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CHEMICAL ANALYSIS OF SURFACE LAYERS OF THE DUMPS SOIL OF THE CITY OF AUGUSTINÓPOLIS, TOCANTINS

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ABSTRACT

The dumps are considered potential sources of heavy metals, since various types of waste are disposed of inappropriately in this area and can contaminate the air, surface water and groundwater, and encouraging the spread of disease through vectors. This study aims to analyze the soil surface layers of the landfill in the municipality of Augustinópolis, Tocantins, about the presence of some heavy metals. It is a field research, with analysis of pH and heavy metals in the soil of the dump in order to compare the values obtained with the guiding values of the CONAMA resolution n □ 420/2009. Thus, it was possible to observe that the municipality of Augustinópolis not adapted so far the requirements of the National solid waste Policy. The pH acid presented at different sampling points in the depths of 0-20 cm, 20-40 cm and 40-60 cm, and in some specimens also alkaline in the depths are complied with. With respect to heavy metals in the soil of that dump, it is necessary to point out that were found lead, copper, cadmium, manganese, zinc and nickel, however, at concentrations below the guiding values for prevention and intervention of CONAMA resolution Nº 420/2009 not considered toxic, however, can cause damage to the environment and public health.

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INTRODUCTION

Inadequate waste management is a common problem in Brazil, since in many regions of the country they still receive open-air dumps as their final destination. Due to the damage they can cause to the environment and public health, it is that this problem has been the subject of numerous debates among the managers of the different spheres of government (municipal, state and federal). ABRELPE data published in 2015 show that approximately 60% of Brazilian municipalities transport 30 million tons of waste a year to inappropriate places, and this amount is increasing annually, even though this practice is prohibited and culminate in pollution since the year 1981 in the country (ABRELPE, 2015). To corroborate this information, Silva Filho (2017) points out that in 2016 there was a setback in the solid waste situation in the country, since the data referring to the final destination of MSW show a worsening when compared to the year 2015, where of 41.7 million tons of waste were dumped in landfills. In the year 2016, some 3,331 municipalities sent over 29.7 million tons of waste, equivalent to 41.6% of the collected waste, which are transported to landfills or controlled landfills, which are sites that do not have a set of systems and measures indispensable

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to avoid damage and degradation to the environment. In addition, from 2015 to 2016, there was an increase in the number of dumps in the country and a decrease in sanitary and controlled landfills (SARMIENTO, 2017). Given this, inadequate waste management is also a reality faced by the state of Tocantins. According to the State Solid Waste Plan of Tocantins, only three of the 139 municipalities that make up the state of Tocantins offer an adequate final destination for the waste generated by its population, which is the sanitary landfill: Palmas, Gurupi and Araguaína. It is also worth mentioning that seven municipalities have controlled landfills and the remaining municipalities have landfills (MORAES, 2017). Aniceto and Horbe (2012) point out that referring to the problem of dumps, one of the most disturbing questions is the contamination of the soil and vegetation by heavy metals from the areas that are used for these purposes. Several heavy metals can be found in dumps, such as arsenic, nickel, copper, copper, lead).

Such metals are found in wastes, such as: bulbs, batteries, batteries, waste paint and cans. Besides these objects, it is possible to find in these areas other toxic products that affect the environment, vegetation and health. According to Guedes (2008) several heavy metals (lead, zinc, cadmium, chromium, mercury, among others) can be found in materials of different waste classifications in the dump, being these highly toxic and harmful to the environment and public health. Muñoz (2002) argues that environmentalists and authorities are increasingly concerned about the amount of heavy-metal waste dumped in landfills, as well as spreading these through the manure to the soil and water sources. In this context, Biondi (2010) points out that in the mid-1990s, soil contamination from the dissemination of heavy metals became a problem worldwide, and was recognized as a cause of health damage and the environment. Research in the field of soil science and environmental contamination developed by international scholars confirmed the importance of soil to conserve the environment ecologically balanced, since it acts as a barrier or agent of dissemination of contaminants to watercourses. In order to minimize impacts and soil contamination, the National Environmental Council (CONAMA) published in 2009 Resolution nº. 420/2009, which addresses tolerable parameters and "values" for the presence of chemical substances in the soil. in order to affect the quality of the product. In addition, said resolution determines the guidelines that must be followed to manage the environment in areas polluted by man's activities with such substances, also states that polluted areas pose a risk to public health and the environment; and stresses the importance of implementing strategies to prevent soil and groundwater from being contaminated, since they are essential for sustainable development, constitute a public patrimony and are sources of reserves to supply the population when necessary (BRAZIL, 2009).

CONAMA notes that on August 31, 1981, Law No. 6,938 was published, which refers to the National Environmental Policy, which establishes that the person responsible for pollution and degradation has the duty to restore and / or repair the damages generated to the environment. Therefore, Law No. 10,406, published on January 10, 2002, imposes, in its art. 1.228, paragraph 1, that for the possession of land it is imperative to preserve the flora, fauna and natural resources, as well as to maintain the environment and the historical and artistic heritage balanced, in addition, one must prevent the contamination air and water (BRASIL, 2009). Regarding this issue of landfill, heavy metals, and lack of MSW management, the need to carry out a study in the municipality of Augustinópolis - Tocantins arose, since the waste generated by its population is dumped in an open dump. In addition, wastes containing heavy metals are carried by the collection car to the garbage dump, without receiving any previous treatment, which connotes the lack of management, and is a matter of risk to the environment and public health. Based on this assumption, this study had as objective to analyze superficial layers of the soil of the city of Augustinópolis, Tocantins, regarding the presence of some heavy metals and to compare the values obtained with the reference values of the Resolution of the National Council of the Environment - CONAMA 420/2009. The present study is a result of the dissertation of Masters in Environmental Sciences of the University of Taubaté - UNITAU defended in June of 2018.

RESULTS AND DISCUSSION

In this study, soil samples from the city of Augustinópolis, Tocantins, were collected. Thus, from the on-site visit to the Augustinópolis municipal dump, it was possible to verify that MSW are not segregated according to their classification, and are disposed of in agglomerated form in this area, so that residues from domestic activities are dumped together with those coming from construction, or with the services of health services. In addition, such waste is not treated before it is transported for final disposal, which increases the probability of further degrading the environment and the health of the population. In the municipality of Augustinópolis the waste is disposed of inadequately, as the municipality did not meet the requirements of the National Solid Waste Policy. However, it is worth mentioning that the work of the municipal landfill is being completed, although according to the PNRS published in 2010, municipalities should eliminate landfills by the year 2014, but many Brazilian municipalities did not comply with these recommendations in the given period, and one of them was Augustinopolis.

The extension of the term to extinguish the dump from 2018 to 2021 also benefited the municipality, as the manager freed from paying a fine for non-compliance with the relevant legislation. In this context, Siqueira and Moraes (2009) affirm that the solid urban waste produced by the population from their different occupations causes damages to human health, besides causing negative impacts and sanitary problems to the environment, and social, economic and administrative problems . Many cities, besides not carrying out the preliminary treatment of the garbage generated by the population, still offer to these as final destination the open dump, thus contributing to increase the level of contamination of air, soil and groundwater sources and surface water. In relation to the heavy metals found in the soil samples from the city of Augustinópolis - TO, it is important to note that concentrations of only 6 metals were detected: cadmium (Cd), copper (Cu), nickel (Ni) , lead (Pb), zinc (Zn) and manganese (Mn). The results obtained were compared with the guideline values of CONAMA Resolution No. 420/2009 (Table 5), considering that in the state of Tocantins there are no specific parameters for soil evaluation. Table 2 refers to the values of heavy metals and pH found in soil samples extracted from the 0 to 20 cm depth of the 15 demarcated points. The samples from 0 to 20 cm showed that the pH was alkaline at points P4 (8.37); P3 (7.63); P1 (7.27) and P2 (7.23).

Table 1. List of guiding values for soils and groundwater, CONAMA Resolution 420/2009

Substances	CAS n°	Soil (mg.kg-1 dry weight) (1)				
		Quality reference	Prevention	Investigation		
				Agricultural APMax	Residential	Industrial
Cadmium	7440-48-4	E	1,3	3	8	20
Lead	7440-43-9	E	72	180	300	900
Copper	7440-50-8	E	60	200	400	600
Manganese	7439-96-5	E	-	-	-	-
Nickel	7440-02-0	E	30	70	100	130
Zinc	7440-66-6	E	300	450	1.000	2.000

Source: BRAZIL, 2009.

Table 2. Average values of pH and heavy metals detected in samples from 0 to 20 cm depth, collected from surface layers of the landfill of the city of Augustinópolis, Tocantins, July 2016

Heavy metals mg/kg									
			Ph	Cu Copper	Mn Manganese	Zn Zinc	Cd Cadmium	Pb Lead	Ni Nickel
Depth	Sample of Points		$CaCl_{2\ 0,01\ mol/L}$						
	P1	A	7,27	12,45	11,83	16,27	0,10	10,54	0,55
		B							
		C							
	P2	A	7,23	10,91	10,45	15,33	0,07	1,90	0,81
		B							
		C							
	P3	A	7,63	12,96	7,62	91,31	0,07	6,56	0,86
		B							
		C							
	P4	A	8,37	10,55	11,88	10,57	0,04	2,47	0,53
		B							
		C							
	P5	A	5,33	0,49	13,83	2,75	0,01	0,00	0,18
		B							
(0-20)		C							

On the other hand, the acid pH was demonstrated in soil samples collected from point P5 (5.3), and collected from the area that is outside the dump on a private property. Relevant to this, Giordano; Filho and Carvalho (2011) state that pH changes not only the activity of the enzymes, but also the coefficient of solubility and toxicity of the various compounds present in the dumps. The pH also indicates the deterioration stage in which the solid residues are, therefore, the pH near 6.0 indicates that the landfill or landfill is in the acid stage of deterioration, however, when it has pH near 8.0 , this is in the last stage of anaerobic deterioration, which corresponds to the methanogenic stage. With respect to heavy metals, the highest values in descending order of Copper at points P3 (12,96), P1 (12,45), P2 (10,91), P4 (10 , 55), the most significant of which is found in P3 and P1. The soil sample P5 was collected outside the landfill area, and sample P1 was removed from the top of the dump and P2 was extracted at a distance of 100 m from P1. When comparing these results with those of CONAMA reference number 420/2009, it was verified that the values are below the reference value of prevention, therefore copper was not found in amount harmful to the soil, the environment and public health. Manganese was increased at points P5 (13.83), P1 (11.83) and P4 (11.88). It is worth mentioning that Resolution CONAMA 420/2009 does not present reference value for this element. According to the Laborsolo (2013), Manganese (Mn) is considered a cationic micronutrient, being the eleventh element most found in nature. Its existence in the soil is the result of oxides, carbonates, silicates and sulfides. The presence of Manganese comes from the connection between pH, oxidoreducation, amount of organic matter and harmony with other elements, among them: iron (Fe) and Calcium (Ca). It is added that the reduced pH contributes so that the amount of Mn is smaller, however, when the pH is high, it contributes to the oxidation.

In this context, Biondi *et al.* (2011) emphasizes that although the prevention values for Fe and Mn are not determined by the CONAMA resolution 420/2009, it is extremely important to know the natural concentrations of Mn and Fe in soils, since, besides being plant micronutrients, the their existence as main elements of rocks make them interesting for the studies of geochemistry, in addition to pointing, indirectly, the concentrations of other heavy metals. Zinc was found to be higher in the P3 (91.31), P1 (16.27) and P2 (15.33) samples, and lower in the P4 (10.57) and P5 (2, 75). According to CONAMA parameters, Zinc is present in the soil of the city of Augustinópolis, however, in an insignificant amount to contaminate the soil and cause damages to the environment.

In contrast to the findings of this study, Nascimento (2017), when evaluating the soil quality of the disused dump in the municipality of Brejinho in the state of Rio Grande do Norte, found total values of Cr, Mn, Pb and Zn, with concentrations of 21, 10%, 424.07%, 2,150.85% and 17,500.00%, simultaneously. It was also verified that Zn was the metal with the greatest variation in its concentration, having exceeded the Quality Reference Value in soils of Rio Grande do Norte (PRESTON *et al.*, 2014) and, in addition, (PASTOR and HERNANDES, 2012), which increases the concern about the presence of this element in the soil. Cadmium was detected more concentrated in samples extracted from P1 (0,10). According to the values in the table CONAMA 420/2009, the average levels of Cadmium detected in the different sampling points are lower than the value of prevention, which is a positive result, since Cadmium values above those recommended for prevention can cause significant damages to the environment environment, and especially health. According to Pan *et al.* (2010) and Fontaine *et al.* (2008), cadmium can seriously impair health, affecting bones and kidneys even more often, even in individuals not exposed to

Table 3. Mean values of pH and heavy metals detected in samples from 20 to 40 cm depth, collected from surface layers of the soil of the Augustinópolis municipality, Tocantins, July 2016

Depth	Sample of Points		Ph $CaCl_{2\ 0,01\ mol/L}$	Cu Copper	Mn Manganese	Zn Zinc	Cd Cadmium	Pb Lead	Ni Nickel
				Heavy metals mg/kg					
(20-40)	P1	A B C	7,40	6,27	7,70	14,41	0,05	1,31	0,55
	P2	A B C	7,23	7,76	10,72	18,96	0,05	10,15	0,72
	P3	A B C	7,57	4,78	6,64	99,15	0,16	0,72	0,42
	P4	A B C	7,90	4,10	6,22	32,81	0,07	13,57	0,38
	P5	A B C	5,33	0,29	10,27	1,32	0,01	0,00	0,15

work, or it may affect adults and children who have been exposed to small concentrations of cadmium. Cadmium is more concentrated in the organs than in the muscles or fats, moreover, it can be found in greater quantity in the kidneys in relation to the liver. Regarding Nickel, it is pointed out that this metal was detected at different sampling points in concentrations below the reference parameters of CONAMA Resolution 420/2009. According to Ecycle (2018) there is a tolerable amount of nickel that does not cause harm, however, if extrapolated, it can cause serious damage to the human body as well as microorganisms present in the soil and seas, and even birds can be affected. For this reason, NiPERA (Nickel Producers Environmental Research Association) was established to establish safe levels of exposure to nickel not only for individuals who come into contact with the metal in their working environment, but also for all existing forms of life and for the environment. Contrasting the results of the study, Milhome *et al.* (2018) point out that in the evaluation of the soil of the Iguatu - CE dump in the presence of heavy metals, metals such as Nickel (Ni) and Cadmium (Cd) are not found in the analyzed samples. Regarding Lead, it is noteworthy that this metal was more evident in samples collected from points P1 (10,54) and P3 (6,56). These results indicate that this metal is low, according to the prevention value adopted by CONAMA Resolution 420/2009, this result being a positive point, since lead is highly toxic, and for that reason, when it occurs in high concentrations entails serious harm to public health. Relevant to this, Moreira and Moreira (2004) affirm that lead (Pb) can cause serious neurological disorders in adults, especially in children, since this metal is capable of generating irreversible damages, such as: reduction of Q.I. and cognitive impairment. The same authors note that an amount of 10 µg L-1 in a child's blood and 40 µg dL-1 in an adult are sufficient to cause damage to the nervous system. Corroborating with findings from the study, Pinto Filho *et al.* (1990) observed the presence of the following metals: Cu, Cd, Cr, Fe, Mn, Ni, Pb, and Zn in monitoring the total and present values of heavy metals in the city of Apodi-RN. In addition, they found that these metals were in a smaller quantity in the city of Apodi - RN, when they compared the results obtained with the amount of heavy metals found in contaminated soil in the city of Assú - RN, in a study carried out by Pinto Filho *et al*. al. (2010), where they detected Cu, Cd, Cr, Fe, Mn, Ni, Pb 95.24 mg / kg and, 4.25 to 6.43 mg / kg. Table 3 shows the distribution of the heavy metals and pH values found in the soil samples, which were collected at a depth of 20 to 40 cm. It was observed in Table 3 that in the soil samples collected at depths of 20 to 40 cm, the pH was alkaline at points P4 (7.90), P3 (7.57), P1 (7.40) and P2 (7.23). Acid pH was verified in the soil samples extracted from the P5 point (5.33). It should be noted that the pH values obtained in the depth of 20 to 40 cm presented little difference when compared to the samples collected from the depth of 0 to 20 cm.

Regarding the Copper content, it is noteworthy that it was found higher at points P2 (7.76) and P1 (6.27). Such metal was found in a lower concentration in the depth of 20 to 40 cm, when compared to the findings in the 0 to 20 cm samples. It is important to mention that Cu levels in this depth (20 to 40 cm) are lower than the values of prevention recommended by CONAMA Resolution 420/2009, so they are not harmful to the environment and public health. Manganese was shown to be increased at points P5 (10,27) and P2 (7,70). However, when comparing the Mn values obtained in the samples of 20 to 40 cm with those of the depth of 0 to 20 cm, it was evidenced that in the 0 to 20 cm was found increased in 4 sample points and in the 20 to 40 cm in only two. As mentioned above, CONAMA does not indicate reference content for this metal, however, its presence in the soil is directly related to pH and oxidation. Zinc was found in higher values in the samples of points P3 (91,31) and P1 (16,27). According to the guiding values of CONAMA, Zinc was detected in the soil of the city of the study, however, in a non-considered prevention and intervention content. The cadmium presented low levels in the different sampling points, being greater the one found in P1 (0,10). According to guiding values of CONAMA (2009) for this metal, the cadmium present in the samples collected from points P3 and P1 are lower than the prevention value, which is 1.3, which is a positive result as previously mentioned, due to this metal is highly harmful to individual and collective health, even when the population is exposed to small amounts. With regard to Nickel, it is emphasized that this metal was found in the samples of 20 to 40 cm of depth in concentration inferior to the value of prevention and intervention recommended by the resolution CONAMA 420/2009. As for lead, it is reported that the P4 point (13.57) was the one with the highest concentration, but it is lower than the values of prevention and intervention of the CONAMA resolution.

Table 4. Mean values of pH and heavy metals detected in samples from 40 to 60 cm depth, collected from surface layers of the landfill of the city of Augustinópolis, Tocantins, July 2016

Depth	Sample of Points		Heavy metals mg/kg						
			pH $CaCl_{2\ 0,01\ mol/L}$	Cu Copper	Cu Copper	Cu Copper	Cu Copper	Cu Copper	Cu Copper
(40-60)	P1	A B C	7,37	6,48	6,92	13,77	0,05	9,99	0,62
	P2	A B C	7,20	7,13	8,61	31,36	0,07	2,49	0,73
	P3	A B C	7,50	5,35	7,37	53,54	0,06	5,37	0,58
	P4	A B C	7,73	4,50	6,67	8,67	0,04	1,33	0,34
	P5	A B C	5,63	0,21	7,52	0,80	0,01	0,00	0,16

This result is also positive, since this metal is highly toxic. Corroborating with the findings of the study, Becegato *et al.* (2010) investigated the spatial distribution of radioactive elements and heavy metals in a dump that was deactivated in the municipality of Lages-SC, showing average levels of Cadmium, Chromium, Nickel and Lead between 0.2; 13.1; 7.2 and 8.9, which are lower than the quality, prevention and intervention values of the CETESB table. On the other hand, Moreira *et al.* (2010) developed a study with the objective of determining the peculiarities of the urban solid grounded waste, detected 1.62 mg / kg Cadmium, 107.19 mg / kg - Chromium, 65.07 mg / kg - Crude, 34.43 mg / kg Iron, 281.43 mg / kg Manganese, 43.60 mg / kg Nickel, 28.62 mg / kg - Lead and 0.78 mg / kg Zinc, with total zinc not significant, when compared to other metals, since the others were found in amounts higher than CETESB and CONAMA parameters. Lopes *et al.* (2010) when carrying out a study on heavy metals in natural zones and municipalities of the state of Rio Grande do Norte, found total metals values between 6.43 mg / kg for Cadmium, 95.24 mg / kg Chromium, 106.23 mg / kg for Lead and 48.42 mg / kg for Nickel. These findings pointed to soil contamination, since the levels detected are higher than the guiding values of the CETESB table of 2014. Relevant to this, Cavalett; (As), cadmium (Cd), chromium (Cr), lead (Pb) and mercury (Hg) in an area in the neighborhood Embocuí, municipality of Parananguá - Pr, which analyzed the concentrations of arsenic (As), cadmium (Pb), chromium (Cr) and mercury (Hg) were used in higher concentrations when compared to other metals. However, such concentrations were evidenced in lower values than those contaminated for soil established by the Company for environmental sanitation technology - CETESB (2005). Pb and Hg were detected above the reference value for natural soil, which requires monitoring and monitoring of these levels, to verify if the soil can become contaminated with them. Table 4 shows the distribution of the heavy metals and pH values found in the soil samples, which were extracted at a depth of 40 to 60 cm.

It is visualized in the samples extracted from the depth of 40 to 60 cm, that the pH is alkaline at points P4 (7.73) and P3 (7.5). However, pH was present in soil samples taken from the P5 point (5, 63), which were collected from the area outside the dump. It was also observed in the samples of 40 to 60 cm, that the Copper content was more significant at the point P3 (7,13) and P1 (6,48). It is worth noting that the samples taken in the depths of 40 to 60 cm showed less amount of this metal when compared to the other depths, but this result does not indicate damages to the environment and public health, since the values obtained are lower than the values mentors of CONAMA. Manganese was elevated with representativeness only at points P2 (8,61), but did not cause damages to the environment and public health. It is important to highlight that Zinc was found in smaller values than the samples collected at depths of 0 to 20 cm and of 40 to 60 cm, at lower levels than the CONAMA resolution parameters, being a finding also positive, since it was not found in concentration that could cause damage to the environment. Cadmium presented higher levels at the sampling point P2 (0.07), which was found in this depth at a lower concentration than the depths of 0 to 20 and 40 to 60 cm, and lower than CONAMA values. Lead was found to be higher in the samples from point P1 (10.54), but also lower than CONAMA guiding values, since even though it was detected in the analyzed soil, it showed low concentrations. Nascimento (2017), when evaluating the soil quality in a dump that was deactivated in the city of Brejinho, in the state of Rio Grande do Norte, detected total concentrations of the following Cr, Mn, Pb and Zn metals, which showed an increase in the its contents 21.10%, 424.07%, 2.150.85% and 17.500,00%. Preston *et al.* (2014) point out that Zinc was the metal that presented the most variation in its concentration in both environments, since its content exceeded the guiding value of CONAMA quality reference, besides being a metal with high mobility when compared to the others, which is a worrying factor (PASTOR, HERNANDES, 2012).

Pinto Filho *et al.* (2012) in a study on soil monitoring of the city of Apodi - RN found total concentrations of the Cd, Cr and Ni metals lower than the Quality Reference Values - VRQ of CONAMA, thus concluding that the area of the dump of said municipality poses a risk of contamination by such elements. On the other hand, the aforementioned authors point out that the detected concentrations of Cu and Zn are within the Value of Prevention - VP, and this result is a warning for a probable contamination of the place where the Apodi - RN dump by metals heavy. In addition, Lead was evidenced in concentrations higher than the intervention values of CONAMA, such finding shows that the area used for final disposal of urban solid waste may constitute one of the causes that will lead to contamination of the soil and water. On the other hand, Santana and Barroncas (2007) and Oliveira (2007), when conducting research on the heavy metal content present in waters in the state of Manaus, found that the values obtained were higher than those established by CONAMA, thus indicating contamination of the waters analyzed.

Conclusion

When evaluating the presence of heavy metals and pH in the soil layers of the city of Augustinópolis - TO, it was possible to verify the presence of acid and alkaline pH in some samples. With regard to the heavy metals present in the soil of said dump, it is necessary to point out that Lead, Copper, Cadmium, Manganese, Zinc and Nickel were found in concentrations lower than the guiding values of CONAMA Resolution No. 420/2009, therefore, the levels detected are not considered to be toxic. However, this does not prevent that in layers deeper than these metals can be found in levels higher than those of the aforementioned resolution. In addition, with the passage of time and increase of waste dumped in the dump, such metals can cause greater damage to the environment and public health, which needs monitoring of the area and greater attention of the manager, which should provide a final destination more the waste produced by the population.

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