Supplementary Material

Effective radium concentration in topsoils contaminated by lead and zinc smelters by Girault et al., Science of the Total Environment, 2016

SM1. Experimental uncertainties on $EC_{Ra}$

The relative uncertainties on $EC_{Ra}$ of this study topsoil samples are shown in Fig. S1 versus $EC_{Ra}$. The two main contributions to the uncertainty on $EC_{Ra}$ of a single sample come from the counting statistics and the dilution correction during sampling (Girault and Perrier, 2012a). The increase of the uncertainty at low $EC_{Ra}$ is due to the smaller counting rate. For the N set, two subsamples were available: the bulk subsample and the < 2 mm grain-size subsample (Fig. 3 in the main text). As the $EC_{Ra}$ values for these two subsamples were compatible (see below), they were averaged, leading to a significant reduction of the uncertainties. In the case of the T set and the reference samples, the amount of available mass was smaller (50 g instead of 100 g or 200 g), and the measured radon concentration was therefore smaller for the same $EC_{Ra}$, leading to larger uncertainties, still largely sufficient for the present purpose.

Fig. S1. Relative experimental uncertainty in per cent as a function of the measured $EC_{Ra}$ value, separately for D samples, N samples, T samples and reference samples, and all other soils measured so far in other locations.
SM2. Systematic comparison of the subsamples available for N samples

For the N set, the distribution of the difference between $EC_{Ra}$ of the < 2 mm grain-size subsample minus $EC_{Ra}$ of the bulk subsample divided by the average of the two subsamples is shown in Fig. S2. This provides a finer comparison of the two values, one against the other, than in Fig. 3 in the main text. The average of this distribution is 2.1±0.9 % and its standard deviation is 9.6±0.6 %. While the effect is small, there is a statistically significant excess of the $EC_{Ra}$ of the < 2 mm subsample above the $EC_{Ra}$ of the bulk subsample. On average, the absolute difference is 0.46±0.17 Bq·kg$^{-1}$. The effect is compatible with the understanding that finer fractions in general are characterized by larger $EC_{Ra}$ (Girault and Perrier, 2012b), which is consistent with the known affinity of radium with clay minerals (Greeman et al., 1999). This small effect will be neglected in this study. Overall, the distribution is well reproduced by a Gaussian having the same mean and RMS, shown as the full line in Fig. S2.

![Fig. S2.](image)

Fig. S2. Relative difference in per cent between $EC_{Ra}$ measured for < 2 mm fraction with respect to the bulk sample.
SM3. Statistical test of the interpolated map

The overall quality of the $EC_{Ra}$ map displayed in Fig. 6 in the main text, which covers about 783 km$^2$, can be tested in the following manner. At each location where an $EC_{Ra}$ value is available, a new map is calculated by using all points except the considered point. Then, the value actually measured at that location is compared with the value proposed by the map. The distribution of such first-exclusion residuals is shown in Fig. S3. The average is 0.36±1.90 %. Thus, there is no systematic bias, but there is a dispersion of 26 %, which is rather large. This test indicates that the $EC_{Ra}$ from the map is meaningful, but the experimental value has a smaller uncertainty, on average, than the dispersion of the map. This suggests that the map is still insufficiently constrained, and that the data at this site contain more structures than accounted for by the map. This conclusion is also suggested by the observation that the distribution differs significantly from the Gaussian distribution having the same mean and same RMS, shown by the full line in Fig. S3. The distribution of the residuals, in particular, shows several peaks, which suggests local structures unaccounted for by the interpolated map, a fact clearly visible with the profiles shown in Fig. 7 in the main text. Therefore, the interpolated map can be useful to get a global view, but is not sufficient to account for localized rapid variations. This problem is inherent with kriging of natural data. Geology of bedrock, geographical surface processes, and human activities tend to create local zones of large dispersion at the borders of discrete, more uniform domains of various sizes.

Fig. S3. Difference between the $EC_{Ra}$ value measured at one location minus the value given by the interpolated map calculated without this particular data point.
SM4. $E_{\text{Ra}}$ and chemical elements

Other chemical analyses are compared with $E_{\text{Ra}}$ for the D and N sets (Fig. S4). $E_{\text{Ra}}$ increases with organic matter content (Fig. S4a), for which radium has a strong affinity (Greeman et al., 1999; Hidaka et al., 2007). In addition, the $E_{\text{Ra}}$ increase may also be related to the presence in topsoil of some bacteria, able to degrade and remobilize some minerals or grains and to increase the emanation factor $E$ of the topsoil through the formation of biofilms at the surface of the mineral grains.

No clear relation is observed between $E_{\text{Ra}}$ and uranium concentration (Fig. S4b). Such uranium concentrations are commonly found in agricultural soils exempt of uranium pollution, consistent with the fact that no U contamination is reported in the studied area (Sterckeman et al., 2002). This suggests that radium in the topsoils of the studied site may mainly result from secondary mineralization. Although the number of samples is small, these all are taken from ploughed cultivated lands and show relationships between $E_{\text{Ra}}$ and both Ag and Se concentrations of the soil (Fig. S4c,d). The increase of $E_{\text{Ra}}$ with Ag and Se concentrations may be related to the pollution from the smelters (Sterckeman et al., 2002), partly complicated for Se through its particular mobility in soils, but possibly also to the presence of fertilizers in the topsoils and to the sedimentary bedrock.

Fig. S4. Soil sample characterization versus $E_{\text{Ra}}$ for N samples (circles) and D samples (diamonds): (a) organic matter content, (b) uranium concentration, (c) silver concentration, and (d) selenium concentration.
SM5. Quality of the measurements of MS

Similarly to the $EC_{Ra}$ data-set, the methodology used to measure MS on one hand, and the effect of the < 2 mm grain-size fraction on the other hand, have been studied (Fig. S5). To do this, we used the entire N set for which MS was determined directly in the field, in the laboratory on the bulk subsamples, and in the laboratory on the < 2 mm grain-size fraction subsamples. The MS values obtained in the laboratory on the bulk subsamples and on the small grain-size fraction subsamples are compatible, with a mean relative difference of 7±3 % only (Fig. S5a). Crushing and sieving of the < 2 mm grain-size fraction subsamples may also tend to homogenize the sample and to reduce the dispersion of the results between samples.

Comparisons of the MS values in the field with those on the bulk and the small grain-size fraction subsamples in the laboratory lead to larger differences (Figs. S5b,c). Indeed, measurements performed in the laboratory show significantly larger MS, with mean relative differences of 23±5 % for bulk subsamples and 18±4 % for the small grain-size fraction subsamples, compared to measurements performed in the field. These differences are relatively small, given the fact that the methodology and the instruments were different, which suggests that the use of the hand-held field magnetic susceptibility meter (KT-9 Kappameter, Exploranium, Canada) can be generalized in the field for systematic surveys and to obtain rapidly a first-order MS value of the topsoil (Hammade et al., 2004).
Fig. S5. Comparison of the magnetic susceptibility values for the entire N set: (a) between MS on bulk sample in the laboratory and MS of the < 2 mm sample fraction in the laboratory, (b) between MS measured on bulk sample in the laboratory and MS measured in situ, (c) between MS measured on the < 2 mm sample fraction in the laboratory and MS measured in situ.
The measurements of low-field magnetic susceptibility, $\chi_m$, in BRGM and IPGP are compared for a subset of N samples (Fig. S6). $\chi_m$ values obtained in IPGP in 2013 are 14±4 % smaller than those obtained in BRGM in 2002 on the same samples. The agreement between the two sets of values is satisfactory, given the fact that the exact methodology and the instruments were different (see main text), and that samples could have evolved due to the long storage between 2002 and 2013. Relative variations between samples, however, are in remarkable agreement. The $\chi_m$ data obtained in BRGM and in IPGP, therefore, can be combined safely for the present study.

**Fig. S6.** Comparison of $\chi_m$ measurements performed on the same samples in BRGM in 2002 and in IPGP in 2013.
SM6. $EC_{Ra}$ and MS versus geographical units

The regional relationship between $EC_{Ra}$ and $\chi_m$ emerges also from the two dimensional plot (Fig. S7). The samples from the Pévèle and the Gohelle form rather separated clouds, while the samples from the Deûle Valley and the Scarpe Plain are scattered over the available range. When considering the separation line drawn in Fig. S7, 72 % of the points from the Gohelle lie above the line, while 76 % of the points from the Pévèle lie below. The separation is not total, but considerably better than what can be achieved with $EC_{Ra}$ or $\chi_m$ alone. While the barycenters of the clouds are well separated in Fig. S7, a large dispersion is observed, of the same order of magnitude as the mean separation.

![Fig. S7. $\chi_m$ versus $EC_{Ra}$ separately for the four geographical units defined in the main text.](image-url)
SM7. MS and lead concentration versus geographical units

The relationship between $\chi_m$ and $C_{Pb}$ is shown in Fig. S8. While $\chi_m$ values larger than $30 \times 10^{-7}$ m$^3$·kg$^{-1}$ are characterized by $C_{Pb}$ larger than 400 mg·kg$^{-1}$, the opposite is not true, and the relationship between $\chi_m$ and $C_{Pb}$ depends dramatically on the geographical unit.

The dependence of $\chi_m$ on the geographical unit is not only an effect of the distance to the ME smelter, as shown in Fig. S9a, but the relation for distances larger than 5 km depends on the geographical unit, and does not appear dominated by distance. This could be due to the fact that $\chi_m$ is dominated by a diffuse source or a smelter contribution depending on the region, for example because of the mean wind trends (Fig. 1 in the main text), or by pedogenic or remodeling processes that have now washed away the local origin of the pollution, and mixed the pollution input with natural enhancements of $\chi_m$. Clearly, $\chi_m$ can be used safely as a proxy of TE pollution only for distances smaller than 5 km at this studied site. The dependence of $EC_{Ra}$ on the geographical unit is also shown in Fig. S9b.

![Fig. S8. $\chi_m$ versus $C_{Pb}$ separately for the four geographical units defined in the main text.](image)

![Fig. S9. (a) $\chi_m$ and (b) $EC_{Ra}$ measured in the laboratory as a function of the distance to the ME smelter, separately for the four geographical units defined in the main text.](image)
SM8. MS versus $EC_{Ra}$ and zinc concentration

The second TE produced by ME and NY smelters in large quantities is Zn, with concentrations in topsoils varying from 500 mg·kg$^{-1}$ to about 4000 mg·kg$^{-1}$ for the samples having also the largest $C_{Pb}$ (Fig. S10). Fig. S10 is similar to Fig. 11 in the main text for the case of Pb. Indeed, for these topsoils sampled at distances mostly larger than a few kilometers from either the ME smelter or the NY smelter, Pb and Zn concentrations are correlated. It is clear again that, while the most Zn polluted samples have large $\chi_m$, the opposite is not true, and samples with significant TE concentrations can have small $\chi_m$, but then large $EC_{Ra}$, which suggests significant fine clay fraction.

![Diagram](image-url)

**Fig. S10.** $EC_{Ra}$ versus $\chi_m$ for three domains of zinc concentration.
SM9. Magnetic parameters of topsoils at the studied site

IRM curves are shown in Fig. S11, complementing earlier data shown in figure 19 in Clozel-Leloup et al. (2001). All samples are saturated above 0.3 T. Magnetic minerals with higher coercivity are probably missing or, more presumably, present with a very small concentration with no measurable effect. This tends to show that the main carrier of remanence is a mineral having a weak coercivity like magnetite or maghemite.

Some differences are nevertheless observed within the D set (Fig. S11a,b). At low magnetic field, all the samples studied show similar behavior, except samples D3 and D7. The saturation is obtained for larger magnetic field in the case of samples D6 and D1 compared with all other samples studied. As shown in Fig. S12, samples D3 and D7 are located less than 2 km around the ME smelter and show intermediate $E_{C_{Ra}}$. Samples D6 and D1 are located more than 4 km away from the ME smelter and show smaller $E_{C_{Ra}}$ (Fig. S12). Samples characterized by similar $E_{C_{Ra}}$ exhibit generally similar IRM curves, a point that should be studied in more detail.

![Fig. S11.](image)

(a) Normalized Isothermal Remanent Magnetization (IRM) acquisition curves obtained in IPGP with the D samples in 2013. (b) Gradient of the IRM as a function of the applied magnetic field (Kruiver et al., 2001).
The saturation obtained at 0.8 T has been used to determine the $\text{IRM}_{0.8T}/\chi_m$ ratio (Fig. S13). These results confirm that probably the main carrier of magnetization is magnetite. Indeed, it is well accepted that presence of sulfides or minerals other than magnetite can be characterized by a ratio greater than $20 \times 10^3$ A.m$^{-1}$. In Fig. S13, the $\text{IRM}_{0.8T}/\chi_m$ ratios tend to rise up to an asymptotic value equal to a reference level, defined by the 6 reference samples. Although the size of the magnetic grains can have an effect, this trend could be explained by an increase of magnetite content close to the smelters.
Thermo-magnetic experiments in weak field were done for a total of 10 samples. In Fig. S14 are shown the results obtained for four samples. These samples have been selected because they show the main characteristics of all samples for which thermo-magnetic experiments have been conducted (see Table S1). The shape of the curves during heating shows a drop among a wide range of temperature, varying between 500 °C and 600 °C. This is consistent with the presence of magnetite or substituted magnetite coarse grains (PSD grains). A mixture of maghemite is also characterized by the drop of MS over the Curie temperature of magnetite (575 °C). A bump from 280 °C to 300 °C reveals the presence of a secondary magnetic mineral, which in this case could be a ferrimagnetic iron sulfide. The Curie temperature of pyrrhotite is 325 °C and the oxidation product of pyrrhotite is generally oxy-hydroxides (Belzile et al., 2004). However, sulfur concentration is generally low in our studied topsoils, and both the increase of MS for the cooling curves and the disappearance of the bump could be due to other mineralogical transformations.

Fig. S14. Thermo-magnetic experiments for four selected samples of the study site.