ORIGINAL PAPER

Seifeddine Sellami^{1,2} · Ouahida Zeghouan³ · Mechi Lassaad^{4,5} • Younes Moussaoui^{6,7} · Brahim Kebabi¹

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Abstract

This study describes the determination of lead and pH in Setif soils. Soil samples from the town of Setif were taken from a total of

100 subsurface soils, systematically sampled (regular 1×1 km grid). The lead concentration was determined by atomic absorption and the average lead concentrations ranged from 24 to 384 mg kg^{-1} . The distribution of the different concentrations of lead and iso-concentration was distributed on the map of the exchange site with Arc GIS software. Compared with their local soil background values, higher concentrations of Pb were observed to different extents. The distribution of Pb concentrations has been explained by urban traffic.

Keywords Pollution . Soil . Fuel . Lead . Setif

Introduction

Industrial, agricultural, and urban development has been accompanied by real health problems related to environmental pollution. Industrial companies release into the environment a significant number of pollutants such as lead, elements likely to contaminate the environment (water, air, soil, plants) and to have a real impact on human health (Garnier [2005\)](#page-7-0). The

Responsible Editor: Abdullah M. Al-Amri

 \boxtimes Mechi Lassaad mechilassaad@yahoo.fr

- ¹ Pollution and Water Treatment Laboratory, Department of Chemistry, Faculty of Exact Sciences, University of Constantine 1, Constantine, Algeria
- ² Department of Materiel Sciences, Faculty of SESNV, University Larbi Tébessi, Tebessa, Algeria
- ³ Center for Research in Biotechnology (CRBt), Constantine, Algeria
- ⁴ Chemistry Department, Faculty of Science, Ha'il University, P.O. Box 2440, Ha'il 81451, Saudi Arabia
- ⁵ Material, Environment and Energy Laboratory (UR14ES26), Faculty of Sciences of Gafsa, University of Gafsa, Gafsa, Tunisia
- ⁶ Organic Chemistry Laboratory (LR17ES08), Faculty of Sciences of Sfax, University of Sfax, Sfax, Tunisia
- ⁷ Faculty of Sciences of Gafsa, University of Gafsa, Gafsa, Tunisia

environmental risks associated with soil pollution in Pb are increasingly worrying.

Anthropogenic lead in soil pollution is mainly due to automobile traffic, industrial activities (Delmas et al. [2002\)](#page-7-0), sewage treatment, waste incineration, agricultural use of fertilizers and pesticides, the production of paints, and pigments (Oulhote et al. [2011](#page-7-0); Triantafyllidou and Edwards [2012](#page-8-0)), which may have adverse effects on ecosystems (Facchinelli et al. [2001](#page-7-0)).

Bioavailability or lead in soil is dependent on soil properties (Luo et al. [2014](#page-7-0)) and an assessment of lead toxicity based on total metal concentrations may therefore overestimate or underestimate the actual availability and risk of lead in soil. It can also threaten the health of animals and humans along the food chain. However, only a fraction of the total concentration of metals in the soil is available to be absorbed and have toxic effects on soil organisms, defined as the bioavailability of metals (Peijnenburg et al. [2007\)](#page-7-0).

In Algeria, lead tetraethyl is still used to improve the performance of gasoline. It is used for its anti-knocking role. It also allows lubricating the valves of the engines (Guibet and Montagne [2011\)](#page-7-0).

The global consumption of fuels containing lead in Algeria reached 2.71 million tons in 2017 (1.18 million tons in normal gasoline, 1.53 million tons in super gasoline: Journée d'études sur la médiatisation de l'essence sans plomb SONATRACH Division Raffinage Production des Essences sans Plomb Post-Réhabilitation des Raffineries 23 Mai [2012\)](#page-7-0).

The harmful effect of lead on the environment and on human health has been widely studied (Delon [1986](#page-7-0); Cunningham and Berti [1993](#page-7-0); Pichard [2002;](#page-7-0) Dumat et al. [2006;](#page-7-0) Al-Dabbas et al. [2015;](#page-7-0) Etchevers et al. [2014](#page-7-0); Hojati [2017\)](#page-7-0). Lead containing petrol seems to be the main source of contamination in the cities. This has led governments in developed countries to ban the addition of lead to fuels (Dela Guardia et al. [1983\)](#page-7-0).

The purpose of this study is to determinate the concentration of lead in the soil of the city of Setif, one of the most populated cities in Algeria. Samples were taken from an area of approximately 100 km^2 including the city and surrounding areas.

Materials and methods

All chemicals and reagents were obtained from Sigma Aldrich and were of analytical grade or equivalent.

Site description

The city of Setif is located in the east of Algeria, in a highland region; it is 300 km east of the capital Algeria and rises to 1100 m altitude. It covers an area of 127 km², with a large population, estimated at more than 410,000 inhabitants (2015). It occupies a predominant position among the cities of the highlands. It is also a major crossing point because it is crossed by the East-West Main road, as well as the N° 09 national road and the N° 5 national road (Fig. [1\)](#page-2-0). Setif soils are generally sandy to clayey in texture and mostly classified as arid soils and are calcareous. Minerlogically, most of the soils are dominated by kaolinite, illite, smectite, and chlorite-typical for most arid and semi-arid soils (Djenba [2013](#page-7-0)).

Sampling

The sampling points were systematically distributed in the town of Setif and its surroundings, based on a regular $1 \times$ 1 km grid. Thus, 100 grid cells were sampled (Fig. [2](#page-3-0)). In the city center, where most soils were very anthropogenic, samples were collected from gardens, cemeteries, and parks. Geographic coordinates were taken at each sampling point using a GPS. Samples were taken in February, March, and April 2015 at a depth of 0 to 2 cm. The soil samples were dried in the open air and sieved to 2 mm, according to the French standard NF X31-101 (French Agency for Standardization (AFNOR) [1994\)](#page-7-0) and kept in closed plastic bags until analysis.

Measurement of the concentration of lead in the soil

To determine the concentration of lead in the soil, we followed two steps:

Mineralization

The digestion step is an essential step because it limits the interferences related to the organic matter. In our study, wet mineralization was favored and carried out as follows: A 5-g sample of the soil sample was digested in a solution containing 5 mL of nitric acid (65%), 10 mL of hydrochloric acid (37%), and 10 mL of the water. The whole is kept in a sand bath set at a temperature of about 300 °C until complete drying of the sample. Fifty milliliters of water is then added to the sample. After stirring and filtration, the concentration of lead is determined by flame atomic absorption spectroscopy (FAAS).

Calibration and quantification

The lead concentration was determined by flame atomic absorption spectroscopy (FAAS). This method was the most feasible and could be suitably adapted to a higher measurement concentration of more than 30 elements; the residual concentration of Pb was determined by atomic absorption spectrometry (Analytik Jena NovAA 400). A calibration curve $(1-5 \text{ mg } L^{-1})$ lead was prepared by appropriate dilution of a stock standard solution of lead nitrate (equivalent to 1 g L^{-1} lead) (Fig. [3](#page-4-0)). The lead wavelength (λ max) is equal to 283.3 nm. The software used to determine the absorbance is Win AAS (Version 3.15.0). The detection limit of this device is 0.25 ppm (Amiard et al. [1987](#page-7-0)). A Cyber Scan pH 510 digital pH meter equipped with a combined glass electrodecalomel was used for the pH measurement.

The standard was given by the following: $Abs = 0.004$ $[Pb^{2+}]$, where $[Pb^{2+}]$ is in milligram per liter. Furthermore, the coefficient of determination (R^2) was found to be 0.997.

Estimation of lead content in gasoline

The analysis of lead in gasoline marketed in the town of Setif was carried out by X-ray fluorescence using a 9-W Panalytical Epsilon 3 spectrophotometers. This energy-dispersive X-ray spectrophotometer is designed for elemental analysis. The system is controlled by a computer on which the OMNIAN analysis software is installed. The sample is placed under helium flow during the analysis. The X-ray fluorescence spectrum was recorded with a silver filter with a thickness of 100 μm with a potential difference of 30.00 kV and a current of 300 μA.

Fig. 1 Location of the study area with the 100 sampling points

Fig. 2 Site of the soil sampling of the region of the town of Setif

pH measurement

Accurately weighed 10 g of the ground and sieved soil sample was weighed in a clean glass beaker of 50 mL and 25 mL deionized water was added to form a 1:2.5 soil/water slurry solution. Then, the beaker, containing the mixture, was placed on an automatic stirrer and stirred for 30 min. For the measurement of pH, the

meter was calibrated with the standard buffer solutions of pH 4 and 7 before use. The pH measurements of the soil/water mixtures were carried out immediately after the soil samples were brought to the laboratory. The measurements were done by immersing the calibrated pH meter probes into the upper part of the slurry solution of the mixtures until the readings were stable (Odiyo et al. [2005\)](#page-7-0).

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Fig. 3 Calibration curve, Abs = $f([Pb^{2+}])$

Results and discussions

Results

The X-ray fluorescence analysis of gasoline marketed in the town of Setif shows that it contains 0.982 g L^{-1} of lead. This value corresponds to 1.53 g of tetraethyl lead (PTE) per liter of gasoline. It also contains much lower contents the following elements as Br (Fig. 4).

The results of the atomic absorption analysis of lead in our samples collected in the town of Setif are summarized in Table 1. Based on the results shown in Table 1, the distribution of the different concentration of lead and isoconcentration was distributed on the exchange site map with Arc GIS software (Fig. [5\)](#page-6-0). The average lead concentration in the town of Setif is 67.705 mg kg⁻¹. A minimum of 24.097 mg kg^{-1} was measured for sample N° 53 and a maximum of 383.621 mg kg−¹ was measured for sample N° 26. Generalized low-level contamination raised the overall concentrations to 30–100 mg kg^{-1} (Davies [1995](#page-7-0)).

Fig. 4 X-ray fluorescence spectrum of gasoline marketed in the town of Setif; red curve with lead; green curve without lead

Table 1 (continued)

Ech	N	E	pH	$[Pb^{2+}]$ (mg kg ⁻¹)
66	36° 12' 11.95	5° 24' 56.64	8.03	66.831
67	36° 12' 11.95	5° 25' 36.68	8.00	33.239
68	36° 12' 11.95	5° 26' 16.77	7.93	97.105
69	36° 12' 11.95	5° 26' 56.95	8.08	33.774
70	36° 12' 11.95	5° 27' 36.00	8.09	51.187
71	36° 12' 44.36	5° 21' 36.00	8.16	30.453
72	36° 12' 44.36	5° 22' 16.00	7.96	219.912
73	36° 12' 44.36	5° 22' 55.86	7.83	57.274
74	36° 12' 44.36	5° 23' 35.62	7.64	101.253
75	36° 12' 44.36	5° 24' 16.28	8.38	55.712
76	36° 12' 44.36	5° 24' 56.64	8.06	121.938
77	36° 12' 44.36	5° 25' 36.68	8.11	35.039
78	36° 12' 44.36	5° 26' 16.77	8.25	40.378
79	36° 12' 44.36	5° 26' 56.95	7.99	33.261
80	36° 12' 44.36	5° 27' 36.00	8.11	61.418
81	36° 13' 16.66	5° 21' 36.00	8.26	47.332
82	36° 13' 16.66	5° 22' 16.00	8.18	129.934
83	36° 13' 16.66	5° 22' 55.86	8.30	44.834
84	36° 13' 16.66	5° 23' 35.62	8.20	69.594
85	36° 13' 16.66	5° 24' 16.28	8.26	25.160
86	36° 13' 16.66	5° 24' 56.64	8.13	141.861
87	36° 13' 16.66	5° 25' 36.68	8.15	29.263
88	36° 13' 16.66	5° 26' 16.77	8.24	77.112
89	36° 13' 16.66	5° 26' 56.95	8.02	28.901
90	36° 13' 16.66	5° 27' 36.00	7.58	142.521
91	36° 13' 48.00	5° 21' 36.00	8.18	43.596
92	36° 13' 48.00	5° 22' 16.00	8.21	90.754
93	36° 13' 48.00	5° 22' 55.86	7.92	30.948
94	36° 13' 48.00	5° 23' 35.62	8.07	88.973
95	36° 13' 48.00	5° 24' 16.28	8.38	35.482
96	36° 13' 48.00	5° 24' 56.64	8.35	65.097
97	36° 13' 48.00	5° 25' 36.68	8.30	40.305
98	36° 13' 48.00	5° 26' 16.77	7.95	110.265
99	36° 13' 48.00	5° 26' 56.95	8.14	39.437
100	36° 13' 48.00	5° 27' 36.00	8.08	101.624

Discussion

Algeria is still using petrol containing lead tetraethyl (PET) as an antiknock additive at a concentration of 1.53 $g L^{-1}$. This leads to soil pollution by lead. The city of Setif is suffering from this pollution. It is much more pronounced inside the city is especially in the city center where the road traffic is high. It is less important outside the city, especially in areas with no roads. Total Pb concentrations have a median of 67.705 mg kg^{-1} with a considerable range (24.097 and 383.621 mg kg⁻¹). Thirteen percent of total Pb concentrations are less than 30 mg kg⁻¹, but elsewhere, widespread low-level contamination has raised overall concentrations to 30–100 mg kg⁻¹ (67%). In our study, the standard AFNOR, French Standard X 31-151 of 100 mg kg^{-1} is exceeded in 20% of the points of the city with a maximum of 383.621 mg kg⁻¹ at position N° 26 (AFNOR [1994\)](#page-7-0). This point is located next to a NAFTAL fuel distribution station. Most of the contaminated soil is located in the city center; the other points are located in the industrial zone ready for a road heavily used by vehicles, where the traffic is heavy.

Several studies have shown that lead deposition at ground level is positively correlated with road traffic density (Nawazish et al. [2012](#page-7-0)). High levels of lead in urban areas are mainly attributable to automobile exhaust and traffic emissions, in particular, leaded petrol and lubricating oils (Sharma and Dubey [2005](#page-8-0)).

Such an increase in lead concentrations in areas with heavy traffic has been observed in other cities. Indeed, despite the strong increase in the use of unleaded fuels in European countries, the level of lead in urban soils remains high due to the non-biodegradability of metals (Sánchez-Martin et al. [2000;](#page-7-0) Imperato et al. [2003\)](#page-7-0). According to the study department French roads and motorways, most of the lead particle deposition takes place in the first 20 m of the road. Ground-level lead concentrations are inversely proportional to the distance from the road (Sánchez-Martin et al. [2000;](#page-7-0) Imperato et al. [2003;](#page-7-0) Setra [2004;](#page-8-0) Genc and Ulupinar [2010;](#page-7-0) Teju et al. [2014\)](#page-8-0) indicating their linear dependence to the traffic density to the vehicular emissions. In developing countries, however, lead tetraethyl-containing gasoline is still widely used. For example, in Algeria, 89% of gasoline consumption is leading (Maas et al. [2010](#page-7-0)).

These data point to the existence of a causal link between the density of road traffic and the contamination of the environment by heavy metals, especially lead.

The chemical properties of lead in the soil are related to pH values; it is the factor that most influences the mobility and bioavailability of lead (Rieuwerts et al. [1998](#page-7-0)). For this type of study, pH is not only important in itself but also because it depends on the greater or lesser availability of the waterborne elements. At the pH values obtained (soils of 7.7–8.4, considered moderately alkaline), most of the metals in this range are in the form of low-solubility salts, being soluble at acidic pH values, as in the case of manganese, which means that it is not very likely to encounter toxicity problems in plants caused by trace elements (McBride [1994;](#page-7-0) Itanna [1998](#page-7-0)). This study showed us that pH did not influence the concentration of Pb measured in the 100 samples.

Conclusion

Pollution status, relationships with soil properties, and the main sources of Pb in topsoils from different land uses in the city of Setif, one of the most populated cities in Algeria, were studied. Compared with their local soil background values, higher concentrations of Pb were observed to different extents. Accordingly, industrial and urban soils showed higher concentrations and enrichments of Pb, rather than other land uses.

The spatial distribution of Pb concentrations has been explained by urban traffic. Lead concentrations showed spatial autocorrelation and high values were distributed over a large

Fig. 5 Spatial distribution of lead concentration and isoconcentration

area. The sampling strategy of this study (regular grid with a mesh size of 1×1 km) is adequate to describe such models. The sampling strategy can be a useful tool for providing land managers with spatial data over large areas from a land management perspective. In addition, this work has allowed us to see the real impact of land use. Factories and road traffic have a significant effect on environmental pollution and in particular soils. The petrol containing lead tetraethyl is also a major source of environmental contamination by lead. Soil pH did not influence the concentration of Pb.

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