Metal Speciation in Sludges: a Tool to Evaluate Risks of Land Application and to Track Heavy Metals Contamination in Sewage Network

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Research Article

Keywords: urban sewage sludge, agronomic properties, heavy metal speciation, WWTP contamination.

Posted Date: July 26th, 2021

DOI: https://doi.org/10.21203/rs.3.rs-672007/v1

Abstract

Agricultural spreading of dewatered sewage sludge from wastewater treatment plants is economically profitable but care must be taken to ensure that there is neither degradation of the agronomic quality of the soils nor contamination of them in the long term, particularly by accumulation of heavy metals. To evaluate the variability of the sludge in a given geographical area, we studied the sludge coming from five treatment plants in northern Algeria. We determined parameters that account for the agronomic quality of sludges and total content of Ag, Cd, Co, Cr, Cu, Ni, Pb, Ti and Zn. We evaluated the bioavailability of theses metals by determining their speciation by sequential extraction, each metal being distributed among five fractions: easily exchangeable, acido-soluble, bound to carbonates and partly to Fe-sulphides, bound to Fe- and Mn-oxides, bound to organic matter or sulphides, contained in poorly soluble minerals. We found that all the analysed sludges had satisfactory properties from an agronomic quality point of view. High total Ni content indicated that three sludges were not spreadable under French or Chinese regulations. Metal speciation, however, showed that Ni was contained in very poorly bioavailable fractions, and therefore presented a low risk in the soils concerned. In contrast, the total Cu was below the regulatory limit values, but contained in very bioavailable fractions with a risk of toxic effects by accumulation over less than 10 years. These results showed that regulations must take into account the bioavailability with regard to the characteristics of the soils on which sludge will be spread. Metal speciation in the sludge also made it possible to identify the zone of the sewerage network on which the sources of contamination must be sought and gave indications on the nature of these sources.

Introduction

Increasing urbanization, industrialization, and population pressures have resulted in growing challenges in wastewater management on a global scale (Allaoui et al. 2015). The disposal of residual sewage sludge issued from wastewater treatment plants (WWTP) in dedicated landfills or, by incineration, are options adopted in many parts of the world, but both strategies are expensive and can lead to environmental problems (Walter et al. 2006; Amir et al. 2005). Spreading dewatered sewage sludge (DSS) on agricultural land is another disposal option used in several countries because of its potential for improving soil physical properties and for containing significant nutrients for plant growth (Hernàndez et al. 1991; Martìnez et al. 2003; Singh and Agrawal, 2008). This practice aims to provide a sustainable solution while allowing a reduction in the use of fertilizers, but provided that two important constraints are met: the conservation of the agronomic properties of the soil (Tarchouna et al. 2010; Cherfouh et al. 2018) and the absence of accumulation of contaminants such as heavy metals (Alloway and Jackson, 1991; McBride, 1995) or organics (Lamastra et al. 2018; Alvarenga et al. 2015).

When DSS is used as organic amendments for agricultural purposes, its large amount of organic matter can indeed improve the biological activity and the physical properties of the soil (Clapp et al. 1986; Cherfouh et al., 2018), but the presence of heavy metals is probably the main critical impediment to overcome (Mo et al. 2000). Thus, it was noted that applying sewage sludge to soil might provide potentially toxic metals under labile forms (McBride, 1995). Several studies proved that urban sewage sludge contains significant concentrations of heavy metals because municipal sewage treatment plants are likely to receive industrial and other wastewater. Heavy metals in sludge constitute a relevant constraint limiting their valorization on agricultural soils, in particular, because of the high contents and their bioavailability to the soil-plant system.

Several studies deal with the content of heavy metals and their potential mobility in DSS. There are, however, surprisingly few studies which deal, within a given economic and climatic zone, with the variability within DSS with regard to these parameters, despite the fact that this essential information has to be taken into account in public policies that guide the use of sludges.

In Algeria for example, the quantity of sewage sludge produced annually by around 200 WWTP (Bouchaala et al. 2017) is not known with certainty but certainly higher than 200 000 tons of which only 25% are spread on agricultural lands. As the DSS have been shown to have agricultural value (McConnel et al. 1993), it would be economically profitable to increase this percentage. The use of DSS in excess, however, can have adverse effects such as water and soil toxicity and reduced yields (Chouial et al. 2017). It is therefore necessary to assess the toxic potential of DSS and its variability between treatment plants.

The total heavy metal contents of a DSS are easy to obtain by chemical analysis, usually after sample acid digestion and subsequent Inductively Coupled Plasma measurement. They are useful to assess a potential contamination of a DSS and are usually the only parameters considered by public regulation. They are, however, insufficient to deliver indication about the bioavailability of the metals, which depends on their chemical species (Ma and Rao, 1997; Su et Wong, 2003; Amir et al. 2005; Walter et al. 2006). These can be determined by sequential extraction, a functional technique which can be applied to soil, sludge or sediment samples for determining the distribution of metals in various fractions (Tessier et al, 1979; Lemière et al. 2001), some of which correspond to potentially bioavailable metals (Fluentes et al. 2004). Sequential extraction consists of the sequential use of specific reagents under different pH conditions (Gleyzes et al. 2002). One of the most widely used protocols (Tessier et al. 1979) defines five geochemical fractions: easily exchangeable, bound to carbonates (acid-soluble), bound to Fe and Mn oxides (reducible), bound to organic matter or sulphides (oxidizable) and contained in primary and secondary minerals (residual). Depending on the physicochemical conditions of the soil, the metals found in the first four fractions can be mobilized and made bioavailable.

In this context, the objective of this work was to evaluate the characteristics and variability of five urban residual sludges coming from urban WWTP located in the same Mediterranean area through the determination of the relevant agronomic parameters, the concentration and the speciation of heavy metals (Ag, Cd, Co, Cr, Cu, Pb, Ti, Zn) by sequential extraction. The indirect question was raised whether the origin of potential contaminations in the wastewater network can be determined.

Material And Methods

The DSS samples studied were taken from drying beds from five activated sludge of WWTP whose capacity ranges from 5,000 to 120,000 inhabitant equivalent, located in Algeria (Fig. 1). The technical characteristics of the WWTP are given in Table 1. All the sludges were of urban origin and resulted from an activated sludge process. For each WWTP, 5 samples taken on the same day were mixed to form an average sample. Samples were air-dried, then dried in oven at 55°C, grinded in an agate mortar, sieved through a 160 µm mesh sieve and stored in polyethylene bottles at 4 ° C. For each sample, an aliquot was weighed for determining water content after drying at 105°C.

Table 1
Technical characteristics of the wastewater treatment plants (WWTP) (IE: inhabitant equivalent)

WWTP	Date of commissioning	Capacity (IE)	Discharge (m3 day-1)	Outlet
Azeffoun (AZF)	07/2006	5 000	/	Mediterranean Sea
Boukhalfa (BKH)	11/2006	25 000	3 750	Sébaou River
Tizi-Ouzou (EST)	07/2000	120 000	18 000	Sébaou River
Tadmaït (TDM)	05/2007	13 000	1 950	Sébaou River
Boumerdes (BMD)	01/ 2001	75 000	8000	Tatareg River

For each analysis, three analysis replicates for each sample were performed in order to meet statistical acceptance requirements. All extraction solutions were prepared using ultrapure water (conductivity = 18 $\mu S.cm^{-1}$) and trace metal grade chemical reagents (Merck).

Electrical conductivity and pH were determined using a 1/10 [w:w] sludge-to-water ratio. Cation exchange capacity (CEC) was determined using the cobalthexamine method (Aran et al. 2008; Tarchouna et al. 2010). Total organic carbon (TOC) and total N (tN) were measured on solid samples using a CHNS (Shimadzu, Flash2000). The organic matter content was calculated using the formula MO (%) = CO (%) x 1.72, based on the assumption that average soil organic matter is composed by 58% of carbon. (Pribyl, 2010). Aqueous extracts were realized using a 1:10 [w:w] sludge-to-water ratio, agitation for 16h and 0.45 µm filtration. On aqueous extracts, the water-extractible organic carbon (WEOC) was measured using a TOC-meter (TOC-V CSH, Shimadzu) by difference between total carbon and inorganic carbon. Ions concentrations in solution (nutrients and other major species) were measured by ionic chromatography (Dionex-DX-120).

Sequential extraction was performed using a five steps procedure modified from Tessier et al. (1979). Centrifugation was performed after each step at 4500 rpm for 15 min, the supernatant was filtered at 0.45µm on pre-washed nitrocellulose membrane before to be placed in polypropylene bottles where pH was adjusted at pH 2 with concentrated HNO_3 (72%) in order to prevent hydrolysis of metals before analysis. The centrifugation pellet was recovered, washed by stirring 2h at room temperature with 40ml of ultrapure water then centrifuged for 15 mn. The obtained pellet was then submitted to the next step. All bottles and flasks were previously cleaned with HNO_3 10% and rinsed.

- Step 1 – **Fraction F-ex**. 2g of soil or sludge were shaken in 20mL of KNO_3 1M for 16h at RT. The supernatant obtained after centrifugation corresponds to an easily exchangeable fraction.
- Step 2 – **Fraction F-ac**. The pellet obtained after Step 1 was stirred for 3h at RT with sodium acetate 1M adjusted at pH = 5. The supernatant obtained after centrifugation corresponds to a strongly adsorbed fraction, bound mainly to carbonates or to part of the Fe-sulphides (Flyhammar, 1998).
- Step 3 – **Fraction F-red**. The pellet obtained after Step 2 was stirred for 2h at 65°C in 80mL of 0.25 $mol.L^{-1}$ hydroxylammonium chloride at pH 1.5. The supernatant obtained after centrifugation corresponds to a fraction bound mainly to Fe and Mn (hydr)oxides.
- Step 4 – **Fraction F-ox**. The pellet obtained after Step 3 was suspended in hydrogen peroxide 30% (30mL, pH = 2), stirred 5h at 85°C and centrifuged. The obtained pellet was stirred for 0.5h in 20mL of 3.2 $mol.L^{-1}$ ammonium acetate acidified at pH = 2 with HNO_3 20% v/v. The supernatant obtained after centrifugation corresponds to a fraction bound mainly to organic matter or sulphides.
- Step 5 – **Fraction F-res**. The residual fraction was obtained after aqua-regia extraction assisted by micro-wave (120°C, 900W, 1h) of the pellet obtained after Step 4.

The concentration of metals in the extraction solutions of the different fractions was measured using the inductively coupled plasma atomic emission spectrometry (ICP-AES) method. Statistical analysis was conducted using the XLSTAT software.

Results And Discussion

Agronomic quality of sludges

The main agronomic parameters are given in Table 2. All the studied DSS had significant OM and tN contents, which offers good prospects for agricultural use. The cation exchange capacity (CEC) was in the range expected from the high OM content. The pH values were standing between slightly acid 6.4 and alkaline 8.1. Such values were not expected to cause problems, particularly with regard to the mobility of trace metals (Yong and Phadungchewit, 1993). The tN content ranged between 3.0 and 4.4 %, a result similar to that of other studies (Stark and Clapp, 1980). The C/N ratio ranged between 5.2 and 7.6. Some authors consider that such low values may promote nitrogen leaching. C/N ratio should ideally be raised to around 20 by adding bulking agents having a high C/N ratio (Tisdale and Nelson, 1993). Others, however, using the same type of sludge, showed that, in Mediterranean areas, biomass production was better improved by using sludge-alone amendment rather than sludge added to bulk agent amendment (Bousselhadj et al. 2004).

Regarding available P and K values, significant variability was observed between DSS samples (Table 2). PO_4^{3-} varied from 4.6 to 0.2 and K^+ from 3.7 to 0.6 $g.kg^{-1}$. These values are in the range of total P and K values found in other studies (Wen et al. 1997; Samars et al. 2008; Tavazzi et al. 2012), which confirms their useful practical use as fertilizer. The measured electrical conductivity (EC) is only indicative, because there is no standard value for this type of measurement, which, in addition, is quite rare in the literature. It gives an indication of the salinization hazard for soils sensitive to this problem. In our case, the values for a 1:10 water extract varied from 409 to 1844 $\mu S.cm^{-1}$, which would correspond to 762 to 3432 $\mu S.cm^{-1}$ for a 1:5 water extract (Perez-Espinosa et al. 2000). These values are lower or in the range of values observed elsewhere (Perez-Espinosa et al. 2000), therefore without specific salinization hazard.

Table 2 Agronomic parameters of the studied urban dewatered sewage sludges depending of the WWTP location (EC: electrical conductivity, tN: total N, CEC: cation exchange capacity), OM: organic matter

							Aqueous extract		
	pH	EC $\mu S.cm^{-1}$	tN %	C/N	CEC $cmol.kg^{-1}$	OM %	PO_4^{3-} $g.kg^{-1}$	K^+ $g.kg^{-1}$	WEOC $g.kg^{-1}$
AZF	6.4	610	3.8	5.7	36	37.1	4.6	2.1	12.5
BKH	7.7	947	3.7	6.2	39	39.3	0.9	2.5	14.6
EST	7.7	1844	4.4	5.8	36	43.7	1.7	3.7	24.9
TDM	7.7	409	3.0	7.6	33	39.4	0.4	0.6	3.2
BMD	8.1	679	3.6	5.2	38	32.2	0.2	1.6	3.4

Total content of heavy metals

The total content of the studied heavy metals did not vary significantly between DSSs (Table 3). For metals for which there is a legal maximum value, all SSs values were below the permitted threshold, except for Ni. TDM and BDM samples had Ni content higher than the French and Chinese legal ceiling value and sample AZF had Ni content higher than Chinese ceiling value. TDM and BDM sample had a Cr content lower, but rather close to the Chinese limit value. High Ni and Cr content in DSSs were frequently observed in other studies (Juarez et al. 1987; Zufiaurre et al. 1998; Lasheen et Ammar, 2009). High content of heavy metals in WWTP sludges usually do not originate from domestic effluents, but from industries that discharge effluents in the sewer system or from entry of runoff stormwater into the sewer system (Sörme and Lagerkvist, 2002; Singh and Agrawal, 2008).

Cr and Ni compounds may come from metal surface treatment or damascening industries. Ni compounds may also come from ceramic manufacturing industries and Cr compounds from textiles and tanning industries (Islam et al. 2017). In our study, the high Ni and Cr content in DSSs must be related to the fact that in the studied area there is no strict quality control of effluents from small industries which discharge directly in the sewer network.

Table 3 Total content of heavy metals ($mg.kg^{-1}$ of dry matter ± std) in sludge and ceiling values application to the land. Fr: France NF U44-041; US: U.S. EPA CRF 503.13; Ch: China GB4284-84. In red, values higher than one of the legal ceiling value

Metal	Samples of sewage sludge					Legal ceiling content			
	AZF	BKH	EST	TDM	BMD	Fr	US	Ch	
								pH<6.5	pH≥6.5
Ag	5.1 ± 0.3	1.8 ± 0.1	4.6 ± 0.4	7.4 ± 0.1	1.1 ± 0.1	#	#	#	#
Cd	0.8 ± 0.1	0.5 ± 0.1	0.6 ± 0.1	1.0 ± 0.1	0.7 ± 0.1	20	85	5	20
Co	27 ± 1	9.5 ± 0.5	11 ± 1	14 ± 0.3	18.6 ± 0.1	#	#	#	#
Cr	323 ± 4	247 ± 16	294 ± 19	449 ± 5	428 ± 28	1000	3000	600	1000
Cu	120 ± 34	120 ± 5	145 ±8	210 ± 2	154 ± 9.0	1000	1500	250	500
Ni	139 ± 2	107 ± 7	138 ± 11	243 ± 2	202 ± 15	200	420	100	200
Pb	69 ± 7	92 ± 5	109 ± 14	90 ± 2	94 ± 12	800	300	300	1000
Ti	1087 ± 14	923 ± 67	946 ± 69	1134 ± 9	1092 ± 80	#	#	#	#
Zn	343 ± 17	365 ± 17	820 ± 57	569 ± 10	373 ± 26	3000	2800	500	1000

Unavailable data.

No legal maximum value was found for Ag, Co and Ti. Ag content in the studied DSSs ranged from 1.1 to 7.4 mg.kg^{-1}. These values can be considered to be low in comparison with the few data available in the literature. A study from USEPA (2009) considered 74 sludge samples representative of U.S. WWTPs and found that Ag content was ranging from 2 to 195 mg.kg^{-1} (20 on average), 50% of the samples having a value higher than 13. Pradas del Real et al. (2016) reported a value equal to 14 mg.kg^{-1} for a sludge from Switzerland.

Cobalt is of special interest because it can act on biogeochemical cycles, in particular with regard to the availability of nitrogen for plants (Perez-Espinosa et al. 2002). Here the Co content in sludges ranged from 9.5 to 27 mg.kg^{-1}, which can be considered as high and even outstanding values compared to the scarce data available in the literature, that range from 1 to 13 mg.kg^{-1} (Grummitt, 1976; Perez-Espinosa et al. 2002; Pradas del Real et al. 2016; Malinowska and Jankowski, 2020). The higher value observed here (27 mg.kg^{-1}, AZF sample) is, however, unlikely to have an effect on plant growth (Perez-Espinosa et al. 2002). A cumulative effect of DSS application over several years, however, is not to be ruled out, depending on the mobility of Co in the soil.

Titanium in sludges was more studied due to the increasing use in recent decades of TiO_2 nanoparticles, especially in personal care products, and because it is used as a catalyst for photocatalytic degradation of organic pollutant in wastewater (Wielinsky et al. 2021). Data on bulk TiO_2 content in DSSs, however, are also scarce. Values ranging from 305 to 1800 mg.kg^{-1} were measured in DSS issued from European WWTPs (Johnson et al. 2011; Pradas del Real et al. 2018; Wielinsky et al. 2021). Lazareva and Keller (2014) calculated, considering market studies, that the Ti content in sludges from New-York, London and Shanghai would range from 40 to 208 mg.kg^{-1}. Here the Ti content in DSS ranges between 946 and 1092 mg.kg^{-1}, values relatively high with regard to the literature. Titanium, mainly as TiO_2, is widely used products from paints to personal care products (Braun, 1997). Poorly controlled house painting activity may be the cause of the high concentrations observed here.

Considering the total metal content, sludge from BKH and EST sewage treatment plants can be recommended as a fertilizer or as an organic soil amendment. For Ni, AZF sludge exceeds the Chinese standard, TDM and BDM sludges exceed both French and Chinese standards and therefore cannot be applied without costly prior treatment (Veeken et Hamelers, 1999; Wong et al. 2000). It would be, however, more relevant to trace the origin of nickel in the corresponding localities to avoid its transfer to the sewer network. Anyway, these data underline the importance of quality control of sludges with regard to heavy metals.

Statistical analysis (PCA, principal component analysis) (Fig. 2) was able to identify two groups of metals with differentiated behaviours. Thus, PCA shows good correlations between metals in the (Cu, Ni, Cr, Cd, Ti) group, as well as in the (Pb, Zn) group, these two groups not being correlated with each other. Co was anticorrelated with Pb and Zn. The two first components explained 83,6% of the variance. The position of the BKH and TDM points is explained by lower and higher values, respectively, for metals from the (Cu, Ni, Cr, Cd, Ti) group. The position of the EST point is explained by higher values for Pb and Zn and low value for Co; the opposite being observed for the AZF point.

Speciation of heavy metals

In Mediterranean soils where the sludges are spread, the fractions most likely to release bioavailable metals are the F-ex, F-ac fractions, as well as the F-oxi fraction. The latter corresponds to metals bound to sulphides, which are rapidly oxidized in a dry environment and, in the case of organic matter, of pH higher than 6.5 (Cherfouh et al. 2018).

The studied metals showed differentiated behaviours with, except for Ag, a great consistency between the WWTPs (Fig. 3, numerical values are given as Supplementary Material). For all metals, the exchangeable fraction (F-ex) was lower than 3.5 %.

- Ti, Cr and Ni were found mostly in the residual fraction (F-res), i.e. contained in minerals (more than 90% for Ti and Cr and more than 80% for Ni), therefore poorly bioavailable (Sims and Kline, 1991). Small amounts of these metals (<10%) were in the oxidable fraction (F-oxi), i.e. mainly bound to organic matter or sulphides and, for Ni, 8-12% were in the reducible fraction (F-red), i.e. mainly bound to Fe or Mn oxides, in agreement with other studies (Ahumada et al. 2004; Islam et al. 2017; Yang et al. 2017).
- The distribution of Co among the fractions looks like that of Ni, with a greater proportion in the F-oxi and F-red fractions. High values of the latter were observed for samples BDM and AZF. Cumulative content in the F-ex, F-ac, F-oxi fraction (max. 3.3 $mg.kg^{-1}$ in the AZF sludge) were low enough, however, to rule out long-term risk with regard to plant growth.
- Zn an Pb were mostly in the F-red fraction, as observed elsewhere (Silveira et al. 2006; Chen et al. 2008; Zufiaurre et al. 1998), with, for Zn, a non-negligible proportion (4.2 to 15.9%) in the acid-soluble fraction (F-ac).

- Cu was mainly distributed between F-red, F-oxi and F-res fractions, with a F-ac fraction ranging from 1.7 to 7.3%. Compared to other metals, Cu is well known to be mainly associated with the oxidizable fraction, which is confirmed by our results with best affinity of this fraction comparatively to Cr, Zn, Ni, Pb and Co. This behaviour is similar to that observed by other authors (Chen et al. 2008; Walter et al. 2006, Zufiaurre et al. 1998).
- Cd was the only metal having a low or under detection limit residual fraction (F-res). Most Cd was distributed between the F-ac and the F-red fractions, with a significant part (10.3 to 15.8%) in the F-oxi fraction. Similar distribution has already been described by in sludge from in middle-south region of China (Chen et al. 2008). The low Cd contents in the fractions were low enough to rule out a long-term risk.
- Ag was the only metal whose distribution was quite different from one sludge to another.

The specific behavior of each metal with respect to each fraction results in similarities between stations in the distribution of metals, as shown in figure 4. There were, however, significant differences between WWTPs, which are best highlighted by statistical analysis (Fig. 5). The BKH and EST sludges were characterized by lower values for most of the metal fractions F-red, F-oxi and F-res, and proportionally higher values for the exchangeable fractions F-ex and F-ac. In contrast, the AZF, BDM and TDM sludges were characterized by higher values for F-res, F-oxi and F-red fractions of metals. AZF and sludges were separated from the TDM sludge mainly due to a higher Co values in the F-oxi fraction.

The potential risk highlighted above due to high Ni and, to a lesser extent, Cr, can be put into perspective by the speciation data. More than 80% of Ni and Cr were found in the F-res fraction, the least likely to be made bioavailable by a change in acidity or redox potential in the soil. The pH usually greater than 6 of the soils of the region where these sludges can be spread is not favourable to the solubilization of Ni- or Cr-bearing metallic particles or minerals (Smith, 1994). Here the sum of the F-wat, F-ac and F-oxi Ni fractions, all capable of rapid release of bioavailable Ni, ranged from 6 (BDM) to 13 (TDM) $mg.kg^{-1}$. Considering that sludge application is around 20 $t.ha^{-1}$, neglecting leaching and plant uptake, and using 1.5 $kg.dm^3$ as soil bulk density, it would take 230 (TDM) to 500 (BDM) years to accumulate in the topsoil 10 cm the bioavailable Ni content above which toxic effects can be observed (Kumari et al. 2018). The speciation of Ni can be very different in other places. In a Slovenian sludge studied by Scancar et al. (2000), more than 81% of the high Ni content (621 $mg.kg^{-1}$) were contained in potentially labile fractions. In contrast to Ni, while the total Cu content was below the authorized limits, the sum of the F-wat, F-ac and F-oxi fractions, all capable of rapid release of bioavailable Cu, ranged from 26 (BKH) to 102 (TDM) $mg.kg^{-1}$. Considering the same hypothesis than for Ni, it would take 3 (TDM) to 11 (BKH) years to accumulate in the topsoil 10 cm the bioavailable Cu content above which inhibition of nitrification can be observed (3.8 $mg.kg^{-1}$ soil) (Cela and Sumner, 2002). These considerations underline the insufficiency of the regulations which only consider the total metal contents and not the conditions of their bioavailability.

Whatever the agronomic value of the sludges, the speciation of the metals in sludges makes it possible to identify the sites on which the search for sources of contamination would be necessary. Analysis of the treated wastewater gives information on the contamination at the moment of sampling, while the sludge gives information on the contamination integrated on the entire deposition time. Here the sources must be searched within the sewage network of the AZF, TDM and BDM WWTPs. The analysis showed that the contaminations concerned several metals simultaneously, the higher values of total Ni being accompanied by higher values for most F-red, F-oxi and F-res fractions of Cd, Co, Cr, Cu and Ti. Possible sources can be industries or cottage industries related to painting (Lokhande et al. 2011; Tesfalem and Abdrie, 2017), metalworking and metal plating (Quin et al. 2018), tannery, textile dyeing (Imtiazuddin and Mumtaz, 2013; Uma et al. 2016). Here we identified metal plating industry in the BDM area and metalworking activities in the TDM area. An exhaustive identification of the sources is, however, an activity in its own right which must be carried out in collaboration with the competent regulatory services.

Conclusion

The analysis of sludges from various WWTPs made it possible to assess their variability within an area characteristic of a developing Mediterranean country. All the analysed sludges had satisfactory properties from an agronomic quality point of view. Analysis of the total content of heavy metals showed that some sludges were not usable under French or Chinese regulations. The speciation of metals by sequential extraction underlined, however, that these regulations do not take into account the bioavailability of metals in the spreading environment, here Mediterranean soils. For three of the studied sludges, the total Ni content was higher than maximum legal values while Ni was contained at more than 80% in very poorly bioavailable fractions. In contrast, the total Cu content was below the maximum legal values while this metal was contained in fractions capable of rapid release of bioavailable Cu. The risk of plant toxicity in the short and medium term by spreading these sludges was consequently more linked to Cu than to Ni. Considering that sludge application was around 20 $t.ha^{-1}$, without leaching and plant uptake considerations, and using 1.5 $kg.dm^3$ as soil bulk density, it was possible de calculate the time that would be required to accumulate bioavailable metal in the topsoil before reaching the threshold above which toxic effects appear. It therefore appears necessary to develop standards which take into account their bioavailability in the soils on which they will be spread.

The speciation of the metals in sludges also makes it possible to identify the sewage network area on which the sources of contamination must be sought. The sludge gives information on the contamination integrated on the entire deposition time, and the metal species indicate what type of source should be sought. Note that the same type of approach could be applied to organic contaminants.

Declarations

Author contributions RC, field sampling, laboratory work, data curation, writing (initial draft); YL, data analysis, writing; AD, doctoral scholarship acquisition; PM, scientific supervision, conceptualization, methodology, writing (review and editing).

Funding The doctoral scholarship of RC was provided by the Algerian Ministry of High Education and Scientific Research (MESRS) and the Mouloud Mammeri University. Financial support was provided by a grant from the Université de Toulon.

Data Availability All data generated or analysed during this study are included in this published article and its supplementary information files.

Ethics approval and consent to participate

Not applicable

Consent for publication

Not applicable.

Competing interests

The authors declare no competing interests.

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Figures

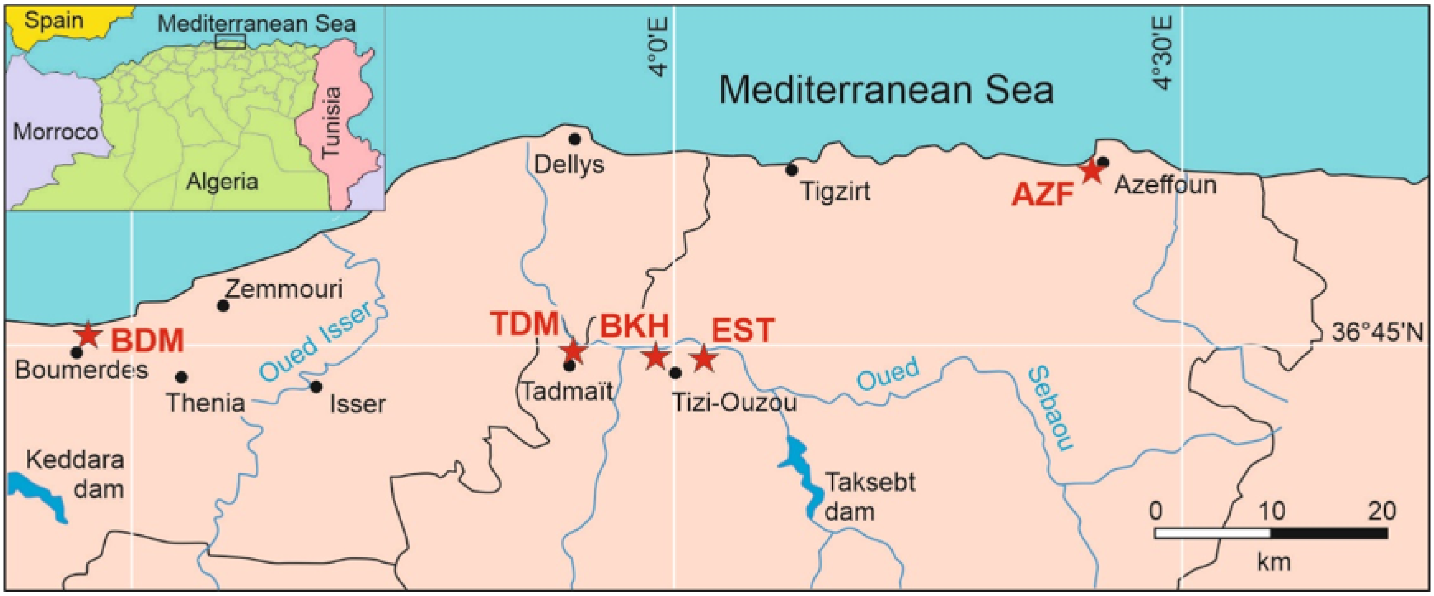

Figure 1

Geographic localization of treated wastewater plants

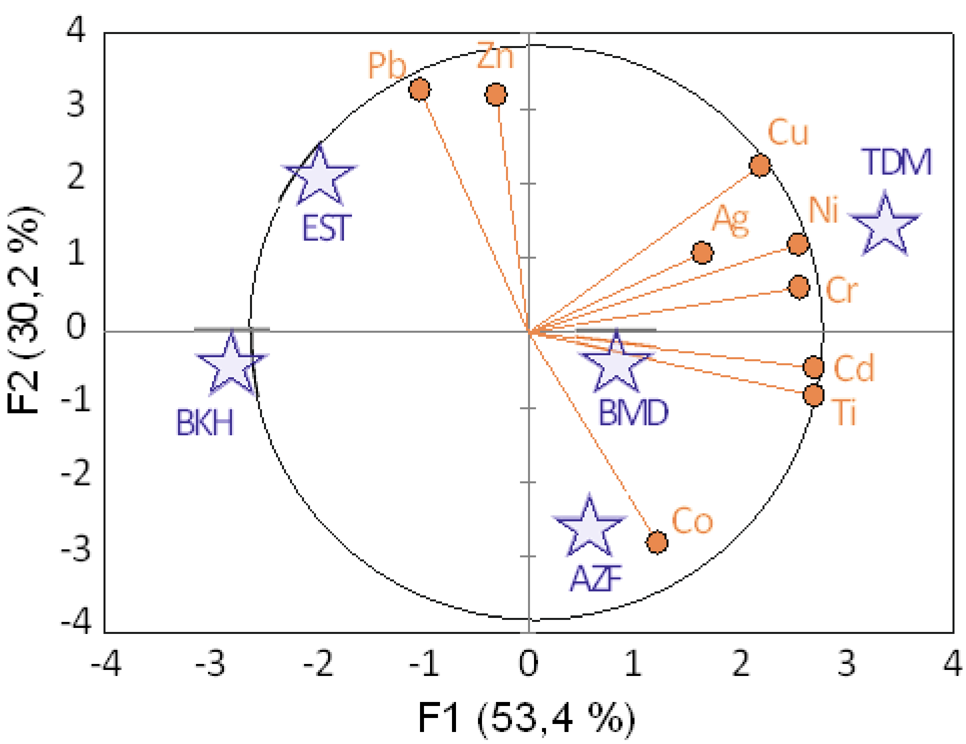

Figure 2

PCA biplot on the first two factorial axes for total metal content. Stars correspond to the observed different WWTPs. Percent on each factorial axis gives the explained variance

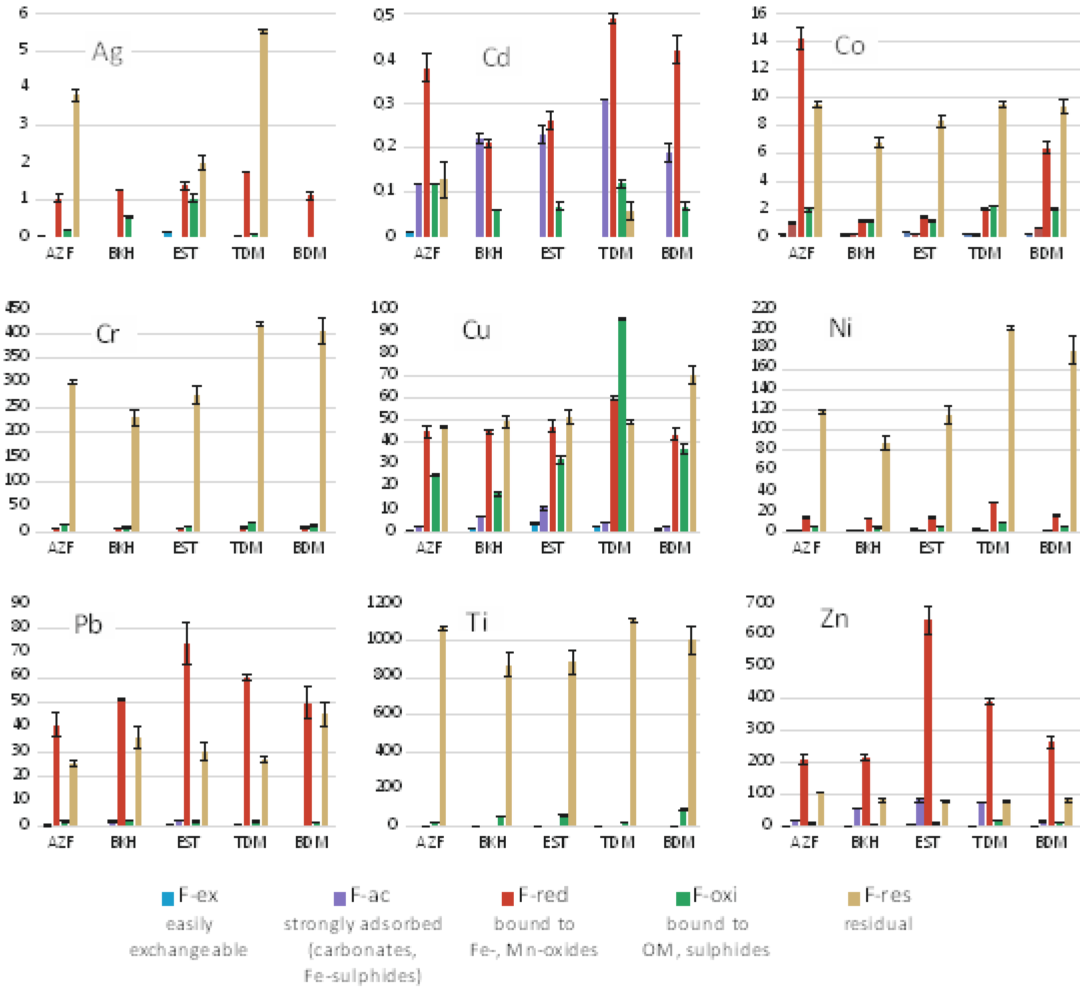

Figure 3

Metal speciation in the studied sludges from various WWTPs, values in mg kg-1

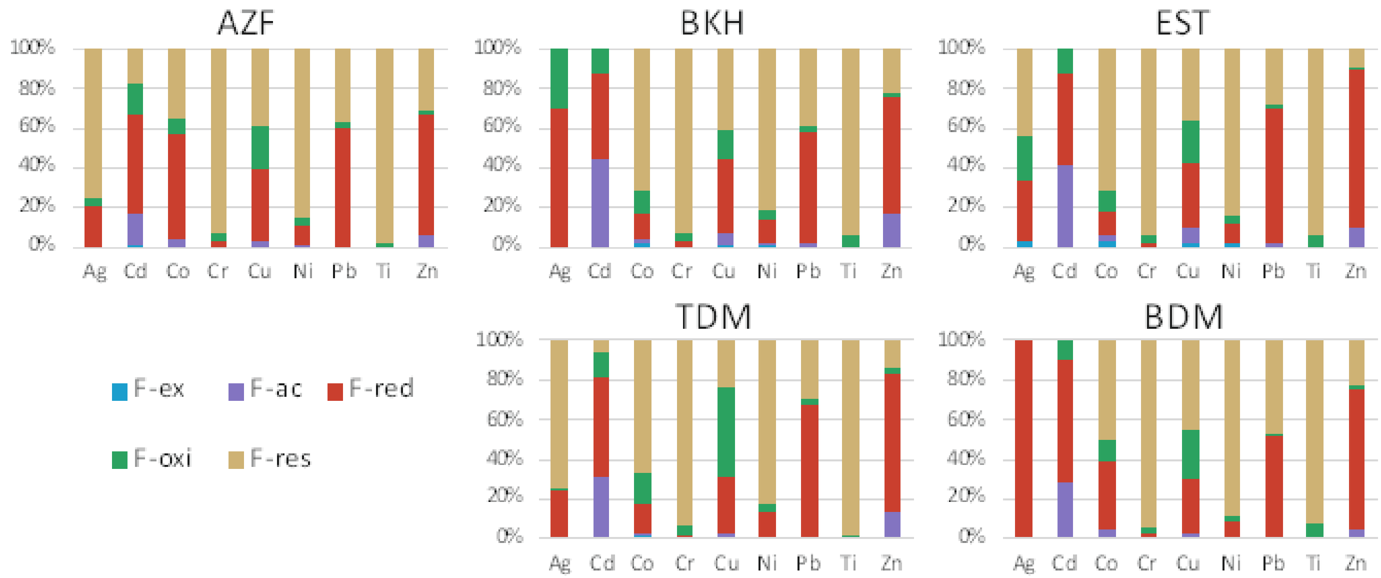

Figure 4

Metal speciation in the studied sludges from various WWTPs. Percent for each fraction in a given sludge.

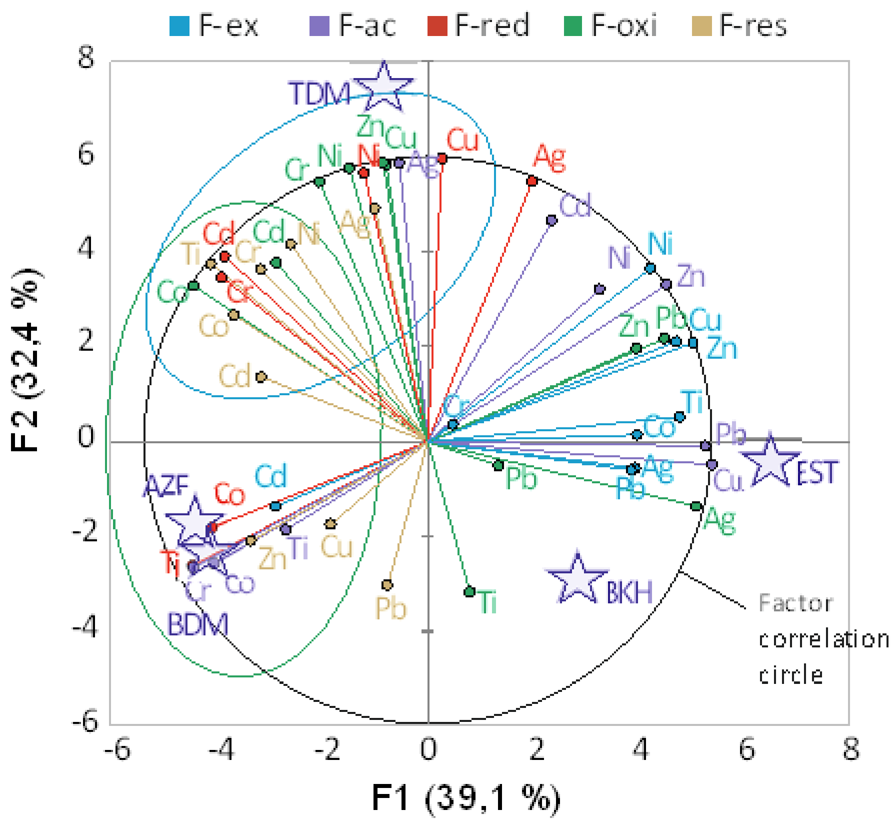

Figure 5

PCA biplot on the first two factorial axes for the whole set of data. Colour of points/letters indicate the metal fraction. Stars correspond to the observed WWTPs

Supplementary Files

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