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Heavy Metals and Polycyclic Aromatic Hydrocarbon Contents of Soil and Selected Vegetable from Waste Disposal Sites in Rivers State

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Abstract

This experiment was designed to evaluate the levels of heavy metals and polycyclic aromatic hydrocarbons in edible vegetables grown around dumpsites and are consumed by people living within the communities. The concentration of heavy metals and PAHs in soils and vegetables from five waste disposal sites in Rivers State were investigated using standard analytical procedures. End determination of the heavy metals and PAHs was achieved with a flame type atomic absorption spectrophotometer (AAS), and Gas chromatography flame ionization detector (GC-FID) respectively. Some results obtained from the soil sample show the range of various heavy metals included Pb, 3.55-6.14 mg/kg; As, 0.425-2.43 mg/kg; Cr, 4.07-9.79 mg/kg and Zn, 3.34-9.05 mg/kg. The results from the *Talinum triangulare* leaf sample show the range of various heavy metals-Pb, 0.33-1.55 mg/kg; As, 0.308-0.618 mg/kg; Cr, 0.038-0.072 mg/kg; Zn, 4.118-11.242 mg/kg; Co, 0.301-0.520 mg/kg; and Cu, 2.862-7.242 mg/kg. All the concentration of the 16 PAHs obtained from the analysis had relatively lower concentrations than the maximum allowable concentration. Their control samples showed no trace of PAHs in both the soil and leaf samples. Among the analysed PAHs, there was a predominance of phenanthrene (0.842 mg/kg) for soil and (0.58 mg/kg) for the vegetable, which was above the maximum limit of 0.14 mg/kg and can pose serious health risks to consumers of these dumpsite vegetables. Treatment of industrial effluents and phyto-extraction of excess metals from polluted environments could reduce health risk. Also recommendations on the proper handling of wastes to reduce possible toxic metal and PAH loads at dumpsites have also been highlighted.

Keywords: Heavy metals; Polycyclic aromatic hydrocarbons; Soil; *Talinum triangulare*; Rivers state

Introduction

Heavy metals and polycyclic aromatic hydrocarbon concentrations in soil and plants are associated with biological and geochemical cycles and are influenced by anthropogenic activities such as agricultural practices, industrial activities and waste disposal methods [1,2]. Studies have shown that soils at refuse dumpsites contain different kinds and concentrations of heavy metals, depending on the age, contents and location [3,4]. People's attitude towards the environment is also of concern. People must be informed and educated to know the effects of indiscriminate disposal of waste. In the light of the above statements, this study seeks to examine some heavy metals and polycyclic aromatic hydrocarbons content in soils and selected vegetables from waste dumps in Rivers State and their effect on human health. It also seeks to suggest lasting and sustainable solutions to the problems by making recommendations that will help control the situation if adhered to. Investigations were carried out in 5 major areas of Rivers State, Nigeria namely Abuloma, Igbo-Etche, Onne, Oroigwe and Rumuolumeni; where soil and *Talinum triangulare* leaf (water leaf) samples were picked at random in the composite method of sample collection and analyzed for heavy metals and polycyclic aromatic hydrocarbons content.

Materials and Methods

Sample collection: Samples of *Talinum triangulare* were also collected from the above five dumpsites within Rivers State, where the soil samples were obtained and the control sample from a farmland in Federal Government Girls' College Abuloma. A total of five *Talinum triangulare* plant and five soil samples each were collected from the five different dumpsites and put into pre-cleaned polyethylene bags and foil paper, respectively. Three evenly distributed locations were identified at each dump site as sample collection points. At each point solid waste were removed at the surface. Soil sample (10 cm deep) was then taken at each point following standard procedure [3]. The soil samples were put in clean foil paper and sealed to prevent contamination during transportation and taken immediately to the laboratory. At the laboratory, care was taken to prevent contamination of the samples. Clods and crumbs were removed and mixed uniformly.

Analysis of Soil and Plant Samples

Sample blank solutions were prepared using the same procedure described for the samples. Same quantities of reagents including water were used for sample and blank. All chemicals used were of analytical grade.

Procedure for soil pH and metal analysis

Soil pH analysis: Soil sample of 20 g was weighed from each dump site and then added to 20 ml of distilled water in the ratio of 1:1. This was left for 30 minutes but was stirred intermittently. The electrode pH was rinsed with distilled water and dipped into the sample solution and a stable reading was recorded.

Soil metal analysis: The soil samples were sieved through a 2 mm sieve to remove the stones and other remaining coarse particles. 5 g of air-dried, soil sample was weighed into a 100 ml beaker and 2 ml of aqueous HNO3 and 6 ml of aqueous HCl in the ratio 1:3 was added to the already weighed soil sample. The mixture was digested by heating on a heating mantle to ensure the mixture attains near-dryness so as to enable proper leaching of the soil sample. The digested sample was filtered using distilled water to dilute or alternatively, the mixture could be rinsed through a filter paper into a 50 ml volumetric flask. Distilled water was used to make up the digested filtrate to 50 ml mark in the volumetric flask. The digested soil was then presented to the flame type atomic absorption spectrophotometer (AAS) (Model HANNA H1 8314), so that the respective metals of interest can be read out. The mean values of three determinations per sample were recorded.

Procedure for Talinum triangulare pH and metal analysis

Talinum triangulare pH analysis: Portions of 100 g of *Talinum triangulare* was weighed and soaked in 5 L of distilled water in a plastic container. The pH of this water (where the leaves was soaked) was determined using a pH meter.

Talinum triangulare metal analysis: In the laboratory, samples of *Talinum triangulare* were washed with distilled water and allowed to dry in moisture extraction oven at 105°C. The oven dried sample was ground into fine powder using pestle and mortar, and sieved through a 2.0 mm mesh sieve to obtain a dried powdered sample that was used for all the analyses. Approximately 5.0g of the powder was transferred to a 100 ml beaker; and then digested with 10 ml of HNO3-HCLO4-HF. The contents of the beaker were heated at 200°C for 1 h in a fume cupboard, and then cooled to room temperature. Then, 20 ml of distilled water was added and the mixture was filtered using Whatman No. 42 filter paper to complete the digestion of organic matter. Finally, the mixture was transferred to a 50 ml volumetric flask, filled to the mark, and allowed to settle. Concentrations of lead (Pb), chromium (Cr), zinc (Zn), arsenic (As), cobalt (Co) and copper (Cu), were determined using a flame type atomic absorption spectrophotometer (AAS) (Model HANNA H1 8314). The mean values of three determinations per sample were recorded. Appropriate quality assurance procedures and precautions were carried out to ensure reliability of the results.

Procedure for polycyclic aromatic hydrocarbon analysis on soil and Talinum triangulare leaf samples (using sohxlet method (epa 3540c)

A 10 g of homogenized wet soil samples were measured in crucible using weighing balance (MettlerPM 2000) to the nearest 0.01 g.

For Leaf: the leaves were crushed and 10 g were measured to the nearest 0.01g. 10g of activated sodium sulphate was added to the sample and mixed to dry the sample and to make it loose before transferring it into a Whatman extraction thimble. The extraction thimbles were then placed into Sohxlet apparatus as stipulated in EPA 3540C, and the samples were refluxed for approximately 2 h (12cycles) using Dichloromethane as an extraction solvent. The extracts were concentrated to 2 ml using K-D apparatus prior to injection into GC-FID (Gas Chromatography-Flame Ionisable Detector) (6890 N-Agilent Gas Chromatograph).

Statistical Analysis

Data were reported as mean ± standard deviation (SD) and was analyzed using One Way Analysis of Variance (ANOVA) while the independent T-test was used to evaluate the degree of significant difference ($p<0.05$) between groups of the variables under investigation.

Result and Discussion

Parameters/Soil Samples	pH	Lead (Pb) mg/kg	Arsenic (As) mg/kg	Chromium (Cr) mg/mk	Zinc (Zn) mg/mk	Cobalt (Co) Mg/mk	Copper (Cu)mg/mk
Abuloma	6.41 ± 0.010 ^{a}	3.63 ± 0.361^{d}	1.77 ± 0.015^{b}	4.07 ± 0.036^{c}	3.34 ± 0.100^{e}	0.581 ± 0.002 ^{b}	3.01 ± 0.014 ^{a}
Onne	5.91 ± 0.143^{b}	6.14 ± 0.020^{a}	0.553 ± 0.003^{c}	6.39 ± 0.042^{b}	9.05 ± 0.036^{a}	0.633 ± 0.003^{b}	0.972 ± 0.002^{c}
Oroigwe	6.11 ± 0.015 ^{a}	5.86 ± 0.015^{b}	0.425 ± 0.002^{c}	9.79 ± 0.025 ^{a}	5.85 ± 0.030^{d}	0.337 ± 0.001^{c}	1.23 ± 0.035^{b}
Igbo-Etche	6.04 ± 0.025 ^{a}	3.55 ± 0.010 ^{d}	2.43 ± 0.025 ^{a}	4.33 ± 0.020 ^{c}	7.44 ± 0.020 ^{c}	1.26 ± 0.031^{a}	0.442 ± 0.005^{c}
Rumuolumeni	5.68 ± 0.106^{b}	4.26 ± 0.020 ^{c}	0.877 ± 0.003^{c}	6.003 ± 0.010^{b}	8.87 ± 0.015^{b}	0.421 ± 0.005^{b}	1.82 ± 0.044^{b}
Control	6.63 ± 0.050^{a}	3.10 ± 0.032 ^{d}	0.282 ± 0.004^{c}	3.27 ± 0.020 ^{d}	3.04 ± 0.025 ^{e}	0.261 ± 0.004 ^{c}	0.11 ± 0.003^{c}
canadian Env. Quality Guidelines	6.6 - 7.3	70	12	4.9	150	40	63
a)-e) value with different superscripts in the same column are singnificantly different at the 0.05 level ($p≤0.05$) Source: maximum permitted concentrations as defined by Canadian Environment Quality Guidelines [5].							

Table 1: Heavy metals concentrations (mg/kg; dry weight) in dump site soil samples collected from the study area. Values are means ± standard deviation for 3 replicates (n=3).

Parameters/Leaf Samples	pH	Lead (Pb) mg/kg	Arsenic (As) mg/kg	Chromium (Cr) mg/mk	Zinc (Zn) mg/mk	Cobalt (Co) Mg/mk	Copper (Cu)mg/mk
Abuloma	6.92 ± 0.010 a	0.33 ± 0.020 c	0.308 ± 0.002 d	0.038 ± 0.002 d	4.118 ± 0.001 c	0.401 ± 0.002 b	4.014 ± 0.003 c
Onne	5.97 ± 0.020 b	1.261 ± 0.004 a	0.521 ± 0.001 b	0.063 ± 0.001 b	10.024 ± 0.001 a	0.506 ± 0.001 a	5.621 ± 0.004 b
Oroigwe	6.25 ± 0.025 a	0.82 ± 0.015 b	0.429 ± 0.002 c	0.059 ± 0.002 c	8.299 ± 0.001 b	0.301 ± 0.002 c	7.242 ± 0.002 a
Igbo-Etche	6.67 ± 0.026 a	0.406 ± 0.003 b	0.618 ± 0.002 a	0.055 ± 0.002 c	9.611 ± 0.007 b	0.44 ± 0.009 b	2.862 ± 0.003 d
Rumuolumeni	5.77 ± 0.010 b	1.55 ± 0.020 a	0.436 ± 0.003 c	0.072 ± 0.002 a	11.242 ± 0.025 a	0.52 ± 0.002 a	5.202 ± 0.002 b
Control	6.73 ± 0.020 a	0.29 ± 0.013 c	0.292 ± 0.002 d	0.031 ± 0.002 d	4.002 ± 0.002 c	0.26 ± 0.004 d	2.221 ± 0.003 d
WHO/FAO	5.5 -7.0	0.3	0.43	2.3	99.4	50	73.3

a)-d) value with different superscript in the same column are significantly different at the 0.05 level ($p \leq 0.05$) Source: Maximum permitted concentration as defined by WHO/FAO-CODEX [6].

Table 2: Heavy metals concentrations (mg/kg; dry weight) in dump site Talinum triangulare leaf samples collected from the study area. Values are means ± standard deviation for 3 replicates (n=3).

Parametersisoil collezdon pant	Abuloma	Onne	Igbo-Etche	Control	Maximum Allowable Concentration
Naphthalene mg/kg	bdl	0.069 ± 0.001 b	0.087 ± 0.002 a	bdl	1.8
A cenaphthene mg/kg	bdl	bdl	bdl	bdl	570
A cenaphthylene mg/kg	bdl	0.083 ± 0.002 b	0.104 ± 0.002 a	bdl	852
Fluorene mg/kg	0.018 ± 0.001 b	0.05 ± 0.003 a	bdl	bdl	560
Anthracene mg/kg	0.043 ± 0.001 b	0.075 ± 0.003 a	bdl	bdl	12,000
Phenathrenemg/kg	0.034 ± 0.002 c	0.15 ± 0.005 b	0.192 ± 0.003 a	bdl	0.14
Flooranthene mg/kg	0.045 ± 0.002 c	0.113 ± 0.003 b	0.123 ± 0.003 b	bdl	3,100
Pyrene mg/kg	0.002 ± 0.0003 b	bdl	0.203 ± 0.002 b	bdl	2,300
1,2-Dibenzanthracene mg/kg	bdl	0.072 ± 0.002 a	0.055 ± 0.003 b	bdl	0.09
Chrysene mg/kg	0.038 ± 0.003 b	bdl	0.326 ± 0 17 a	bdl	88
B enzo [k] fluoranthene mg/kg	0.05 ± 0.006 a	0.028 ± 0.003 b	bdl	bdl	9
B enzo [b] fluoranthene mg/kg	bdl	0.074 ± 0.003 b	0.546 ± 0.002 a	bdl	0.9
B enzo [a] pyrene mg/kg	0.003 ± 0.0002 b	bdl	0.08 ± 0.0006 a	bdl	0.09
Indeno [12,3-cd] pyrene mg/kg	0.07 ± 0.003 a	bdl	0.005 ± 0.0007 b	bdl	0.9
1,2,5,6-Dibenzathracene mg/kg	0.115 ± 0.003 a	0.008 ± 0.0005 b	bdl	bdl	0.9
1,12-B enzoperylene mg/kg	0103 ± 0.002 a	0.1 ± 0.005 b	bdl	bdl	0.9

Values with different superscript letters (a,b,c) in the same row are significantly different at the 0.05 level ($P \leq 0.05$); bdl=below detectable limit i.e.,<0.0001 mg/kg. Source: Maximum allowable concentration from the International standard for Tiered Approach to Corrective Action Objectives (TACO).

Table 3: PAH concentration (mg/kg; wet weight) in soil samples from the study areas. Values represent mean ± standard deviation of three replicates; (n=3).

Parameters/leaf collection point	Abuloma	Onne	Igbo- Etche	Control	Maximum Allowable Concentration
Naphthalene(mg/kg)	bdl	0.061 ± 0.002[b]	0.073 ± 0.001[a]	bdl	1.8
Acenaphthlene(mg/kg)	bdl	bdl	bdl	bdl	570
Acenaphthylene(mg/kg)	bdl	0.075 ± 0.002[b]	0.097 ± 0.002[a]	bdl	852
Fluorene(mg/kg)	0.41 ± 0.002[a]	0.025 ± 0.003[b]	bdl	bdl	560
Anthracene(mg/kg)	0.01 ± 0.002[b]	0.05 ± 0.003[a]	bdl	bdl	12,000
Phenanthrene(mg/kg)	0.5 ± 0.023[a]	0.12 ± 0.02[c]	0.14 ± 0.015[b]	bdl	0.14
Fluoranthene(mg/kg)	0.38 ± 0.015[a]	0.112 ± 0.001[c]	0.113 ± 0.002[b]	bdl	3,100
Pyrene(mg/kg)	0.07 ± 0.015[a]	bdl	0.132 ± 0.002[a]	bdl	2,300
1,2-Dibenzathracene(mg/kg)	bdl	0.055 ± 0.003[a]	0.007 ± 0.001[b]	bdl	0
Chrysene(mg/kg)	0.14 ± 0.01[a]	bdl	0.12 ± 0.01[b]	bdl	88
Benzo [k] fluoranthene(mg/kg)	0.02 ± 0.015[b]	0.017 ± 0.001[a]	bdl	bdl	9
Benzo [b] fluoranthene(mg/kg)	bdl	0.022 ± 0.003[b]	0.039 ± 0.001[a]	bdl	1
Benzo [a] pyrene(mg/kg)	0.03 ± 0.015[b]	bdl	0.056 ± 0.002[a]	bdl	0.9
Indenol [1,2,3-cd]pyrene(mg/kg)	0.0027±0.0002[a]	bdl	0.002 ± 0.002[b]	bdl	0.09
1,2,5,6-Dibenzanthracene(mg/kg)	0.051 ± 0.002[a]	0.005 ± 0.0003[b]	bdl	bdl	0.9
1,12-Benzoperylene(mg/kg)	0.05 ± 0.003[a]	0.021 ± 0.002[b]	bdl	bdl	0.9

Values with different superscript letters (a,b,c) in the same row are significantly different at the 0.05 level (P≤0.05). bdl=below detectable limit i.e., < 0.0001mg/kg. Source: Maximum allowable concentration from the International standard for Tiered Approach to Corrective Action Objectives (TACO).

Table 4: PAH concentration (mg/kg; wet weight) in Talinum triangulare leaf samples from the study areas. Values represent mean ± standard deviation of three replicates; (n=3).

Discussion

Heavy metals

Metals play an integral role in the life processes of microorganisms. Some metals, such as calcium, cobalt, chromium, copper, iron, potassium, magnesium, manganese, sodium, nickel and zinc, are essential, serve as micronutrients and are used for redox-processes; to stabilize molecules through electrostatic interactions; as components of various enzymes; and for regulation of osmotic pressure [7]. Many other metals have no biological role (eg. silver, aluminium, cadmium, gold, lead and mercury) and are nonessential and potentially toxic to microorganisms. Generally, in the areas studied, the concentrations of Pb, As, Zn, Co and Cu in the soils were below the compared maximum permissible limits of Canadian Environmental Quality Guidelines [5], except for Cr. This also reflected in the low level of these metals obtained from the control sites in comparison with those obtained from the study sites. It was suggested that the soil contamination may be considered when concentrations of an element in soils were two-three times greater than the average background levels [8]. Therefore the soil of the various dump-sites in the study area may be considered contaminated based on the fact that heavy metal contents in the control soil in this study was low. From the mean results, there is an indication that Cr is the contaminant in the dump-site soils where these waste disposal contents applied to these soil resulted in some degree of contamination. This does not pose any health risk as chromium when transferred from the soil to the edible plant in the right quantity, is required for carbohydrate, lipid metabolism and the utilization of amino acids, unless consumed in excess amount which can be toxic to humans [9]. Plant grown on soils possessing enhanced metal concentrations have increased heavy metal ion content. The uptake of metal ions has been shown to be influenced by the metal species and plant parts. The results obtained from this study have shown high levels of heavy metals in soil and *Talinum triangulare* obtained from the various dumpsites. Water leaf also accumulated As and Cr above the WHO maximum limit while the level of Cr, Co, Cu and Zn was below the maximum limit of World Health Organization. The *Talinum triangulare* vegetable is in high demand in Rivers State and other areas within the locality because they are part of the daily staple food. Continuous consumption of these vegetables will inevitably result to health consequences. There is a need for regular evaluation of trace metals in these vegetables by Federal and State protection agencies. The studied plant can be used for environmental monitoring based on metal loads. It has also revealed that concentrations of most of the metals analyzed for in plants varied positively with their corresponding levels in soil. Although the levels obtained for most of the metals were within the acceptable standards, indiscriminate dumping of refuse and cultivating edible plants on dumpsite soils should be discouraged as an unpleasant situation may result.

Polycyclic aromatic hydrocarbons

The ratio of PAH profiles maybe used to track their origin as petrogenic, biogenic and pyrogenic sources [10-12]. From the result of the analysis carried out on the soil sample for checking the concentration of PAHs, it was observed that out of the recommended 16 PAHs normally analysed for in samples, acenaphthene was not detected in the soil samples analysed. Acenaphthene is chemically used on a large scale to prepare naphthalic anhydride and is a precursor to dyes and optical brighteners [13]. Naphthalene was not detected in the soil sample obtained from Abuloma, but was observed in the soil samples from Onne and Igbo-Etche with the respective concentration of 0.069 and 0.087 mg/kg. Acenaphthylene, was also not observed in the Abuloma soil sample but had the values of 0.083 mg/kg and 0.104 mg/kg in soil samples from Onne and Igbo-Etche respectively. Fluorene, on the other hand was present in soil samples from Abuloma and Onne with the concentration values of 0.018 mg/kg and 0.05 mg/kg respectively and absent in the sample from Igbo-Etche. Anthracene concentration of 0.043 mg/kg and 0.075 mg/kg was observed in Abuloma and Onne soil samples but was absent in the soil obtained from Igbo-Etche. Phenanthrene and Fluoranthene were both present in all the three soil samples. The concentration of phenenthrene was 0.034, 0.15 and 0.192 mg/kg for Abuloma, Onne and Igbo-Etche respectively; while the concentration for fluoranthrene was 0.045, 0.133 and 0.123 mg/kg respectively for the above three locations. Pyrene was observed to be below detectable limits for the soil obtained from Onne but was observed in the soil sample from Abuloma (0.002 mg/kg) and Igbo-Etche (0.203 mg/kg). 1, 2-Dibenzanthracene was also below detectable limit in Abuloma soil sample but was observed in the soil sample from Onne (0.072 mg/kg) and Igbo-Etche (0.203 mg/kg). The four ring PAH, Chrysene was detected in the soil sample from Abuloma (0.038 mg/kg) and Igbo-Etche (0.326 mg/kg) but was not detected in the Onne soil sample. Benzo [k] fluoranthene, the five ring PAH was detected in Abuloma soil sample (0.05 mg/kg) and Onne soil sample (0.028 mg/kg) but was not detected in Igbo-Etche soil sample. Benzo [b] fluoranthene on the other hand was not detected in the soil sample from Abuloma dumpsite but was minutely present in Onne dumpsite soil (0.074 mg/kg) and Igbo-Etche dumpsite soil (0.546 mg/kg). For Benzo [a] pyrene, and Indeno[1,2,3-cd]pyrene, their contents were observed in Abuloma dumpsite soil sample (0.003 and 0.07 mg/kg) and Igbo-Etche dumpsite soil sample (0.08 and 0.005 mg/kg) respectively. The five ring PAH, 1, 2, 5, 6-Dibenzathracene was detected in Abuloma and Onne dumpsite soil sample at 0.155 and 0.008 mg/kg respectively; while the six ring PAH 1,12-Benzoperylene followed the same trend above with 1,2,5,6-Dibenzathracene having its concentration at 0.103 and 0.100 mg/kg respectively.

The results in Table 4 shows that some of the tested vegetables have been contaminated with minute amount of PAHs with different mean concentrations ranging from 0.002 to 0.41 as against the values obtained from Zohair [14] which had higher values of polycyclic aromatic hydrocarbon. It was notice from the results that the 3-4 rings PAHs were predominates.

However phenanthrene and flouranthene is the most abundant individual PAH compounds in vegetables under investigation. These compounds are more water-soluble than the higher molecular weight PAHs and so may be more susceptible to uptake from soils as well as deposition from polluted air. The higher PAHs content in green vegetables such as *Talinum triangulare* could be explained by their contact surface to the ambient air during growth [15].

In the investigation of the uptake of trace elements and PAHs by vegetables grown in soils contaminated by trace elements and PAHs, Erik et al. [15] found higher concentrations of these contaminants in vegetables grown in contaminated soils than those grown on uncontaminated soils. Plants also take up these pollutants through various pathways, including root uptake and atmospheric deposition from gaseous or particulate forms [16]. Human health is endangered by the consumption of vegetables grown on soils contaminated by crude oil spills and their residues.

Conclusion

Indiscriminate disposal of waste in the various dumpsites, led to the accumulation of heavy metals and PAHS in soil and consequently into the vegetable. These concentrations varied among the tested soil and vegetable, which reflect the differences in their uptake capabilities and their further translocation to edible portion of the plants. With the high rate of pollutants uptake by a commonly consumed edible vegetables such as *Talinum triangulare*, and the crude oil related activities taking place in Rivers State, human exposure to PAHs through food absorption is a matter of concern. The major hydrocarbon components of crude oil are paraffin, cycloparafffins and aromatic substances containing one or more benzene rings. Polycyclic aromatic hydrocarbons have been detected in Nigerian crude oil [17]. Hence, proper refuse disposal methods, maintenance, and enlightenment of the public could have prevented many of these contaminations. It is therefore very imperative to control waste disposal methods, as the impact on the food chain, ecosystem and human health is significant.

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