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Multi-temporal accumulation and risk assessment of available heavy metals in poultry litter fertilized soils from Rio de Janeiro upland region

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Abstract Poultry litter is widely used as fertilizer in soils and can be a relevant source of heavy metals for agricultural environments. In this study, poultry litter fertilization of long-term (< 1–30 years) was evaluated in tropical soils. Our main goal was to investigate the occurrence of temporal variation in the available fraction of heavy metals (Cu, Cr, Zn, Pb, Cd, and Mn) in soils, in addition to their environmental loads through new indexes for risk assessment. The highest mean concentrations in poultry litter were the following: 525 mg kg^{-1} for Mn, 146 mg kg^{-1} for Zn, and 94.4 mg kg^{-1} for Cu. For soils, concentrations were higher for the same heavy metals: Mn (906 mg kg^{-1}), Zn (111 mg kg^{-1}), and Cu (26.3 mg kg^{-1}). Significant accumulation ($p < 0.05$) in fertilized soils was observed for Cu, Cr, and Zn. The high estimates of poultry litter input based on geological background (LI_{GB}) for Cu, Cr, and Zn coincided with the accumulation observed in soils, confirming the effectiveness of the index. The risk of biogeochemical transfer based on fertilized soils (LI_{FS}) decreased for Cu, Cr, and Zn between 10 and 30 years of soil fertilization. For Mn, a very high LI_{FS} was estimated in all long-term fertilized soils. The proposed indices, based on heavy metal concentration, can be used in risk assessments to guide future studies that analyze other environmental matrices possibly impacted by manure and poultry litter fertilization.

Keywords Environmental risk · Trace elements · Agricultural soils · Tropical soils

Introduction

Improving a sustainable agricultural production plays a crucial role in meeting the United Nations target set in the Sustainable Development Goals (UN-SDG), which aims to eradicate hunger and malnutrition through food security. In this context, agricultural wastes (poultry litter and manure) have been widely used as soil fertilizers, and such use has been a matter of debate (Bolan et al. 2004; Gerber et al. 2008; Williams 2013).

The use of poultry litter has shown to be effective to increase crop yields, besides improving chemical, physical, and biological properties of agricultural soils (Bolan et al. 2010). Among chemical attributes, poultry

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litter can be considered an effective source of nitrogen (N), phosphorous (P), and potassium (K), reducing the inorganic fertilizer application, as well as giving a productive destination to poultry farming wastes (Celestina et al. 2018; Vollú et al. 2018). However, the disadvantageous side is the exposure of agricultural environments to sanitary products and food additives used in the poultry production cycle. Among possible contaminants, veterinary antibiotics, natural hormones produced by chicken, and heavy metals can be mentioned (Azeez et al. 2009; Ho et al. 2014; Parente et al. 2018).

Poultry litter may contain from trace to high heavy metal loads that are usually added as supplementary nutrients, such as copper (Cu), zinc (Zn), and manganese (Mn), or occur unintentionally, as raw material contaminant may contain cadmium (Cd), chromium (Cr), and lead (Pb) (Han et al. 2000; Suleiman et al. 2015; Wang et al. 2015). According to Zhang et al. (2012), large amounts of heavy metals have been detected in Chinese chicken manure from 1990 to 2010.

Moreover, both mineral fertilizers and pesticides raise heavy metal soil contamination well above the geological background (Atafar et al. 2010; Gonçalves et al. 2014). On a global scale, Brazil is one of the greatest fertilizer consumers. Indeed, only in 2015, the country demanded nearly 30.2 million (t) of mineral fertilizers (IEA 2016). In addition, the country is a major consumer of pesticides, with > 550,000 t marketed in 2016 (IBAMA 2017).

Continuous heavy metal inputs over agricultural soils may increase the risk of human chronic exposure to toxic levels through contaminated food (Khan et al. 2008, 2015). In addition, poultry litter organic matter forms soluble complexes with heavy metals, which may compromise groundwater and surface resources (Gerber et al. 2008; Li and Shuman 1997).

In general, many previous studies have addressed the problems related to heavy metal input in soils from poultry litter and manure using total or pseudo-total digestion methods (Azeez et al. 2009; Cang et al. 2004; Jiang et al. 2011; Karci and Balcıoğlu 2009). However, the use of available fraction extraction methods would be more appropriate to assess the potential risk of absorption by plants, as well as leaching and contamination of water resources (Andrade et al. 2009).

Regarding environmental risk assessment, there are several approaches on human and ecological health, in addition to the main fate and accumulation trends (Chen et al. 2015; Shi et al. 2018; Wu et al. 2015). Risk assessment models can be important tools for evaluating soil contamination impacts and predicting future measure managements to maintain ecosystem balance (Kowalska et al. 2018). However, as far as we know, the models that consider the contribution of poultry litter or manure application on soils are scarce.

Therefore, the overall goal of this study was to assess the heavy metal accumulation of available fraction in agricultural soils over a long period (< 1 to 30 years) of poultry litter fertilization. In addition, we propose a new index with two variations as tools to environmental risk assessment. The indices are based in the heavy metal available fraction in poultry litter, geological background, and fertilized soils.

The study area was chosen as a model of a tropical environment, since Rio de Janeiro upland region is highly weathered, with annual mean rainfall > 2500 mm (Dourado et al. 2012). Moreover, its slope relief contributes to erosive processes that may lead to heavy metal soil–water mobilization through leaching and runoff.

Material and methods

Study area and sampling

Poultry farms are located in São José do Vale do Rio Preto (SJVRP) municipality, upland region (615 m a.s.l., mean elevation) of Rio de Janeiro state, in southeastern Brazil. Poultry litter samples were collected at the end of the production cycle (45 days). Soil samples (A horizon) classified as Typic Hapludox (USDA 1999) and poultry litter were sampled between October 2015 and December 2017, freeze-dried, and sieved at 75 μm. Thirty poultry litter (PLitter) samples were collected from 17 poultry farms, as well as 65 soil samples (in agricultural activity) were obtained. For soils, 15 samples were collected inside poultry houses (Shed soil) from 4 poultry farms, and 50 fertilized soil samples were obtained in accordance with the following classification in 5 groups: short-term soil (ST soil—15 samples), with < 1 year of agricultural use, medium-term soil (MT soil—10 samples) with 1.5 years, long-term soil 1 (LT soil 1—15 samples) with 10 years, LT soil 2 (8 samples) with 15 years, and LT soil 3 (7 samples) with 30 years (Fig. 1). Additionally, two background pool soil samples were also collected at forest and grass sites without agricultural use.

Analytical procedures and quality control

Extraction method was previous described by Fiszman et al. (1984). Basically, for each 1 g of sample 20 mL of HCl (0.1 M) were added. After that, the extract solution was kept for 16 h to extract the available fraction of heavy metals. Purification was made with slow filter paper Whatman® n° 42, 2.5 μm (Kent, England). Ultra-pure water from a Milli-Q® System (18.2 Ω m—high purity deionized water, Millipore/Merck, Darmstadt, Germany) and a 0.22 μm filter were used to prepare aqueous solutions. Standard solutions in the working range were prepared from the stock solutions (1000 mg L^{-1}, Merck, Germany).

Heavy metals (Cu, Cr, Zn, Cd, Pb, and Mn) were determined by flame atomic absorption spectrometry (FAAS), using a Varian® spectrometer (AAS240FS, Santa Clara, USA), equipped with deuterium background correction. The analyses were carried out in duplicate, including the analytical blanks. Concentrations were calculated as the mean of two measurements, considering acceptable up to 15% coefficient of variation. Quality control for heavy metal quantification was made by standard addition (Mitra 2003). Our recovery results for metal determination standard addition were satisfactory (80–110%), according to Association of Analytical Communities (AOAC 2011) (Online Resource Table S1). All procedures, including calibration curves, were used following some protocols (APHA 1998; Dorneles et al. 2008; Lino et al. 2016). The method detection limits (MDLs) were calculated using the following formula: (3 × Sb)/Xb × (V/M), where Sb is the standard deviation of seven measurements of the blank; Xb is the mean of the angular coefficient of the calibration curve; V is the final volume of the sample solution; and M is the sample mass. MDLs in mg kg^{-1} were 0.12, for Cu; 0.8, for Cr; 1.4, for Zn; 0.1, for Cd; 1.8, for Pb; and 0.6, for Mn.

Poultry litter load index

Poultry litter load index (*LI*) is firstly proposed here to provide a relative ranking of heavy metal load due to poultry litter application in soils. In this context, two approaches are proposed herewith: poultry litter load based on geological background (LI_{GB}), and poultry litter load based on fertilized soils (LI_{FS}).

The first approach, i.e., LI_{GB}, assesses the potential load of heavy metals derived from poultry litter on non-impacted soils by agricultural activities.

LI_{GB} for a single element is defined as:

$$LI_{GB} = \frac{C\ \text{poultry litter}_n}{GB_n}$$

where $C\ poultry\ litter_n$ is the heavy metal concentration (mg kg^{-1}) measured in each poultry litter sample, and GB_n is the geological background for each element in soils (mg kg^{-1}). We propose that the LI_{GB} be classified into five levels, adapted from "single pollution index" described in Kowalska et al. (2018), as follows: very low ($LI_{GB} < 0.1$), low ($0.1 \leq LI_{GB} < 1$), moderate ($1 \leq LI_{GB} < 3$), high ($3 \leq LI_{GB} < 5$), and very high ($LI_{GB} \geq 5$).

The second approach, i.e., LI_{FS}, is proposed in this study in order to provide a relative ranking of heavy metal transfer from poultry litter to environment. The index is based on the fact that the poultry litter application on soil should contribute to increase heavy metal concentrations in this matrix.

LI_{FS} for a single element is defined as:

$$LI_{FS} = \frac{C\ \text{poultry litter}_n}{C\ \text{soil}_n}$$

where $C\ poultry\ litter_n$ is the mean concentration (mg kg^{-1}) measured for each heavy metal in poultry litter samples, and $C\ soil_n$ is the concentration of each fertilized soil sample (mg kg^{-1}). The proposed classification is the same for the previous index.

Statistical analysis and heat map

Data normality was verified by Shapiro–Wilk test. Due to the non-normal distribution, the Kruskal–Wallis test was chosen with Dunn's posttest which compares all pairs of columns. For all statistical tests, the significance level adopted was 5% ($p < 0.05$). GraphPad Prism 5.0® statistical program was the software used for performing graphs and tests. Heat maps interpolate a raster surface from points using a two-dimensional minimum curvature spline technique. The resulting smooth surface passes exactly through the input points.

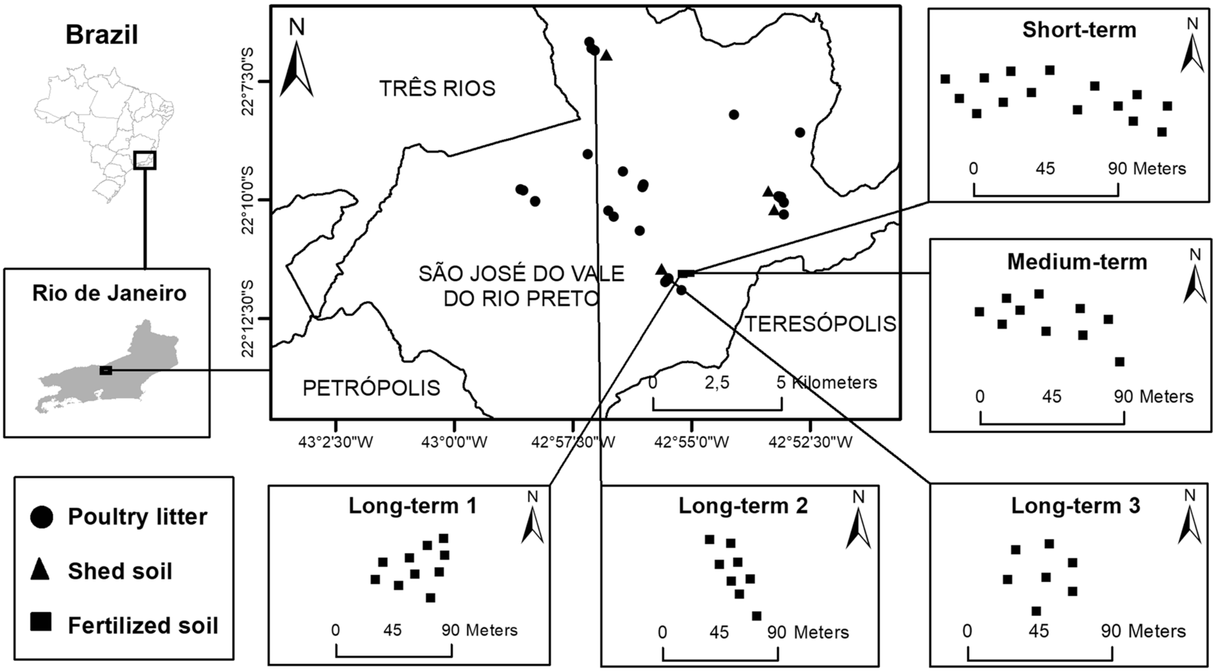

Fig. 1 Study area and sampling points

Results and discussion

Heavy metals in poultry litter samples

Among heavy metals, Mn had the highest concentrations 525 ± 294 mg kg^{-1} (mean ± SD), followed by Zn (146 ± 85.5 mg kg^{-1}) and Cu (94.4 ± 54.5 mg kg^{-1}). Essential for plants, these elements are expected to occur unintentionally in *Eucalyptus* spp. sawdust and digested soybean and maize, the main materials forming poultry litter (Nagajyoti et al. 2010). However, since the extraction method is suitable for evaluating the available fraction, it is expected that the measured levels of heavy metals are due to their addition in the feed. Manganese monoxide, zinc, and copper sulfate, as example, are added to husbandry feed. Previous studies reported Cu concentration in feed 15 times higher than the 8 mg kg^{-1} required, and 100 times higher than 40 mg kg^{-1} needed Zn (Cang et al. 2004; Gerber et al. 2008; Nicholson et al. 1999). Copper concentrations in poultry litter were in a similar range than those reported in previous studies (81.8–134 mg kg^{-1}), where strong extraction methods were used (Ravindran et al. 2017; Xiong et al. 2010). Chromium (Cr) occurred in all poultry litter samples, with low mean concentration (2.21 ± 1.19 mg kg^{-1}) compared to previous studies (30.5–225 mg kg^{-1} (Karcı and Balcıoğlu 2009; Zhang et al. 2012). In addition, studies reported very high Cr concentration in poultry feed (162–936 mg kg^{-1}) (Cang et al. 2004; Zhang et al. 2012). For Pb, all poultry litter samples were below the MDL, while Cd was detected in only 37% of them, ranging from <MDL to 0.55 mg kg^{-1}. According to Wang et al. (2013), Cd concentrations in poultry manure from China increased 196% between 2002 and 2008, reflecting a progressive risk of human exposure to Cd through transfer of this toxic metal to water resources and edible plants.

Heavy metal load based on recommended poultry litter application

The technical recommendations of poultry litter application in agricultural soils are generally based on their N and P concentrations, in addition to the required content for each crop (Bolan et al. 2004). However, analytical methods are often inaccessible to farmers, which may lead them to apply doses far above those required, resulting in an environmental overload (Gerber et al. 2008). The Brazilian Agricultural Research Corporation (Embrapa) established a safety criterion for poultry litter application between 5 and 20 t ha^{-1} to soils from Rio de Janeiro state (Embrapa 2013). Considering the higher

Table 1 Heavy metal loads based on the poultry litter application recommended for agricultural soils

Heavy metals	Max. conc.[a] (mg kg^{-1})	Max. application[b] (kg ha^{-1})	Four applications—year[c] (kg ha^{-1})	Limit USA[d]—year (kg ha^{-1})	Limit Brazil[e]—year (kg ha^{-1})
Cu	252	5.04	20.2	75	137
Cr	5.08	0.10	0.41	150	154
Zn	232	4.64	18.6	140	445
Cd	0.55	0.01	0.04	1.9	4
Mn	975	19.5	78.0	n.d.	n.d.

n.d. not determined

[a] Maximum concentration measured in poultry litter samples (all samples were <MDL for Pb)

[b] Maximum recommended application (20 t ha^{-1})

[c] Heavy metal load based on four applications per year

[d] US-EPA Part 503 (1994) load limit permitted from sewage sludge

[e] Conama no. 375/ 2006 load limit permitted from sewage sludge

heavy metal concentration measured in poultry litter and the maximum recommended application, we predicted the worst-case scenario (Table 1). This approach is a useful concept in risk management that allows assessing the maximum potential risks. The estimate of four applications per year is based on short cycle crops.

Due to the lack of regulatory limits for heavy metals in manure, we compared the present estimative with the annual load limit established for sewage sludge applied to soils from USA and from Brazil. Although the estimated annual load (kg ha^{-1}) is high for some elements, values are below the set limits for soil application. The high estimated Mn load should be carefully considered, since its geological background is high and there are no soil quality values established by Brazilian legislation (Conama no. 420/2009). In agreement with our results, Mattias et al. (2010) pointed out that pig slurry increased available fraction of Cu, Zn, and Mn in Brazilian agricultural soils. Among global agricultural producers, Brazil, China, India, Russia, and USA account for 50% of the heavy metal input into agricultural soils through manure fertilization (Leclerc and Laurent 2017). Therefore, it is crucial to establish limits for heavy metal loading in soils due to fertilization with animal waste.

Poultry litter load index based on geological background

Poultry litter load indices (LI_{GB}) varying from high ($3 \leq LI_{GB} < 5$) to very high ($LI_{GB} \geq 5$) were estimated for Cu, Zn, and Cr. The high Cu and Zn concentrations found in poultry litter samples influenced the estimated LI_{GB} (Fig. 2).

Using other estimative model, Xiong et al. (2010) also reported high Cu load in soils due to manure fertilization. According to Brazilian legislation (IN no. 25/2009), soil fertilization with manure is exclusively permitted for pasture. However, in the study area, there is no inspection to avoid this type of application to other crops. Negative impacts related to Cu and Zn release in soils include co-selection for antibiotic resistance genes (Baker-Austin et al. 2006; Ji et al. 2012). In addition, high Cu and Zn levels in soils can cause toxicity to plants, chronic exposure to animal husbandry through pasture, and increase risk of human exposure through food (Khan et al. 2015; Xiong et al. 2010). The moderate to very high LI_{GB} estimated for Cr was influenced by its low geological background concentration (0.80 mg kg^{-1}). Chromium is toxic to most vascular plants even at very low concentrations (0.10 mg kg^{-1}), affecting physiological processes including reduction of seed germination

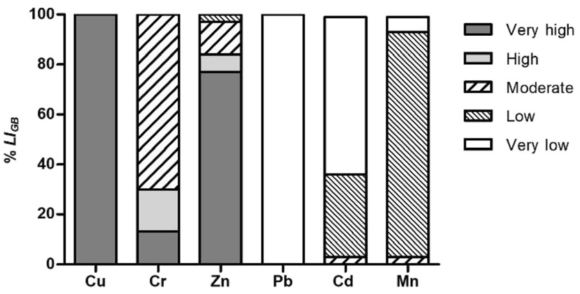

Fig. 2 Percentage of poultry litter load index based on geological background (LI_{GB}) for each heavy metal

and root growth rate (Nagajyoti et al. 2010). The toxic elements Pb and Cd had very low ($LI_{GB} < 0.1$) to low load indices ($0.1 \leq LI_{GB} < 1$), because of their low concentrations in samples. Among heavy metals, Mn had the highest poultry litter concentrations. However, a predominantly low LI_{GB} was estimated for Mn, which seems to be a consequence of the high geological background (974 mg kg^{-1}) measured in the study area.

Heavy metals in soil samples

The available fraction for each heavy metal in fertilized soils did not exceed the prevention limit of Brazilian legislation (Conama no. 420/2009), based on strong acid extraction methods. However, the same legislation recommends that reference values should be considered at the regional level. In this context, most of the sample sets presented concentrations above the measured geological background (Table 2).

Copper concentrations in all fertilized soils (14.1 ± 12.1 mg kg^{-1}) were similar to those reported in soils from USA and Nigeria (11.2–12.4 mg kg^{-1}), where strong digestion methods were applied (Azeez et al. 2009; Gupta and Charles 1999). Ninety-eight percent of the soil samples presented higher concentrations than the background value (Cu 0.13 mg kg^{-1}). The highest value among mean Cu concentrations was found in LT soil 3 (26.3 ± 14.4 mg kg^{-1}), which was 200 times higher the background level. The highest mean Cr concentration was 3.02 ± 1.94 mg kg^{-1} in a soil inside shed. In total fertilized soils, the mean Cr concentration (1.54 ± 1.31 mg kg^{-1}) was lower than the levels reported in previous studies 7.67–80.2 mg kg^{-1} in agricultural soils (Azeez et al. 2009; Karci and Balcıoğlu 2009). In addition, 62% of soil samples had concentrations above the background value (0.80 mg kg^{-1}).

The Zn concentrations of fertilized soils (66.8 ± 69.2 mg kg^{-1}) were higher than those found in previous studies, ranging 31.4–52 mg kg^{-1} (Azeez et al. 2009; Gupta and Charles 1999; Jaja et al. 2013). Moreover, 91% of the samples had Zn concentrations above the reference value (11.9 mg kg^{-1}). Despite its supplementation in animal feed, Zn is widely added in commercial fertilizers due to its metabolic function related to plant protein synthesis, respiration, and photosynthesis (Gonçalves et al. 2014).

The highest value among mean Pb concentrations was found in MT soil (4.79 ± 1.38 mg kg^{-1}). However, our results suggest that poultry farming did not constitute the main Pb source to soils, since poultry litter samples showed concentrations below MDL. Atafar et al. (2010) reported mean Pb concentrations in chemically fertilized soils ranging from 3.59 (before cultivation) to 8.76 mg kg^{-1} (after harvest). According to Gonçalves et al. (2014), low-quality micronutrient sources containing toxic metals, including Pb, are not uncommon in Brazil. Previous studies reported poultry litter as Pb source to soils, with highest concentrations between 14.7 and 22 mg kg^{-1} (Gupta and Charles 1999; Jaja et al. 2013).

Among all soil samples, only 8% were above Cd reference value (0.40 mg kg^{-1}). The highest Cd concentrations occurred in ST soil (0.36 ± 0.09 mg kg^{-1}). Previous studies measured higher Cd concentrations (0.74–2.07 mg kg^{-1}) in fertilized soils with poultry litter and manure (Azeez et al. 2009; Gupta and Charles 1999). Moreover, Dziubanek et al. (2017) highlighted high Cd concentrations (13.2–68.5 mg kg^{-1}) in soils treated with fertilizers and sewage sludge in Poland. According Gonçalves et al. (2014), among agrochemicals, phosphate sources present high levels of toxic metals to agricultural soils, which is especially important for Cd.

Manganese (Mn) concentrations were the highest among all elements, reaching 906 ± 902 mg kg^{-1} in samples from LT soil 2. The high Mn background value (974 mg kg^{-1}) surely influenced the higher concentrations compared to previous studies ranging from 33 to 227 mg kg^{-1} (Azeez et al. 2009; Gupta and Charles 1999). Rehman et al. (2018) reported the mean Mn level of 285 mg kg^{-1} on agricultural soils from Pakistan. In agreement with our findings, the latter authors suggested the Mn was mainly originated from geological sources and from agrochemicals. Moreover, Mn is an essential macronutrient for plant metabolic functions and this metal can be applied to soils through commercial fertilizer formulations, in addition to be the second most abundant metal in the Earth's crust (Gonçalves et al. 2014).

Temporal trend in heavy metal concentrations in soils

The ST soil to LT soil 3 areas present a temporal variation (< 1 to 30 years) related to the time of land use. The accumulation trend of Cu, Cr, Zn, and Pb in the same area, with two periods of poultry litter fertilization, is presented on Fig. 3a, while Fig. 3b illustrates trends over the years in three different areas.

Table 2 Heavy metal concentrations (mg kg^{-1}) in geological background (GB), soil inside the shed (Shed soil), short-term fertilized soil (ST soil), medium-term soil (MT soil), long-term soils (LT soils 1, 2, and 3), and basic statistics

Heavy metal	Sample	Mean GB[a]	Mean	SD	Median	Max.[b]	Min.[c]
Cu	Shed soil	0.13	12.8	5.19	12.0	27.1	6.9
	ST soil		10.2	11.8	4.14	33.3	0.11
	MT soil		15.5	4.05	16.5	18.9	5.57
	LT soil 1		5.50	2.91	4.49	12.1	2.79
	LT soil 2		19.7	14.6	14.3	53.1	8.53
	LT soil 3		26.3	14.4	23.8	44.6	6.85
Cr	Shed soil	0.80	3.02	1.94	3.12	7.24	0.64
	ST soil		0.51	0.52	0.21	1.62	0.21
	MT soil		2.73	0.95	3.12	3.79	0.64
	LT soil 1		0.58	0.20	0.48	0.99	0.48
	LT soil 2		1.57	0.93	1.28	2.82	0.48
	LT soil 3		3.42	0.58	3.48	4.26	2.55
Zn	Shed soil	11.9	87.6	76.8	60.9	326	23.3
	ST soil		38.1	48.2	22.4	173	1.03
	MT soil		111	85.3	87.2	351	63.0
	LT soil 1		27.0	20.3	27.5	73.0	1.29
	LT soil 2		84.2	90.7	49.3	290	23.8
	LT soil 3		102	52.8	101	166	20.0
Pb	Shed soil	1.80	<MDL	n.d.	n.d.	<MDL	<MDL
	ST soil		1.69	2.16	0.48	6.30	0.48
	MT soil		4.79	1.38	5.11	6.33	1.11
	LT soil 1		2.40	1.93	1.22	5.69	1.22
	LT soil 2		5.15	2.26	6.50	7.56	1.22
	LT soil 3		5.71	2.54	6.44	8.22	2.19
Cd	Shed soil	0.40	0.18	0.10	0.15	0.43	0.04
	ST soil		0.21	0.13	0.24	0.45	0.07
	MT soil		0.07	0.00	0.07	0.07	0.07
	LT soil 1		0.36	0.09	0.34	0.53	0.23
	LT soil 2		0.04[d]	n.d.	n.d.	<MDL	<MDL
	LT soil 3		0.04[d]	n.d.	n.d.	<MDL	<MDL
Mn	Shed soil	974	286	267	216	933	33.7
	ST soil		293	398	72.1	1216	9.99
	MT soil		212	210	145	570	16.6
	LT soil 1		626	222	647	845	43.1
	LT soil 2		906	902	665	2017	8.68
	LT soil 3		567	766	44.7	1714	9.27

SD standard deviation, <*MDL* below method detection limit, *n.d.* not determined

[a] Mean geological background concentration (GB) from pool soil samples of a local forest and field

[b] Maximum concentration

[c] Minimum concentration

[d] Concentration <MDL in soil areas in which at least one quantified sample was estimated through the equation: Df × MDL, where Df is the detection frequency in each area (Das et al. 2017)

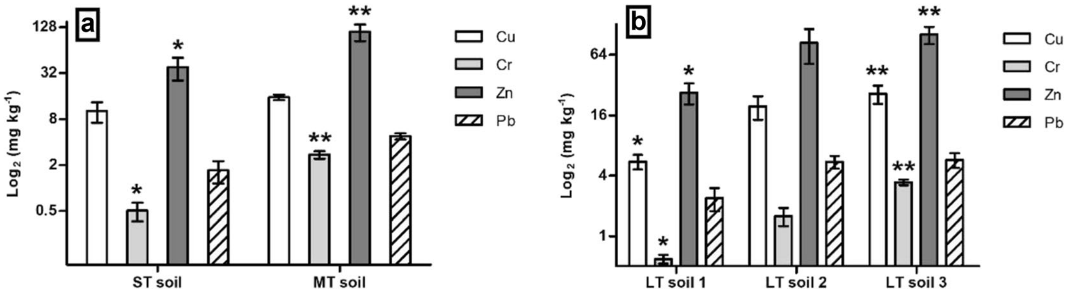

Fig. 3 **a**, **b** Mean heavy metal concentration ($\log_2$ mg kg^{-1}) in fertilized soils

We found a similar trend of accumulation over the years—ST soil to MT soil (Fig. 3a) and among LT soils (Fig. 3b) related for the four elements, with significant difference ($p < 0.05$) highlighted with asterisks. The significant accumulation confirms the effectiveness of the LI_{GB} index as a preliminary risk assessment tool, since the index pointed out great Cu, Cr, and Zn load. In addition, the continuous poultry litter application changed the soil chemical parameters over the years. Organic carbon content (and consequently organic matter (OM)), increased from 2.2% in ST soil to 6.8% in LT soil 3. Poultry litter also influenced in increasing soil pH (reaching > 6) and cation exchange capacity (CEC), from 13 to 25 Cmol$_c$ dm^{-3} in ST and LT soil, respectively. Soil chemical parameters are presented in Online Resource Table S2. In acidic conditions, soil OM and CEC have a great capacity to influence the adsorption of cationic species in soils (Violante et al. 2010). According to Jaja et al. (2013), poultry litter application sharply increased Cu concentration in soil upper layer (0–10 cm). In these situations, Cu is mainly adsorbed on OM and clay minerals (ATSDR 2004). Among cation species, Cr (III) and Zn (II) are the most frequent forms, tending to complex both with organic and inorganic binders, resulting in low mobility due to sorption reactions (ATSDR 2005, 2012a; Gerber et al. 2008). Although Pb also showed an increasing trend over the years, poultry litter samples were below the MDL. Our results suggest that agrochemical applications could be the main source of Pb inputs, since this practice usually occurs during the same period of poultry litter fertilization.

Although Cd can be immobilized by increased OM content (ATSDR 2012b), we observed an opposite trend over the years, compared to the other measured elements. There was a decreasing temporal trend in Cd concentrations over the period of land use. In soils with acidic conditions, Cd tends to be available in the soil solution (Dziubanek et al. 2017). Therefore, the lowest pH (5.1) in MT soil suggests that the concentrations below MDL in this sample set can be due to the greatest Cd mobility.

Regarding Mn, a slight increase over the years was observed, suggesting that Mn content from poultry litter is being mobilized or changing to less available chemical states. Mn can be immobilized in soils through cation exchange reactions, being retained by clays at low concentrations and desorbed by ion exchange reactions on soil solution at high concentrations (ATSDR 2012c). The bioavailability of this metal can be increased at pH < 5.5 and by redox potential, resulting in increasing Mn (II) levels in soil matrix, which is the most soluble and available chemical species for plants (Millaleo et al. 2010).

Poultry litter load index based on fertilized soils

The proposed index reflects the ratio between the mean of each element in poultry litter samples and the concentration measured in fertilized soils. The index is based on the assumption that if the input of heavy metals is greater than the measured in soils, a biogeochemical transfer is occurring. In this case, the lower concentrations in soil samples are indicative that the heavy metals were transferred to the biota and other environmental matrices (e.g., deeper layers of the soil, leaching, runoff, and air particles).

According to the index LI_{FS}, high to very high load percentages were estimated for Cu, Cr, Zn, and Mn in fertilized soils (Fig. S1). Considering these critical heavy metals and the long-term application of poultry litter in the study region, we present heat maps based on LI_{FS} for long-term fertilized areas 1, 2, and 3 (Fig. 4).

Predominantly high and very high LI_{FS} were estimated in LT soil 1 (10 years of fertilization). Azeez et al. (2009) observed, in a similar period of fertilization (9 years), Cu, Pb, and Mn mobilization to depth soil layers (80–120 cm). In addition, heavy metal mobilization through

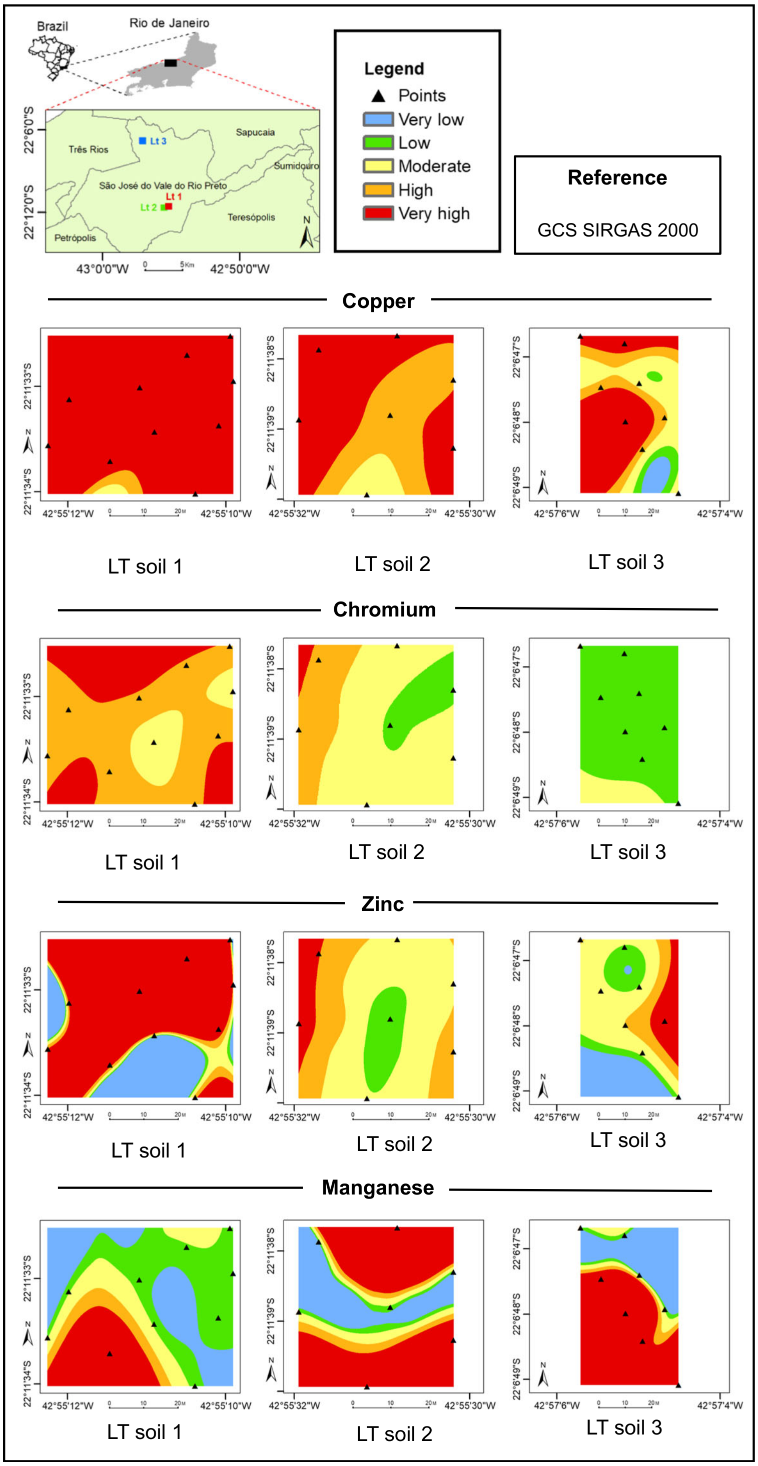

Fig. 4 Heat maps based on LI_{FS} for Cu, Cr, Zn, and Mn in long-term soils (LT soils 1, 2, and 3)

environmental matrices is expected, leading to risks of accumulation by edible plants (Khan et al. 2015; Mattias et al. 2010; Millaleo et al. 2010).

On the other hand, temporal trends of decreasing LI_{FS} were estimated for Cu, Cr, and Zn over the years (LT soil 1 to 3). The decreased risk of biogeochemical transfer was probably influenced by changes in soil chemical parameters due to poultry litter application, such as increased pH, OC, and CEC (Online Resource Table S2). Among heavy metals, Mn presented a different pattern maintaining very high LI_{FS} in all areas (Fig. 4). According to this preliminary tool of environmental risk assessment, in addition to crops, water resources and surrounding drainage basins should be monitored with respect to possible high heavy metal availability.

Conclusions

Through the assessment based on technical recommendations of poultry litter application in agricultural soils, it was possible to estimate high annual loads of Mn, Zn, and Cu. However, due to the high soil variability, heavy metal load should be monitored considering geological background. In this context, our proposal of a load index based on geological background (LI_{GB}) was effective as a preliminary environmental risk assessment tool. The LI_{GB} predicted very high (≥ 5) loads of Cu, Cr, and Zn, in agreement with the observed significant accumulation of these metals in fertilized soils over the years. According to the second proposed index, based on fertilized soils (LI_{FS}), the risk of biogeochemical transfer changed with the assessed heavy metal and over the years of poultry litter fertilization. The estimated LI_{FS} decreased for Cu, Cr, and Zn between 10 and 30 years of soil fertilization. For Mn, very high LI_{FS} were estimated in all long-term fertilized soils. The LI_{FS} can be a simple and effective tool to guide future monitoring studies in agricultural areas where poultry litter and manure are largely applied. In this context, heavy metal bioaccumulation mainly by edible plants should be investigated. Furthermore, the possible impacts of heavy metal contamination on water resources through leaching and runoff should be monitored.

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References

Andrade, M. G., Melo, V. F., Souza, L. C. P., Gabardo, J., & Reissmann, C. B. (2009). Heavy metals in soils of a lead mining and metallurgy area. II—Forms and plant availability. *R. Bras. Ci. Solo, 33*, 1889–1897.

AOAC - Association of analytical communities (2011). Standard Format and Guidance for AOAC Standard Method Performance Requirement (SMPR) Documents (Version 12.1). 27p. http://www.aoac.org/aoac_prod_imis/AOAC_Docs/ISPAM/3.5SMPRGuidelinev12.1.pdf. Accessed 1 Oct 2018

APHA - American Public Health Association. (1998). In L. S. Clesceri, A. E. Greenberg, & A. D. Eaton (Eds.), *Standard methods for the examination of water and wastewater. American Water Works Association, Water Environment Federation* (20th ed. ed.). Baltimore: United Book Press, Inc..

Atafar, Z., Mesdaghinia, A., Nouri, J., Homaee, M., Yunesian, M., Ahmadimoghaddam, M., & Mahvi, A. H. (2010). Effect of fertilizer application on soil heavy metal concentration. *Environmental Monitoring and Assessment, 160*, 83–89.

ATSDR - Agency for Toxic Substances and Disease Registry (2004). Toxicological profile for copper. https://www.atsdr.cdc.gov/toxprofiles/tp132.pdf (accessed 21 October 2018).

ATSDR - Agency for Toxic Substances and Disease Registry (2005). Toxicological profile for zinc. https://www.atsdr.cdc.gov/toxprofiles/tp60.pdf (accessed 21 October 2018).

ATSDR - Agency for Toxic Substances and Disease Registry (2012a). Toxicological profile for chromium. https://www.atsdr.cdc.gov/toxprofiles/tp7.pdf (accessed 21 October 2018).

ATSDR - Agency for Toxic Substances and Disease Registry (2012b). Toxicological profile for cadmium. https://www.atsdr.cdc.gov/toxprofiles/tp5.pdf (accessed 21 October 2018).

ATSDR - Agency for Toxic Substances and Disease Registry (2012c). Toxicological profile for manganese. https://www.atsdr.cdc.gov/toxprofiles/tp151.pdf (accessed 21 October 2018).

Azeez, J. O., Adekunle, I. O., Atiku, O. O., Akande, K. B., & Jamiu-Azeez, S. O. (2009). Effect of nine years of animal waste deposition on profile distribution of heavy metals in Abeokuta, south-western Nigeria and its implication for environmental quality. *Waste Management, 29*, 2582–2586.

Baker-Austin, C., Wright, M. S., Stepanauskas, R., & McArthur, J. V. (2006). Co-selection of antibiotic and metal resistance. *Trends in Microbiology, 14*(4), 176–182.

Bolan, N. S., Adriano, D. C., & Mahimairaja, S. (2004). Distribution and bioavailabilty of trace elements in livestock and poultry manure by-products. *Critical Reviews in Environmental Science and Technology, 34*, 291–338.

Bolan, N. S., Szogi, A. A., Chuasavathi, T., Seshadri, B., Rothrock, M. J., Jr., & Panneerselvam, P. (2010). Uses and management of poultry litter. *World's Poultry Science Journal, 66*, 673–698 https://www.researchgate.net/profile/Aa_Szogi/publication/231872388_Uses_and_management_of_poultry_litter/links/0f31753399554a3206000000.pdf (accessed 21 October 2018).

Cang, L., Wang, Y., Zhou, D., & Dong, Y. (2004). Heavy metals pollution in poultry and livestock feeds and manure under intensive farming in Jiangsu Province, China. *Journal of Environmental Sciences, 16*(3), 371–374.

Celestina, C., Midwood, J., Sherriff, S., Trengove, S., Hunt, J., Tang, C., Sale, P., & Franks, A. (2018). Crop yield responses to surface and subsoil applications of poultry litter and inorganic fertilizer in south-eastern Australia. *Crop & Pasture Science, 69*, 303–316.

Chen, H., Tenga, Y., Lu, S., Wang, Y., & Wang, J. (2015). Contamination features and health risk of soil heavy metals in China. *The Science of the Total Environment, 512–513*, 143–153.

Conama n° 420 de 28 de dezembro de 2009 - Conselho Nacional do Meio Ambiente. http://www.mma.gov.br/port/conama/res/res09/res42009.pdf (accessed 21 October 2018).

Conama n° 375 de 29 de agosto de 2006 - Conselho Nacional do Meio Ambiente. http://www2.mma.gov.br/port/conama/res/res06/res37506.pdf (accessed 22 October 2018).

Das, K., Malarvannan, G., Dirtu, A., Dulau, V., Dumont, M., Lepoint, G., Mongin, P., & Covaci, A. (2017). Linking pollutant exposure of humpback whales breeding in the Indian Ocean to their feeding habits and feeding areas off Antarctica. *Environmental Pollution, 220*, 1090–1099.

Dorneles, P. R., Lailson-Brito, J., Fernandez, M. A., Vidal, L. G., Barbosa, L. A., Azevedo, A. F., Fragoso, A. B., Torres, J. P., & Malm, O. (2008). Evaluation of cetacean exposure to organotin compounds in Brazilian waters through hepatic total tin concentrations. *Environmental Pollution, 156*(3), 1268–1276.

Dourado, F., Arraes, T. C., & Fernandes e Silva, M. (2012). The "Megadesastre" in the mountain region of Rio de Janeiro state—causes, mechanisms of mass movements and spatial allocation of investments for reconstruction post disaster. *Anu. Inst. Geociênc. UFRJ, 35*(2), 43–54.

Dziubanek, G., Baranowska, R., Ćwieląg-Drabek, M., Spychała, A., Piekut, A., Rusin, M., & Hajok, I. (2017). Cadmium in edible plants from Silesia, Poland, and its implications for health risk in populations. *Ecotoxicology and Environmental Safety, 142*, 8–13.

Embrapa (2013). Manual de calagem e adubação do Estado do Rio de Janeiro. Editor técnico, Luiz Rodrigues Freire et al. Brasília, DF. Embrapa; Seropédica, RJ. Editora UFRRJ. 434p.

Fiszman, M., Pfeiffer, W. C., & Lacerda, L. D. (1984). Comparison of methods used for extraction and geochemical distribution of heavy metals in bottom sediments from Sepetiba Bay, RJ. *Environmental Technology Letters, 5*, 567–575.

Gerber, P., Opio, C., Steinfeld, H. (2008). Poultry production and the environment—a review. In: O. Thieme, D. Pilling (Eds.) *FAO Animal Production and Health Proceedings, No. 9. Rome*. FAO - Food and Agriculture Organization of the United Nations. Poultry in the 21st Century: avian influenza and beyond. Proceedings of the International Poultry Conference, held 5–7 November 2007, Bangkok, Thailand. http://www.fao.org/3/a-i0323e.pdf (accessed 17 October 2018).

Gonçalves Jr., A.C., Nacke, H., Schwantes, D., Coelho, G.F. (2014). Heavy metal contamination in Brazilian agricultural soils due to application of fertilizers. Environmental Risk Assessment of Soil Contamination, Dr. Maria C. Hernandez Soriano (Ed.) https://www.intechopen.com/books/environmental-risk-assessment-of-soil-contamination/heavy-metal-contamination-in-brazilian-agricultural-soils-due-to-application-of-fertilizers (accessed 10 September 2018).

Gupta, G., & Charles, S. (1999). Trace elements in soils fertilized with poultry litter. *Poultry Science, 78*, 1695–1698.

Han, F. X., Kingery, W. L., Selim, H. M., & Gerard, P. D. (2000). Accumulation of heavy metals in a long-term poultry waste-amended soil. *Soil Science, 165*(3), 260–268.

Ho, Y. B., Zakaria, M. P., Latif, P. A., & Saari, N. (2014). Occurrence of veterinary antibiotics and progesterone in broiler manure and agricultural soil in Malaysia. *The Science of the Total Environment, 488–489*, 261–267.

IBAMA - Instituto Brasileiro do Meio Ambiente e dos Recursos Naturais Renováveis (2017). Relatórios de comercialização de agrotóxicos. Boletim 2016/Químicos e Bioquímicos/Vendas de ingredientes ativos por UF. http://www.ibama.gov.br/agrotoxicos/relatorios-de-comercializacao-de-agrotoxicos#boletinsanuais (Accessed 28 May 2018).

IEA - Instituto de Economia Agrícola. (2016). Safra 2016/17 Revigora as Vendas do Segmento de Fertilizantes. *Análises e Indicadores do Agronegócio, 11*(9), 1–6 http://www.iea.sp.gov.br/ftpiea/AIA/AIA-57-2016.pdf (accessed 02 April 2018).

IN n° 25/2009 – Instrução Normativa n° 25, de 23 de julho de 2009—Normas sobre as especificações e as garantias, as tolerâncias, o registro, a embalagem e a rotulagem dos fertilizantes orgânicos simples, mistos, compostos, organominerais e biofertilizantes destinados à Agricultura http://www.dpv24.iciag.ufu.br/new/dpv24/Apostilas/IN%20MAPA%2025%202009.pdf (Accessed 28 May 2018).

Jaja, N., Mbila, M., Codling, E. E., Reddy, S. S., & Reddy, C. K. (2013). Trace metal enrichment and distribution in a poultry litter-amended soil under different tillage practices. *The Open Agriculture Journal, 7*, 88–95.

Ji, X., Shen, Q., Liu, F., Ma, J., Xu, G., Wang, Y., & Wu, M. (2012). Antibiotic resistance gene abundances associated with antibiotics and heavy metals in animal manures and agricultural soils adjacent to feedlots in Shanghai, China. *Journal of Hazardous Materials, 235–236*, 178–185.

Jiang, X., Don, R., & Zhao, R. (2011). Meat products and soil pollution caused by livestock and poultry feed additive in Liaoning, China. *Journal of Environmental Sciences, 23*, S135–S137.

Karcı, A., & Balcıoğlu, I. A. (2009). Investigation of the tetracycline, sulfonamide, and fluoroquinolone antimicrobial compounds in animal manure and agricultural soils in Turkey. *The Science of the Total Environment, 407*, 4652–4664.

Khan, S., Cao, Q., Zheng, Y. M., Huang, Y. Z., & Zhu, Y. G. (2008). Health risks of heavy metals in contaminated soils and food crops irrigated with wastewater in Beijing, China. *Environmental Pollution, 152*, 686–692.

Khan, A., Khan, S., Khan, M. A., Qamar, Z., & Waqas, M. (2015). The uptake and bioaccumulation of heavy metals by food plants, their effects on plants nutrients, and associated health risk: A review. *Environmental Science and Pollution Research International, 22*(18), 13772–13799.

Kowalska, J. B., Mazurek, R., Gasiorek, M., & Zaleski, T. (2018). Pollution indices as useful tools for the comprehensive evaluation of the degree of soil contamination—A review. *Environmental Geochemistry and Health, 40*, 2395–2420. https://doi.org/10.1007/s10653-018-0106-z.

Leclerc, A., & Laurent, A. (2017). Framework for estimating toxic releases from the application of manure on agricultural soil: National release inventories for heavy metals in 2000–2014. *The Science of the Total Environment, 590–591*, 452–460.

Li, Z., & Shuman, L. M. (1997). Mobility of Zn, Cd, and Pb in soils as affected by poultry litter extract—I. Leaching in soil columns. *Environmental Pollution, 95*(2), 219–226.

Lino, A. S., Galvão, P. M. A., Longo, R. T. L., Azevedo-Silva, C. E., Dorneles, P. R., Torres, J. P. M., & Malm, O. (2016). Metal bioaccumulation in consumed marine bivalves in Southeast Brazilian coast. *Journal of Trace Elements in Medicine and Biology, 34*, 50–55.

Mattias, J. L., Ceretta, C. A., Nesi, C. N., Girotto, E., Trentin, E. E., Lourenzi, C. R., & Vieira, R. C. B. (2010). Copper, zinc and manganese in soils of two watersheds in Santa Catarina with intensive use of pig slurry. *R. Bras. Ci. Solo, 34*, 1445–1454.

Millaleo, R., Reyes-Díaz, M., Ivanov, A. G., Mora, M. L., & Alberdi, M. (2010). Manganese as essential and toxic element for plants: Transport, accumulation and resistance mechanisms. *Journal of Soil Science and Plant Nutrition, 10*(4), 476–494.

Mitra, S. (2003). *Sample preparation techniques in analytical chemistry*. Chemical Analysis. Hoboken, John Wiley & Sons https://doi.org/10.1002/0471457817 (accessed 29 January 2018).

Nagajyoti, P. C., Lee, K. D., & Sreekanth, T. V. M. (2010). Heavy metals, occurrence and toxicity for plants: A review. *Environmental Chemistry Letters, 8*, 199–216.

Nicholson, F. A., Chambers, B. J., Williams, J. R., & Unwin, R. J. (1999). Heavy metal contents of livestock feeds and animal manures in England and Wales. *Bioresource Technology, 70*, 23–31.

Parente, C. E. T., Azeredo, A., Vollú, R. E., Zonta, E., Azevedo-Silva, C. E., Brito, E. M., Seldin, L., Torres, J. P. M., Meire, R. O., & Malm, O. (2018). Fluoroquinolones in agricultural soils: Multi-temporal variation and risks in Rio de Janeiro upland region. *Chemosphere, 219*, 409–417. https://doi.org/10.3389/fenvs.2018.00118.

Ravindran, B., Mupambwa, H. A., Silwana, S., & Mnkeni, P. N. S. (2017). Assessment of nutrient quality, heavy metals and phytotoxic properties of chicken manure on selected commercial vegetable crops. *Heliyon, 3*, e00493. https://doi.org/10.1016/j.heliyon.2017.e00493.

Rehman, Z. U., Khan, S., Shah, M. T., Brusseau, M. L., Khan, S. A., & Mainhagu, J. (2018). Transfer of heavy metals from soils to vegetables and associated human health risk in selected sites in Pakistan. *Pedosphere, 28*(4), 666–679.

Shi, Y., Xu, X., Li, Q., Zhang, M., Li, J., Lu, Y., Liang, R., Zheng, X., & Shao, X. (2018). Integrated regional ecological risk assessment of multiple metals in the soils: A case in the region around the Bohai Sea and the Yellow Sea. *Environmental Pollution, 242*, 288–297.

Suleiman, N., Ibitoye, E. B., Jimoh, A. A., & Sani, Z. A. (2015). Assessment of heavy metals in chicken feeds available in Sokoto, Nigeria. *Sokoto J. Vet. Sci., 13*(1), 17–21.

USDA. (1999). *Soil taxonomy: a basic system of soil classification for making and interpreting soil surveys* (2.ed ed.). Washington: United States Department of Agriculture. Natural Resources Conservation Service. Soil Survey Staff 169p.

US-EPA Part 503 (1994). United States Environmental Protection Agency. A Plain English Guide to the EPA Part 503 Biosolids Rule. EPA/832/R-93/003. 180p.

Violante, A., Cozzolino, V., Perelomov, L., Caporale, A. G., & Pigna, M. (2010). Mobility and biovailability of HM and metalloids in the soil. *Journal of Soil Science and Plant Nutrition, 10*(3), 268–292.

Vollú, E., Cotta, S. R., Jurelevicius, D., Leite, D. C., Parente, C. E., Malm, O., Martins, D. C., Resende, A. V., Marriel, I. E., & Seldin, L. (2018). Response of the bacterial communities associated with maize rhizosphere to poultry litter as an organomineral fertilizer. *Frontiers in Environmental Science, 6*. https://doi.org/10.3389/fenvs.2018.00118.

Wang, H., Dong, Y., Yang, Y., Toor, G. S., & Zhang, X. (2013). Changes in heavy metal contents in animal feeds and manures in an intensive animal production region of China. *Journal of Environmental Sciences, 25*(12), 2435–2442.

Wang, H., Dong, Y., & Wang, H. (2015). Hazardous metals in animal manure and their changes from 1990 to 2010 in China. *Toxicological and Environmental Chemistry, 96*(9), 1346–1355.

Williams, C.M. (2013). Poultry waste management in developing countries. In: FAO - Food and Agriculture Organization of the United Nations. Poultry Development Review. 127p. http://www.fao.org/docrep/013/al718e/al718e00.pdf Accessed 21 October 2018.

Wu, S., Peng, S., Zhang, X., Wu, D., Luo, W., Zhang, T., Zhou, S., Yang, G., Wan, H., & Wu, L. (2015). Levels and health risk assessments of heavy metals in urban soils in Dongguan, China. *Journal of Geochemical Exploration, 148*, 71–78.

Xiong, X., Yanxia, L., Wei, L., Chunye, L., Wei, H., & Ming, Y. (2010). Copper content in animal manures and potential risk of soil copper pollution with animal manure use in agriculture. *Resources, Conservation and Recycling, 54*, 985–990.

Zhang, F., Li, Y., Yang, M., & Li, W. (2012). Content of heavy metals in animal feeds and manures from farms of different scales in Northeast China. *International Journal of Environmental Research and Public Health, 9*, 2658–2668.