

Tracing Source Pollution in Soils Using Cadmium and Lead Isotopes

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Tracing the source of heavy metals in the environment is of key importance for our understanding of their pollution and natural cycles in the surface Earth reservoirs. Up to now, most exclusively Pb isotopes were used to effectively trace metal pollution sources in the environment. Here we report systematic variations of Cd isotope ratios measured in polluted topsoils surrounding a Pb–Zn refinery plant in northern France. Fractionated Cd was measured in soil samples surrounding the refinery, and this fractionation can be attributed to the refining processes. Despite the Cd isotopic ratios being precisely measured, the obtained uncertainties are still large compared to the total isotopic variation. Nevertheless, for the first time, Cd isotopically fractionated by industrial processes may be traced in the environment. On the same samples, Pb isotope systematics suggested that materials actually used by the refinery were not the major source of Pb in soils, probably because refined ore origins changed over the 100 years of operation. On the other hand, Cd isotopes and concentrations measured in topsoils allowed identification of three main origins (industrial dust and slag and agriculture), assuming that all Cd ores are not fractionated, as suggested by terrestrial rocks so far analyzed, and calculation of their relative contributions for each sampling point. Understanding that this refinery context was an ideal situation for such a study, our results lead to the possibility of tracing sources of anthropogenic Cd and better constrain mixing processes, fluxes, transport, and phasing out of industrial input in nature.

Introduction

The anthropogenic impact on the trace metal cycle has been significant since the Roman period (1–3) but became more important in the past 150 years. Numerous researchers have tried to determine the source of the metal pollution in the environment by using variations in concentrations and enrichment factors relative to natural “crustal” inputs. Up

to now, most exclusively Pb isotopes were used to effectively trace metal pollution sources in the environment using sediments (4, 5), peat bogs (6, 7), ice and snow (8), lichens (9–11), soils (12, 13), and others (14–16). Nevertheless, other trace metal pollution was detected in the environment, including that from Cd.

Cadmium isotope ratios have been commonly measured in meteorites and other extraterrestrial samples to study the mass-dependent fractionation for cosmochemical applications (17–20). Because no or less significant Cd isotopic variations were found in natural terrestrial samples, including ore deposits (20–22), environmental Cd tracing was done exclusively by the use of concentration variations (23–26). However, the low boiling point (765 °C) of Cd favors the solid-phase–gas-phase change (used in chemical industries for metal purification) and may lead to isotope fractionation if total transformation from solid to gas, or gas to solid, is not reached or if Cd phases are physically separated from one another during the phase change reaction. Recently, large Cd isotopic fractionations were reported for industrially partly evaporated Cd metal (20, 22, 27, 28), suggesting that anthropogenic processes may lead to a few per mil (‰) variation of the ¹¹⁴Cd/¹¹⁰Cd isotope ratio. As a result, Cd isotopically fractionated by industrial processes reaching the environment might be detected. Whereas Pb isotopes will directly trace sources, Cd isotopes might trace anthropogenic fractionations.

In this study, we searched for anthropogenic fractionated Cd in soils sampled near an important Pb–Zn refinery plant, from which dusts and slag Cd isotopic composition were already reported (22) and shown to be fractionated from natural soil and rock samples. Here, we demonstrate that precise Cd isotope measurements provide a new tracer tool in the environment for source pollution identification. Along with Pb isotopes, cadmium isotopic composition may then be used in other polluted areas to identified metal anthropogenic sources.

Materials and Methods

Samples used in this study were agricultural soils, and dusts and slag from a Pb–Zn refinery plant (Metaleurop) located in Noyelles-Godault, Northern France. Previous studies have been clearly successful in the identification of the refinery as the major source of trace metal contamination in soils (29, 30), and samples were selected according to the trace metal dispersion around the refinery (30). The polluted soil fraction we used in this study was restricted to the first top 40 cm of a 1.5–2 m depth core (topsoil), where the Cd depth migration is limited (31), and sampled over a radius of 500–4000 m around the plant (30). The soil samples were dried at a temperature below 40 °C, crushed, and sieved to 2 mm. A representative subsample was crushed to 0.315 mm before being powdered at a few micrometer grain size in order to obtain the most homogeneous powder possible for isotopic analysis. The tilled topsoils have probably recorded and averaged the atmospheric fallouts of the past 100 years or so, linked to this major refinery plant, built in 1894 (31). The industrial dust samples were collected on filters, and slag was sampled at the exit of the plant furnace the same day.

Sample concentrations were determined using atomic absorption spectrophotometry with electrothermal atomization (30). Lead and cadmium isotopic analysis were done using MC–ICP–MS available at CRPG. For Pb and Cd isotopic measurements, between 50 and 100 mg of sample were digested in a mixture of different subboiled and suprapur concentrated acids (HNO₃–HF–HCl, HNO₃–H₂O₂) and the

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TABLE 1. Distance from the Refinery (m) of Topsoil Sampling Points and Cd and Pb Contents and Isotopic Composition of Topsoil, Slag, and Dust Samples^a

sample	distance from refinery (m)	direction	Pb ($\mu\text{g}\cdot\text{g}^{-1}$)	Cd ($\mu\text{g}\cdot\text{g}^{-1}$)	$^{206}\text{Pb}/^{207}\text{Pb}^*$	$^{208}\text{Pb}/^{204}\text{Pb}^*$	$^{206}\text{Pb}/^{204}\text{Pb}^*$	$\delta^{114}\text{Cd}/^{110}\text{Cd}^* (\text{‰})$	2(sd)
soil	693	SE	1004	19	1.1549	38.04	18.014	-0.46	0.26
soil	891	N	672	13	1.1576	38.10	18.052	-0.58	0.13
soil	954	N	1132	21	1.1569	38.11	18.053	-0.37	0.12
soil	990	N	1050	20	1.1563	38.11	18.044	-0.50	0.10
soil	1046	N	884	16	1.1565	38.13	18.061	-0.31	0.07
soil	1138	SE	507	10	1.1579	38.08	18.055	-0.06	0.14
soil	1145	N	779	14	1.1565	38.10	18.047	-0.66	0.09
soil	1746	SW	429	7	1.1574	38.12	18.066	-0.37	0.08
soil	1958	NE	320	6	1.1583	38.08	18.061	-0.13	0.16
soil	2178	NE	240	5	1.1575	38.11	18.067	-0.48	0.17
soil	2821	N	198	4	1.1584	38.08	18.062	-0.12	0.09
soil	2856	NW	101	2	1.1667	38.24	18.228	0.20	0.11
soil	4291	NE	155	4	1.1633	38.15	18.141	-0.46	0.10
slag			17968	13	1.1040	36.93	17.129	0.36	0.10
dust 1			141219	12195	1.1305	37.39	17.620	-0.64	0.13
dust 2			173916	1431	1.1273	37.35	17.576	-0.64	0.06

^a Soils are ordered as a function of the distance from the refinery. The external reproducibility of the measurements is expressed as 2 times the standard deviation (2(sd)). Cadmium reference is Cd Spex solution (see text for details).

element of interest was isolated. Lead was previously purified on anion-exchange resin according to the technique described by Manhès et al. (32). A total Pb blank was less than 1 ng and was negligible compared to the amount of Pb processed through the column. Sample lead isotopic compositions were measured with a MC-ICP-MS (Isoprobe, micromass, now GV Instruments) equipped with nine Faraday cups allowing the measurement of all the Pb isotopes, Tl isotopes, and ^{200}Hg simultaneously. The NIST SRM 981 Pb and NIST SRM 997 Tl were used to correct for instrumental mass bias, according to the empirical technique used by Maréchal et al. (33) and reported by White et al. (34) for lead application. The correction is based on the relationship measured between Pb and Tl mass bias. Reference values used for both Pb and Tl reference materials were taken from Thirlwall (35). Repeated measurements of the NIST SRM 981 Pb yielded recalculated values (using the Pb–Tl relationship) within the uncertainties of the assigned values with the following standard reproducibility ($2 \times$ standard deviations (2(sd))) better than 0.5‰ for the ratios including the ^{204}Pb and better than 0.2‰ for the other ratios. More details on the Pb isotopic analyses used with this study are reported elsewhere (3, 11, 36). The Cd from samples was also purified by using anion-exchange chromatography and by following the procedure previously reported by Cloquet et al. (22). The total procedural Cd blank level is less than 200 pg and considered negligible in front of the amount of Cd isolated from the sample. Instrumental mass bias was corrected by using the standard–sample–standard technique, and the pure Spex Cd solution (certiprep lot no. 7-29Cd) was used as reference (delta zero). This instrumental mass bias technique was found useful and accurate for precise Cd isotope measurement, as previously discussed (22). The pure Spex Cd solution used as reference in this study has the same isotopic composition as the JMC Cd solution used by another team (20). Cadmium isotopic composition is reported in delta notation (‰) as already suggested (27), and uncertainties obtained are estimated to 0.12‰ (2σ , 2 times the deviation from the mean) for the $^{114}\text{Cd}/^{110}\text{Cd}$ ratio (22). All the Cd isotopic ratios measured are coherent with a mass-dependent fractionation. Details on the method used for the Pb and Cd measurements were published elsewhere (22, 36).

Results

Table 1 presents Pb and Cd concentrations as well as isotopic compositions of 13 soils, 2 different dusts, and 1 slag. Distance and direction from the refinery of the studied soils are also reported.

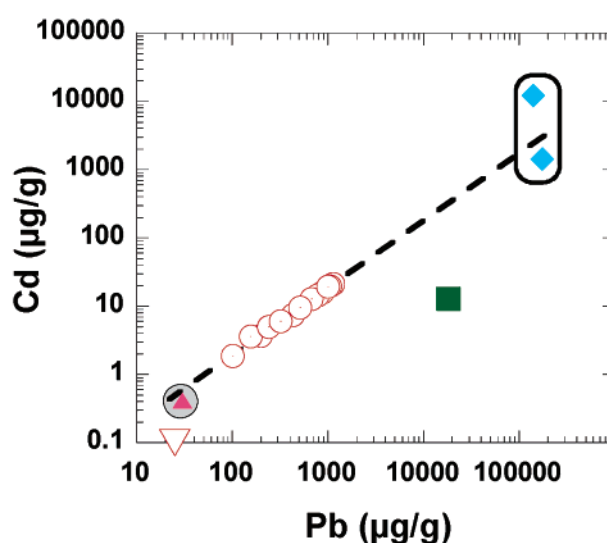


FIGURE 1. Cadmium concentrations versus lead concentrations in samples. Open circles represent the polluted topsoils, filled diamonds represent the dusts from the refinery, the filled square represents the slag from the refinery, and the filled triangle represents the median value for reference topsoils from northern France (37), and the gray area is the range of the value (see text for details). The inverted open triangles represent the upper continental crust (38).

Concentrations. Pb and Cd concentrations measured in soils aligned along a single trend (Figure 1), suggesting a common source for these two elements. Dusts from the refinery plant have high Cd concentrations (Table 1) and define a compositional field which plots on the high side of the soil trend. The slag sample has also a high Pb content but has 100- to 1000-fold less Cd than the dust samples (Table 1). It plots significantly outside the trend defined by the soils (Figure 1). Reference topsoils (31, 37) sampled away from the refinery plant, and thought to be nonsignificantly contaminated by refinery emissions, have Pb contents (median $30.3 \mu\text{g}\cdot\text{g}^{-1}$, $n = 38$) slightly higher than the average upper silicate continental crust (38) but higher Cd, varying from 0.28 to $0.73 \mu\text{g}\cdot\text{g}^{-1}$ (median, $0.41 \mu\text{g}\cdot\text{g}^{-1}$). These reference topsoils plot at the low concentration end of the polluted soil trend, whereas estimations of the average upper crust composition plot slightly under the trend (Figure 1). The distribution of the data in Figure 1 strongly suggests a mixed origin of Cd and Pb in soils, between refinery dusts, probably

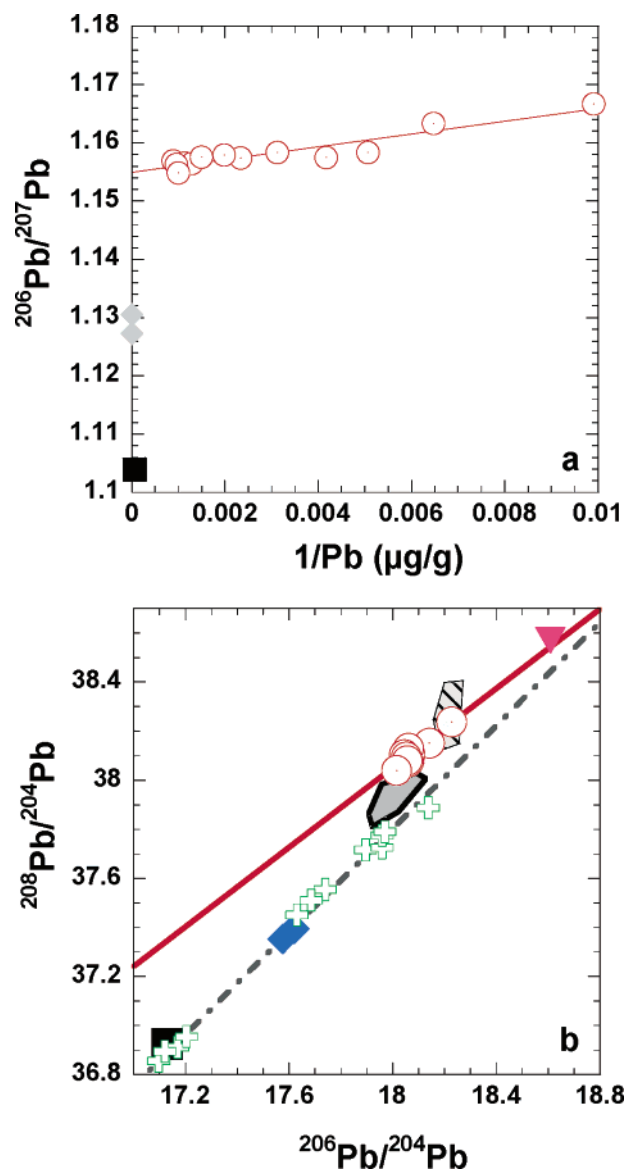


FIGURE 2. (a) Mixing diagram $^{206}\text{Pb}/^{207}\text{Pb}$ vs $1/\text{Pb}$ and (b) three isotopes diagram $^{208}\text{Pb}/^{204}\text{Pb}$ vs $^{206}\text{Pb}/^{204}\text{Pb}$. Open circles represent polluted topsoils, filled diamonds represent the dusts from the refinery, the filled square represents the slag from the refinery, the filled inverted triangle represents a reference topsoil from northern France, far away from the refinery (41). The black line is a regression through polluted soils, and the dashed line is the regression through dusts and slag. The plain gray area represents waste combustor materials (36), and the hatched gray area represents ores from Sardinia and Spain refined in the early years of the plant activity used in the past in the refinery (44). Crosses are actual aerosols deposited in the area (39). Uncertainties are included in the points.

emitted to the atmosphere through the chimney, and the local agricultural background.

Lead Isotopes. Lead isotopic ratios measured in polluted soils defined a single line in a Pb–Pb diagram (Figure 2a). This alignment certainly results from a simple binary mixing and suggests that Pb in polluted soils has two main sources. However, the Pb isotopic composition of slag and dust samples is significantly less radiogenic than that of polluted soils and does not plot on the polluted soil trend (Figure 2a). Our data on refinery materials are however compatible with other published data on similar materials from the same refinery (39, 40) and suggest Pb isotopic heterogeneity among the different sample types. In a $^{208}\text{Pb}/^{204}\text{Pb}$ vs $^{206}\text{Pb}/^{204}\text{Pb}$

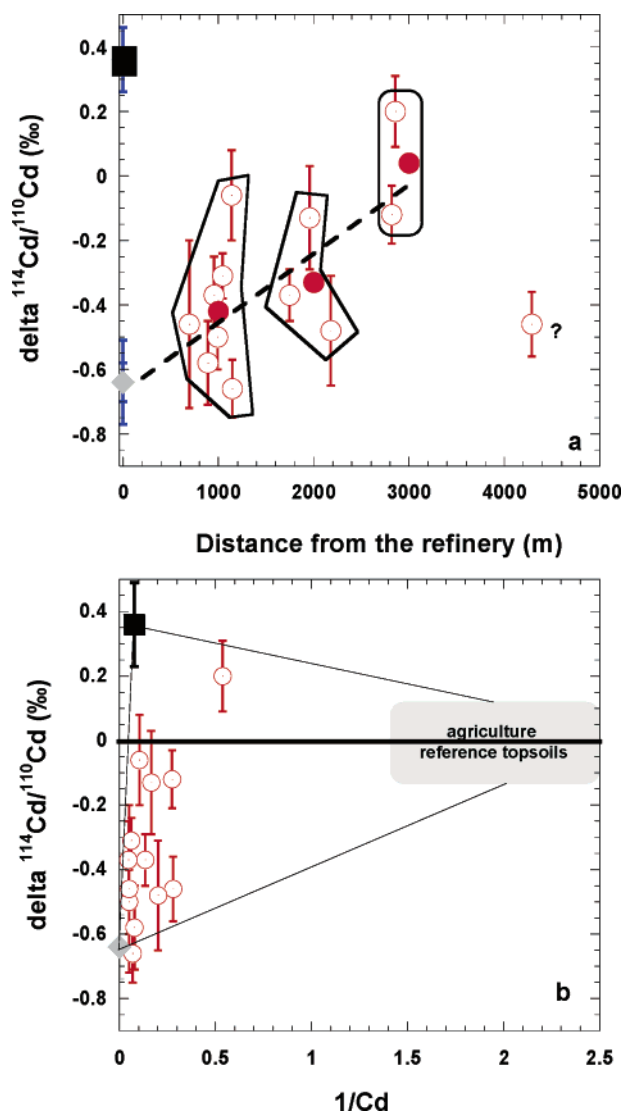


FIGURE 3. (a) Cadmium isotopic composition of polluted topsoils and refinery materials expressed as $\delta^{114}\text{Cd}$ (‰) versus the sampling distance from the refinery (meters). Filled circles are the mean of the equidistant soils from the refinery, open circles represent the polluted topsoils, filled diamonds represent the dusts from the refinery, and the filled square represents the slag. The dashed line is the regression through the mean of the equidistant soils. (b) Cadmium isotopic composition versus the inverse cadmium concentration ($\mu\text{g/g}$). The gray area is the field for the reference topsoils for which the isotopic composition was estimated at 0‰. Other symbols are the same as in a. Error bars represent the external reproducibility (2(sd), 95% confidence).

three isotopes space (Figure 2b), the soils form a single line. The slag and dusts also form a single line but different from that defined by the soils. A reference topsoil sample (41) plots at the radiogenic end of the trend defined by polluted soils, whereas municipal waste combustor materials (36) plot in a somewhat intermediate position between soils and slag–dust samples. These municipal waste combustor materials are thought to represent the average composition of industrial Pb used in France for the past 10–15 years (36, 42).

Cadmium Isotopes. Measured cadmium isotopic compositions varied from 0.4 to -0.6‰ in terms of $\delta^{114}\text{Cd}$. This variation is found between slag and dusts, respectively, the two dusts having the same isotopic composition. All the soils measured yielded a $\delta^{114}\text{Cd}$ comprised between these values ranging between -0.6 and 0.2‰ (Figure 3a). Only one soil

analyzed has a $\delta^{114}\text{Cd} > 0\text{‰}$, and most soils have a $\delta^{114}\text{Cd} < -0.3\text{‰}$. In a $\delta^{114}\text{Cd}$ vs $1/\text{Cd}$ mixing diagram (Figure 3b), the soils do not align along a single line. This suggests that at least three different sources having distinct Cd isotopic compositions and concentrations are present in these soils.

Discussion

Lead Isotopes. The spatial distribution of metal concentrations in polluted soils (Table 1) clearly demonstrate that the refinery plant is the main source of Cd and Pb in the area (29, 30). Lead isotopes also indicate that Pb in polluted topsoils is a mixture of at least two isotopically distinct sources. The low-Pb and radiogenic-Pb end-member is best represented by reference topsoils, whereas the Pb-rich and unradiogenic end-member is less straightforward to identify. The Pb concentration distribution around the refinery plant strongly suggests this anthropogenic activity as being the source of Pb enrichment, but the isotopic composition of slag and dust collected recently do not fit as an end-member (Figure 2a). Lead isotope ratios measured in polluted soils provide meaningful information, but the interpretation is not straightforward since Pb isotopic ratios do not identify the actual industrial dusts and slag as being the source of Pb pollution in soils. Nevertheless, this is likely explained by the fact that different Pb ore bodies (or a single Pb deposit) may have very different Pb isotopic compositions (43). The composition of slag and dust measured here represents the composition of the different ore materials refined the day of sampling, whereas the Pb-rich topsoil isotope composition reflects an average of the ore materials refined over the operating years. Indeed, during the early 20th century, this refinery used Pb–Zn ores from Sardinia, Italy, and from southern Spain, which Pb isotopic composition would perfectly fit the polluted soil composition today (44) (Figure 2b). Moreover, actual aerosols sampled near the refinery (39) form a line with the dust and slag Pb isotopic composition but not with the soil isotopic ratios (Figure 2b). Aerosols were collected in different locations around the refinery, during winter and during summer, and their isotopic compositions suggest either mixing sources between the actual refinery emissions and other modern Pb sources or (and) isotopic heterogeneity of Pb ores actually refined (36). The discrepancy between soils and modern atmospheric fallout confirms that the soils integrated Pb (and other metals) over the operating years of the refinery, during which emission and fallout fluxes must have greatly varied. Consequently, the unradiogenic end-member in soils is certainly a time-integrated averaged composition of ore materials refined over the years, including those from Sardinia and Spain.

Contrarily to Pb, Cd isotopic composition of feeding ores is assumed to be homogeneous as suggested by the isotopic homogeneity of terrestrial rocks analyzed so far. Changing ore sources and metal fluxes will not be an issue because variations in Cd isotope ratios will trace anthropogenic fractionation.

Cadmium Isotopes Contribution. The large cadmium isotopic variation measured between industrial dust and slag samples is coherent with a Cd isotopic fractionation occurring during evaporation–condensation processes (28). The slag sample has the heaviest composition with a $\delta^{114}\text{Cd}$ of 0.36‰ , whereas both dust samples yielded the same and the lowest $\delta^{114}\text{Cd}$ of -0.64‰ (Table 1). Assuming that the slag sample represents the last fractions of evaporated Cd in the refinery in an equilibrium evaporation system and that the $\delta^{114}\text{Cd}$ of the initial ore material was homogeneous and close to 0‰ , as observed for many geological samples, a fractionation factor $\alpha_{\text{sol-gas}}$ of only 1.0001 is needed to fit the measured composition of the slag. This α value is much lower than the 1.007 previously reported (28) for a simple evaporation of

molten Cd under vacuum at 180 °C . The Cd comprised in dusts was certainly the result of gas condensation in the refinery chimney. The Cd isotopic composition of dusts then reflects that of the gas Cd at a given moment of the evaporation process. Indeed, considering a quasi 100% evaporation of the feeding Cd ore, the $\delta^{114}\text{Cd}$ of the average gas should be close to 0‰ . Equilibrium condensation in a Rayleigh system would lead to gas fractions depleted in heavy Cd. A fractionation factor $\alpha_{\text{gas-condensate}}$ of 0.9998 would generate a $\delta^{114}\text{Cd}$ of about -0.6‰ for the last 15% Cd gas to condense. Cadmium in dusts may then originate from this last Cd gas fraction. The data support the fact that even if very low fractionation factors are involved, industrial processes may generate isotopically fractionated materials.

By contrast to Pb isotopes, all the analyzed polluted topsoils yielded intermediate Cd isotopic composition between slag and dusts, suggesting that these industrial materials strongly dominate the Cd budget in the soils. The $\delta^{114}\text{Cd}$ in soils is roughly correlated with the distance from the refinery plant (Figure 3a). Indeed, all samples except one may be grouped in equidistant points at $\pm 200\text{ m}$. Although there is a significant variation of the measured $\delta^{114}\text{Cd}$ in samples from each group, the average isotopic composition of polluted soils closer to the refinery plant shows systematically lower $\delta^{114}\text{Cd}$ values, toward that of the two dust samples (Figure 3a). The average $\delta^{114}\text{Cd}$ of polluted soils in the 3000 m group is close to 0‰ . One polluted soil located further away ($> 4000\text{ m}$) has a low $\delta^{114}\text{Cd}$ of -0.46‰ and does not plot on the general trend. This sample has also a high Cd concentration, similar to some soils in the 1000 m group (Table 1). This suggests that the dispersion around the refinery plant is not perfectly radial and that it is probably strongly influenced by wind directions and emission fluxes at the chimney (39). Nevertheless, the distribution of the data points in Figure 3a likely represents mixing between a ^{114}Cd -depleted source, dusts from the refinery plant, and a source having a ca. 0‰ $\delta^{114}\text{Cd}$ value.

The $\delta^{114}\text{Cd}$ values and Cd concentrations relationship found for the polluted topsoils (Figure 3b) may be explained by the contribution of at least three Cd origins: (1) industrial dusts, (2) slag, and (3) the local agriculture-related background represented by the reference topsoils. The slag contribution, either from wind mobilization of residual tailings or from the use as a field lane material, may explain the distribution of $\delta^{114}\text{Cd}$ values for soils of a single equidistant group. Assuming the Cd isotopic fractionation between dust and slag was similar over the operating years of the refinery, their relative Cd contribution to surrounding polluted soils may be in the triangle space defined by the composition of slag, dust (average of the two samples), and agriculture reference topsoils ($0.5\text{ }\mu\text{g/g}$ Cd and $\delta^{114}\text{Cd} = 0\text{‰}$) (Figure 3b). Cadmium from the local background (reference topsoils) may reach 20–25% but contributes to less than 10% in most soils. About 65% of the polluted soil samples comprise more than 60% Cd from dusts. The maximum contribution from slag Cd is estimated to be less than 80%, considering the uncertainties on the measurements, for one polluted soil sampled at 3000 m away from the refinery plant. These calculations confirm that dust materials are the primary contributors to soil Cd pollution in this area of northern France. In any case, the mass contribution of dusts never exceed 2% in the soils to satisfy the mass isotopic balance mixing equations (45). The relative contributions of the different Cd sources in soils calculated here are the result of more than 100 years of refining activities in the area and certainly not representative of the recent Cd–Pb inputs, as suggested by Pb isotopes.

This study showed that Cd isotopes are complementary to Pb isotopes and help to better constrain the dynamics of polluted environments. In many areas worldwide, estimated

Cd excess relative to natural inputs may be very high compared to other associated metals (25, 26). Cadmium isotopes might be used to document mixing processes, fluxes, transport, and phasing out of industrial input in nature.

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