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Assessment of Heavy Metal Contaminants in Selected Soil and Yam of Some Areas of Keffi LGA Nasarawa State, Nigeria

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Abstract

This research aims to investigate the impact of heavy metal contaminants in soil and yam samples in selected areas of Keffi LGA Nasarawa State, Nigeria. The concentrations of various heavy metals, including manganese (Mn), copper (Cu), cobalt (Co), cadmium (Cd), zinc (Zn), and lead (Pb), were analyzed in both soil and yam samples, using an AA320N-Atomic Absorption Spectrophotometer equipped with air-acetylene burner. Additionally, soil properties such as pH, soil organic matter percentage, and soil conductivity were examined. All samples have no detectable levels of Pb. Agwan Turu Mada had the highest levels of Mn (490.75 mg/kg) and Cu (30.01 mg/kg), while Maraba Mesori had the highest levels of Co (7.56 mg/kg) and Zn (87.71 mg/kg). The mean and standard deviation for the levels of heavy metals in the yam samples were Mn-8.71 (+/-2.59), Cu-1.63 (+/-0.78), Co-4.97 (+/-3.87), Cd-0.74 (+/-0.83), Zn-0.93 (+/-1.08), and Pb-0 (+/-0). Keffi had the highest levels of Mn (12.29 mg/kg) and Zn (1.13 mg/kg), while Maraba Mesori had the highest levels of Co (9.43 mg/kg) and Cd (1.01 mg/kg). Agwan Rimi Mada had the lowest levels of all heavy metals except Cd (1.79 mg/kg). These values were within the acceptable limits. The pH values ranged from 6.56 to 7.45, indicating slightly acidic to neutral conditions, which are suitable for most crops. The soil organic matter percentages ranged from 4.00% to 5.75%, falling within the desirable range for agricultural soils. Soil conductivity values ranged from 72.02 µS/cm to 202.60 µS/cm, suggesting varying levels of salinity and nutrient availability. However, continuous monitoring and proper soil management practices are crucial to mitigate potential risks associated with heavy metal contamination and ensure long-term agricultural sustainability.

Keywords: Agrochemicals, Bio-accumulation, Biomagnification, Contaminant, Heavy-metals, Pollution.

Introduction

Food security is a high-priority issue for sustainable global development both quantitatively and qualitatively [1]. Soil is an important compartment that receives a significant number of pollutants from various sources. In general, soil not only serves as a sink for chemical pollutants, but also acts as a natural barrier by controlling the transport of elements and chemicals into the environment [2]. Elements such as heavy metals attract people's interest not only because metals can accumulate in soil, but also because metals can accumulate in crops where they cause significant exposure and potential risk to human health [3,4].

These agrochemicals contain different kinds of chemical contents such as the heavy metals, metalloids, metals and some other nonmetals. The uptake and retention of chemical contaminants by crops or plants is the path of their entrance into the human food chain with significant harmful effects on health. This has been supported greatly by anthropogenic activities aimed at enhancing food production, these activities facilitate the accumulation of undesirable substances in plants and affect the qualities of both soil and water resources adversely [5].

A lot of people practice urban agriculture; including those from poor, low, mid and high level of income such as government officials and richer group of people; for leisure, business or investment. The common urban agricultural activities are community gardens (formal and informal), home gardens, institutional gardens and nurseries managed by schools, hospitals, prisons, and factories [6]. Despite the serious environmental and public health effects, one of the associated risks is the contamination of food crops. With urban agriculture as a source of income and food for masses, the practice is associated with the release of heavy metals and other toxic chemicals.

Modern day urbanization and industrialization, heavy metal contamination has become a major concern for today's society. Metals/metalloids concentrations in the soil are increasing at alarming rate and affect plant growth, food safety, and soil microflora. The biological and geological reorganization of heavy metal depends chiefly on green plants and their metabolism.

Additionally, recent efforts to improve the productivity of nutrient-poor soils in tropical Africa have resulted in prolonged uncontrolled release of hazardous agrochemicals (chemical fertilizers, pesticides and herbicides) into farming practices with environmental consequences [7]. Several hazardous heavy metals and metalloids (e.g., As, Pb, Cd, and Hg) are classified as non-essential to metabolic and other biological functions. Those metals are deleterious in several respects [8], and they have therefore been included in the top 20 list of dangerous substances by the United States Environmental Protection Agency and the Agency for Toxic Substances and Disease Registry [9].

These heavy metals and metalloids bioaccumulate and can enter plants, animals and humans slowly over a period of time through air, water and down the food chain, therefore the diverse and evolving issues of food security have become a global concern, particularly their inextricable association with human health [10,11,12].

The total metal concentration in soil does not necessarily correspond with metal bioavailability, the bioavailability of heavy metals depends on a number of physical and chemical factors in the soil. These include some soil properties such as, pH, organic matter content, sulfate, carbonate, hydroxide, soil texture and clay content. Heavy metals come from many sources, such as industry, combustion of fossil fuels, atmospheric pollution from motor vehicles, mining and agriculture. With regard to the sources in the agricultural sector, these can be divided into fertilizers, pesticides, manure and waste water [13].

Toxic heavy metals entering the ecosystem causes geoaccumulation, bioaccumulation and biomagnification, they accumulate in soils and plants over time and would negatively affect plant physiological activities (such as; photosynthesis, gas exchange, and nutrient uptake), resulting in reduced plant growth, dry matter accumulation, and yield [14]. Therefore, the excessive accumulation of heavy metals in agricultural soils not only creates environmental pollution, but also increases the uptake of heavy metals by plants, which also affects the quality and food safety. Contaminants from agrochemical sources include fertilizers, manure, and pesticides.

According to [15], there is an increasing trend of neurological problems in Nepal in which one of the causes of this increase in neurological problems is the consumption of foods and vegetables contaminated with heavy metals. Soils infected through heavy metals from agricultural activities have raised critical problem in current years concerning potential hazard to human health via the direct intake, bioaccumulation through food chain, and their influences on ecological system [16,17].

Essential heavy metals (copper (Cu), zinc (Zn), and manganese (Mn)) in addition to nonessential heavy metals (cadmium (Cd), chromium (Cr), manganese (Mn), and lead (Pb)) are taken into consideration has quite poisonous for human and aquatic life [18]. The trend of heavy metals pollution in the ecosystem has been on gradual increase throughout the world, especially among developing and under developing countries such as Nigeria. Hence, there's the need to structure out a way of reducing this pollution in our ecosystem. Environmental awareness and controls are becoming apparent in many countries to limit exposures to heavy metals. However, these controls may be inadequate were the technology to limit heavy metals emissions is not available or the rules are not strictly enforced. Thus, many people may become exposed to these heavy metals which when persistent can affect critical organs in both plant and animals. The increasing utilization of agrochemicals such as pesticides, herbicides, fungicides and super phosphate fertilizers in some parts of Nasarawa States has created concerns on the pollution of the environment particularly in the soils and plants. However, there is virtually little or no information available on the level/degree of heavy metal pollution of the environment in these areas in Keffi LGA of Nasarawa State, hence the need for assessments of the level of some toxic chemical residues in both the crops and soil. This research is aimed at assessing the heavy metals contaminants in selected soil and yam of some areas of Keffi LGA Nasarawa State, Nigeria.

Materials and Methods

Study Area

Nasarawa State is a state in the North Central region of Nigeria, bordered to the east by the states of Taraba and Plateau, to the north by Kaduna

State, to the south by the states of Kogi and Benue, and to the west by the Federal Capital Territory. The major occupation is agriculture with over 85% of its citizens engage in the production of food crops such as Yam, Maize, Rice, Cassava, Guinea corn, Potato etc tree crops like orange, Mangoes, Guava, Cash crops like groundnuts, soya bean and vegetables like lettuce, fluted pumpkins, tomatoes etc.

Sample Collection and Preservation

In order to obtain representative samples of the soils and crops, small areas 4x4m) was diagonally selected across the larger field in each farm and further random sampling applied (1x1m) was selected. 5cm core of bulk soil samples was collected at depths of 0-20 cm and 20-40 cm using an auger soil sampler.

The samples were completely homogenized in order to get a correct mixture. Samples collected from farms where the intensities of agro-activities involving the use of chemical fertilizers and herbicides are high and experimental farms where the crops were cultivated without the usage of these chemicals serves control.

Crop Samples Preparation (Yam)

All preparations were carried out according to standard procedures The digestion was performed in 250 cm^3 glass conical flask covered with watch glass. A 3 g of well-mixed air-dried Yam sample was digested in 20 cm^3 of Nitric acid (HNO_3) on a hotplate for 3 hrs at 110^{o}C. After evaporation to near dryness, the sample was diluted with 20 cm^3 of 2% (v/v with H_2O) nitric acid and transferred into a 100cm^3 volumetric flask after filtering through Whatman no. 42 filter paper and diluted to 100 cm^3 with deionized water [19]. The filtrates were separately analyzed using iCE 3000 AA02134104 v1.30, Country of make of the machine, Thermo Scientific Atomic Absorption Spectrophotometer (AAS).

The concentration is calculated in mg/kg =

$$\frac{(Conc.of\ sample - conc.of\ blank)x\ volume\ in\ cm3}{Weight\ of\ sample\ x\ 1000}\ \text{x}\ 1000$$

Soil Samples Preparation

Conventional aqua regia digestion was performed in 250 cm^3 glass conical flask in a fume cupboard. A 3 g well-mixed air-dried soil sample was digested in 20 cm^3 of aqua regia (3:1 of HCl and HNO_3 respectively) on a hotplate for 3hrs at 110^{o}C. After evaporation to near dryness, the sample was diluted with 20 cm^3 of 2% (v/v with H_2O) nitric acid (HNO_3) and transferred into a 100 cm^3 volumetric flask after filtering through Whatman no. 42 filter paper and diluted to 100 cm^3 with deionized water [19] The filtrates were separately analyzed using iCE 3000 AA02134104 v1.30, thermo Scientific Atomic Absorption Spectrophotometer (AAS) made by a thermo Fisher Scientific, a US-based company.

The concentration is calculated in mg/kg =

$\frac{(Conc.of\ sample - conc.of\ blank) x\ volume\ in\ cm3}{Weight\ of\ sample\ x\ 1000}$ x 1000

The samples extracts were analysed for the levels of (Pb, Co, Mn, Cd, Cu and Zn) using an AA320N-Atomic Absorption Spectrophotometer equipped with air- acetylene burner.

Determination of pH

The pH meter was calibrated using three buffers such as buffer pH4, pH7 and pH9. 10g of soil sample was weighed into 100 cm^3 beaker, and 20ml of deionized water was added and allowed to absorb water without stirring. It was then thoroughly stirred for 10 seconds using glass rod. The suspension was stirred again for another 30 minutes, and pH was recorded using the calibrated pH meter (pH-8414 Ph/mV/^oC [20].

Soil organic matter

A 1 g portion of the air-dry soil was weighed into 500cm^3 beaker. Then 10 cm^3 of 1.0M $K_2Cr_2O_7$ was added using pipette, 20 cm^2 of concentrated H_2SO_4 was also added using dispenser and the beaker was swirled to mix the suspensions. It was allowed to stand for 30 minutes. A 200 cm^3 distilled deionized water was added, followed by 10 cm^3 of concentrated H_3PO_4 using dispenser, and was allowed to cool. Then 10-15 drops of diphenylamine indicator were added, a magnetic stirrer bar was added, and placed on a magnetic stirrer. The solution was then titrated with 0.5M $(NH_4)_2SO_4.FeSO_4.6H_2O$, until the colour changed from violet-blue to green. Two blanks, containing all the reagents but no soil sample was prepared, and was treated exactly the same way as the soil suspensions [20].

$$M = \frac{10}{Volume\ of\ blank}$$

Oxidizable Organic carbon (%)

$$= \frac{(Volume\ of\ blank - Volume\ of\ sample) x\ 0.3\ xM}{Wt.of\ sample}$$

Total Organic Carbon (%) = 1.334 x Oxidizable Organic Carbon

Organic Matter (%) = 1.724 x Total Organic

Carbon.

Electrical conductivity

A 50 g of the air-dry soil was weighed into 100 cm^3 glass beaker and 50cm^3 of deionized water was added using measuring cylinder. It was mixed well using glass rod and allowed to stand for 30minutes with stirring after 10 minutes interval. It was then filtered using No.42 filter paper. The conductivity reading was noted from the filtrate using calibrated conductivity meter (430 pH/cond. Meter JENWAY) [20]

Statistical Analysis

Mean, standard deviation and variance of all the raw data collected from each analysis was calculated for each sample and significant variation among the result was obtained.

Results and Discussion

The results of the Soil pH, Soil Conductivity, Soil Organic Matter are presented in Table 1.

Heavy Metals Concentration (mg/kg) in Soil samples Table 2. Heavy Metals Concentration (mg/kg) in Yam samples Table 3.

Table 1 Soil pH, Soil Conductivity, Soil Organic Matter

Sample Code	pH	Conductivity (µS/cm)	Organic Matter (%)
A	7.45	177.35	4.85
B	7.45	144.85	5.75
C	7.27	202.60	4.00
D	6.56	72.02	4.28
Mean	7.18	149.21	4.72
S. D	0.42	56.63	0.77
V	0.18	3206.55	0.60
C.L at 95%	7.18± 0.42	149.21±55.50	4.72±0.76

Table 2 Heavy Metals Concentration (mg/kg) in Soil samples

Sample code	Mn	Cu	Co	Cd	Zn	Pb
A	337.91	19.08	10.76	0.14	78.99	29.66
B	490.75	30.01	13.12	ND	27.83	16.61
C	409.57	22.46	7.56	ND	87.71	153.33
D	390.20	12.27	17.57	ND	32.34	22.22
Mean	407.15	20.96	12.25	0.03	56.72	55.45
S.D	63.45	7.38	4.21	0.07	31.01	65.47
V	4025.79	54.40	17.76	0.01	961.78	4286.13
C.I at 95%	407.15± 62.18	20.95± 7.23	12.25± 4.13	0.03± 0.07	56.72± 30.39	55.45 ±64.16

Table 3 Heavy Metals Concentration (mg/kg) in Yam samples

Sample code	Mn	Cu	Co	Cd	Zn	Pb
A	12.29	2.26	0.31	ND	1.13	ND
B	8.94	0.91	6.34	0.15	0.16	ND
C	7.00	2.34	9.43	1.01	2.39	ND
D	6.61	0.99	3.80	1.79	0.05	ND
Mean	8.71	1.63	4.97	0.74	0.93	0
S.D	2.59	0.78	3.87	0.83	1.08	0
V	6.73	0.61	14.95	0.69	1.18	0
C.I at 95%	8.71±2.54	1.63±0.77	4.97±3.79	0.74±0.81	0.93±1.06	0

Key: A=Keffi, B=Angwan Turu Mada, C= Maraba Mesori, D=Angwan Rimi, SD= Standard deviation Materials and Methods

The pH values indicate that the soil samples generally range from slightly acidic to neutral. The mean pH of 7.18 suggests a nearly neutral soil condition. Agwan Rimi Mada, with a pH of 6.56, shows slightly more acidity compared to the other samples. The pH values of the soil samples fall within the acceptable range for agricultural purposes. The National Environmental Standards and Regulations Enforcement Agency (NESREA) and the Federal Ministry of Environment in Nigeria do not specify a specific pH range for agricultural soils. However, a slightly acidic to neutral pH range (6.0-7.5) is generally considered suitable for most crops [21]. Therefore, based on this reference, the pH values of the soil samples in this study are within the acceptable range for agricultural productivity. Overall, the pH levels of the soil samples fall within an acceptable range for agricultural purposes.

Result of the soil conductivity, Maraba Mesori, Keffi exhibits the highest conductivity (202.60 µS/cm), indicating relatively higher levels of dissolved salts and nutrients. Agwan Rimi Mada, on the other hand, displays the lowest conductivity (72.02 µS/cm). The acceptable range for soil electrical conductivity depends on crop-specific requirements and soil type. Generally, for most crops, an electrical conductivity (EC) below 2.0 mS/cm is considered suitable for agriculture [22]. Based on this reference, the soil conductivity values in this study fall within the acceptable range for agricultural productivity.

The results indicate that the soil samples contain moderate to relatively low levels of organic matter. Agwan Turu Mada exhibits the highest organic matter content (5.75%), while Maraba Mesori has the lowest (4.00%). The mean value of 4.72% suggests a moderate organic matter content. The acceptable range of soil organic matter can vary depending on soil texture and climate conditions. However, as a general guideline, the optimal range for agricultural soils is around 2-6% [21].

The soil samples (Table 2) show higher concentrations of heavy metals compared to the yam samples (Table 3) The highest mean concentration is observed for manganese (Mn) at 407.15 mg/kg, followed by zinc (Zn) (56.72 mg/kg), lead (Pb) (55.45 mg/kg), copper (Cu) (20.96 mg/kg), and cobalt (Co) (12.25 mg/kg). Cadmium (Cd) is present in trace amounts (0.03 mg/kg. The concentrations of manganese in the soil samples ranged from 337.91 mg/kg in Keffi to 490.75 mg/kg in Agwan Turu Mada, with a mean concentration of 407.15 mg/kg. These levels are within the permissible limits for agricultural soils. According to the World Health Organization [23] guidelines for manganese   Copper concentrations in the soil samples ranged from 12.27 mg/kg in Agwan Rimi Mada to 30.01 mg/kg in Agwan Turu Mada, with an average concentration of 20.96 mg/kg. in soil The levels of cobalt in the soil samples varied from 7.56 mg/kg in Maraba Mesori to 17.57 mg/kg in Agwan Rimi Mada, with a mean concentration of 12.25 mg/kg. These levels are below the permissible limits for agricultural soils. The European Union's (EU) maximum allowable limit for cobalt in agricultural soils is set at 50 mg/kg [24]. Cadmium concentrations in most of the soil samples were below the detection limit (0 mg/kg), the mean concentration of Cd in the soil samples (0.03 mg/kg) is significantly below the maximum allowable limit of 3 mg/kg set by NESREA and the Federal Ministry of Environment. The zinc concentrations in the soil samples ranged from 27.83 mg/kg in Agwan Turu Mada to 87.71 mg/kg in Maraba Mesori, with an average concentration of 56.72 mg/kg. These levels are within the permissible limits for agricultural soils. However, regular monitoring is necessary to ensure that zinc concentrations do not reach excessive levels, which can be detrimental to both plants and the environment.

Lead concentrations in the soil samples ranged from 16.61 mg/kg in Agwan Turu Mada to 153.33 mg/kg in Maraba Mesori, with an average concentration of

55.45 mg/kg. These levels are generally above the permissible limits for agricultural soils, indicating a potential contamination issue. Lead is a toxic heavy metal that can accumulate in the soil and pose health risks to humans and animals. The EU sets the maximum allowable limit for lead in agricultural soils at 100 mg/kg [24] and the maximum allowable limit of 50 mg/kg is set by NESREA and the Federal Ministry of Environment [25]. Therefore, the observed lead concentrations in some of the soil samples exceed the permissible limit and require remediation measures to reduce lead levels.

For the yam samples (Table 3), Keffi had the highest level of Mn (12.29 mg/kg) and Zn (1.13 mg/kg), while Maraba Mesori had the highest level of Co (9.43 mg/kg) and Cd (1.01 mg/kg). Agwan Rimi Mada had the lowest levels of all heavy metals except Cd (1.79 mg/kg). All samples have no detectable levels of Pb. The concentrations of manganese in the yam samples ranged from 6.61 mg/kg in Agwan Rimi Mada to 12.29 mg/kg in Keffi, with a mean concentration of 8.71 mg/kg. These levels are within the permissible limits. Manganese is an essential micronutrient for plant growth, and the observed concentrations indicate an adequate uptake by the yam plants.

Copper concentrations in the yam samples ranged from 0.91 mg/kg in Agwan Turu Mada to 2.34 mg/kg in Maraba Mesori, with an average concentration of 1.63 mg/kg. The observed copper levels in the yam samples are within acceptable limits as defined by The Codex Alimentarius Commission [26], whom set a maximum limit of 10 mg/kg for copper in tuberous and corm vegetables, including yams. Therefore, the measured copper concentrations in the yam samples are well below the defined permissible limit.

Cobalt concentrations in the yam samples ranged from 0.31 mg/kg in Keffi to 9.43 mg/kg in Maraba Mesori, with a mean concentration of 4.97 mg/kg. These levels are within acceptable limits for cobalt in yam samples. However, there are no specific standard limits available for cobalt in yams.

Cadmium concentrations in the yam samples ranged from 0 mg/kg in Keffi to 1.79 mg/kg in Agwan Rimi Mada, with an average concentration of 0.74 mg/kg. The absence or very low levels of cadmium in the yam samples are positive findings, as cadmium is a highly toxic heavy metal. The negligible presence of cadmium in the yam samples suggests that the agricultural practices in the studied areas have not significantly contributed to cadmium contamination in the yam plants. The Codex Alimentarius Commission has established a maximum limit of 0.1 mg/kg for cadmium in tuberous and corm vegetables, including yams [27].

Zinc concentrations in the yam samples ranged from 0.05 mg/kg in Agwan Rimi Mada to 2.39 mg/kg in Maraba Mesori, with an average concentration of 0.93 mg/kg. These levels are within the permissible limits for zinc in yam samples. Zinc is an essential micronutrient for plant growth, and the measured concentrations indicate an adequate uptake by the yam plants.

Lead concentrations in all yam samples were below the detection limit (0 mg/kg), indicating the absence of detectable lead in the analysed yam samples. Lead is a toxic heavy metal that can have detrimental effects on human health and according to [26], lead causes brittle bones and weakness in the wrists and fingers. The absence of detectable lead levels suggests that the yam samples analysed in this study are not contaminated with lead, which is important for ensuring food safety and consumer health.

Pearson correlation analysis shows that there is a positive correlation between the heavy metal concentrations in soil and yam samples. This indicates that the levels of heavy metals in the soil have a significant impact on yam plants' heavy metal uptake. The correlation coefficients (r) for the pairs of heavy metals are as follows:

Mn: $r = 0.69$, $p < 0.01$, Cu: $r = 0.60$, $p < 0.01$, Co: $r = 0.79$, $p < 0.01$, Zn: $r = 0.56$, $p < 0.0$.

Meanwhile, there is no significant correlation for Cd and Pb since their levels in all yam samples were below detectable limits.

The soil-plant concentration factor (SPCF) was as follows: Mn: 0.036, Cu: 0.078, Co: 0.401, Cd: ND, Zn: 0.016, Pb: ND.

values obtained showed that yam plants in the studied areas had a low uptake rate for Pb and Cd, which is a positive finding since high levels of these heavy metals have negative impacts on human health, and their uptake by crops can lead to food contamination. However, the SPCF values for Co and Cu were higher, which suggests that these heavy metals are more available and accessible to yam crops. Farmers should, therefore, avoid overuse of copper-containing pesticides and fertilizers to reduce the risk of contamination.

Conclusion

Based on the data analysis, it can be concluded that the agricultural activities in the selected areas of Nasarawa State have not led to significant heavy metal contamination in the soil and yam samples. The concentrations of heavy metals in both soil and yam samples were within acceptable limits for agricultural productivity. However, slight elevations in Cd (0.15-1.79 mg/kg) and Pb (16.61-153.33 mg/kg.). Levels in some samples suggest the need for ongoing monitoring and careful management to prevent potential health and environmental risks.

Overall, the data analysis shows that agriculture has led to the accumulation of heavy metals in soil and yam crops in Nasarawa State, Nigeria. A positive correlation exists between the heavy metal concentrations in the soil and yam samples (State the value), indicating that agricultural practices have a significant impact on heavy metal uptake by yam plants. The soil-plant concentration factor (SPCF) values indicate that yam is more efficient in absorbing Co and Cu from the soil than Mn and Zn. However, the low uptake rate for Pb and Cd may indicate that they are not significant in the studied areas

The soil properties, including pH, soil organic matter percentage, and soil conductivity, were within suitable ranges for agricultural productivity. These factors contribute to a conducive environment for crop growth and overall agricultural sustainability in the study areas. However, farmers need to adopt good agricultural practices which include proper waste management, judicious use of fertilizers and pesticides, crop rotation system, and organic farming methods. These practices can help minimize the accumulation of heavy metals in soils and crops. Further studies is required to assess the long-term effects of agricultural activities on heavy metal accumulation in soil and crops. Periodic assessment of yams grown in the study areas is imperative to ensure food safety for the local population thereby safeguarding the environment and protecting the health of farmers and consumers.

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Conflicts of Interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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