-west to north-east axis symmetry. The central industrialized and most populated zone around the Gohelle to the south-west shows a south-west to north-east axis symmetry. The central industrialized and most populated zone around the Gohelle to the south-west shows a south-west to north-east axis symmetry.

To produce an interpolated map of EC\textsubscript{Ra} of topsoils, a standard kriging algorithm (Grid_3D from VisualNumerics) is used to account for the irregular spacing of the samples, based on a smooth spline function for spatial averaging. No constraints are imposed on the boundaries of the mapped domain. It is the first time that sufficient data are available to produce an EC\textsubscript{Ra} map for topsoils. The predictability of this map is discussed in the Supp. mat. (Fig. S3). The main structures, that we comment below, do not depend on the exact choice of interpolation parameters. Previous studies (Girault et al., 2012; Girault and Perrier, 2014), while showing profiles of geological relevance, could not be used to produce a map. The obtained map (Fig. 6), while it is an interpolation that should be taken with caution, reflects and emphasizes data structure, with a few large-scale zones and smaller spots (of 1 to 2 km size) concentrated in some domains. To the north-east, EC\textsubscript{Ra} contours match the topographic lines of the Pévèle (Figs. 5 and 6). By contrast, the Gohelle to the south-west shows a south-west to north-east axis symmetry. The central industrialized and most populated zone around ME and along the Deûle Canal exhibits more granulated structures. The large-scale zones seem to match more with the geographical units than with possible wind transport and dispersion (see Fig. 1). From the interpolated map, we calculate a proper spatial average of EC\textsubscript{Ra} of 7.38 ± 0.03 Bq·kg\textsuperscript{-1} (Table 1) over the studied zone, corrected for the irregular spacing. The 6 reference samples located outside the studied zone have EC\textsubscript{Ra} between 2.88 ± 0.24 Bq·kg\textsuperscript{-1} and 9.45 ± 0.57 Bq·kg\textsuperscript{-1}, and an arithmetic average of 5.6 ± 1.0 Bq·kg\textsuperscript{-1}.

The spatial variations of EC\textsubscript{Ra} are then studied along two orthogonal profiles (Fig. 7) where all points at a distance smaller than 3.5 km from the profile lines (shown in Fig. 5) are included. For the AA' profile located across the Deûle Canal (Fig. 7a), the EC\textsubscript{Ra} homogeneity is remarkable at distances <15 km and >25 km. Although interpolation from the map along the profile (Fig. 6) is consistent with the data, the smoothing of the map ignores clear step-like variations, for example between positions 25 to 30 km and around position 23 km (Fig. 7a). Similar observations are made along profile BB' located along the Deûle Canal (Fig. 7b).

**Table 1**

Summary of effective radium concentration, magnetic susceptibility and lead concentration. The Deûle Valley and the Scarpe Plain are located between the Pévèle and the Gohelle (Fig. 1). Average values are arithmetic means. Spatial averages are means corrected for irregular point spacing and are computed from interpolated maps.

<table>
<thead>
<tr>
<th>Data</th>
<th>All zones</th>
<th>Pévèle</th>
<th>Deûle Valley</th>
<th>Scarpe Plain</th>
<th>Gohelle</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of samples</td>
<td>n = 186</td>
<td>n = 52</td>
<td>n = 34</td>
<td>n = 57</td>
<td>n = 43</td>
</tr>
<tr>
<td>Surface area (km²)</td>
<td>738</td>
<td>188</td>
<td>105</td>
<td>158</td>
<td>287</td>
</tr>
<tr>
<td>EC\textsubscript{Ra} (Bq·kg\textsuperscript{-1})</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Range</td>
<td>0.70 ± 0.06 to 12.53 ± 0.49</td>
<td>2.45 ± 0.15 to 10.53 ± 0.45</td>
<td>1.54 ± 0.07 to 11.34 ± 0.80</td>
<td>0.70 ± 0.06 to 12.53 ± 0.49</td>
<td>4.28 ± 0.20 to 11.70 ± 0.86</td>
</tr>
<tr>
<td>Average</td>
<td>7.55 ± 0.15</td>
<td>6.44 ± 0.22</td>
<td>8.33 ± 0.33</td>
<td>7.78 ± 0.32</td>
<td>7.96 ± 0.20</td>
</tr>
<tr>
<td>X\textsubscript{10} (10\textsuperscript{-7} m\textsuperscript{3}·kg\textsuperscript{-1})</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Range</td>
<td>0.89 ± 0.01 to 47.30 ± 0.47</td>
<td>0.89 ± 0.01 to 11.30 ± 0.11</td>
<td>1.95 ± 0.02 to 19.70 ± 0.20</td>
<td>1.36 ± 0.01 to 47.30 ± 0.47</td>
<td>2.02 ± 0.02 to 18.00 ± 0.18</td>
</tr>
<tr>
<td>Average</td>
<td>5.00 ± 0.37</td>
<td>3.44 ± 0.28</td>
<td>5.57 ± 0.56</td>
<td>5.53 ± 1.02</td>
<td>5.74 ± 0.54</td>
</tr>
<tr>
<td>C\textsubscript{Ra} (mg·kg\textsuperscript{-1})</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Range</td>
<td>18.70 ± 0.94 to 2205 ± 55</td>
<td>18.70 ± 0.94 to 525 ± 26</td>
<td>19.89 ± 0.99 to 388 ± 19</td>
<td>26.6 ± 1.3 to 2205 ± 55</td>
<td>24.2 ± 1.2 to 1580 ± 7.9</td>
</tr>
<tr>
<td>Average</td>
<td>125 ± 15</td>
<td>78 ± 11</td>
<td>91 ± 12</td>
<td>246 ± 44</td>
<td>50.8 ± 1.9</td>
</tr>
</tbody>
</table>

The spatial variations of EC\textsubscript{Ra} are then studied along two orthogonal profiles (Fig. 7) where all points at a distance smaller than 3.5 km from the profile lines (shown in Fig. 5) are included. For the AA' profile located across the Deûle Canal (Fig. 7a), the EC\textsubscript{Ra} homogeneity is remarkable at distances <15 km and >25 km. Although interpolation from the map along the profile (Fig. 6) is consistent with the data, the smoothing of the map ignores clear step-like variations, for example between positions 25 to 30 km and around position 23 km (Fig. 7a). Similar observations are made along profile BB' located along the Deûle Canal (Fig. 7b).
3.2. Comparison of $EC_{Ra}$ with soil analytical results

Despite the limited statistics of the D set, the fine fraction is found positively correlated with $EC_{Ra}$ (Fig. 8a). The enrichment of radium in the fine fraction seems to be general (Greeman et al., 1999). This fact could reflect preferential adsorption of radium to some clay minerals (Hidaka et al., 2007), but the large dispersion in Fig. 8a indicates that additional effects must contribute.

No systematic relationship is observed between $EC_{Ra}$ and Fe in the range 1 to 8% (Fig. 8b). Indeed, while some samples suggest a fast increase of $EC_{Ra}$ from 5 Bq·kg$^{-1}$ to 12 Bq·kg$^{-1}$ when Fe concentration increases from 1.0 to 2.5%, this pattern is not shared by other samples characterized by $EC_{Ra}$ < 7 Bq·kg$^{-1}$. One mechanism leading to efficient adsorption of radium in soils could be controlled by Fe (Ames et al., 1983; Flexser et al., 1993), but coexisting with another Fe independent mechanism. This suggests that radium adsorption in soils may be controlled differently by chemical, mechanical, and biological processes of alteration. A similar dual behavior is observed with As (Fig. 8c), likely related to the As/Fe ratio in topsoils (Girault et al., 2011a).

The relationship between $EC_{Ra}$ and Hg concentration seems significant despite limited statistics (Fig. 8d), possibly suggesting common preferential adsorption of radium and Hg to the fine clay fraction, Fe-oxy-hydroxides, and organic matter. Further chemical analyses are considered in Supp. mat. (Fig. S4).

3.3. Comparison of $EC_{Ra}$ with MS

For the N set, MS measured in the laboratory is consistent for bulk and <2 mm grain-size subsamples (Supp. mat., Fig. S5a). In addition, MS measured in the laboratory for bulk and <2 mm grain-size subsamples is consistent on average with MS measured in the field (Supp. mat., Fig. S5b, c). This demonstrates that the measurement of MS in the field can be generalized to obtain rapidly first-order MS of topsoils.
To further check the reliability of the MS data, the data obtained in 2002 in BRGM were compared with the data obtained in 2013 in IPGP (Supp. Mat., Fig. S6). In the following, we use the $\chi_m$ data obtained in the laboratory for bulk samples.

In the whole data-set, $\chi_m$ values range from $(0.89 \pm 0.01) \times 10^{-7}$ to $(47.30 \pm 0.47) \times 10^{-7}$ m$^3$ kg$^{-1}$, with an average of $(5.00 \pm 0.37) \times 10^{-7}$ m$^3$ kg$^{-1}$ (Table 1). The largest $\chi_m$ is obtained for the ditch sample (N set), characterized by $E_{C_{Ra}}$ of $3.45 \pm 0.15$ Bq kg$^{-1}$, and the second largest, with $(41.10 \pm 0.41) \times 10^{-7}$ m$^3$ kg$^{-1}$, is obtained for a processing residue located near ME and characterized by the smallest $E_{C_{Ra}}$ ($0.70 \pm 0.06$ Bq kg$^{-1}$). These maximum $\chi_m$ values are, however, far from being exceptional. A similar peak value of $\chi_m$ ($43.3 \times 10^{-7}$ m$^3$ kg$^{-1}$) was reported in an industrial zone in China (Xia et al., 2014), and larger maximum $\chi_m$ values are reported: for example, $114.7 \times 10^{-7}$ m$^3$ kg$^{-1}$ in Styria (Hanesch and Scholger, 2002) or $121 \times 10^{-7}$ m$^3$ kg$^{-1}$ in Mexico City (Morton-Bermea et al., 2009).

The spatial variations of $\chi_m$ also display remarkable spatial coherence over the full site scale, as illustrated by the interpolated map (Fig. 7).

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**Fig. 7.** Orthogonal profiles of $E_{C_{Ra}}$ and $\chi_m$ versus distance. Location of profiles is shown in Fig. 5. Bold grey lines correspond to the profiles from the interpolated maps (Figs. 6 and 9).

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**Fig. 8.** Soil sample characterization versus $E_{C_{Ra}}$ for N samples (circles) and D samples (diamonds): (a) fine fraction content, (b) iron concentration, (c) arsenic concentration, and (d) mercury concentration.
9). The west of the industrial site concentrates $\chi_m > 10 \times 10^{-7} \text{ m}^3 \cdot \text{kg}^{-1}$ at distances larger than 15 km from ME, and are unlikely due to the smelters. This region is densely populated (INSEE, 2012), with the agglomeration of Lens (Fig. 1) surrounded by large numbers of highways. This relation between MS of topsoils and population density is consistent with the work of Jordanova et al. (2014). An extended uniform domain to the south and to the east of ME shows $\chi_m < 4 \times 10^{-7} \text{ m}^3 \cdot \text{kg}^{-1}$. Spots of high $\chi_m$ characterize the Deûle Valley near ME (Fig. 9), likely resulting from the smelter activities. As observed for $EC_{Ra}$, the interpolated map of $\chi_m$ provides an improved estimate of the spatial average of $(4.83 \pm 0.06) \times 10^{-7} \text{ m}^3 \cdot \text{kg}^{-1}$ for the studied zone. This is significantly larger than the average $\chi_m$ of $(2.54 \pm 0.34) \times 10^{-7} \text{ m}^3 \cdot \text{kg}^{-1}$ obtained for the 6 reference samples outside the studied zone.

The large-scale spatial homogeneity of $\chi_m$ is shown along the two orthogonal profiles (Fig. 7). Whereas regions of the profiles have a rather stable mean $\chi_m$ value, typically for distances <15 km and >24 km in profile AA’ (Fig. 7a), fluctuations around the mean tend to be larger for $\chi_m$ than for $EC_{Ra}$. However, we observe the opposite for distances >25 km in profile BB’ (Fig. 7b). Larger and erratic fluctuations of $\chi_m$ characterize the central and most industrialized zones in both profiles. Most of the small-scale structures in the $\chi_m$ profiles do not seem to be correlated with small-scale structures in the $EC_{Ra}$ profiles.

### 3.4. $EC_{Ra}$ and MS versus geographical domains

Large-scale organization is further evidenced by considering separately the four geographical units of the studied area (Fig. 10 and Table 1). The Pévèle and the Gohelle show narrower $EC_{Ra}$ distributions than the Deûle Valley and the Scarpe Plain, but significantly different averages: $6.44 \pm 0.22 \text{ Bq} \cdot \text{kg}^{-1}$ for the Pévèle and $7.96 \pm 0.20 \text{ Bq} \cdot \text{kg}^{-1}$ for the Gohelle. These differences remain for $EC_{Ra}$ and $\chi_m$ when spatial averaging is performed (Table 1). By contrast, $C_{Pb}$ is more similar in both regions: $78 \pm 11 \text{ mg} \cdot \text{kg}^{-1}$ for the Pévèle and $50.6 \pm 3.9 \text{ mg} \cdot \text{kg}^{-1}$ for the Gohelle. Significantly different distributions are noticed in the Deûle Valley and the Scarpe Plain for the three variables $EC_{Ra}$, $\chi_m$, and $C_{Pb}$. Finally, mean $C_{Pb}$, when averaged spatially using the interpolated map (Table 1), shows the same value for the Pévèle and the Deûle Valley (about 60 mg·kg⁻¹), a smaller value for the Gohelle (about 48 mg·kg⁻¹), and a larger value for the Scarpe Plain (about 120 mg·kg⁻¹). The regional relationship between $EC_{Ra}$ and $\chi_m$ is further considered in the Supp. mat. (Fig. S7).

### 3.5. Lead concentration versus $EC_{Ra}$ and MS

Other effects of TE are observed when $\chi_m$ is considered together with $EC_{Ra}$, for three different domains in $C_{Pb}$ (Fig. 11). Samples with $C_{Pb}$ between 100 and 300 mg·kg⁻¹ form a cloud with a mean $\chi_m$ of $(4.46 \pm 0.38) \times 10^{-7} \text{ m}^3 \cdot \text{kg}^{-1}$ and a mean $EC_{Ra}$ of $8.17 \pm 0.29 \text{ Bq} \cdot \text{kg}^{-1}$, while samples with $C_{Pb}$ smaller than 100 mg·kg⁻¹ form a cloud with a similar mean $\chi_m$ of $(4.38 \pm 0.25) \times 10^{-7} \text{ m}^3 \cdot \text{kg}^{-1}$ and a significantly smaller mean $EC_{Ra}$ of $7.33 \pm 0.16 \text{ Bq} \cdot \text{kg}^{-1}$. The dispersion of $\chi_m$ around the mean appears larger for $C_{Pb}$ smaller than 100 mg·kg⁻¹ than for $C_{Pb}$ between 100 and 300 mg·kg⁻¹, i.e., $2.9 \times 10^{-7} \text{ m}^3 \cdot \text{kg}^{-1}$ versus $2.4 \times 10^{-7} \text{ m}^3 \cdot \text{kg}^{-1}$ (Fig. 11). Although the processing residues have extremely large $C_{Pb}$ (>800 mg·kg⁻¹; Supp. mat., Fig. S8), the largest $\chi_m$ (>15 × 10⁻⁷ m³·kg⁻¹), and $EC_{Ra}$ < 5 Bq·kg⁻¹, most samples with large $\chi_m$ tend to cluster at large $EC_{Ra}$.

The stability of $\chi_m$ versus $C_{Pb}$ hides a more complex relationship, essentially dominated by the regional spatial dependence (Figs. 10 and S7). This is also visible when looking versus distance to the ME smelter (Supp. mat., Fig. S9). In a given region, an increase of $C_{Pb}$ is clearly correlated with an increase of $\chi_m$, a fact easily obscured because of the similar amplitudes of the effect of the increase of other TE concentrations and the effect of regional variations. Similar effects are observed with Zn (Supp. mat., Fig. S10).

The particular relationship observed here between $\chi_m$ and $EC_{Ra}$ can be compared with other sites (Fig. 12). Sites from Nepal include topsoils, sediments, and laterites (Girault et al., 2011b). Topsoils sampled near a road show $\chi_m$ values similar to the ME area, which could suggest that these soils are contaminated by traffic. This explanation, however, is not convincing, because the traffic in Nepal at this high altitude cannot compare with the exposure of the Northern France region. A more likely explanation would be, in both cases, significant soil and bedrock contribution to $\chi_m$. Alternatively, higher $\chi_m$ values for topsoils could reflect the well-known Le Borgne effect of enhancement of $\chi_m$ for topsoils (Le Borgne, 1955), but, as most samples from the ME area come from agricultural ploughed land, this particular effect should have been washed away.

Sediments taken around reference profiles in unpolluted areas display a remarkable correlation between $\chi_m$ and $EC_{Ra}$ (Fig. 12), with significantly smaller $\chi_m$ values (between 0.09 × 10⁻⁷ m³·kg⁻¹ and 4 × 10⁻⁷ m³·kg⁻¹). This type of relationship is confirmed by sediments sampled between surface and 1 m depth in the compound of the French Magnetic Observatory of Chambon-la-Forêt, located in the Orléans forest in the center of France. Overall, despite their internal variability, topsoils from the ME area cover a relatively small fraction of the domain observed so far in Fig. 12.

### 4. Discussion

#### 4.1. Significance and interpretation of the effective radium concentration

The observed properties of $EC_{Ra}$ reflect several factors. First, well-identified regional compartments clearly emerge within the studied area. Second, on top of this soil source, two effects can be superimposed: (1) redistribution of the soils by erosion and colluviation, and (2) re-modeling of the soils by industrial or urban changes. These two effects can lead to soil mixing and transport, possibly from the loessic soils of the Pévèle and the Gohelle to the colluvial and alluvial soils of the Deûle Valley and the Scarpe Plain (Deschodt et al., 2012). The homogeneity of the loess characteristics and $EC_{Ra}$ values within both the Pévèle and the Gohelle suggests that soil transport in the opposite direction is not an important effect.
For most samples taken in agricultural land, ploughing should have homogenized the first 30 cm of soil, which may also have contributed to smooth out laterally the EC$_{Ra}$ values. Furthermore, for these agricultural soils, in the case of EC$_{Ra}$ as for all other parameters, it should be kept in mind that, while some source terms, natural or industrial, have time-scales larger than decades, what remains in the soil has been modified by changes in land use and crop uptake. Like TE, heavy radionuclides, including radium, are assimilated by roots, but this seems to concern mostly mosses, shrubs, and trees (Noskova et al., 2010). To a first approximation, we can interpret EC$_{Ra}$ data using the idea that it reflects the ability of soils to fix, leach, and transfer radium to the external biosphere, which can be proposed as a locally-calibrated proxy or a local (meter or sample-scale) reference for the same set of processes affecting TE pollution and $\chi_m$. Thus, the knowledge of EC$_{Ra}$ provides some knowledge of part of the variability of TE concentrations and $\chi_m$, which is what we observed in our data-set. Then, some schemes emerge to make use of EC$_{Ra}$ in order to clarify the specific distributions produced by the pollution sources.

The effect of the industrial activities, at least the part leading to TE release, can be separated into three components: (1) the spreading of solid mineral waste, for example the mixing of processing products with local soils in various constructions or storages; (2) the release of liquid waste, leading to river sediments which can end up later in agricultural land, in particular during a flood; and (3) aerial dust dispersion, the latter being the dominating component in the ME area (Douay et al., 2008). Furthermore, for agricultural soils, and even more for woody soils, the effects of urban activities can also be important (Douay et al., 2009).

Samples resulting from direct solid inputs are characterized by low EC$_{Ra}$ values, as no uranium ore has been processed at this site. Conversely, in this context of little bedrock exposure and thick Quaternary sediments coverage, it is not unreasonable to assign small EC$_{Ra}$ values to processing plants in the absence of other information. Samples with larger EC$_{Ra}$ could reflect larger fine fractions, as suggested by Fig. 8a. In general, clay content increases radium adsorption of soils during pedogenesis (Greeman et al., 1999; Girault et al., 2011a), which could also be associated with larger TE affinity and explain the features of Fig. 12. Globally, the quantity EC$_{Ra}$ can be considered as a condition parameter of the soil, before being subjected to TE aerial deposition. Subsequent evolution would be characterized by $\chi_m$. It is therefore important to characterize the magnetic features of the samples in more details.

Fig. 10. Distributions of EC$_{Ra}$, $\chi_m$, and $C_{Pb}$ separately for the four geographical units defined in Fig. 1. Average and range of values are gathered in Table 1.

Fig. 11. EC$_{Ra}$ versus $\chi_m$ for three domains of $C_{Pb}$. 

<table>
<thead>
<tr>
<th>Sample</th>
<th>Data</th>
<th>Number of data</th>
<th>$EC_{Ra}$ (Bq kg$^{-1}$)</th>
<th>$\chi_m$ ($10^{-7}$ m$^3$ kg$^{-1}$)</th>
<th>$C_{Pb}$ (mg kg$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pevele</td>
<td>(n=52)</td>
<td>0 to 10</td>
<td>5 to 10</td>
<td>2 to 8</td>
<td></td>
</tr>
<tr>
<td>Deule Valley</td>
<td>(n=34)</td>
<td>0 to 10</td>
<td>5 to 10</td>
<td>2 to 8</td>
<td></td>
</tr>
<tr>
<td>Scarpe Plain</td>
<td>(n=57)</td>
<td>0 to 10</td>
<td>5 to 10</td>
<td>2 to 8</td>
<td></td>
</tr>
<tr>
<td>Gohelle</td>
<td>(n=43)</td>
<td>0 to 10</td>
<td>5 to 10</td>
<td>2 to 8</td>
<td></td>
</tr>
</tbody>
</table>
IRM curves show that all samples are saturated above 0.3 T (Supp. mat., Fig. S11a, complementing Fig. 19 in Clozel-Leloup and Théveniaut, 2001). Magnetic minerals with higher coercivity are probably missing or, more presumably, present with a very low concentration and not measurable. The similar shape of the IRM gradient for all the D samples (Supp. mat., Fig. S11b) suggests that the main carrier of remanence is a mineral of weak coercivity like magnetite or maghemite (Kruiver et al., 2001).

Although identification of minerals is rather complicated (Maher and Thompson, 1999; Evans and Heller, 2003; Liu et al., 2012), the main carrier of magnetization is probably magnetite, with possibly an increase of magnetite content close to the smelters (Supp. mat., Fig. S13). This is indeed supported by the Day diagram (Day et al., 1977; Dunlop, 2002; Liu et al., 2012) in Fig. 13 (see Table S1 in the online version at http://dx.doi.org/10.1016/j.scitotenv.2016.05.007, for the sample description), that provides information on the size of the magnetic grains. While the determination of hysteresis parameters reflects the contribution of the whole sample, which is a combination of magnetic multi-domain (MD) and single domain grains (SD), the characteristics of the main carrier of magnetization (probably magnetite) lie in the pseudo-single domain (PSD) area next to the MD area in a Day diagram. This is compatible with what is reported by other authors in similar circumstances (Xia et al., 2014).

Thermo-magnetic experiments in weak field were performed for 10 samples. For all samples, the curves are similar to those of the four selected samples (Supp. mat., Fig. S14). The results confirm the presence of magnetite or substituted magnetite, possibly in coarse grains, and a mixture with maghemite. However, it is not possible at this stage to clearly define the type of magnetite, a point that remains always a delicate matter (Franke et al., 2009). A secondary magnetic mineral could be a ferrimagnetic iron sulfide such as pyrrhotite and its oxidation products oxy-hydroxides (Belzile et al., 2004), but sulfur concentration is generally low in our studied topsoils.

If coarse magnetite is the main carrier of $\chi_m$, no enhancement of $EC_{Ra}$ is expected near the smelters. On the other hand, two factors that might contribute to the $\chi_m$ of regional soils are the organic carbon content and the presence of iron oxides (Porsch et al., 2014), which contribute both to $EC_{Ra}$ also. The observed relation between $\chi_m$ and $EC_{Ra}$ then would mainly reflect the sampling and these natural sources of $\chi_m$ enhancement. Indeed, the large-scale regular grid of the N samples would enhance the regional signal with respect to the local introduction of coarse magnetite, visible only in the vicinity of the smelters.

5. Conclusion

In this paper, we have studied the benefit of effective radium concentration ($EC_{Ra}$) to the mapping and characterization of trace elements pollution in topsoils at an industrial site that has produced extensive dust emissions for almost a century. It is the first time that radon emanation measurements of soils are carried out in such an industrialized and urbanized context, in the absence of uranium ore processing pollution. Thanks to the large number of sampling sites ($n = 186$), a map of $EC_{Ra}$ could be produced for the first time.

In the studied area, soil $EC_{Ra}$ was low (10 Bq·kg$^{-1}$) and no local anomaly was identified. Thus, the measurement of $EC_{Ra}$ probably reflected the local variations of radium concentrations in the topsoil. The remarkable uniform $EC_{Ra}$ values in the Pévèle and the Gohelle...
showed that natural domains in agricultural soils were preserved despite the long history of land use and human activities. Remodeling seems to contribute to large mixing only in the alluvial plains, where natural mixing processes also may play a major role. Thus, the cartography of $E_{Ra}$ outlines natural domains in a complex region, which is important information in order to be able to differentiate anomalous and normal parameters of a given soil.

Spatial variability of $\chi_{m}$ is not necessarily easy to interpret, because the large signals from the smelter emissions are rapidly diluted away from the smelters by diffuse traffic emissions and other urban TE emitters, and the natural variations due to local pedogenetic factors and bedrock. However, when studied together with $E_{Ra}$, regional structures can be more easily identified. In the studied site, with spatial scale of 20 to 40 km, the polluted area shares features with several natural domains (i.e., here the geographical units), and $E_{Ra}$ provides a useful tool to disentangle the spatial structure induced by the pollution sources within the spatial structure of the local background.

The significant blurring and dispersion of $E_{Ra}$ and $\chi_{m}$ could be the main signature of pollution and soil degradation processes due to human activity. Such dispersion, unobserved in sediments unaffected by pollution, could indicate unknown polluted areas. More work is needed to characterize this dispersion and whether it can be used to define a soil degradation factor. In general, the current knowledge on the evolution of soils in heavily urbanized contexts is poor, especially in the presence of industrial pollution. Reference samples are usually in small numbers, while what is commonly called reference or background can be complex and deserves extreme attention (Dung et al., 2013).

Having a reference region for agricultural soils, in the absence of pollution, in various geological contexts would thus be valuable.

To make progress on the interpretation of $E_{Ra}$ in the presence or not of TE pollution, a better understanding of radiometric transport processes in soils is needed, as well as the transfer of radium to the biosphere (Noskova et al., 2010). The use of $E_{Ra}$ as a proxy of the ability of a soil to fix and release TE could be tested in the laboratory using for example leaching experiments. In the case of TE residing in the soils for long periods of time since their industrial production, the biological factor in the evolution of the signatures is an important parameter (Stefanowicz et al., 2009). For the production of the $\chi_{m}$ signature of soils, extensive data-sets suggest a largely abiogenic system where the formation of secondary ferrimagnetic minerals is essentially controlled by the weathering capacity to supply iron to the surface soils (Blundell et al., 2009). The subsequent co-evolution of the soils and its TE, with or without large $\chi_{m}$, might be totally different. For example, microbial degradation of hydrocarbon by iron reducing bacteria produces a unique $\chi_{m}$ signature (Atekwana et al., 2014), which could be overwhelmingly present in urban industrial zones. Such reactions could also lead to TE leaching, and therefore signatures in terms of $E_{Ra}$.

While the use of $E_{Ra}$ remains at its infancy, measuring this parameter is easy and cost-effective in large numbers of samples, and deserves some attention in the field of soil pollution. Given the importance of improving our ability to diagnose soils as well as other parts of our environment, it is the duty of applied and fundamental Earth scientists to work together to create new methods and improve the efficiency of the existing ones.

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References


