ASSESSMENT OF LEACHATE AND SOIL CONTAMINATION WITH HEAVY METALS AROUND DEPOSIT SITES IN PODUJEVA AND PRIZREN

Tafë Veselaj[1,4], Rifat Morina[2], Valdet Gashi[3], Fatbardh Sallaku[4]

[1] *Kosovo Environmental Protection Agency, Street "Luan Haradinaj" Government Building 10000 Prishtine, Kosove*

[2] *Faculty of Food Technology University of Mitrovica "Isa Boletini", PIM Trepca 40000 Mitrovice, Kosove*
E-mail: rifat.morina@umib.net

[3] *Global Green LTD, Rifat Berisha Str. No. 23/1, 10000 Prishtine, Kosove*

[4] *Agriculture University of Tirana - Faculty of Agriculture and Environment w/n Kamez Albania*

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ABSTRACT

The leachate of heavy metals from waste landfills can affect and pollute the agriculture land around. The purpose of this research was to study the concentration of heavy metals in the soil influenced by the solid waste leachates from landfills. Heavy metals which were analyzed were Zn, Cd, Ni, Cu, Pb, Cr, Fe, As and Hg. At the same time, the soil texture was ascertained so as to determine the wastewater penetration into the depth of the land. The results show that leachates from landfills possess contamination potential for water surface and soil. Heavy metals concentrations both in soil samples and in water samples showed that all the metals analyzed are present. In soil samples, the concentration of Ni was over EU and national standards, which was in the range of 78.1 - 92 mg/kg, around landfills in Prizren and Podujeva and in water samples the concentration of Ni was 0.14 - 0.16 mg/L. The Pb concentration was 52 mg/kg, in soil samples around Podujeva landfill, while the lead concentration in the water samples in Podujeva, was 0.14 mg/L.

Keywords: landfill leachate, heavy metals, land contamination.

INTRODUCTION

The migration of the population from rural areas towards urban areas has contributed to increasing the waste generation in these areas, creating serious waste management challenges for the operating companies and municipalities. At the same time, the rapid increase of waste generation has led to the emergence of many environmental problems. The problem became even bigger when considering that the waste management network was not established yet in the all territory. This situation in Kosovo led to the creation of many illegal landfills. In 2017, 1062 illegal landfills have been identified in 16 municipalities [1]. All these illegal waste dumps represent an environmental problem with a high cost of elimination. Illegal waste landfill sites represent a great concern for the environment in other countries as well [2]. Illegal landfills are of different sizes, positions and can be found near rivers, landscape, street settlements, etc. Illegal waste disposal has had numerous environmental consequences, including but not limited the deterioration of land, ground and surface water, and the air quality. The waste impact depends on waste composition and illegal disposal practices [3]. After 2002 - 2005, a sanitary landfill was built for urban waste, thus marking a turning point for better waste management in Kosovo.

In spite of major investments in landfill construction, following their operationalization many negative

effects of discharges of these landfills were observed. To assess the impact of landfills on the environment, the study included samples from the soil surface and surface water around Podujeva and Prizren landfills. The Podujeva landfill is a municipal landfill wherein 10315.42 tons of wastes are disposed annually, while the waste landfill in Prizren is a regional landfill and 79661.07 tons of wastes are disposed on this site each year [4]. The leachates from the new landfills are more contaminated compared to the older landfills [5]. In the European Union, different countries have good and bad practices in terms of waste management and landfills. In the 21st century, sustainable waste and landfill management have become a necessity in all stages of impact, starting from designing operation or closure process.

As a country in transition, Kosovo has yet to reach the required EU landfill management standards. On the one hand, this causes financial loss, higher emission of pollutants and shorter lifetime of a landfill. In general, mixed waste limits re-use, recycling, conversion alerts, increases cost and lowers the efficiency of waste management technology performance [6]. On the other hand, researchers reported that more than 20 % of nitrogen will leach from waste, therefore, recirculation of infiltrations stimulates microbial activity, increasing the rate of ammonia (release of ammonia from residues in the liquid phase [7]. The new waste dumps, usually, their leachates, are highly contaminated with ammonia which results from hydrolysis and nitrogen fermentation from the fraction content of the biodegradable substrates [8]. In addition, landfill leachates may contain complex organic compounds, hydrocarbons, metals with different concentrations, which, depending on the distance of the circulation on the ground, present their impact on surface and ground waters. In a study that was conducted in Sweden, in the wastewaters of 12 municipal landfills, 90 organic compounds and 50 inorganic compounds were identified [9]. Concentrations of pollutants in leachates also depend on rain and season. The leachates landfills in the dry season are more polluted, due to evaporation on one side and reduced atmospheric rainfall than the rainy season, when concentrations of pollutants in leachates are smaller [10]. Leachates flows into the surrounding environments are due to the lack of adequate control facilities [11]. The land and the waters around the dumps site have a great potential to be contaminated by the polluting emissions. Therefore, the prevention of leachates flow and their prior treatment is a basic principle of standards according to local and European laws. Treatment of these waters also carries the high cost for the waste management company. In European countries, such as in Germany, the cost of treating these waters varies between 12 and 75 € per m^3 [12].

The total damage costs of air pollution due to poor waste management is estimated at € 11 million - € 22 million per year [13]. Soils may have a range of heavy metals with a different concentration on the surrounding, such as the geological environment, anthropogenic and natural activities occurring [14]. The landfill leachate usually contains heavy metals As, Cd, Cr, Cu, Pb, Hg, Zn, Ni, and xenophobic organic substances, the discharge of which causes serious environmental threats to the surrounding soil [15].

The aim of this research was to study the concentration of heavy metals in the soil and surface waters influenced by the solid waste leachates from landfills around Podujeva and Prizren in Kosove.

EXPERIMENTAL

Nine soil samples were taken in two regions around landfills in Podujeva and Prizren. The distance of the soil sampling from Podujeva landfill was 73 - 432 m, where 4 soil samples were taken while the distance of the soil sampling around Prizren landfill was 31 - 731 m, and 5 soil samples were taken (Fig. 1). The samples were collected at a depth of 30 - 40 cm, in 2015. The collection of soil samples was conducted according the instructions from Guidelines Model for Sampling (ISO 10381-1: 2002), Guidelines on Sampling Techniques (ISO 10381-2: 2002), and Guidelines on Safety (ISO 10381-3: 2001) [16]. The samples were dried (dessicated) at a room temperature for two weeks. Afterwards, the soil was grinded, filtered in a size of 2 mm, followed by homogenization and the end preparation for laboratory analysis. The samples were then heated to 95 ± 10°C for about 15 minutes. After the samples were cooled, 5 mL of HNO_3 was added and heating was applied for another 30 minutes. The digests were again allowed to cool (priori to that 2 mL of Milli-Q water and 3 mL of 30 % H_2O_2 was added) and heated to 95 ± 5°C. After the digests were cooled again, another 1 mL of 30 % H_2O_2 was added. The heating was continued until the sample volumes were reduced to approximately 5 mL.

The digests were then allowed to cool again before being diluted to 50 mL with Milli-Q water. The materials samples were analyzed for the concentration of heavy metals, such as Zn, Cd, Ni, Cu, Pb, Cr, Fe, As and Hg. The heavy metals were analyzed with Agilent Technologies 4200 MP-AES according US EPA Method 3050B. In the meantime, Hg was analyzed with ICP-MS laboratory apparatus using the ISO 11466/1995 method. The comparison of heavy metal limits values was conducted based on the Kosovo Administrative Instruction on Allowing the Norms of Hazardous Substances and Harmful Presence in Soil and Council Directive 86/278/EEC (Table 1). The determination of soil texture, as a physical property, was also carried out (Table 2). Soil texture will provide information about: the ability infiltrators of land (soil permeability), field capacity of the soil for water, suitability for urban uses, etc.

The sampling of the two landfills for the water flow (leachate) was conducted, according to ISO 5667-6 [16]. Sampling points were deployed in the downstream direction. Water samples were taken in 6 phases, during the period between 2015-2016. The Water Sample point was 511.0 meters away from the Podujeva landfill whereas in Prizren was 976.0 meters from the landfills. Total number of samples for both landfills was 12. Every time after conducting the sampling, 100 mL were separated for each sample, which was previously filtered with a 0.45 μm filter and added 2 to 25 mL of HNO_3, depending on the sample type. The comparison of heavy metal limit values are according the Kosovo Administrative Instruction NO.30/2014, (Annex II-limited values of discharge), Kosovo Administrative Instruction NO.15/2012 of Waste Landfills Management (Annex 1; Maximal allowed concentration on discharging filtration from landfill) and Council Decision of 19 December 2002, establishing a criteria and procedures for the acceptance of waste at landfills pursuant to Article 16 of and Annex II to Directive 1999/31/EC (Table 3).

The determination of heavy metals from the water flow (leachates) sample was conducted with the atomic absorber (SAA - Perkin Elmer model Analyst 400). The heavy metals identified are: Pb, Cd, Cr, Cu, Ni, Zn, Fe. For the determination of heavy metals method ISO 6351 was used. Heavy metals, As and Hg are determined with the same atomic absorber, but with the hydraulic system technique for As was (EN ISO 11969: 1996), and for Hg - (ISO 12846: 2012). The atomic absorber calibration was done every time before analyzing the samples.

Table 1. Limit values of heavy metals in water discharge according to Kosovo and the EU standards.

Metals	Unit	Limits of wastewater*	Limits of waste**	EU limits ***
Cr	mg/L	1.0	0.5	2.5
Cd	mg/L	0.02	0.5	0.3
Ni,	mg/L	0.5	2.0	3
Zn,	mg/L	1	10.0	15
Cu,	mg/L	0.5	10.0	30
Fe,	mg/L	2	-	-
Pb	mg/L	0.5	2.0	3
As	mg/L	0.1	1.0	0.3
Hg	mg/L	0.01	0.1	0.03

** Kosovo Administrative Instruction No.30/2014, manners, parameters and limit values of wastewater discharge in the water body (Annex II-limited values of discharge);*

*** Kosovo Administrative Instruction No.15/2012 of Waste Landfills Management, Annex 1;*

**** Council Decision of 19 December 2002, Article 16 and Annex II to Directive1999/31/EC.*

Table 2. Texture of soil samples of urban waste landfills.

Waste landfill	Fractions	Particle size, mm	%	Accuracy	Method
Landfill of Podujeva	Sand	>0.02	58.5	+/-10%	Pipet
	Lyme	0.02-0.002	34.6	+/-10%	Pipet
	Clay	<0.002	6.9	+/-10%	Pipet
Landfill of Prizren	Sand	>0.02	61.3	+/-10%	Pipet
	Lyme	0.02-0.002	27.6	+/-10%	Pipet
	Clay	<0.002	11.1	+/-10%	Pipet

Table 3. Limit values of heavy metal concentrations in soil (Kosovo & EU).

Parameters	Limit values mg/kg*	Limit values mg/kg**
Zn	300	150-300
Cd	2	1-3
Ni	50	30-75
Cu	100	50-140
Pb	50	50-300
Cr	50	-
Fe	-	-
As	20	-
Hg	1	1-1.5

** Norms of Hazardous Substances and Harmful Presence in Soil allowed by Kosovo Administrative Instruction;*

*** Norms of Hazardous Substances and Harmful Presence in Soil allowed by Council Directive 86/278/EEC.*

This is achieved by applying all the steps provided in the manual for using the software WinLab32 AA Flame installed on PCs and SAA-s.

RESULTS AND DISCUSSION

The soil and water samples leachates were analyzed to determine the concentration of 9 heavy metals; Zn, Cd, Ni, Cu, Pb, Cr, Fe, As, Hg. The most important one was to investigate the correlation between heavy metal concentrations in leachate and soil. The measured values differ depending on the landfills points sampling. Samples of landfills in Podujeva and Prizren (Figs. 2 and 3) have resulted the presence of all heavy metals. The average values of heavy metals in Prizren leachates landfill show that there is a high level of contamination with Cd 0.11 mg/L, (Fig. 2), which is over the limited values of the Kosovo Standard for wastewater discharges in the water body. However, the Cd was not detected in the Podujeva samples. The concentration of Cr, Ni, Zn,

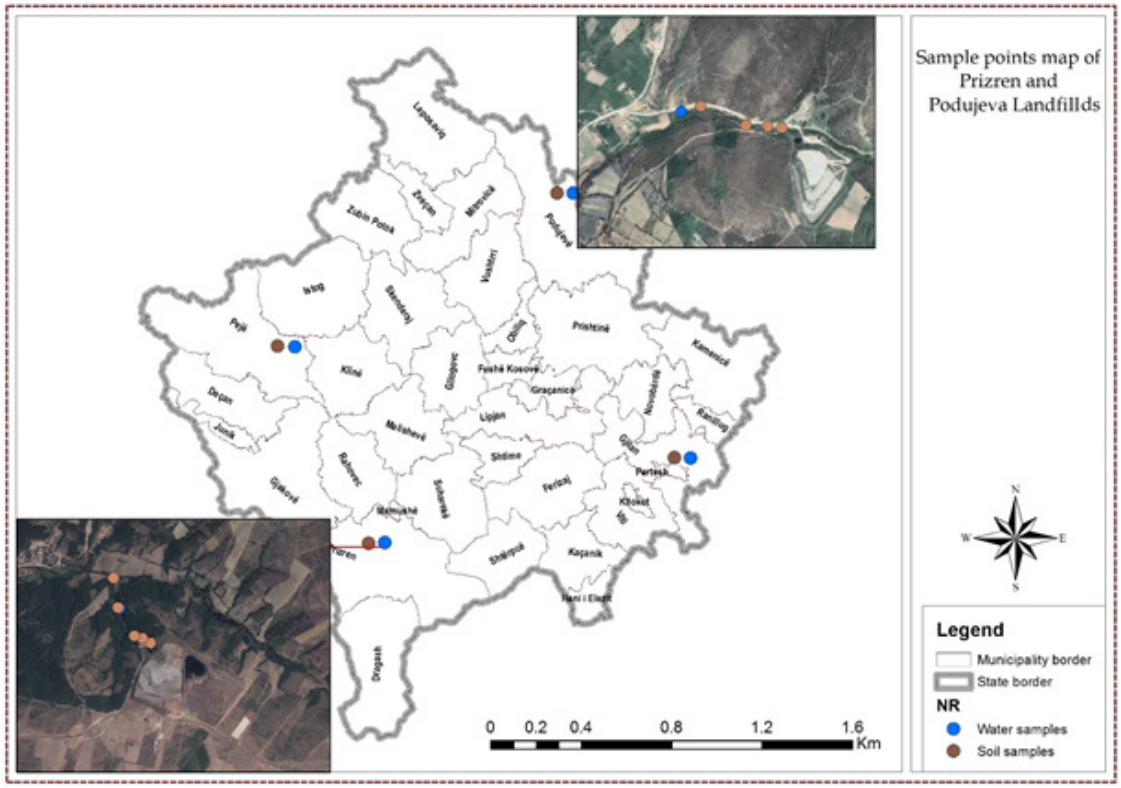

Fig. 1. Sampling points of water and soil around urban waste landfills in Podujeva and Prizren.

Cu, Fe, Pb were found to be below the limit values of the standard, although these metals resulted present in all samples leachates.

The values of As and Hg are presented in μg/L due to the low values of these metals in the leachate water samples. High concentrations of these metals were not found in the points landfills.

The determination of soil texture will provide insights about: soil permeability, field capacity of soil for water, suitability for urban uses, etc. The following frac-

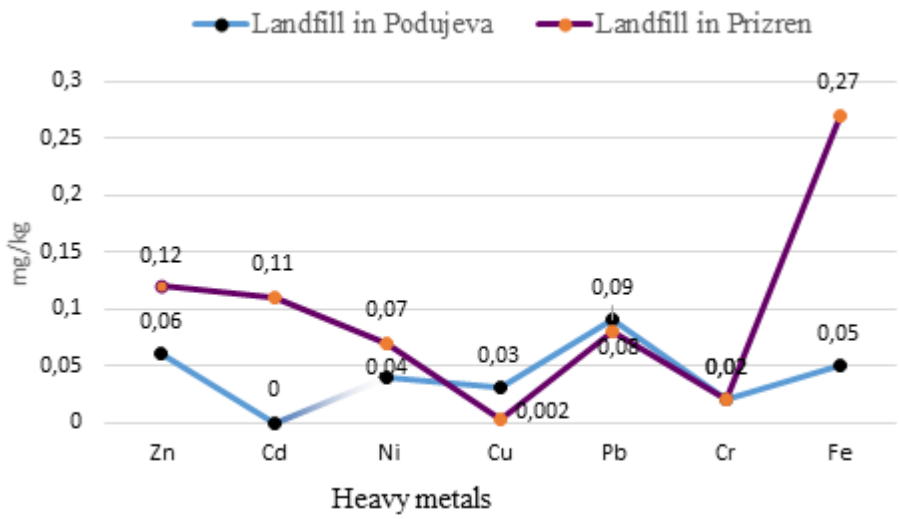

Fig. 2. The average concentration of heavy metals in landfill leachate in Podujeva (a) and Prizren (a).

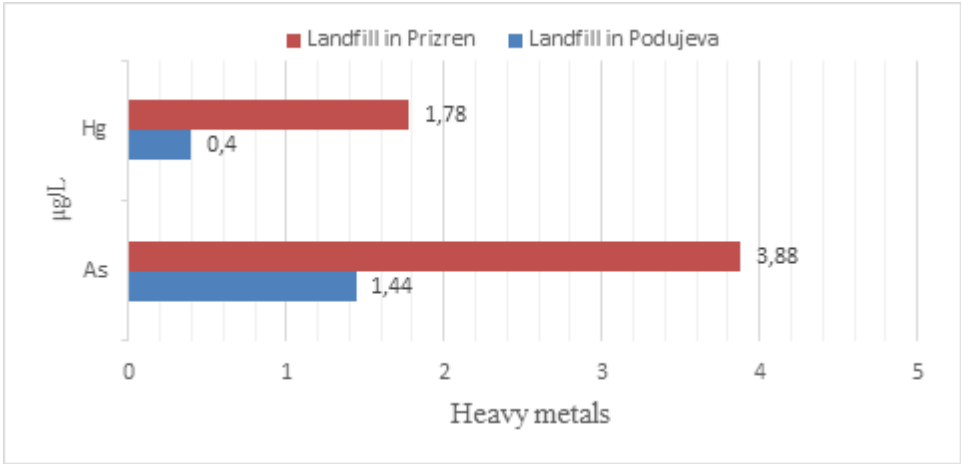

Fig. 3. Variation of arsenic and mercury concentrations in landfills leachate.

tions of soil texture were determined: sand represented as 58.5 to 61.3 %, lyme 27.6 - 34.6 %, and clay starting from 6.9 to 11.1 %. The highest percentage of sand resulted in soil samples in Prizren was 61.3 % and the lowest in Podujeva - 58.5 %. The highest percentage of Lyme resulted in soil samples in Podujeva was 34.6 % and lowest in Prizren - 27.6 %. Meanwhile, clay as the highest percentage resulted in soil samples of Prizren was 11.1 % and lowest in Podujeva - 6.9 %. (Table 2). The heavy metal concentrations have been found below the limit in soil samples, according to the Kosovo Administrative Instruction on Allowing Norms of Hazardous Substances and Harmful Presence in Soil and the 86/278/EEC Council Directive (Table 1). The heavy metals concentration analyses of soil samples in Prizren produced the following results: Zn 51.35 mg/kg, Cd 1.15 mg/kg, Ni 78.1 mg/kg, Cu 22.04 mg/kg, Pb 44.70 mg/kg, Cr 39.25 mg/kg, Fe 4510.80 mg/kg, As 17.70 mg/kg, Hg 0.02 mg/kg. (Fig. 4). The concentration of Ni in the collected soil samples in Prizren and Podujeva was found to be over the limit value according to the Kosovo Administrative Instruction in Allowing Norms of Hazardous Substances and Harmful Presence in Soil and the 86/278/EEC Council Directive. The Pb value were over the limit values in soil sample in Podujeva (Fig. 4).

The values of Cd, Cr, and As for both landfills soil samples are near the limited allowance according to the Kosovo Standard. The concentration of Zn, Cd, Ni, Cu, Pb and Hg was found to be higher in the soil samples collected from the Podujeva landfill, as compared to the soil samples collected in the Prizren landfill (Fig. 4). The iron is more concentrated in the soil samples from Prizren than Podujeva (Fig. 5).

Heavy metal concentration in the collected soil sample was found to be in the following order: Fe > Ni > Zn > Pb > Cr > Cu > As > Cd > Hg. The correlation

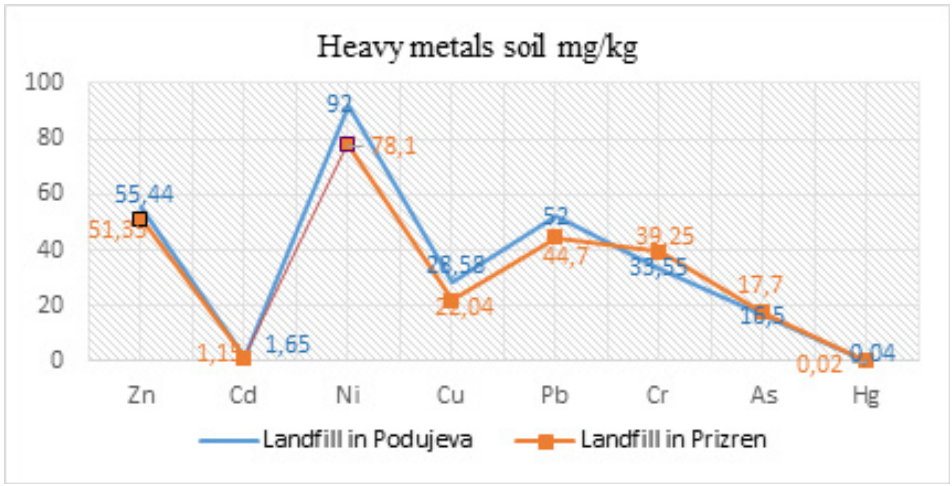

Fig. 4. Heavy metal concentrations in soil samples around landfills in Podujeva and Prizren.

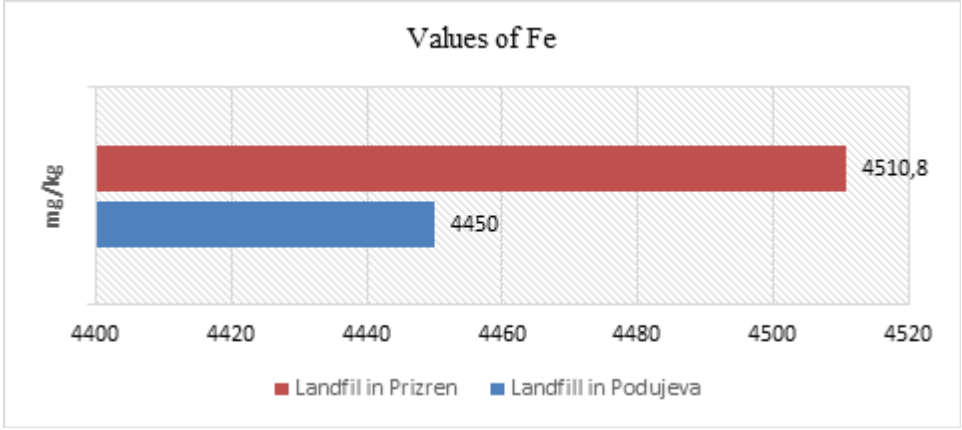

Fig. 5. The Fe values in soil samples in Prizren and Podujeva landfills.

between these metals suggests that most of them have a common source.

The texture of the soil has a direct impact on the way that soil reacts to certain environmental conditions. In our case, the soil sand fraction is between 58.5 - 61.3 %, where the earths' pores have a smaller porosity, but are characterized by a larger pore diameter, enabling a better drainage and water flows rapidly through it. This characteristic enables heavy metals to pass easily into the depths of the ground and groundwater.

CONCLUSIONS

The metal levels were much higher in soil than in leachate, since the metals are generally less mobile and adsorb onto soils. Based on the concentration of heavy metals that were found in soil samples, we can conclude that soils around landfills are polluted with heavy metals, especially with Ni and Pb in Podujeva landfill. The texture of soil indicates that the sand is the dominant factor, which enables the wastewater penetration into the depth of the soil. The determination of heavy metals in soil also shows that there is a direct correlation of content to the concentration of metals in leachates. All metals are assessed and present in the landfill soil and in leachate. Our study confirms that the insulating layer of the landfill is a low function, inadequate leachate management and the porous geo-physical characteristics of the sub-surface at the landfill site. Inefficient management of landfills, the lack of infrastructure investments, inefficient implementation of waste laws, and other environmental laws, have made the landfills to become a permanent high pollution source. The water flow control is considered to be one of the most urgent environmental issues, because of the discharge leachate around the areas, which has resulted from the lack of adequate control of landfills.

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