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# Use of Potentially Toxic Elements in sedimentable industrial dust to trace their input in soils (Northern France)

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## Highlights

- Coal, ores and slags dominate urban dusts near the industrial seaport of Dunkerque
- PTE bearing particles of industrial origin affect the soil quality
- Mo–Cr–Ni association as a specific tracer of metallurgic dusts in soils

## Abstract

**Purpose** At the vicinity of metallurgical and steel activities, notable contamination of Potentially Toxic Elements (PTE) is measured in discrete environmental compartments (soils, biosphere, atmosphere). The main question addressed in this study pertains to the influence of industrial dust fallout on PTE concentrations in soils. The study was conducted near the seaport of Dunkerque, belonging to one of the most industrialised and dust-emitting sites of France.

**Materials and methods** A composite sample of dust fallout was collected over a 4-month-period in urban areas downwind of nearby industries. SEM-EDS and ICP-AES/MS analyses were conducted on this sample to identify metallurgical particles and highlight the main tracer elements of industrial activities. Then, a comprehensive characterization of soils was conducted to map the spatial distribution of metallic pollution levels in the study area. Nearby soil parameters analysis (grain-size distribution, pH, CEC, SOM, calcium carbonates and water contents), the soil chemical composition was identified using XRF and ICP-AES/MS analyses.

**Results and discussion** We quantified the proportion of particles of industrial origin in the composite dust sample at 88% of the total fraction, stressing the importance of metallurgical activities near the seaport of Dunkerque. This dust sample shows particularly high enrichment factors (EF) for Cd, Cr, Ni, and Mo with values of 235, 108, 78 and 169 respectively. The use of different pollution assessment indexes evidences that Mo–Cr–Ni associations appear particularly interesting to trace the incorporation of metallurgical sedimentable dusts into soils. Thus, we identified the presence of

distinct high-PTE patches related to industrial dust deposition in the studied soils, with a parallel decrease in their quality index (*i.e.* Mo Geo Accumulation Index indicating moderate to heavy contamination).

**Conclusions** Our study revealed that the soils located close to the industrial area are the most affected by industrial dust deposition. Several factors explaining the spatial distribution of the soil contamination levels are examined, and it seems that distance from emission sources is not necessarily the most relevant. The study suggests that distribution of plant cover or buildings may act as barriers preventing soils from being exposed to dust deposits.

**Key words** Urban soils · Potentially toxic elements (PTE) · Metallurgy · Industrial emissions · Sedimentable dust · Pollution indexes.

## 1 Introduction

Since 2007, more than 50% of the world's population lives in urban areas (United Nations, Department of Economic and Social Affairs, Population Division 2019). Urbanization and the accompanied anthropogenic activities contribute significantly to the degradation of the environmental compartments and ecosystems, notably through the release of pollutants (Qiao and Huang 2022; Li et al. 2022). This environmental pollution is strongly accentuated by the presence of industries notably metallurgical activities (Schulin et al. 2007; Khademi et al. 2019). Numerous studies demonstrate the specific impacts of industrial dust emissions on the environment (Lamaison 2006; Kfoury et al. 2016). The main emitters are cement factories, metallurgy, steel and coking plants or chemical industries and most of the industrial dusts can be distinguished by size, morphology and chemical composition (Deboudt et al. 1997; Dall'Osto et al. 2008; Hleis et al. 2013). Due to their impact on health and air quality, the monitoring of industrial fine particles (particularly in the atmosphere) is very active in northern France (Potier et al. 2019; Moufarrej et al. 2020).

Unlike coarse and fine particles, sedimentable (>20 µm) particles also present in ambient air cannot penetrate deeply into the respiratory system but can alter human health either by

dermal contact and/or ingestion (Yamamoto et al. 2006; Siciliano et al. 2009). Furthermore, they represent a significant part of atmospheric particles emitted by metallurgical and steel industries (Hleis et al. 2013; Lanzerstorfer 2018). In the Dunkerque agglomeration (Northern France) (Fig. 1), metallurgical and steel industries were established in this region during the 20th century, with the development of a large seaport. According to GeoHazards data (Géorisques 2021a), metallurgical industries located on the western part of this seaport emitted 27% of the atmospheric total dust in France in 2021 (more than 2700 t). Regarding the fact that almost 195,000 inhabitants live in this industrialised agglomeration (INSEE 2024), the fate of these industrial emissions is a major health and environmental issue (Ebert et al. 2000; Dehoog et al. 2005; Laversin 2006).

In the town of Gravelines (Fig. 1), the deposition of dust from the nearby industrialised seaport of Dunkerque to the city centre is particularly recurrent. This is particularly the case with winds from the North-East: sedimentable industrial dusts are mobilised and can be deposited in the city (Deboudt et al. 1997), giving rise to complaints by the inhabitants. Most publications on industrial air pollution in the Dunkerque area focus on coarse and fine particles PM<sub>2.5</sub> and PM<sub>10</sub> (particles with

equivalent aerodynamic diameter less than 2.5  $\mu\text{m}$  and 10  $\mu\text{m}$ , respectively) (Hleis et al. 2013; Kfoury et al. 2016; Moufarrej et al. 2020). Due to their lower direct toxicity, the study of the sedimentable dust was less considered. To what extent and how these inputs are integrated into the soil matrix is the main question of the present study. Which areas of the city of Gravelines are most affected by metallic contamination (potentially associated with industrial dust)? What is the influence of industrial dust on the chemical quality of these urban soils? The main objectives of this study are therefore to (1) evaluate soil contamination levels in Gravelines on the basis of measured PTE concentrations (As, Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, Sc, V, Zn),

(2) to describe their spatial distribution and (3) to locally estimate the contribution of industrial dust. To this aim, this study focused on (1) a characterization of dust depositions, in order to identify the clusters of the industrial particles (composition, size and morphology) and their associated PTE, (2) the typology of soils to interpret their reactivity with respect to PTE inputs. For this purpose, different soil parameters (pH, CEC, etc.) of superficial soils (0–5 cm depth) were determined as well as their chemical composition (major, minor and trace elements), and (3) the use of correlation matrix and clustering analysis to highlight relationships between dust characteristics, soil properties and metal contamination levels in soils.

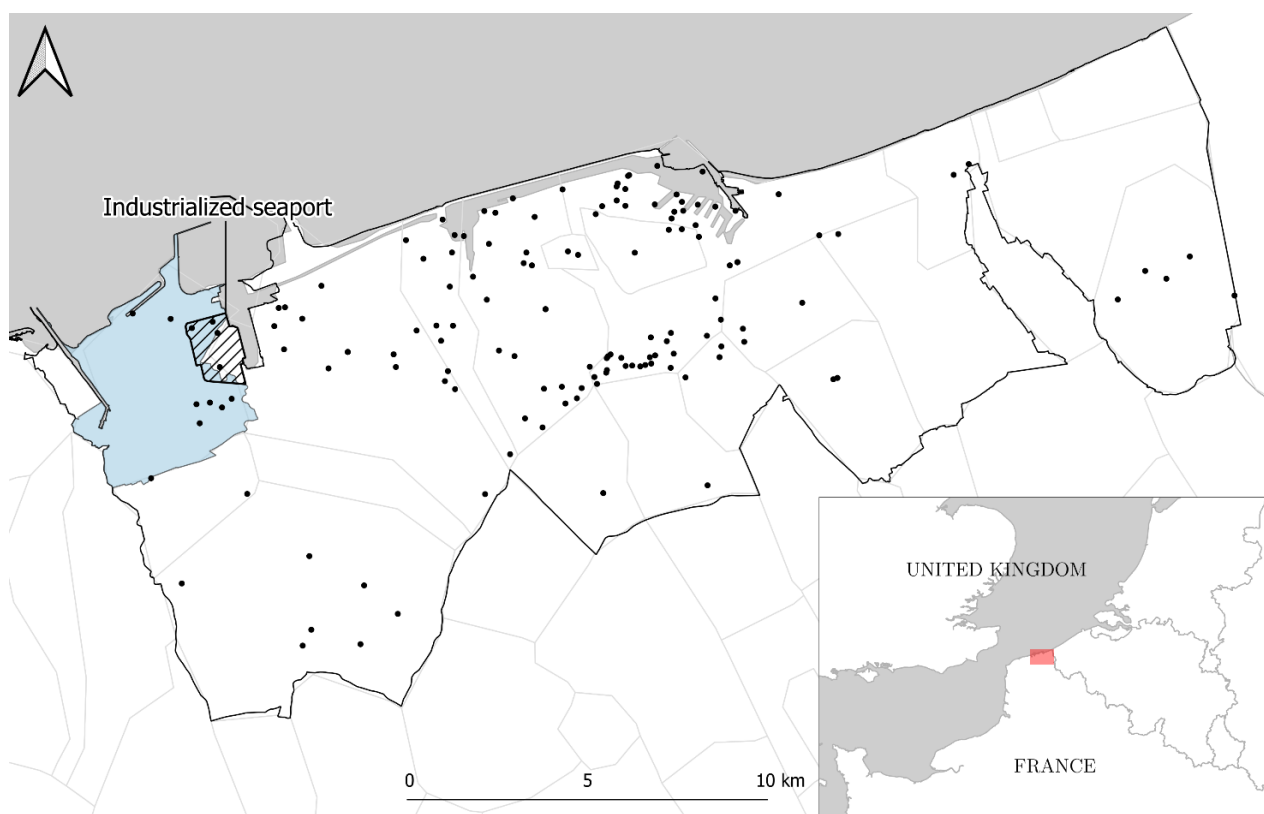


**Fig. 1** Dunkerque agglomeration and the city of Gravelines (in blue). Black dots indicate facilities posing a known major risk for the environment (source: IGN – BD TOPO® Nord 2023)

## 2 Material & Methods

### 2.1 Study area

The city of Gravelines is located on the North Sea coast, in northern France (50°59' N, 2°08' E; area

22.66 sq. km) (Fig. 1). Numerous industries were built near the town in parallel with the construction of the seaport, including three metallurgical production sites and an open-air ore receiving, handling and storage facility. In 2019, the population of the town was 11,014

(INSEE 2019). The climate is temperate with annual temperatures ranging from 2°C to 22°C and average annual precipitation of 727 mm (MERRA-2 meteorological data, 1980-2016). Predominant wind directions in the studied area are Southwest (autumn and winter; wet conditions) and Northeast (spring and summer; mostly dry conditions). The highest speeds (>60 km/h) are recorded for Southwest winds. Urbanised spaces represent 52% of the land use, agricultural spaces 22%, natural spaces 16% and infrastructures 10%.

The area of Gravelines belongs to the Flanders coastal plain mainly composed of marine and alluvial clay and sandy sediments deposited during the Holocene (Leplat et al. 1988). The nature of the soils is characteristic of a pedogenetic evolution on marine formations: mainly clayey-sandy soils rich in calcium carbonates (median value: 13%) (Sterckeman et al. 2004).

## 2.2 Soil and dust sampling

For this study, nine sampling zones were selected in the city of Gravelines (Fig. 2) according to (1) their distance to the emission sources, (2) their location inside or outside the wind corridor where dust deposition is most pronounced (*potential deposition area*) and the inhabitant complaints are numerous, (3) the absence of recent anthropogenic perturbations and (4) their accessibility. The absence of important human perturbations was checked by observation of aerial and satellite photos taken since 1949, combined with the review of the GeoHazards database (Géorisques 2021b).

Eighteen topsoil samples (diameter = 4.5 cm; depth=0–5 cm) were collected from these 9 zones (herbaceous formations). Triplicates were made for each of these 18 topsoil samples to better assess soil heterogeneity (total of 54 soil sub-samples). The whole samples were collected in February 2021 during the winter season using a manual auger and PVC tubes. A composite

sample of dry deposits was collected between February 11 and May 9, 2022, as dry conditions are particularly suitable to mobilize large (>20 µm) dust particles contrary to wet conditions. Three ADA-MASS sensors (NFX43-006, ISO 42-222; 75 mm diameter disks) are placed at 1.80 m above ground level. They are localised in the main streets of the city (Fig. 2), particularly exposed to sedimentable dust deposits (open-field areas with no vegetation or urban barrier). Their location was chosen in order to collect all the industrial dust potentially affecting the city centre. For this composite dust sample, only periods of North-East winds (22.5 and 67.5°; duration: 1072h) were selected.

## 2.3. Characterization of soil and dust samples

### 2.3.1 Soil parameters

The grain-size distribution was determined on wet samples by laser diffraction using a Coulter LS 13 320 instrument (gallium arsenide, 750 nm wavelength, Brea, USA). The instrument measured a particle diameter ranging from 0.375 to 2000 µm. Prior to analysis, samples were passed through a 2-mm-mesh sieve to remove the higher size fraction (roots, stems and leaves). Particle size classes were assigned according to the Soil Science Division Staff (2017) grain-size scale, *i.e.* 0.375–2.0 µm for the clay fraction, 2.0–20 µm for the fine silt fraction, 20–50 µm for the coarse silt fraction and 50–2000 µm for the sand fraction.

Soil pH was measured in water (1:5 soil:solution) using a combined glass electrode and a LPH230T pH-METER (NF ISO 10390). Water content was determined by drying at 65°C in a ventilated oven (NF EN 1097-5). Soil organic matter content (SOM) was estimated by measuring the loss on ignition at 375°C (Brady 1984; Salehi et al. 2011).

The soil cation exchange capacity (CEC) was determined by a spectrophotometric method

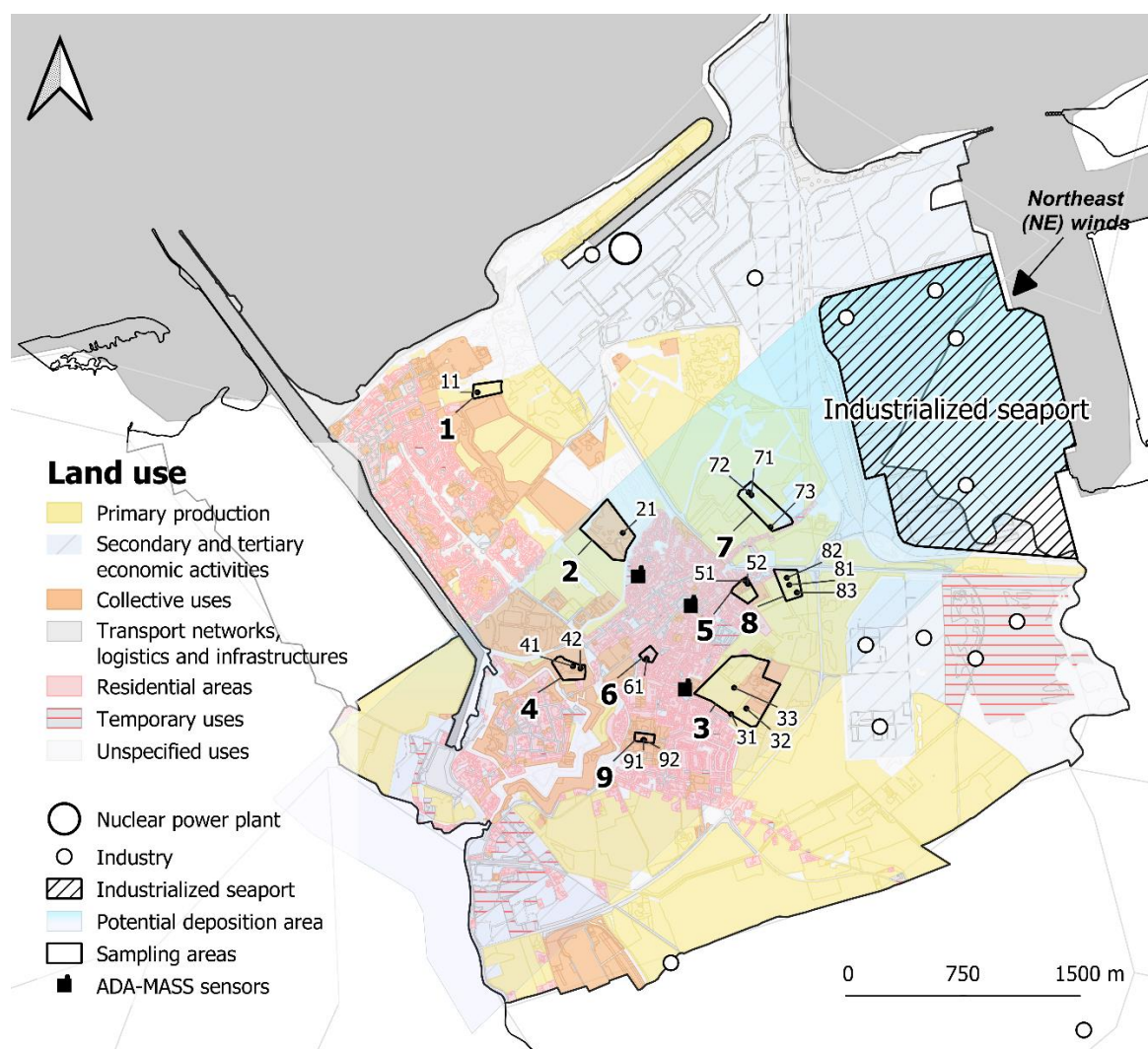


**Fig. 2** Map of Gravelines showing land uses (sources: ©PPIGE Nord-Pas de Calais – OCS2D 2005-2015; IGN – BD TOPO © Nord 2023). Black bold lines and black dots indicate the 9 sampling zones and the 18 sampling locations, respectively. Land cover: meadow and lawn cover on sampling zones 1, 2, 3 and 7; Meadow, shrubs and trees on sampling zone 8; Buildings on sampling zones 4, 5, 6 and 9

based on cobalt-hexammine chloride absorbance according to Aran et al. (2008). 2 g of dry samples were mixed to a 0.01N solution of cobalt-hexammine chloride during 1 hour. The solution was centrifuged for 10 minutes (4000g) and filtered through 0.22  $\mu\text{m}$  filters. The absorbance at 472 nm of the collected mixture was measured to obtain the CEC.

Finally, total carbonate content ( $\text{CaCO}_3$ ) was obtained using a manual calcimeter (OFITTE, Houston, USA; dried and grinded samples) calibrated with pure calcium carbonate. It was estimated by gas pressure developing after reaction of 1 g of fine powdered sample when adding 20 mL of HCl 20%.

The variability of the soil matrix is estimated from the triplicates of the 18 samples collected in Gravelines, which were subjected to all analyses. In addition, 3 analytical replicates were performed on the samples with the highest and lowest values during laboratory phases. These 2 types of uncertainties, linked to the variability of the soils or to laboratory measurements, were compared. Soil variability was systematically greater than measurement uncertainties and was chosen for the presentation of the results. Thus, the absolute uncertainties for the studied soil parameters are as follows: pH  $\pm$  0.3; CEC  $\pm$  0.6 meq/100g; water content  $\pm$  10%;  $\text{CaCO}_3$   $\pm$  2%;

SOM  $\pm 1.4\%$ ; clay  $\pm 1\%$ ; fine silt  $\pm 7\%$ ; coarse silt  $\pm 4\%$ ; sand  $\pm 10\%$ .

### 2.3.2 Major oxide measurement of soil samples

The concentration of 7 major oxides ( $\text{Na}_2\text{O}$ ,  $\text{MgO}$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ ,  $\text{K}_2\text{O}$ ,  $\text{CaO}$ ,  $\text{Fe}_2\text{O}_3$ ) were measured using energy dispersive X-ray fluorescence spectrometry on fused beads (Brucker S2 PUMA ED-XRF). The spectrometer is equipped with a 50 kV Ag anode tube (maximum power: 50 W; maximum high voltage: 50 kV; maximum current: 2 mA; cooling medium: air) and a high-resolution silicon drift detector (SDD). The resolution of the SDD is  $<141$  eV for Mn-K $\alpha$ 1. Spectral data were analysed by Spectra Elements software version 2.0.

To obtain fused soil beads, soil samples (500 to 1000 mg) were dried, sieved (2 mm), grinded, homogenized and calcined at  $1050^\circ\text{C}$  (loss on ignition: LOI). They were mixed with a flux of lithium tetraborate (33%), lithium metaborate (67%) and lithium bromide ( $<1\%$ ) mixture. These flux mixtures were loaded in a Katanax® K1 Prime fluxer and heated up to  $1060^\circ\text{C}$  during 20 minutes. Analytical quality of the XRF measurements was controlled by analysing 11 certified samples of stream sediments. Determination limits (DL) and measurement uncertainties are available in Table S1 (supplementary information).

### 2.3.3 Minor and trace element analysis of soil and dust samples

The total content of 11 minor or trace elements was determined using ICP-AES with an Agilent 5110 (As, Cu, Mn, Zn) and the ICP-MS Agilent 7850 (Cd, Co, Cr, Mo, Ni, Pb, V), Sc was only measured in dust sample. 200 mg of each soil grinded samples and 150 mg of dust sample were digested by using first a concentrated  $\text{HF}$ – $\text{HNO}_3$  acid attack (7.5 mL of a 67:33 v:v mixture) and then 2 others concentrated  $\text{HCl}$ – $\text{HNO}_3$  attacks (9 mL of a 67:33 v:v mixture). Each digestion lasted 48 hours at  $125^\circ\text{C}$  before

evaporation. Digested samples were finally diluted in 9 mL with acidified ultrapure MilliQ® (Millipore 18.2 M $\Omega$ .cm). Each solution was filtered on 0.22  $\mu\text{m}$  filters (cellulose acetate) to remove potential residues. All the reagents were of the optimal/suprapur grade. The accuracy and precision were controlled using 3 sediment and 1 dust standard reference materials (MESS-3, PACS-2, NCSDC-73021 and 1648a., respectively), 12 analytical triplicates and 6 blank samples. The recovery values of the reference standards and the detection limits are available in Table S2 (supplementary information).

### 2.3.4 Scanning Electron Microscopy (SEM) observation of dust sample

SEM images and spot-chemical of individual particle analysis were recorded on the dust fallout sample using a LEO 438 VP scanning electron microscope with an Energy Dispersive X-ray spectrometer (Oxford instruments Isis 300). First, a homogenized subsample was dispersed on double sticky carbon tabs and sputter coated with carbon (Scancoat six Edwards). Carbon as well as nitrogen and oxygen were not considered in this analysis. A total of 1500 particles were automatically analysed (backscattered electron mode; voltage: 25 kV; acquisition time: 40s/particle) to highlight their chemical composition (Mg, Al, Si, K, Ca, Cr, Mn, Fe, Zn (weight%)) and morphology. Obtaining their spherical equivalent diameter allowed estimating their size ( $\mu\text{m}$ ). In parallel, carbon-rich particles were manually identified, as they constitute an important fraction of the sample, but without size information due to the nature of the support.

## 2.4 PTE pollution assessment methodology within a regional frame

Trace metal concentrations were compared to ploughed soils of the French Flemish Coastal plain (Wateringues marine plain), preserved from potential contamination sources (industrial

**Table 1** Trace metal concentrations (mg.kg<sup>-1</sup>; % when\*) and enrichment factors (compared to the upper continental crust (Taylor and McLennan 1995) and Sc concentrations) of dust fallout sample. An EF < 1 indicates a crustal origin

|                              | As | Cd  | Cr   | Co | Cu  | Mn    | Ni  | Mo  | Pb  | V   | Zn    | Al* | Ca* | Fe* |
|------------------------------|----|-----|------|----|-----|-------|-----|-----|-----|-----|-------|-----|-----|-----|
| Concentration in dust sample | 9  | 9   | 1460 | 30 | 197 | 8 356 | 603 | 98  | 147 | 132 | 1 631 | 12  | 7   | 21  |
| EF (Sc)                      | 16 | 235 | 108  | 8  | 20  | 36    | 78  | 169 | 19  | 6   | 60    | 4   | 6   | 15  |

of PTE in particles. An EF ranging from 1 to 10 probably derived from a mixed anthropogenic-terrigeneous source and EF > 10 clearly indicates anthropogenic origin (Cheng et al. 2018)

activities, busy roads, houses) (Sterckeman et al. 2004). Thus, the enrichment factor (EF) and geo-accumulation index ( $I_{geo}$ ) were calculated. To further discuss the results of this study, environmental pollution levels were evaluated using pollution assessment indexes (NIPI, PLI).

#### 2.4.1 Enrichment factors (EF) of metals in dust sample and soils

The EF evaluates the degree of metallic contamination of dust and soils. It distinguishes anthropogenic from natural metal concentrations (Ye et al. 2011; Harb et al. 2015), commonly using aluminium (Al) as a normalizing element (Brady 1984; Duodu et al. 2017). In this case, this element is one of the possible contaminants in dust fallout and thus cannot be used as a reference for the calculation of enrichment factors in dust. Consequently, we used Scandium (Sc) as reference as well as trace metal concentrations in the upper continental crust (Taylor and McLennan 1995) for the dust EF calculation. For the soils, considering the fact that 1) Sc is not measured in the reference material and 2) Al inputs through dust fall are negligible compared to the matrix Al concentrations, this element was used as reference for EF calculations. Consequently, we will not use comparison between the two EF in this article. EF were calculated as follows (Eq. (1)).

$$EF = (C_n/C_e)/(B_n/B_e) \quad (1)$$

where  $C_n$  and  $C_e$  are the concentration of the metal element n and reference element e (Sc or Al) in the sample, and  $B_n$  and  $B_e$  are those in the

reference material (upper crust for dust and Wateringues marine plain for soils).

#### 2.4.2 The geo-accumulation index ( $I_{geo}$ )

The geoaccumulation index ( $I_{geo}$ ) defines the metal contamination level in soil by comparing the present concentration with the natural geochemical background (Müller 1969; Buccolieri et al. 2006). It was calculated for As, Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, V and Zn using Eq. (2):

$$(I_{geo})_n = \log_2\left(\frac{C_n}{1.5 \times B_n}\right) \quad (2)$$

where  $C_n$  is the concentration of the metal n in soil samples and  $B_n$  is its abundance in the regional natural background (Sterckeman et al. 2004). The constant (1.5) is the anthropogenic effect coefficient (Loska et al. 2004).

#### 2.4.3 Pollution assessment indexes: NIPI and PLI

The Contamination Factor (CF) allows the calculation of the two pollution indexes. It is the ratio obtained by dividing the concentration of each metal in the soil sample by the background value (Eq. (3)) (Hakanson 1980).

$$(CF)_n = (C_n/B_n) \quad (3)$$

where  $C_n$  is the concentration of the metal n in soil sample and  $B_n$  is its abundance in the regional background (Hakanson 1980; Gope et al. 2017).

Thus, the Nemerow Integrated Pollution Index (NIPI) (Nemerow 1985) can be calculated to assess the pollution level of a PTE (compared to

the chosen background), taking into account all the sampling sites (Cheng et al. 2014; Zang et al. 2017; Yesilkanat and Kobya 2021). The NIPI can be calculated using the equation (4):

$$(NIPI)_n = \sqrt{\frac{(CF_n)_{ave}^2 + (CF_n)_{max}^2}{2}} \quad (4)$$

where  $(CF_n)_{ave}$  and  $(CF_n)_{max}$  are the mean and maximum values of the CF of metal  $n$  respectively for all sites studied.

The Pollution Load Index (PLI) was calculated to integrate and compare the pollution levels of different sites (Tomlinson et al. 1980; Angulo 1996). The PLI is calculated for one sampling site and for the entire zone (Men et al. 2018), to determine the distribution of pollution and using the following equations (5) and (6):

$$PLI = \sqrt[n]{(CF)_1 \times (CF)_2 \times (CF)_3 \times \dots \times (CF)_n} \quad (5)$$

$$(PLI)_{zone} =$$

$$\sqrt[m]{(PLI)_1 \times (PLI)_2 \times (PLI)_3 \times \dots \times (PLI)_m} \quad (6)$$

where CF is the contamination factor;  $n$  is the number of studied metal elements and  $m$  is the number of sampling sites.

## 2.5 Data analysis

Statistical computing and graphics were performed on R software (R Core Team 2022) using the following packages: ggplot 2 (Wickham 2016), FactoMineR (Lê et al. 2008), factoextra (Kassambara and Mundt 2020), corTest (Yu et al. 2020) and corrplot (Wei and Simko 2021). For these statistical analyses, all concentration values below the detection limit (DL) were replaced by half of the DL, as suggested by Chapman (1996). Maps were made using QGIS 3.10 (QGIS Development Team 2023). SEM data set was submitted to the IDAS hierarchical cluster analysis (HCA) (Bondarenko et al. 1996) to identify the different types of particles in the sample.

## 3 Results

### 3.1. Characterization of dust fallout sample

#### 3.1.1 Chemical composition

PTE concentrations of dust fallout are reported in Table 1. PTE EF were calculated in order to highlight their potential anthropogenic properties (Table 1). Anthropogenic source is very probable for Co and V ( $EF > 5$ ) and clearly highlighted for As, Cd, Cr, Cu, Mn, Mo, Ni, Pb, Zn ( $EF > 10$ ) (Cheng et al. 2018). Furthermore, ICP-AES analyses of Al, Ca and Fe contents indicate high iron concentrations and enrichment factors (21% and  $EF > 10$ , respectively).

#### 3.1.2 Characterization of individual dust particles

The IDAS clusterization highlighted 10 groups of particles within the dust deposition sample, depending on their chemical profile (Table 2). The most represented cluster ( $n^{\circ}10$ ; 44%) is composed of carbon rich particles (Fig. 3.10). Cluster 5 (13%) is characterised by high aluminium concentrations (>90% of the analysed elements) and framboidal morphology (Fig. 3.5). Particles containing at least 20% of iron are found in clusters 1 and 8. Fe-rich particles are represented by cluster 1 (12%) with homogeneous (Fig. 3.1a) or aggregated (Fig. 3.1b) angular forms whereas cluster 8 ( $\approx 5\%$ ) describes Fe-bearing particles associated with Si and characterised by smooth (Fig. 3.8a) or rough (Fig. 3.8b) spherical shapes. Three clusters present high concentrations of silicon: (1) the Si-rich cluster 7 ( $\approx 4\%$ ) with massive shapes (Fig. 3.7); (2) Al-Si-rich particles represented by the cluster 3 ( $\approx 5\%$ ) in non-aggregated (Fig. 3.3a) or aggregated (Fig. 3.3b) shapes; and (3) cluster 9 (9%) with Si-Ca-bearing particles characterised by compact particles with hemispherical shape cavities (Fig. 3.9a), homogeneous angular matrix (Fig. 3.9b) or aggregates (Fig. 3.9c). Calcium is

| Cluster | Abundance | %    | Rich<br>>90% | Important<br>50<>75% | Major<br>20<>50% | Minor<br>10<>20% | Trace <10%        |
|---------|-----------|------|--------------|----------------------|------------------|------------------|-------------------|
| 10      | 633       | 44   | C            |                      |                  |                  |                   |
| 5       | 182       | 12.7 | Al           |                      |                  |                  | Si                |
| 1       | 168       | 11.7 | Fe           |                      |                  |                  | Si Ca             |
| 9       | 134       | 9.3  |              |                      | Si Ca            | Al               | Mn Mg Fe K        |
| 8       | 77        | 5.4  |              |                      | Fe               | Si Fe            | Zn Mn Cr Al<br>Mg |
| 3       | 64        | 4.5  |              | Si                   |                  | Al               | Fe Ca K           |
| 2       | 62        | 4.3  |              |                      | Ca               | Si Fe            | Mg Al             |
| 7       | 62        | 4.3  | Si           |                      |                  |                  | Ca Fe             |
| 4       | 36        | 2.5  | Ca           |                      |                  |                  | Si Fe             |
| 6       | 20        | 1.4  |              | Mn                   |                  | Si               | Ca Fe             |

**Table 2** Main particle clusters identified by SEM–EDS and their abundance in the sample as well as the main constitutive elements

the most represented element in clusters 4 and 2. Cluster 4 ( $\approx 2\%$ ) is Ca-rich ( $> 90\%$ ) (Fig. 3.4) and cluster 2 ( $\approx 4\%$ ) is characterised by high amounts of Ca and minor concentrations of Si

and Fe (Fig. 3.2a, b). Finally, the less abundant ( $\approx 1\%$ ) cluster (6) displays high concentrations of manganese and angular homogeneous shapes.

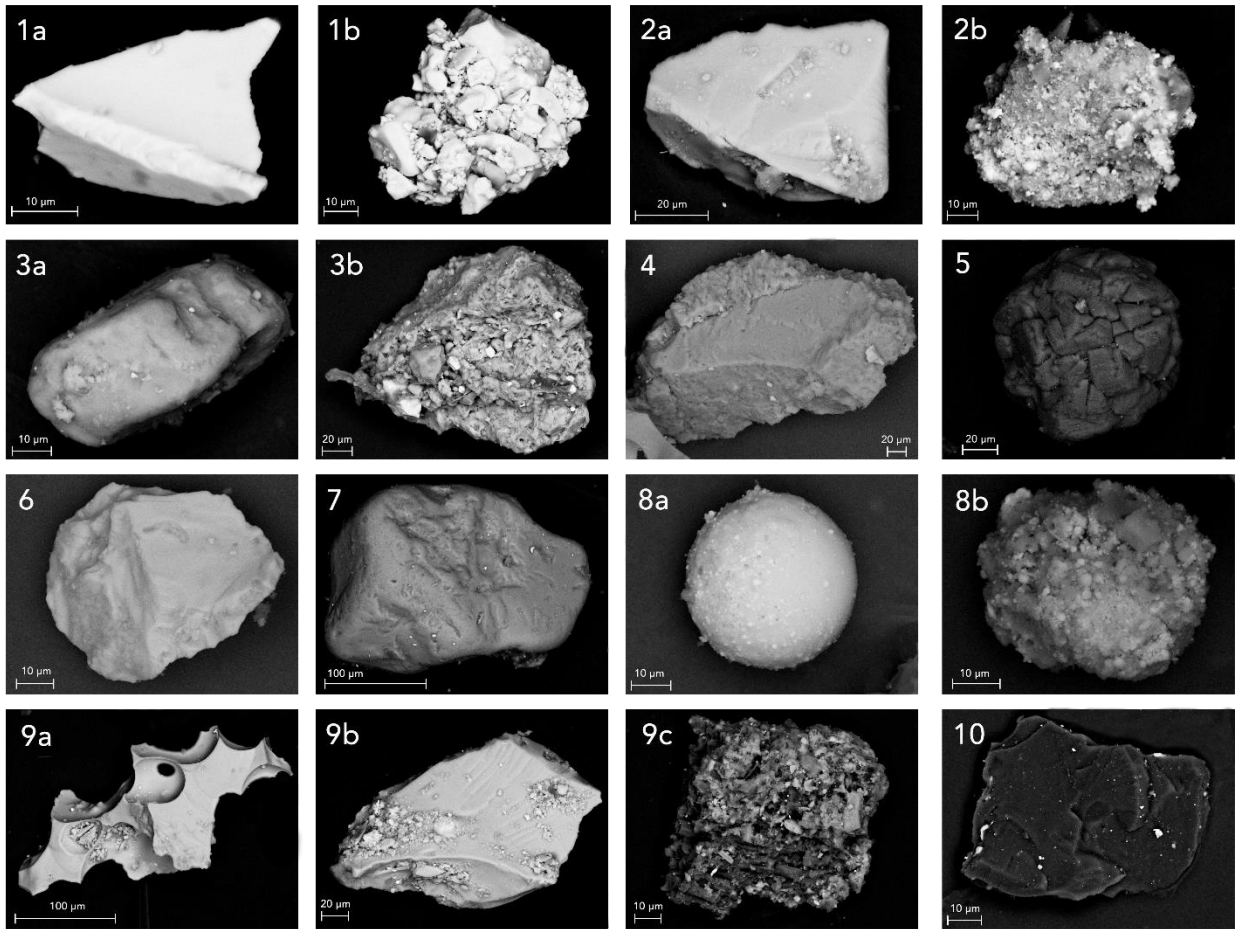


**Fig. 3** SEM observations (backscattered images) of the 10 particle clusters. (1a, b) Fe-rich particles; (2a, b) Ca–Si–Fe rich particles; (3a, b) Al–Si rich particles; (4) Ca-rich particle; (5) Al-rich particle; (6) Mn-rich particle; (7) Si-rich particle; (8a, b) Fe–Si rich particles; (9a, b, c) Si–Ca bearing particles; (10) C-rich particle

### 3.1.3 Size distribution of particles in the dust deposition sample

Most of the analysed particles (70%) have an equivalent spherical diameter ranging between 20 and 75  $\mu\text{m}$ . Twenty percent of them present size ranging from 75 to 125  $\mu\text{m}$  and only 10% between 125 and 315  $\mu\text{m}$ . Size distribution of particles inside 9 clusters is exhibited in Fig. 4. Particles in the C-rich cluster (n°10) could not be

measured because of the inability to distinguish the outline of particles in automatic analysis (due to the carbon coating of the membrane). However, SEM manual observations reflect a large size distribution for this cluster. Clusters 3, 4, 7 and 9 present larger ranges of sizes (standard deviation > 50  $\mu\text{m}$ ) whereas clusters 1, 2, 5, 6 and 8 are characterised by less scattered values (standard deviation < 40  $\mu\text{m}$ ).

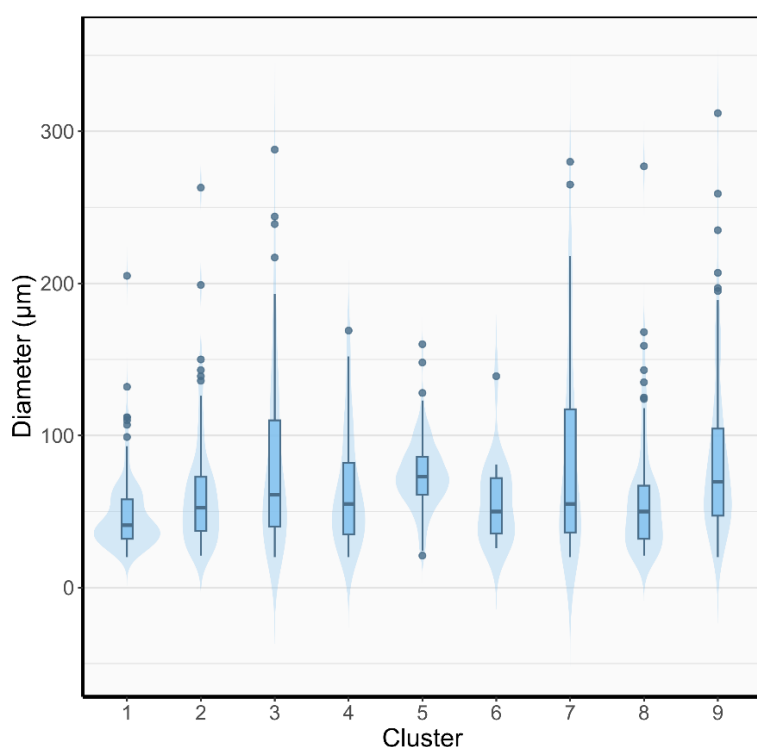


**Fig. 4** Violin plot of particle sizes in the 9 clusters identified by automatic SEM analysis

## 3.2 Soil physico-chemical properties

### 3.2.1 Characterization of soil parameters

The variability of physico-chemical parameters in soils appeared to be rather small between the different samples within the 9 studied zones (Table 3). Soil pH from all areas is rather slightly basic (range: 6.6–7.6; average value: 7.2), with maximum and minimum pH values observed in zones 4 and 1, respectively. The soil texture exhibits some heterogeneities with average silt contents ranging from 23% to 77% and sand from 15% to 73%. Higher clay contents were found in zone 2 (7%), 7 (12%) and 8 (10%) with a

*silt loam* texture. Zone 1 with the highest sand value (73%) was defined by a *loamy sand* texture and the others (zones 3, 4, 5 and 6) by a *sandy loam* one (Richer-De-Forges et al. 2008). Soil organic matter contents (SOM) range on average between 5% and 8% in all sampling location, with the highest content in zone 7 (10.2%). In addition,  $\text{CaCO}_3$  and  $\text{CaO}$  contents are higher in zone 2 (24%; 14.7%) and 7 (25%; 14.5%) whereas minima are observed in zone 1 (3%; <DL). CEC values are globally low (Rengasamy and Churchman 1999) and range between 4.2 meq/100g (zone 1) to 6.7 meq/100g (zone 7). The water contents range between 30% and 56%.

Major oxide measurements indicate homogenous and low Na<sub>2</sub>O, MgO and K<sub>2</sub>O concentrations in all areas, with average values of 0.6%, 1.14% and 1.3%, respectively. Larger concentration ranges are notable for Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub> and CaO, with the highest SiO<sub>2</sub> contents observed in zones 1 and 3 (>80%). The lowest are notable in zones 2 and 7 (<55%) where Al<sub>2</sub>O<sub>3</sub> and CaO concentrations follow an inverse pattern (Al<sub>2</sub>O<sub>3</sub> > 5.5% and CaO > 14%). Finally, Fe<sub>2</sub>O<sub>3</sub> contents range respectively between 1.6-2.7%.

### 3.2.2 Trace element concentrations in the study area

Table 4 displays trace element concentrations in the soils of Gravelines. Chemical characteristics of soils indicate higher concentrations in some elements compared to the surrounding ploughed soils of the Wateringues marine plain (Sterckeman et al. 2004). Molybdenum particularly presents higher values for all the studied samples (range: 0.39-1.76 mg.kg<sup>-1</sup>; average value, 0.74 mg.kg<sup>-1</sup>). Sampling points 11, 31 and 32 present lower concentrations for almost all PTE (Cd, Co, Cr, Cu, Mn, Mo, Ni, V and Zn). Sampling point 33 globally follows the same trend but contains higher concentrations of Cu and Pb (16 and 49.5 mg.kg<sup>-1</sup>, respectively). Zone 4 also presents higher values for these 3 elements. The highest concentrations of some PTE (Cd, Co, Cr Mo, Ni, V and Zn) are measured for the sampling zones 2 and 7 (points 21, 71, 72 and 73) and relatively high levels of Cr, Cu and Mn were also measured in zone 8. Furthermore, trace metal concentrations are lower than those measured in the regional background (Sterckeman et al. 2004) except for Mo and Pb.

### 3.3 PTE enrichments and accumulation indexes in the soils of Gravelines

Enrichment Factor (EF) could not be calculated for the sample 11 because of its aluminium concentration below the detection limit. Concerning the other samples, EF (ranging from 0.7 to 12) mostly indicates a minor enrichment

for the considered trace elements and reflects a diffuse contamination of the soils of Gravelines (depending on soil Al contents and the choice of the Wateringues marine plain background as a reference). As and Pb present no enrichment in 20 and 28% of the soils, respectively. Molybdenum is particularly characterised by a moderate and moderately severe enrichment on 50% and 35% of the studied soils, respectively. Enrichment up to moderately severe in As, Cd, Cu, Pb and Zn is also notable for 2 to 7% of the samples. Moderate enrichments in Cr and Ni are finally recorded for 2% and 4% of the studied soils.

The Nemerow integrated pollution index (NIPI) (Nemerow 1985) ranges between 1.0 (As) to 4.5 (Mo) (Table S3, supplementary information). Almost all the studied PTE are classified with a slight level of pollution (1<NIPI<2), except the Mo for which a heavy level of pollution is observed (NIPI>3). The lowest I<sub>geo</sub> values are noticeable for samples from zones 1 and 3 which globally are classified as *uncontaminated* (excepting minor geo-accumulation indexes in Cu, Mo, Pb) (Table S3). Higher I<sub>geo</sub> values are recorded for samples from zones 4, 5, 8 and 9, presenting minor accumulations in Cd, Cr, Cu, Mn, Ni, Pb, Zn and moderate accumulations in Mo. Zones 2 and 7 showed the highest I<sub>geo</sub> values in the latter elements (except Pb), as well as in Co, V and are classified as moderately to heavily contaminated in Mo.

## 4 Discussion

### 4.1 Identification of dust fallout particles

#### 4.1.1 Nature and origin of the particles

SEM observations and chemical analyses allow to discriminate dust fallout particles (collected during northeast wind conditions) into 10 clusters (Table 2). The cluster 10 (Fig. 3.10) is assigned to coal particles. Its emission is related to the presence of coal unloading facilities in the

**Table 3** Global characteristics of the soils of Gravelines (9 sampling zones). SD: standard deviation

| Sam-<br>pling<br>zone | Statis-<br>tics | pH  | Water con-<br>tent(%) | SOM<br>(%) | CEC<br>(meq/100 g) | CaCO <sub>3</sub><br>(%) | Clay<br>(%) | Fine silt<br>(%) | Coarse<br>silt (%) | Sand<br>(%) | LOI (%) | Na <sub>2</sub> O<br>(%) | MgO<br>(%) | Al <sub>2</sub> O <sub>3</sub><br>(%) | SiO <sub>2</sub><br>(%) | K <sub>2</sub> O<br>(%) | CaO<br>(%) | Fe <sub>2</sub> O <sub>3</sub><br>(%) |
|-----------------------|-----------------|-----|-----------------------|------------|--------------------|--------------------------|-------------|------------------|--------------------|-------------|---------|--------------------------|------------|---------------------------------------|-------------------------|-------------------------|------------|---------------------------------------|
| 1                     | Mean            | 6.6 | 29                    | 7          | 4.2                | 3                        | 1           | 11               | 11                 | 73          | 9       | <DL                      | <DL        | <DL                                   | 87                      | <DL                     | <DL        | <DL                                   |
|                       | SD              | 0.0 | 7                     | 1          | 0.3                | 1                        | 0           | 1                | 2                  | 7           | 1       | <DL                      | <DL        | <DL                                   | 2                       | <DL                     | <DL        | <DL                                   |
|                       | Min             | 6.5 | 22                    | 7          | 4.0                | 2                        | 1           | 10               | 9                  | 65          | 8       | -                        | -          | -                                     | 86                      | -                       | -          | -                                     |
|                       | Max             | 6.6 | 37                    | 8          | 4.5                | 3                        | 2           | 12               | 13                 | 79          | 10      | -                        | -          | -                                     | 89                      | -                       | -          | -                                     |
| 2                     | Mean            | 7.4 | 44                    | 6          | 5.9                | 24                       | 6           | 30               | 29                 | 31          | 24      | <DL                      | 1.0        | 5.7                                   | 50                      | 1.4                     | 14.7       | 2.7                                   |
|                       | SD              | 0.1 | 4                     | 1          | 0.3                | 1                        | 1           | 1                | 0                  | 7           | 7       | <DL                      | <DL        | 0.6                                   | 4                       | 0.1                     | 1.6        | 0.3                                   |
|                       | Min             | 7.3 | 41                    | 5          | 5.7                | 23                       | 6           | 30               | 28                 | 23          | 19      | -                        | 1.0        | 5.0                                   | 45                      | 1.3                     | 12.8       | 2.4                                   |
|                       | Max             | 7.6 | 48                    | 7          | 6.3                | 25                       | 7           | 31               | 29                 | 36          | 32      | -                        | 1.0        | 6.1                                   | 52                      | 1.5                     | 15.8       | 2.9                                   |
| 3                     | Mean            | 7.1 | 33                    | 5          | 4.3                | 5                        | 3           | 31               | 17                 | 49          | 9       | 0.5                      | <DL        | 3.0                                   | 81                      | 1.2                     | 3.6        | 1.6                                   |
|                       | SD              | 0.2 | 6                     | 1          | 0.6                | 2                        | 1           | 12               | 5                  | 22          | 2       | 0.1                      | <DL        | 0.3                                   | 3                       | 0.1                     | 0.6        | 0.6                                   |
|                       | Min             | 7.0 | 24                    | 4          | 3.7                | 3                        | 2           | 14               | 13                 | 3           | 6       | 0.5                      | -          | 2.6                                   | 76                      | 1.1                     | 2.3        | 1.3                                   |
|                       | Max             | 7.6 | 45                    | 7          | 5.4                | 7                        | 6           | 51               | 26                 | 74          | 11      | 0.6                      | -          | 3.5                                   | 85                      | 1.3                     | 4.3        | 3.2                                   |
| 4                     | Mean            | 7.6 | 56                    | 8          | 5.4                | 15                       | 4           | 39               | 21                 | 39          | 14      | <DL                      | 1.1        | 4.0                                   | 68                      | 1.3                     | 8.7        | 2.0                                   |
|                       | SD              | 0.2 | 12                    | 1          | 0.4                | 5                        | 2           | 6                | 1                  | 13          | 2       | <DL                      | 0.0        | 1.0                                   | 5                       | 0.1                     | 3.2        | 0.5                                   |
|                       | Min             | 7.4 | 43                    | 7          | 4.8                | 11                       | 2           | 31               | 19                 | 31          | 12      | -                        | 1.1        | 2.9                                   | 61                      | 1.1                     | 6.3        | 1.5                                   |
|                       | Max             | 7.8 | 76                    | 10         | 5.8                | 23                       | 6           | 50               | 23                 | 63          | 17      | -                        | 1.1        | 5.3                                   | 72                      | 1.4                     | 14.4       | 2.6                                   |
| 5                     | Mean            | 7.3 | 33                    | 6          | 5.0                | 10                       | 4           | 29               | 19                 | 46          | 12      | <DL                      | <DL        | 3.7                                   | 74                      | 1.3                     | 5.9        | 2.0                                   |
|                       | SD              | 0.2 | 4                     | 1          | 0.6                | 1                        | 1           | 3                | 2                  | 7           | 1       | <DL                      | <DL        | 0.4                                   | 1                       | 0.1                     | 0.2        | 0.4                                   |
|                       | Min             | 7.0 | 28                    | 5          | 4.4                | 9                        | 3           | 27               | 15                 | 34          | 11      | -                        | -          | 3.1                                   | 73                      | 1.2                     | 5.8        | 1.3                                   |
|                       | Max             | 7.5 | 38                    | 8          | 5.7                | 11                       | 5           | 36               | 21                 | 54          | 13      | -                        | -          | 4.3                                   | 75                      | 1.4                     | 6.3        | 2.7                                   |
| 6                     | Mean            | 6.9 | 34                    | 7          | 5.0                | 9                        | 4           | 32               | 22                 | 42          | 12      | <DL                      | <DL        | 3.5                                   | 75                      | 1.3                     | 5.3        | 1.7                                   |
|                       | SD              | 0.1 | 1                     | 1          | 0.3                | 0                        | 0           | 1                | 1                  | 1           | 1       | <DL                      | <DL        | 0.1                                   | 1                       | 0.0                     | 0.3        | 0.0                                   |
|                       | Min             | 6.9 | 34                    | 6          | 4.7                | 9                        | 4           | 31               | 20                 | 41          | 11      | -                        | -          | 3.5                                   | 74                      | 1.2                     | 5.0        | 1.7                                   |
|                       | Max             | 7.0 | 35                    | 8          | 5.3                | 9                        | 4           | 33               | 23                 | 43          | 13      | -                        | -          | 3.6                                   | 76                      | 1.3                     | 5.5        | 1.8                                   |
| 7                     | Mean            | 7.6 | 53                    | 8          | 6.7                | 25                       | 8           | 46               | 27                 | 18          | 20      | <DL                      | 1.3        | 5.9                                   | 54                      | 1.4                     | 14.5       | 2.5                                   |
|                       | SD              | 0.1 | 14                    | 1          | 0.3                | 2                        | 2           | 7                | 2                  | 10          | 2       | <DL                      | 0.2        | 0.5                                   | 2                       | 0.1                     | 1.1        | 0.6                                   |
|                       | Min             | 7.4 | 38                    | 6          | 6.3                | 22                       | 6           | 37               | 25                 | 4           | 17      | -                        | 1.1        | 5.2                                   | 52                      | 1.3                     | 12.6       | 1.5                                   |
|                       | Max             | 7.8 | 81                    | 10         | 7.2                | 27                       | 12          | 59               | 31                 | 32          | 22      | -                        | 1.6        | 6.8                                   | 57                      | 1.6                     | 15.5       | 3.1                                   |
| 8                     | Mean            | 7.5 | 44                    | 6          | 5.8                | 15                       | 9           | 53               | 25                 | 15          | 14      | <DL                      | 1.2        | 5.2                                   | 66                      | 1.4                     | 8.8        | 2.4                                   |
|                       | SD              | 0.1 | 10                    | 1          | 0.6                | 0                        | 1           | 4                | 2                  | 7           | 1       | <DL                      | 0.2        | 0.7                                   | 2                       | 0.1                     | 0.3        | 0.2                                   |
|                       | Min             | 7.3 | 32                    | 5          | 5.1                | 14                       | 6           | 48               | 21                 | 9           | 12      | -                        | 1.0        | 4.2                                   | 64                      | 1.3                     | 8.5        | 1.9                                   |
|                       | Max             | 7.6 | 60                    | 8          | 6.8                | 15                       | 10          | 58               | 28                 | 33          | 16      | -                        | 1.4        | 6.4                                   | 70                      | 1.5                     | 9.3        | 2.6                                   |
| 9                     | Mean            | 7.4 | 36                    | 7          | 5.4                | 9.0                      | 5           | 44               | 25                 | 26          | 12      | 0.7                      | 1.1        | 3.5                                   | 74                      | 1.3                     | 5.5        | 2.7                                   |
|                       | SD              | 0.2 | 3                     | 1          | 0.2                | 2.5                      | 1           | 2                | 2                  | 3           | 2       | <DL                      | 0.0        | 0.7                                   | 4                       | 0.1                     | 1.5        | 0.4                                   |
|                       | Min             | 7.2 | 31                    | 6          | 5.2                | 5.7                      | 4           | 42               | 23                 | 22          | 10      | 0.7                      | 1.1        | 2.6                                   | 69                      | 1.1                     | 3.9        | 2.3                                   |
|                       | Max             | 7.8 | 38                    | 8          | 5.6                | 12.4                     | 6           | 46               | 27                 | 30          | 14      | 0.7                      | 1.1        | 4.5                                   | 79                      | 1.4                     | 7.6        | 3.1                                   |

harbour area. [Deboudt et al. \(1997\)](#) also showed the significant use of coal in storage and handling activities in the Dunkerque agglomeration. These carbon-rich particles are potentially associated with trace metal elements

(As, Cd, Cr, Mo, Ni, Pb), according to [Wagner and Hlatshwayo \(2005\)](#). For the cluster 5 (Fig. 3.5), high aluminium concentrations and framboidal morphology of the particles suggest alumina raw material related to industrial

process. This assignment was confirmed thanks to the EDS-SEM analysis of the corresponding raw material as a reference compound (Fig. 3.5). Fe-rich particles in cluster 1 (Fig. 3.1a, b) are considered as iron ore particles used in industrial activities in the field of metallurgy and/or steel making (Laversin 2006). Si and Ca concentrations in cluster 9 match to slag particles generated by Si Mn and/or Fe Mn alloys production (Hernández-Pellón et al. 2017; Baricová et al. 2018). The composition of cluster 8 (Fig. 3.8a, b) is described in the literature as iron oxide (Magiera et al. 2008; Bourliva et al. 2011; Ebert et al. 2012). In the dust sample, these particles also rich in Zn, Mn, Cr, Al and Mg were found as melted-like particles or spheres. They could be ascribed to particulate emissions from a metallurgical plant located in the industrial area; this is in agreement with many studies showing that spherical morphologies result from high-temperature processes related to metallurgical activities/industries (Ebert et al. 2012; Hleis et al. 2013; Zhang et al. 2020). Alumino-silicates (cluster 3) (Fig. 3.3a, b) may originate from the earth's crust (through continental dust), construction activities or industrial processes (coal combustion) (Ebert et al. 2000; Laversin 2006; Genga et al. 2018). Particles rich in Ca and other major elements (Si, Fe) (cluster 2; Fig. 3.2a, b) are interpreted as calcium carbonate alone or mixed with metal oxide. They could be produced by steel factories (Bourliva et al. 2011) but also correspond to raw material or have natural origin. The Si-rich cluster 7 (Fig. 3.7) indicates in the dust sample the presence of quartz coarse grains, abundant in this coastal environment (Manickam and Barbaroux 1987; Vos et al. 2014). Cluster 4 (Ca-rich particles) (Fig. 3.4) can be assimilated to calcium carbonate particles used in steel production. According to Bourliva et al. (2011) and Genga et al. (2018), they can also be generated during building, construction and demolition activities. In the study area, Ca-rich particles are mostly used as raw material for the steel industry (Hleis et al. 2013). In 2005,

Laversin et al. showed the emission of manganese-based particles (cluster 6) in metallurgical industries. Sharp particle shapes could correspond to dust emitted from manganese ore handling. Several studies also demonstrated the predominance of metallurgical and steel industries in the release of manganese in urban particulate matter (Sweet et al. 1993; Howe et al. 2004).

Only 1 of the 10 clusters appeared as a *pristine* cluster composed of mostly sandy Si-rich particles (probably quartz) (cluster 7, ~4%) with variable diameters (Fig. 4). Two mixed clusters were identified with aluminosilicate (n°3, 4.5%) or Ca-rich particles (n°4, 2.5%) coming from either natural, industrial or construction material sources. All the other particles (clusters n°1, 2, 5, 6 and 8: 35.5%) characterised by smaller size distributions are interpreted as emitted by industrial sources: coal, slags, iron ores, metallurgical or steel dust (Table 2). Additionally, the cluster 9 (9.3%, Fig. 3. 9a, b, c) presents different morphologies of industrial emissions with some aggregated particles, explaining the more elongated size distribution of this cluster. Thus, it appears that more than 88% of the particles collected in the city centre of Gravelines during north-east wind conditions have an industrial origin. This is corroborated by the noteworthy enrichment in specific metals (particularly Cd, Cr Mo, Ni, Zn) of the dust sample.

#### 4.1.2 Potential origins of trace elements in the dust deposition sample

A clear anthropogenic source (Table 1) was highlighted for Cr, Mn, Zn, As, Cd, Co, Cu, Ni, Mo, Pb and V. The first 3 elements (Cr, Mn, Zn) were already identified by EDS-SEM analysis in the dust sample (in slag, steel and metallurgical particles). According to the Agency for Toxic Substances and Disease Registry (ATSDR) (ATSDR 2005; ATSDR 2012b; ATSDR 2012a), the main anthropogenic sources of Co, Ni and V in particulate matter are metal mining, smelting

**Table 4** Trace element contents for the 18 top soil sampling points in Gravelines (mg.kg<sup>-1</sup>). In bold, values more than twice higher than the Wateringues marine plain background. The Pollution Load Index (PLI) is indicated for each study area. Tomlinson et al. (1980) classified PLI as: unpolluted (PLI < 1), and polluted (PLI ≥ 1). According to Men et al. (2018) this classification is the same for the (PLI) zone. The Nemerow integrated pollution index (NIPi) (Nemerow 1985) is indicated for each PTE. The NIPi is divided into four levels to indicate the pollution degree: safe (NIPi ≤ 1.0), slight pollution (1.0 < NIPi ≤ 2.0), moderate pollution (2.0 < NIPi ≤ 3.0) and heavy pollution (NIPi > 3.0) (Cheng et al. 2014)

| Sampling zone   | 1          | 2          | 3          | 4          |            |            | 5          |            |            | 6          |            |             | 7          |            |            | 8          |            |            | 9          |            |                 | NIPi<br>Average<br>for the<br>soils of<br>Grave-<br>lines | Percentile |      | Wateringues<br>marine plain<br>background <sup>a</sup> | Regional<br>median <sup>a</sup> |
|-----------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|-------------|------------|------------|------------|------------|------------|------------|------------|------------|-----------------|-----------------------------------------------------------|------------|------|--------------------------------------------------------|---------------------------------|
|                 |            |            |            | 31         | 32         | 33         | 41         | 42         | 51         | 52         | 61         | 71          | 72         | 73         | 81         | 82         | 83         | 91         | 92         | 5th        | 50 th<br>Median |                                                           | 95 th      |      |                                                        |                                 |
| Sampling point  | 11         | 21         | 31         | 32         | 33         | 41         | 42         | 51         | 52         | 61         | 71         | 72          | 73         | 81         | 82         | 83         | 91         | 92         |            |            |                 |                                                           |            |      |                                                        |                                 |
| As              | 4.3        | 6.7        | 5.0        | <b>9.0</b> | 3.6        | 3.9        | 5.3        | 3.9        | 3.7        | 4.0        | 4.7        | 5.1         | 4.4        | 4.0        | 4.9        | 4.6        | 4.5        | 4.4        | 1          | 4.8        | 3.7             | 4.4                                                       | 7.0        | 4.1  | 8.2                                                    |                                 |
| Cd              | 0.24       | 0.33       | 0.26       | 0.25       | 0.23       | 0.37       | 0.30       | 0.40       | 0.32       | 0.31       | 0.39       | <b>0.50</b> | 0.35       | 0.28       | 0.28       | 0.26       | 0.30       | 0.32       | 1.5        | 0.32       | 0.23            | 0.31                                                      | 0.42       | 0.24 | 0.41                                                   |                                 |
| Cr              | 14         | <b>68</b>  | 31         | 32         | 35         | 45         | 47         | 48         | 42         | 38         | <b>68</b>  | <b>77</b>   | <b>60</b>  | 45         | 51         | 48         | <b>68</b>  | 49         | 1.7        | 48         | 29              | 47                                                        | 70         | 28   | 52                                                     |                                 |
| Co              | 1.7        | 6.1        | 2.6        | 2.9        | 3.7        | 4.7        | 4.5        | 3.6        | 3.2        | 3.3        | 4.4        | 5.2         | 5.3        | 3.9        | 4.4        | 4.4        | 3.8        | 3.5        | 1.1        | 4.0        | 2.5             | 3.8                                                       | 5.4        | 3.6  | 9.1                                                    |                                 |
| Cu              | 5          | 9          | 12         | 8          | <b>16</b>  | <b>17</b>  | <b>14</b>  | <b>14</b>  | 9          | 9          | 8          | 13          | 9          | 8          | 10         | 9          | 8          | <b>16</b>  | 1.9        | 11         | 7               | 9                                                         | 16         | 7    | 14                                                     |                                 |
| Mn              | 107        | 316        | 194        | 186        | 224        | 162        | 197        | 280        | 283        | 218        | 279        | 302         | 303        | 412        | 277        | 264        | <b>422</b> | 305        | 1.6        | 263        | 154             | 278                                                       | 413        | 207  | 485                                                    |                                 |
| Ni              | 6          | <b>22</b>  | 9          | 10         | 12         | 15         | 16         | 13         | 12         | 11         | <b>20</b>  | <b>24</b>   | <b>19</b>  | 13         | 15         | 15         | 16         | 13         | 1.7        | 15         | 8               | 14                                                        | 22         | 9    | 19                                                     |                                 |
| Mo              | <b>0.4</b> | <b>0.9</b> | <b>0.4</b> | <b>0.4</b> | <b>0.4</b> | <b>0.7</b> | <b>0.8</b> | <b>0.7</b> | <b>0.7</b> | <b>0.6</b> | <b>1.4</b> | <b>1.8</b>  | <b>0.8</b> | <b>0.5</b> | <b>0.7</b> | <b>0.5</b> | <b>0.8</b> | <b>0.6</b> | <b>4.5</b> | <b>0.7</b> | 0.4             | 0.7                                                       | 1.5        | 0.2  | 0.5                                                    |                                 |
| Pb              | 24         | 24         | 30         | 22         | <b>49</b>  | <b>45</b>  | 39         | 35         | 23         | 36         | 22         | 25          | 26         | 25         | 28         | 32         | 22         | 24         | -          | 30         | 22              | 26                                                        | 46         | 22   | 29                                                     |                                 |
| V               | 15         | <b>68</b>  | 25         | 29         | 38         | 44         | 44         | 35         | 33         | 30         | 52         | 61          | 57         | 44         | 49         | 48         | 50         | 40         | 1.3        | 42         | 23              | 44                                                        | 62         | 34   | 58                                                     |                                 |
| Zn              | 45         | 51         | 39         | 36         | 45         | <b>83</b>  | 64         | <b>72</b>  | 54         | 68         | 58         | <b>82</b>   | 52         | 42         | 46         | 44         | 55         | 60         | 1.6        | 55         | 38              | 53                                                        | 82         | 36   | 67                                                     |                                 |
| PLI<br>per zone | 0.81       | 1.84       | 1.20       |            |            | 1.66       |            | 1.47       |            | 1.36       | 1.84       |             |            | 1.46       |            |            | 1.56       |            |            | 1.47       |                 |                                                           |            |      |                                                        |                                 |

<sup>a</sup> (Sterckeman et al. 2004)

and coal combustion (Karimi Nezhad et al. 2015; Ulrich et al. 2019). However, Ni and V are also often associated with petrochemical industries (Alleman et al. 2010) or with heavy fuel combustion related to shipping transport (Ledoux et al. 2017). The question of dust emitted by sea transport is not supported by V/Ni ratio lower than 0.25, far below the published range values of 2.5-3.5 (Ledoux et al. 2017). Nonetheless, according to the European Pollutant Release and Transfer Register (E-PRTR), the emission of Ni could be linked to local industrial emissions related to the dust recycling from the stainless-steel production. The possible metallurgic and steel plant origin concerns all the studied PTE but other sources should be considered: waste incineration (As, Cd) (Zhao et al. 2014; Ma et al. 2018), pesticide and fertilizer application (As, Cu, Cd, Pb) (Campos 2003; He et al. 2005) or road traffic (Pb, Cu, Zn) (Lee et al. 2006; Kadi 2009). Thus, it can be suggested that Cr, Mn, Co, Ni and V detected in the dust sample were most probably emitted by metallurgical activities, whereas As, Cd, Cu, Zn and Pb may also come from these other urban or peri-urban sources. Molybdenum has clearly an anthropogenic origin in the dust sample (with  $[Mo]=98 \text{ mg.kg}^{-1}$ ;  $EF_{Sc} = 169$ ). It was already detected in  $PM_{10}$  of Dunkerque agglomeration (Alleman et al. 2010). The study of Wong et al. (2021), based on anthropogenic perturbations to the atmospheric molybdenum cycle, pointed out that Mo deposition increased by 100 in industrialised regions because of combustion of coal and smelting processes. Indeed, this metal is commonly used in steels and iron alloys (Yigmatepe et al. 2010; Zhang et al. 2023). Numerous studies indicate also the presence of this element in coals (Orem and Finkelman 2003; Zhang et al. 2004; Wagner and Hlatshwayo 2005).

Deboudt et al. (1997) showed that industrial coarse particles (20-200  $\mu\text{m}$ ) can be deposited up to 5 km from the emission sources, according to the Stokes' law (Diouri 1987). In this sense, industrial particles (50  $\mu\text{m}$  in size) identified in

the dust sample (collected in northeast wind conditions) predominantly come from the nearby industries. From these perspectives, PTE identified as anthropogenic, such as Cr, Mn, Co, Ni, V and Mo as well, appear to be interesting tracers of industrial dust in the study area.

## 4.2 Pedological matrices and their potential affinity to PTE

Physico-chemical study of the soils of Gravelines globally indicated a loamy texture, relatively close to the ploughed soils of the Wateringues marine plain (Sterckeman et al. 2004). A strong correlation ( $R^2=0.99$ ) is notable between  $\text{CaCO}_3$  and CaO contents, indicating that calcium occurs in soils essentially as carbonates.  $\text{CaCO}_3$  is also correlated with the fine fraction, suggesting that carbonates are relatively reactive in the studied soils (Estefan et al. 2017). Correlations between clay, CEC and  $\text{Al}_2\text{O}_3$  ( $R^2>0.77$ ), suggest the presence of clay minerals in the matrices (Kumari et al. 2021). pH values, corresponding to neutral to slightly basic soils, are in agreement with calcium carbonate contents. The same correlations between these elements were highlighted in the soils of the Wateringues marine plain (Sterckeman et al. 2004), also justifying their utilization as referential material.

Furthermore, significant differences in pedological parameters were shown between some sampling zones. Principal component analysis (PCA) was performed on the pedological data set to highlight these differences and better understand the behaviour of the matrices toward metal inputs. PCA showed that the two first principal components contributed to 79.9% of the total variance (Fig. 5). The first principal component (PC1, 66.6%) was mainly formed by  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ , CaO and CEC, discriminating the contribution of quartz in the soil mineralogy ( $\text{SiO}_2$ ; sand) from the clay minerals ( $\text{Al}_2\text{O}_3$ ; clay; silt). The latter contributed to the efficiency of the soil absorption capacity (CEC) (Varadachari et al. 1994; Gobat et al. 2003).

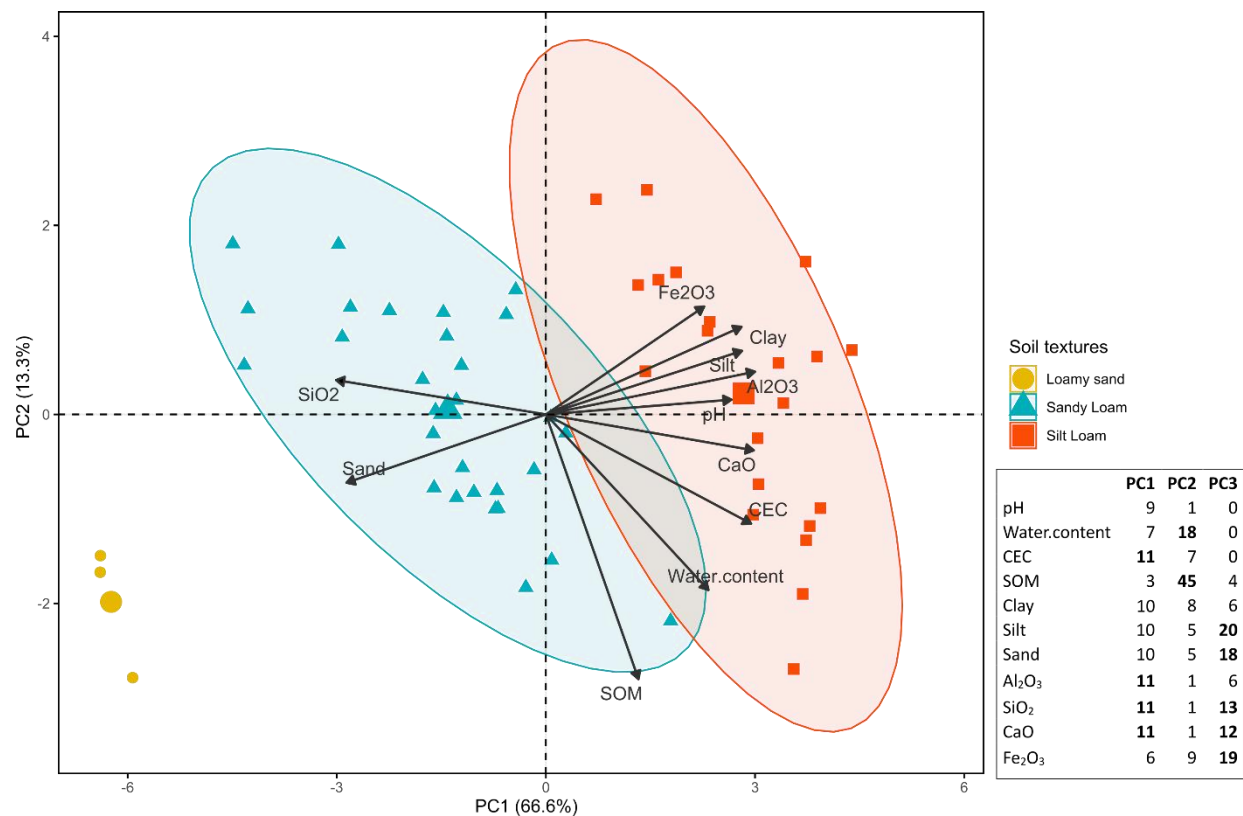


**Fig. 5** Principal component analysis (PCA) illustrating the variations of the pedological variables (arrows) for all the soil samples from Gravelines city and textures (colored symbols). Larger symbols indicate the centroid of values for each soil texture. The percentage of contribution of the different pedological variables in the building of the PCA axis is inset (bottom right). The most important contributors are denoted in bold

The second principal component (PC2, 13.3%) was mainly formed by SOM and water content, probably describing the soil porosity through organic matter aggregates and their water storage capacity (Saxton and Rawls 2006). These variables allowed the discrimination of soil textures according to their capacity of retention and reduction of the mobility of the PTE (Impellitteri et al. 2002; Wolińska et al. 2018; Lasota et al. 2020). Thus, a higher affinity between metals and soil particles is likely in the sampling zones 2, 7 and 8 (silt loam texture) compared to the 3, 4, 5 and 6 ones (sandy loam texture). Loamy sand texture and pedological criteria of the zone n°1 are consistent with a lower reactivity of soils with contaminants.

### 4.3 Contamination levels and potential sources of PTE in the soil matrices

Trace element concentrations in the soils of Gravelines are globally lower than (1) the

regional median values (Table 5), (2) those measured in French and European urban soils and (3) the investigative thresholds proposed by the French ASPITET program, *i.e.* Contribution of pedological stratification for interpreting trace element contents in soil horizons (Baize 2000) (Table 5). The hypothesis of a worrying pollution of soils by metals linked to industrial dust can be rejected. However, numerous PTE present at least minor enrichments compared to the Wateringues marine plain values (local background), indicating a possible influence of industrial dust deposition on the soil PTE budget. It is noteworthy that for such specific soils, the choice of the local background geochemistry appears to be of great importance in highlighting weak enrichments.

A Spearman's correlation matrix was performed in order to highlight PTE associations in industrial dust tracers and their affinity with the soil matrices. Indeed, numerous studies

Table 5 Comparison of trace metal element concentrations (mg.kg<sup>-1</sup>) in urban soils in different cities in France and Europe

| Location                                                 | Mn        | As    | Cd        | Co    | Cr      | Cu     | Mo        | Ni     | Pb      | V       | Zn      | References                    |
|----------------------------------------------------------|-----------|-------|-----------|-------|---------|--------|-----------|--------|---------|---------|---------|-------------------------------|
| Gravelines (France)                                      | 262       | 5     | 0.3       | 4     | 48      | 11     | 0.7       | 15     | 30      | 42      | 55      | This study                    |
| (range)                                                  | (107–422) | (4–7) | (0.2–0.5) | (2–6) | (14–77) | (5–17) | (0.4–1.8) | (6–24) | (22–50) | (15–68) | (36–83) |                               |
| Wateringues maritime plain (local background, France)    | 207       | 4     | 0.2       | 4     | 28      | 7      | 0.2       | 9      | 22      | 34      | 36      | Sterckeman et al. 2004        |
| Regional median (France)                                 | 485       | 8     | 0.4       | 9     | 52      | 14     | 0.5       | 19     | 29      | 58      | 67      | Sterckeman et al. 2004        |
| National median (France)                                 | 628       |       | 0.3       | 12    | 38      | 14     |           | 23     | 26      |         | 59      | Sterckeman et al. 2004        |
| Investigation thresholds by the ASPITET program (France) |           |       | 0.7       | 30    | 100     | 35     |           | 70     | 60      |         | 150     | Baize 2000                    |
| Nancy (France)                                           |           |       | 0.3       |       |         | 32     |           |        | 85      |         | 145     | Zhong et al. 2022             |
| Marseille (France)                                       |           |       | 0.9       |       |         | 87     |           |        | 151     |         | 354     | Zhong et al. 2022             |
| Nantes (France)                                          |           |       | 0.2       |       |         | 49     |           |        | 57      |         | 92      | Zhong et al. 2022             |
| Strasbourg (France)                                      |           |       | 0.0       |       | 42      | 26     |           |        | 92      |         | 85      | Van Geel et al. 2018          |
| United Kingdom                                           |           | 15    | 0.7       |       | 28      | 57     |           | 25     | 183     |         | 251     | Crispo et al. 2021            |
| Turku (Finland)                                          | 235       | 3     | 0.2       | 8     | 37      | 19     | 0.3       | 12     | 20      | 48      | 73      | Salonen and Korkka-Niemi 2007 |
| European community limit values range                    |           |       | 1–3       |       | 70      | 50–140 |           | 30–75  | 50–300  |         | 150–300 | Desaules 2012                 |
| World soils median                                       |           | 6     | 0.4       |       |         | 30     |           | 50     | 35      |         | 90      | Adriano 2001                  |

demonstrated a significant correlation between PTE with similar sources in soils (Cai et al. 2013; Jaffar et al. 2017; Yang et al. 2020). For this purpose, correlations were calculated from the enrichment factors of each anthropogenic PTE (Table S4, supplementary information). Pedological parameters previously described by the principal component 1 (CEC, Al<sub>2</sub>O<sub>3</sub>, CaO, SiO<sub>2</sub>) of the PCA were used in the correlation matrix to define the affinity of PTE with the different fractions of the soil matrices (Table S4). No significant correlation is evident between As, Cd, Cu, Mn, Mo, Pb, Zn concentrations and all the soil parameters. However, Cr, Co, Ni and V concentrations present correlations (R<sup>2</sup>>0.60) with some pedological parameters (CEC, Al<sub>2</sub>O<sub>3</sub> and CaCO<sub>3</sub>), indicating a relative affinity of metal inputs to the absorbent soil matrix.

Almost all the considered trace elements are present in the soils of Gravelines in a slight level of pollution (1<NIPI<2), confirming the diffuse character of the metallic contamination (Hakanson 1980). Molybdenum has a different behaviour and presents a strong level of pollution (NIPI = 4.5). The calculation of EF, I<sub>geo</sub> and pollution indexes for this element has to be relativised considering the very low content of Mo measured in the local background compared to the regional value (0.17 and 0.53 mg.kg<sup>-1</sup>, respectively). However, taking into account (1) the precedent characterization of dust fallout in Gravelines ([Mo] = 98 mg.kg<sup>-1</sup>), (2) the use of Mo in alloys and steel making processes (Maratray 1992; Yigmatepe et al. 2010), and (3) the absence of other significant sources of molybdenum around the city, this element with high NIPI value can be considered as tracer of local industrial (Vejahati et al. 2010). This is also supported by the correlations between EF of Mo, Cr and Ni (R<sup>2</sup>>0.67) in soils (Table S4), as well as their high contents in the dust sample collected in Gravelines (98, 1 461 and 603 mg.kg<sup>-1</sup> respectively). PTE are also associated with coals, as shown by Wagner and Hlatshwayo (2005).

Thus, coals and their transformation products could contribute to the observed enrichments in soils. In the latter, significant correlations ( $R^2 > 0.65$ ) also exist between Co, Ni and V enrichment factors, previously identified as interesting tracers of metallurgical activities in the Dunkerque agglomeration. Several studies have highlighted their coexistence in case of soil contamination under metallurgic industrial influence (Poznanović Spahić et al. 2018; Soltani-Gerdefaramarzi et al. 2021; Wang et al. 2022). It most probably reveals a slight contamination ( $1 < NIPI < 2$ ) by industrial dust coming from the seaport of Dunkerque (mostly of metallurgical origin). However, the contribution of petrochemical sources (Ni-V(-Co) associations) cannot be ruled out (Yuan et al. 2006; Alleman et al. 2010).

*Uncontaminated to moderately contaminated* level of geo-accumulation is notable for Mn, Cd and Zn ( $0 < I_{geo} < 1$ ) in soils. An input of Mn, Cd and Zn in soils through industrial dust deposition cannot be excluded, considering (1) their high concentration in the dust sample ( $Mn > 8000 \text{ mg.kg}^{-1}$ ,  $Cd > 9 \text{ mg.kg}^{-1}$  and  $Zn > 1600 \text{ mg.kg}^{-1}$ ), (2) their utilization in metallurgical and steel processes as explained above, and (3) the strong correlation between Zn and Cd enrichment factors in soils ( $R^2 = 0.81$ ). However, significant correlations ( $R^2 > 0.66$ ) between Zn, Cu and Pb enrichment factors suggest another provenance of these contaminants in soils. Indeed, in the literature, their association is often related to road traffic emissions through the wear and tear of tires (Smolders and Degryse 2002), the ancient use of lead gasoline (De Miguel et al. 1997) or the destruction of mechanical parts of vehicles (e.g. the braking systems) (Guo et al. 2012). Thus, the contamination of soils by Zn, Pb and Cu ( $1.5 < NIPI < 2$ ) could also be partly explained by the impact of non-exhaust road traffic. Besides, the use of Cu as soil amendment could be also considered (Ferreira et al. 2018).

9) and can be distinguished to the previous one by (1) its lower levels of pollution, and (2) the

## 4.4. Spatial vulnerability of the soils toward industrial dust depositions

### 4.4.1 Comparison of the different zones according to the level of metal contamination

The Pollution Load Index (PLI) was calculated considering all the anthropogenic PTE measured (As, Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, V, Zn) (Table 4). The PLI increases on the 9 sampling zones as follows: zone 1 < zone 3 < zone 6 < zone 5 < zone 8 < zone 9 < zone 4 < zone 7 < zone 2. PLI calculations appear particularly influenced by Cr, Ni and Mo concentrations in zones 2, 7 and 8. In contrast, higher contributions of Pb, Zn, Cu are notable for the PLI of zone 4. Calculations indicate a baseline level of pollutants for the zone 1 (PLI close to 1) and a progressive deterioration of the site quality ( $PLI > 1$ ) for the 8 other zones. The global PLI (considering all the sampling zones) also indicates a *progressive deterioration* of the global soils of Gravelines ( $PLI_{Gravelines} = 1.5$ ) (Angulo 1996).

A cluster analysis was performed based on the enrichment factors of the anthropogenic PTE in the soils from zones 2 to 9 (Fig. 6). The objective was to highlight some groups of soils on the basis on PTE associations discussed earlier. Zone 1 is not considered on this figure because of the impossibility to calculate its EF (Al concentrations below the detection limit) as well as its low absorbent capacity (sandy texture) explaining its weak PTE concentrations. Cluster I gathers soil samples of the zones 2, 7 and 8, presenting the highest PLI and  $I_{geo}$  for Mo, Cr, Ni, V and Co. According to the precedent results, these associations reflect contamination of soils by metallurgical dust, coming from the seaport. The impact of industrial dust depositions is particularly notable on these 3 sampling zones, located outside the city and close to emission sources (1.3 - 2 km). Cluster II is composed by the other studied areas (3, 4, 5, 6,

wider panel of contamination elements involved. Indeed, sampling points 31, 32, 51, 52,

61 are the least impacted by all the measured PTE and 33, 41, 42, 91, 92 present intermediate levels of pollution with cluster I. According to

$I_{geo}$  Index (Table S3), a slight industrial influence is notable on zones 4, 5, 6 and 9, through Cr, Ni, and Mo contaminations.

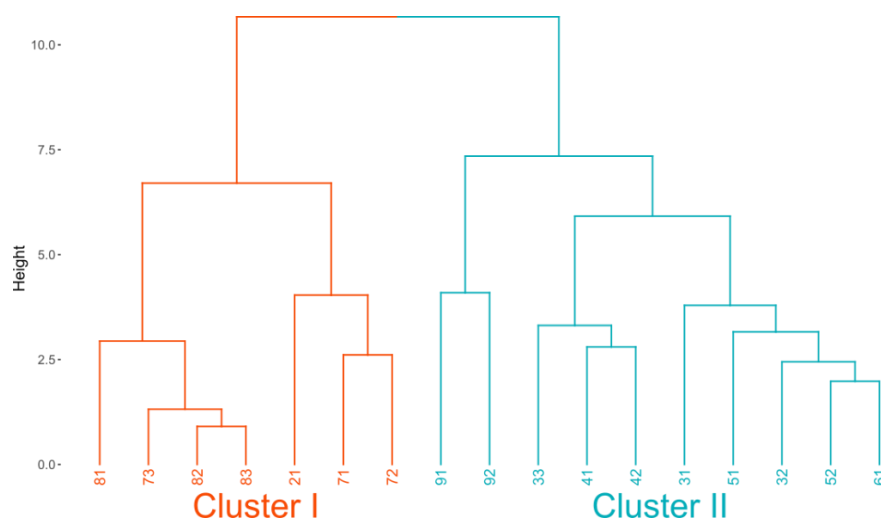


**Fig. 6** Dendrogram obtained from the cluster analysis of Gravelines soil samples (zones 2 to 9) using Ward's method and the Euclidean distance as a function of As, Cd, Cr, Co, Cu, Mn, Ni, Mo, Pb, V and Zn enrichment factors

Otherwise, Cu, Pb and Zn minor enrichments on these zones strongly suggest road traffic sources, in agreement with their location close to the city centre. Minor enrichments on zone 3, especially for sample point 33, could be explained in part by road traffic (Pb) and through soil amendments (Cu). Contrary to those of points 31 and 32, this sample 33 is not protected by surrounding vegetation and is more exposed to atmospheric deposition. To resume, while cluster I associates soils particularly affected by industrial dust, cluster II gathers soils affected by different anthropogenic impacts (for example road traffic or industries). Thus, almost all the studied areas showed a slight but significant contamination by industrial dust.

#### 4.4.2 Testing hypotheses concerning the spatial distribution of contamination by industrial dusts

Several hypotheses could be considered to explain the spatial distribution in soils of the metal concentrations generated by industrial dust: 1) wind remobilization inducing incomplete dust integration in soils, 2) the different capacity of metal retention of soils, 3) the distance from emitters, 4) the presence of barriers to the dust transport. Regarding the

notable deposition of industrial dust in the city of Gravelines during northeast wind episodes (recorded by ALOATEC), the question of the integration of dust in the pedological matrices remains open. An approximate mass balance was calculated, considering the amount of dust deposited on the sensors in periods of northeast winds (ALOATEC). This amount was evaluated for the period 2009-2021 and extrapolated to the period 1990-2021, using a constant deposition rate. Considering 100% of dust integration in soils, the theoretical concentrations obtained were always lower than the actual values in soils. Thus, dust remobilization by wind is not necessary to explain the observed concentrations.

Figure S1 reveals no significant correlation ( $R^2 \leq 0.54$ ) between the Pollution Load Index and CEC, CaO, SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> values. This indicates that the higher PLI in zones 2, 7 and 8 are not only explained by the nature of the matrix (*i.e.* absorbent capacity). The distance of the emission sources to the sampling location may be thought to be the primary factor dictating the level of contamination of the soils. Our data set does not allow to confirm this hypothesis (very poor correlation ( $R^2 < 0.15$ ) between PLI values and the

emission-to-site distance). The absence (or not) of protecting barriers (vegetation or habitations) appears to be another factor explaining the vulnerability of soils to dust deposition. This assumption is based on the facts that (1) the most affected zones (2, 7, 8) are the closest to the western seaport and located outside the city, within large and open primary production areas (Fig. 2), and (2) lower industrial impacts are detected in the residential sector. Thus, soil exposure may constitute an essential parameter to consider, not only when studying the fate of industrial dust but especially according to its future uses (Hirabayashi et al. 2012; Janhäll 2015).

## 5 Conclusion

This study was carried out in one of the most industrialised urban area in France, making it a complex environment in which to determine the sources of PTE contamination in soils. In fact, in addition to the significant emissions of industrial dust into the atmosphere (>2700 t in 2021), urban particles are also released from road traffic, construction or amendments activities. This study benefited from the analysis of a composite dust sample collected in an urban area, which enabled the geochemical signature of metallurgical dust fallout to be determined. Thus, three main tracer elements of industrial particles in soils were identified: Cr, Ni and Mo. Although molybdenum is not routinely studied in urban soils, it appears to be a very interesting tracer of atmospheric input of metallurgical origin in this study. The monitoring of these tracer elements in the soils of Gravelines has shown that all studied zones have been affected by industrial dust deposition at spatially variable concentrations correlated with the soil quality index. Although the soils located close to the industrial area are the most affected, the spatial distribution of soil contamination levels is not solely based on distance from emission sources. Soil exposure to dust fallout (whether or

not it is open to wind corridors) seems to be particularly involved.

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**Authors contribution** *Marine Casetta*: Conceptualization, Methodology, Validation, Formal analysis, Investigation, Writing - Original Draft, Writing - Review & Editing, Visualization; *Lucie Courcot*: Conceptualization, Methodology, Validation, Investigation, Writing - Review & Editing, Supervision; *Jacinthe Caillaud*: Conceptualization, Methodology, Validation, Investigation, Resources, Writing - Review & Editing, Supervision, Project administration, Funding acquisition; *David Dumoulin*: Validation, Investigation, Writing - Review & Editing; *Véronique Alaimo*: Validation, Investigation; *Vincent Cornille*: Investigation; *Gabriel Billon*: Validation, Writing - Review & Editing; *Dominique Courcot*: Resources, Writing - Review & Editing; *Michaël Hermoso*: Resources, Writing - Review & Editing, Supervision; *Sylvie Philippe*: Conceptualization, Methodology, Validation, Investigation, Resources, Writing - Review & Editing, Supervision, Project administration, Funding acquisition

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