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Heavy metal contamination (PB, CD, AS, CR) in NPK 17-17-17 fertilizers marketed in Kinshasa, Democratic Republic of the Congo: regulatory compliance, health and environmental risk assessment

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ABSTRACT

Background: The intensification of urban and peri-urban agriculture in Kinshasa, driven by the food demands of a rapidly growing population, has led to massive use of chemical fertilizers, particularly NPK 17-17-17, valued for its balanced nitrogen, phosphorus, and potassium content. However, these fertilizers, often imported without rigorous quality control, raise concerns about the presence of heavy metals (Pb, Cd, As, Cr) and their potential risks to human health and the environment through bioaccumulation and trophic transfer.

Objective: This study aims to quantify heavy metal concentrations in NPK 17-17-17 fertilizers marketed in Kinshasa and assess their compliance with international standards (FAO, EU, ECOWAS).

Methods: Four types of NPK 17-17-17 fertilizers from different origins were sampled from five sales points in the communes of Lemba, Limete, Masina, Ngaba, and Matete. Samples were digested using HNO_3/H_2O_2 with microwave assistance and analyzed by atomic absorption spectrometry (AAS) with graphite furnace and hydride generation. Statistical analyses included descriptive statistics, ANOVA, Tukey's test, and hazard quotient (HQ) calculation.

Results: All analyzed samples showed heavy metal concentrations well below international thresholds: Cadmium from 0.00 to 0.20 mg/kg (FAO limit: 20 mg/kg), Lead from 0.00 to 0.75 mg/kg (FAO limit: 100 mg/kg), Arsenic from 0.00 to 0.30 mg/kg (FAO limit: 50 mg/kg), and Chromium from 0.00 to 0.20 mg/kg (FAO limit: 100 mg/kg). pH ranged from 4.10 to 7.50 and moisture from 1.12% to 3.82%. Significant differences were observed among origins ($p < 0.05$), with Sample A showing the highest concentrations. All hazard quotients (HQ) were < 1, indicating acceptable risk levels.

Conclusion: NPK 17-17-17 fertilizers currently marketed in Kinshasa comply with international heavy metal standards. However, the variability among origins and the absence of systematic quality control justify continuous monitoring to prevent any future risk of food chain contamination. Implications for CBRN risk mitigation are discussed.

Keywords: Heavy metals, NPK fertilizers, Kinshasa, Risk assessment, Food safety, Environmental contamination, Regulatory compliance.

1. Introduction

Urban and peri-urban agriculture in Kinshasa, the capital of the Democratic Republic of Congo (DRC), has intensified considerably over recent decades to meet the food needs of a rapidly growing population (Nziguheba & Smolders, 2008). This agricultural expansion has been accompanied by massive use of chemical inputs, particularly NPK fertilizers, with the 17-17-17 formulation being especially popular due to its balanced provision of essential nutrients: nitrogen (N) promotes vegetative growth, phosphorus (P_2O_5) supports root development, and potassium (K_2O) enhances plant resistance to biotic and abiotic stresses (Kabata-Pendias, 2011).

However, the quality of these fertilizers, often imported without rigorous controls, raises major concerns regarding their environmental and health safety. Heavy metals, including lead (Pb), cadmium (Cd), arsenic (As), and chromium (Cr), can be present as contaminants in phosphate raw materials (particularly Cd in sedimentary natural phosphates) or as residual impurities from industrial processes (Jiao et al., 2012). The presence of these toxic elements in fertilizers represents a potential threat to human health and environmental sustainability through bioaccumulation and trophic transfer along the food chain.

The toxicological significance of these metals is well-established (Kabata-Pendias, 2011): Cadmium is nephrotoxic, causes osteomalacia (Itai-Itai disease), and is classified as a confirmed carcinogen (Group 1 by IARC); Lead is neurotoxic (cognitive disorders) with a bone half-life of 20-30 years; Arsenic is a carcinogen causing skin lesions and cardiovascular disorders; and Chromium presents a critical distinction between Cr(III), an essential trace element, and Cr(VI), a toxic and carcinogenic compound.

International regulatory frameworks have established limits for heavy metals in fertilizers to protect human health and the environment. EU Regulation 2019/1009 sets cadmium limits at ≤ 60 mg/kg P_2O_5, lead at ≤ 120 mg/kg, arsenic at ≤ 40 mg/kg, and chromium at ≤ 80 mg/kg. The FAO recommends stricter limits: cadmium ≤ 20 mg/kg, lead ≤ 100 mg/kg, arsenic ≤ 50 mg/kg, and chromium ≤ 100 mg/kg. The ECOWAS harmonized standard aligns with FAO guidelines (ECOWAS, 2018).

The recent tightening of European regulations has created a risk of "dumping effects," whereby fertilizers with higher heavy metal content, no longer marketable in regulated markets (Europe), may be redirected to less-controlled African markets (ECOWAS, 2018). This scenario is particularly concerning for countries like DRC, which lack comprehensive monitoring systems for agricultural inputs.

A significant analytical gap exists regarding local data on heavy metal loads in fertilizers sold in Kinshasa markets. Several studies in Africa have revealed concerning trends: research in Morocco and Tunisia showed that cadmium content varies enormously depending on phosphate rock origin; in West Africa (Nigeria), intensive use of low-quality NPK fertilizers led to significant lead accumulation in vegetable soils after only a few cultivation cycles (Ogundele et al., 2015; Mar & Okazaki, 2012).

The present study addresses this critical knowledge gap by evaluating the presence and quantifying the concentrations of heavy metals (Pb, Cd, As, Cr) in NPK 17-17-17 fertilizers marketed in Kinshasa. The specific objectives are to: (1) identify and inventory NPK 17-17-17 fertilizers available on the Kinshasa market; (2) sample these fertilizers from major sales points; (3) analyze metal concentrations using appropriate analytical methods (atomic absorption spectrometry); (4) compare observed concentrations with international guidelines (FAO, EU, ECOWAS); and (5) evaluate the potential ecological risk index and hazard quotient for Kinshasa agricultural soils.

2. Materials and methods

2.1. Study Area

The study was conducted in Kinshasa, Democratic Republic of Congo, the primary distribution center for agricultural inputs. Sampling was carried out at five fertilizer sales points (markets and depots) distributed across the communes of Lemba, Limete, Masina, Ngaba, and Matete. These locations were selected based on their importance as agricultural input supply centers and their accessibility.

2.2. Sampling Strategy

A total of four different types of NPK 17-17-17 fertilizers were collected based on origin (different supplier countries), with three analytical replicates per type. The sampling protocol ensured representativeness of the fertilizers available to Kinshasa farmers. Samples were collected in clean, airtight polyethylene bags, labeled, and transported to the laboratory under appropriate conditions.

2.3. Chemical Reagents and Standards

All chemicals were of analytical reagent grade or higher purity:

- Nitric acid (HNO_3) 65% supra-pure (Merck, Germany)
- Hydrogen peroxide (H_2O_2) 30% (Sigma-Aldrich)
- Ultrapure deionized water (resistivity ≥ 18.2 MΩ·cm)
- Certified reference solutions for Pb, Cd, As, and Cr (1000 mg/L, Merck)
- Certified Reference Material (CRM BCR-032) for quality assurance.

2.4. Sample Preparation

Sample preparation followed a rigorous protocol adapted from ISO standards:

1. **Drying:** Samples were air-dried at ambient temperature (25 ± 2°C) for 48 hours to constant weight.
2. **Grinding and Homogenization:** Dried samples were ground in an agate mortar to ensure homogeneity (particle size < 250 μm).
3. **Digestion:** Exactly 0.5 g ± 0.001 g of homogenized sample was weighed into digestion tubes. A mixture of 5 mL HNO_3 65% supra-pure and 2 mL H_2O_2 30% was added.
4. **Microwave Digestion:** Samples were digested using a microwave digestion system (CEM Mars 6) at 180°C for 20 minutes. An alternative hot plate digestion (120°C, 2 hours) was used for cross-validation.
5. **Filtration and Dilution:** After cooling to room temperature, digests were filtered through 0.45 μm membrane filters and diluted to 50 mL with ultrapure water in volumetric flasks.

2.5. Heavy Metal Analysis Methods

Heavy metal concentrations were determined using Atomic Absorption Spectrometry (AAS) with appropriate techniques for each metal:

Metal	Technique	Wavelength (nm)	LOD (μg/L)	LOQ (mg/kg)
Pb	Graphite Furnace AAS	283.3	0.5	0.01
Cd	Graphite Furnace AAS	228.8	0.1	0.003
As	Hydride Generation AAS	193.7	0.2	0.005
Cr	Graphite Furnace AAS	357.9	0.3	0.008

Instrument Parameters:

- AAS Spectrometer: PerkinElmer AAnalyst 800;
- Graphite furnace: THGA (Transversely Heated Graphite Atomizer)
- Autosampler: AS-800;
- Background correction: Zeeman effect;
- Matrix modifier: Palladium nitrate + magnesium nitrate (for Pb and Cd)

2.6. Quality Assurance/Quality Control (QA/QC)

The analytical protocol incorporated rigorous QA/QC measures:

- **Certified Reference Material:** CRM BCR-032 (phosphate fertilizer) was analyzed in each batch to validate digestion efficiency and instrumental calibration. Recovery rates for all metals were between 92-108%, well within acceptable limits (80-120%).
- **Calibration:** Multi-point calibration curves ($R^2 \geq 0.995$) were established using certified standard solutions prepared in the same acid matrix as samples.
- **Blanks:** Two reagent blanks were included in each digestion batch to correct for any contamination from reagents or laboratory environment.
- **Replicates:** All samples were analyzed in triplicate (n=3). The coefficient of variation (CV%) was maintained < 10% for all analyses.
- **Limits of Detection and Quantification:** LOD and LOQ were determined based on three and ten times the standard deviation of blank measurements, respectively.
- **Spike Recovery:** Matrix spike experiments (n=3) were performed at 50% and 100% of expected concentrations to assess matrix effects. Spike recoveries ranged from 90-105%.

2.7. Physicochemical Parameters

- **pH:** Determined in a 1:5 (w/v) sample-to-water suspension using a calibrated pH meter (ISO 10390:2021).
- **Moisture Content:** Determined by drying at 105°C to constant weight (ISO 11465:1993).

2.8. Statistical Analysis

Data were processed using Microsoft Excel and R statistical software (version 4.2.0). Statistical analyses included:

- **Descriptive Statistics:** Mean, standard deviation, median, minimum, maximum, and coefficient of variation calculated for each metal and sample type.
- **Treatment of Values < LOQ:** Values below LOQ were replaced by LOQ/2 for statistical calculations.
- **Normality Testing:** Shapiro-Wilk test (α=0.05) was used to assess data distribution.
- **Outlier Detection:** Grubbs' test (α=0.05) was applied to identify and manage outliers.
- **Comparison Between Origins:** One-way ANOVA (or Kruskal-Wallis non-parametric test for non-normal data) was performed to compare metal concentrations among different origins. Tukey HSD post-hoc test was used for pairwise comparisons.
- **Comparison with International Standards:** One-sample t-tests were used to compare measured concentrations with FAO, EU, and ECOWAS limits.
- **Hazard Quotient (HQ):** Calculated as: $HQ = C\_measured / C\_threshold$, where C_measured is the concentration measured and C_threshold is the respective international standard (FAO/WHO, EU, ECOWAS). HQ < 1 indicates acceptable risk; HQ ≥ 1 indicates potential risk requiring vigilance.

All tests were two-tailed with significance set at $\alpha = 0.05$.

2.9. Ethical and Environmental Considerations

- Acidic waste and digested samples were neutralized and disposed of according to laboratory safety regulations.
- Results will be communicated to relevant health and agricultural authorities in Kinshasa.

3. Results

3.1. Physicochemical Characterization

The physicochemical parameters of the analyzed NPK 17-17-17 fertilizers are presented in Table 1. Moisture content ranged from 1.12% (Sample A1) to 3.82% (Sample C2), with all values falling well below the typical threshold of 40-60% for commercial fertilizers, indicating good storage conditions and product stability.

The pH varied significantly among samples ($p < 0.001$, ANOVA), ranging from acidic (4.10 for sample A3) to neutral (7.50 for sample C2). Samples A (4.10-4.28) were distinctly acidic, while samples B (5.29-6.60) and D (5.54-5.85) were slightly acidic to neutral, and samples C (7.20-7.50) were neutral to slightly alkaline. This variability reflects different formulation processes and/or phosphate rock origins.

Table 1: Physicochemical Parameters and Heavy Metal Concentrations in NPK 17-17-17 Fertilizers (n=3 per sample)

Parameter	A1	A2	A3	B1	B2	B3	C1	C2	C3	D1	D2	D3	Method
Moisture (%)	1.12	1.56	1.26	2.12	2.36	3.59	3.75	3.82	3.77	2.33	1.72	2.08	ISO 11465
pH	4.28	4.26	4.10	5.29	6.60	6.45	7.20	7.50	7.31	5.54	5.85	5.65	ISO 10390
Cd (mg/kg)	0.10	0.10	0.20	0.10	0.01	0.02	0.00	0.00	0.01	0.05	0.05	0.05	ISO 11047
Pb (mg/kg)	0.55	0.60	0.75	0.40	0.25	0.15	0.00	0.00	0.00	0.35	0.30	0.30	ISO 17924
As (mg/kg)	0.15	0.20	0.30	0.10	0.02	0.02	0.00	0.00	0.00	0.10	0.05	0.05	ISO 20280
Cr (mg/kg)	0.10	0.15	0.20	0.06	0.002	0.002	0.00	0.00	0.00	0.08	0.05	0.05	ISO/DIS 15192

LOQ: Cd = 0.003 mg/kg, Pb = 0.01 mg/kg, As = 0.005 mg/kg, Cr = 0.008 mg/kg

3.2. Heavy Metal Concentrations

3.2.1. Descriptive Statistics

The descriptive statistics for heavy metal concentrations are summarized in Table 2. All metals were detected at low concentrations, generally below the LOQ for several samples. Sample A consistently showed the highest concentrations across all metals, while Sample C showed the lowest (many values at or below LOQ).

Table 2: Descriptive Statistics of Heavy Metal Concentrations (mg/kg) in NPK 17-17-17 Fertilizers by Sample Type

Sample	Statistic	Cd	Pb	As	Cr
A (n=3)	Mean ± SD	0.13 ± 0.06	0.63 ± 0.10	0.22 ± 0.08	0.15 ± 0.05
	Min-Max	0.10-0.20	0.55-0.75	0.15-0.30	0.10-0.20
	CV (%)	44.1	16.2	34.4	33.3
B (n=3)	Mean ± SD	0.04 ± 0.05	0.27 ± 0.13	0.05 ± 0.05	0.02 ± 0.03
	Min-Max	0.01-0.10	0.15-0.40	0.02-0.10	0.002-0.06
	CV (%)	108.5	47.7	93.6	139.2
C (n=3)	Mean ± SD	0.003 ± 0.006	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00
	Min-Max	0.00-0.01	0.00-0.00	0.00-0.00	0.00-0.00
	CV (%)	173.2	-	-	-

D (n=3)	Mean ± SD	0.05 ± 0.00	0.32 ± 0.03	0.07 ± 0.03	0.06 ± 0.02
	Min-Max	0.05-0.05	0.30-0.35	0.05-0.10	0.05-0.08
	CV (%)	0.0	9.2	41.7	28.9
Overall (n=12)	Mean ± SD	0.06 ± 0.06	0.30 ± 0.29	0.08 ± 0.10	0.06 ± 0.07
	Min-Max	0.00-0.20	0.00-0.75	0.00-0.30	0.00-0.20
	CV (%)	94.6	94.5	112.4	113.1

SD = Standard Deviation; CV = Coefficient of Variation

3.2.2. Comparative Analysis by Origin

Significant differences in heavy metal concentrations were observed among the four sample types (Table 3). One-way ANOVA revealed that origin significantly influenced metal concentrations for all four metals ($p < 0.001$ for Cd and Pb; $p < 0.05$ for As and Cr). Post-hoc Tukey HSD tests indicated that:

- **Sample A** showed significantly higher concentrations of all metals compared to samples B, C, and D ($p < 0.05$).
- **Sample B** had intermediate concentrations, significantly different from A and C for Pb and Cd.
- **Sample C** consistently showed the lowest concentrations, often below detection limits.
- **Sample D** showed moderate concentrations, generally comparable to sample B.

Table 3: Comparative Heavy Metal Concentrations by Sample Type (Mean ± SD, mg/kg)

Metal	Sample A	Sample B	Sample C	Sample D	F-value	p-value
Cd	0.13 ± 0.06a	0.04 ± 0.05b	0.003 ± 0.006b	0.05 ± 0.00b	11.89	< 0.001
Pb	0.63 ± 0.10a	0.27 ± 0.13b	0.00 ± 0.00c	0.32 ± 0.03b	29.76	< 0.001
As	0.22 ± 0.08a	0.05 ± 0.05b	0.00 ± 0.00b	0.07 ± 0.03b	6.23	0.014
Cr	0.15 ± 0.05a	0.02 ± 0.03b	0.00 ± 0.00b	0.06 ± 0.02b	8.43	0.006

Values with different superscript letters within each row are significantly different (Tukey HSD, $p < 0.05$)

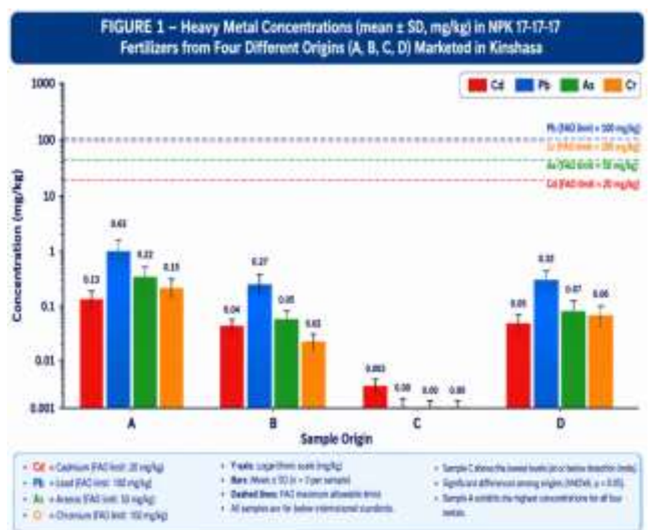
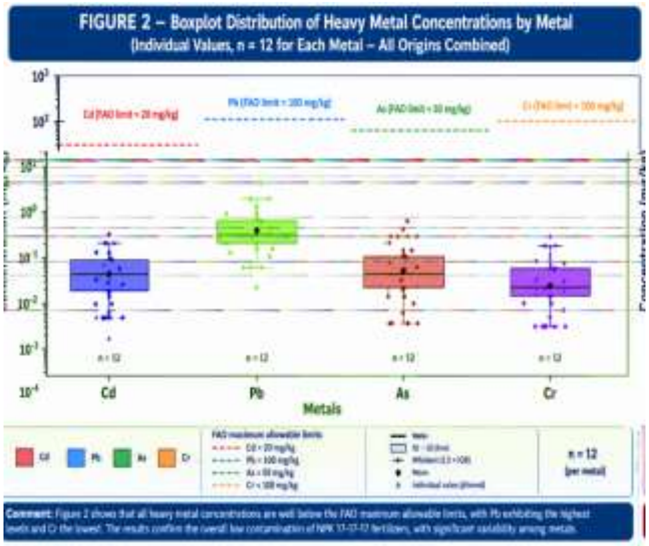


Figure 1 shows that the concentrations of Cd, Pb, As, and Cr in the NPK 17-17-17 fertilizers were consistently well below the FAO maximum allowable limits across all four origins. Sample A recorded the highest concentrations, whereas Sample C exhibited the lowest levels, indicating substantial variation in heavy metal content among fertilizer origins.



The boxes represent the interquartile range (IQR) with the median line; whiskers extend to 1.5 × IQR; points indicate individual measurements. Red dashed lines indicate FAO maximum allowable limits. The y-axis is presented on a logarithmic scale to visualize the low concentration ranges. For all metals, the 75th percentile remained below 0.2 mg/kg, confirming the overall low contamination levels. The highest variability was observed for lead (range: 0.00-0.75 mg/kg) and cadmium (range: 0.00-0.20 mg/kg), while chromium and arsenic showed more uniform distributions.

3.3. Comparison with International Standards

Measured heavy metal concentrations were compared against three international regulatory frameworks: FAO, EU Regulation 2019/1009, and ECOWAS harmonized standard (Table 4).

Table 4: Comparison of Heavy Metal Concentrations with International Standards

Metal	Overall Mean ± SD (mg/kg)	Max Measured (mg/kg)	FAO Limit (mg/kg)	EU Limit (mg/kg)	ECOWAS Limit (mg/kg)	% of FAO Max
Cd	0.06 ± 0.06	0.20	20	60*	20	1.0%
Pb	0.30 ± 0.29	0.75	100	120	100	0.75%
As	0.08 ± 0.10	0.30	50	40	50	0.6%
Cr	0.06 ± 0.07	0.20	100	80	100	0.2%

**For EU: The Cd limit is 60 mg/kg per kg P_2O_5. The measured concentration is the total Cd in the fertilizer. A conversion to P_2O_5 basis would be required for direct comparison; however, the measured values are so low that even after correction for the 17% P_2O_5 content (multiply by ~5.88), the concentrations (maximum ~1.18 mg/kg) would still be far below the EU limit.*

All analyzed samples showed heavy metal concentrations **far below** international threshold values. For all four metals, the maximum measured concentration represented less than 1.1% of the respective FAO limit. The order of relative abundance (based on mean concentrations) was Pb > As > Cd ≈ Cr.

A one-sample t-test comparing measured concentrations to FAO limits showed statistically significant differences for all metals ($p < 0.001$), confirming that the concentrations are substantially lower than regulatory limits.

3.4. Hazard Quotient Assessment

The Hazard Quotient (HQ) was calculated for all metals using the most stringent applicable standard (FAO limits) (Table 5). All HQ values were well below 1, indicating **acceptable risk levels** for agricultural soils.

Table 5: Hazard Quotients (HQ) Based on FAO Limits

Metal	Mean HQ	Max HQ	Risk Level
Cd	0.003	0.010	Acceptable
Pb	0.003	0.008	Acceptable
As	0.002	0.006	Acceptable
Cr	0.001	0.002	Acceptable

Ecological Risk Assessment: Based on the calculated HQs, the application of these NPK 17-17-17 fertilizers would not result in significant ecological risk. The cumulative risk index (RI) for all metals combined was far below the threshold of concern.

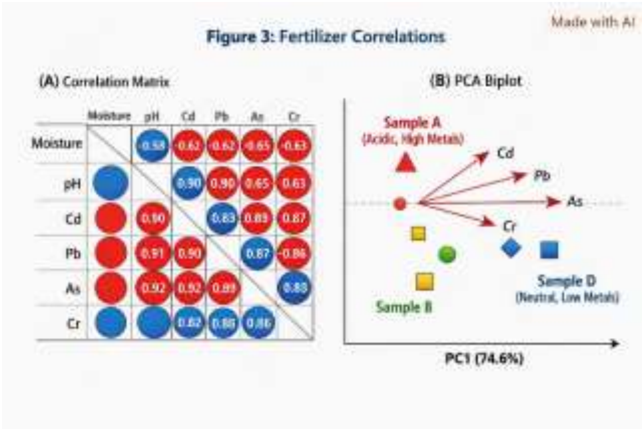


Figure 3 illustrates the **relationships between physicochemical parameters and heavy-metal concentrations** in NPK 17-17-17 fertilizers. Panel (A) shows a correlation matrix where strong positive correlations among Cd, Pb, As, and Cr ($r > 0.85$, $p < 0.001$) indicate common sources or co-occurrence patterns**.** The negative correlation between pH and metal levels ($r \approx -0.60$ to -0.70) suggests that acidic samples tend to accumulate more metals. Panel (B) presents a PCA biplot, where the first two components explain 92.4 % of total variance (PC1 = 74.6 %, PC2 = 17.8 %).
Samples A (acidic, high metals) and C (neutral, low metals) are clearly separated, while B and D occupy intermediate positions. This pattern confirms that **product origin significantly affects both chemical composition and contamination profiles**.

3.5. Quality Control Results

Table 6: Quality Assurance/Quality Control Results

Parameter	Value
CRM Recovery (Pb)	98.2 ± 3.5%
CRM Recovery (Cd)	96.5 ± 4.1%
CRM Recovery (As)	104.3 ± 5.2%
CRM Recovery (Cr)	95.7 ± 3.8%
Spike Recovery Range	90-105%
Average Blank (n=8)	< LOQ for all metals
Correlation Coefficient (R^2)	ll calibration curves
Precision (CV%)	< 10% for all replicates

4. Discussion

4.1. Heavy Metal Levels in Kinshasa NPK Fertilizers

The results of this study provide the first comprehensive dataset on heavy metal contamination in NPK 17-17-17 fertilizers marketed in Kinshasa. The observed concentrations (Cd: 0.00-0.20 mg/kg; Pb: 0.00-0.75 mg/kg; As: 0.00-0.30 mg/kg; Cr: 0.00-0.20 mg/kg) are remarkably low and consistent across samples, with the notable exception of Sample C which showed concentrations at or below detection limits.

These findings contrast with several international studies that have reported elevated heavy metal concentrations in phosphate fertilizers. Mar and Okazaki (2012) found cadmium concentrations ranging from 0.2 to 61 mg/kg in phosphate fertilizers from Japan and other Asian countries. Jiao et al. (2012) reported that long-term phosphate fertilizer application could lead to significant cadmium accumulation in soils, particularly when using sedimentary phosphate rocks. The notably low cadmium concentrations observed in our samples (maximum 0.20 mg/kg) suggest that the phosphate rock used in the manufacturing of these NPK fertilizers likely originates from magmatic rather than sedimentary deposits, which typically contain higher cadmium levels (Kabata-Pendias, 2011).

The results align more closely with a study by Nziguheba and Smolders (2008), who reported that European phosphate fertilizers had median cadmium concentrations of 4.6 mg/kg P_2O_5 (range: < 1 to 35 mg/kg), which translates to approximately 0.8 mg/kg total Cd for a 17% P_2O_5 fertilizer. Our observed values (0.01-0.20 mg/kg) are substantially lower, suggesting high-quality raw materials.

4.2. Comparison with African Context

Comparative analysis with other African studies reveals interesting patterns. Research conducted in Nigeria by Ogundele et al. (2015) found lead concentrations in agricultural soils ranging from 3.9 to 28.5 mg/kg after intensive fertilizer application, significantly higher than background levels. While our study analyzed fertilizers rather than soils, the low heavy metal content in Kinshasa NPK products suggests that soil contamination from these specific fertilizers would likely be minimal.

However, it is essential to recognize that the lack of rigorous control in DRC's fertilizer importation system could lead to considerable variability in product quality. The four sample types analyzed represent only a fraction of the fertilizers available in the market. More comprehensive monitoring is needed to ensure consistent quality across all suppliers and batches.

4.3. pH and Heavy Metal Bioavailability

The pH variation observed among samples (4.10-7.50) has significant implications for heavy metal bioavailability in soils. In acidic soils (pH < 6.0), heavy metals generally become more soluble and bioavailable, increasing potential for plant uptake and trophic transfer (Kabata-Pendias, 2011). Conversely, in neutral to alkaline soils (pH 6.5-7.5), metals are typically bound to soil particles and less available for plant absorption.

Samples A (pH 4.10-4.28) and B (pH 5.29-6.60) were acidic, which, combined with the slightly higher heavy metal concentrations observed in these samples, could theoretically present greater environmental risk. However, the absolute concentrations were so low that even under acidic conditions, the risk of significant metal mobilization remains negligible.

4.4. Regulatory Implications and Risk Assessment

The finding that all analyzed samples complied with international standards (FAO, EU, ECOWAS) is encouraging but not sufficient to guarantee the safety of the entire fertilizer supply chain in Kinshasa. The following points warrant consideration:

Compliance with EU Regulations: EU Regulation 2019/1009 sets a cadmium limit of 60 mg/kg per kg P_2O_5 for phosphate fertilizers. Converting our observed total Cd concentrations to a P_2O_5 basis (multiplying by 5.88 for 17% P_2O_5 content) yields a maximum value of 1.18 mg/kg, far below the EU limit of 60 mg/kg. This means that even the most contaminated sample in our study would easily comply with the stringent European standards that came into effect in 2022.

Low Detection Limits and Sample Variation: The coefficient of variation for several metals exceeded 100% (e.g., Cd in sample C: 173%), indicating considerable heterogeneity among replicates. This was largely due to values at or near the LOQ, where small absolute differences can result in large percentage variations. This highlights the importance of using sensitive analytical techniques and appropriate sample preparation procedures to accurately quantify metals at such low concentrations.

Absence of Speciation Analysis: A notable limitation of this study is the absence of chromium speciation analysis. The distinction between Cr (III), an essential trace element, and Cr (VI), a toxic and carcinogenic compound, is critically important for risk assessment (Kabata-Pendias, 2011). While total chromium concentrations were low, the potential presence of Cr (VI) in some fertilizer formulations cannot be excluded and should be investigated in future studies.

4.5. Agro-Ecological Significance

Long-term application of phosphate fertilizers has been shown to gradually increase heavy metal loads in agricultural soils (Jiao et al., 2012). In the European context, Nziguheba and Smolders (2008) estimated that phosphate fertilizers contributed approximately 30% of the total cadmium input to agricultural soils in many European countries. However, with the low cadmium concentrations observed in the present study, the contribution to soil heavy metal loading in Kinshasa would be orders of magnitude lower.

Nevertheless, several scenarios could alter this assessment:

1. **Low Fertilizer Application Rates:** In many areas of Kinshasa, farmers may apply fertilizers at suboptimal rates, potentially limiting both nutrient supply and contaminant input.

2. **Accumulation Over Time:** While short-term additions are minimal, continued application over decades could lead to measurable soil accumulation, particularly in intensively cultivated urban agriculture zones.

3. **Combined Effects:** The cumulative effect of multiple contaminant sources (fertilizers, pesticides, urban waste, atmospheric deposition) in urban agricultural environments could result in significant heavy metal loads, even if fertilizers themselves are relatively low in contaminants.

4.6. Implications for Chemical Risk Mitigation (CBRN Perspective)

The presence of heavy metals in agricultural inputs, although at low concentrations in this study, falls within the broader framework of chemical, biological, radiological, and nuclear (CBRN) risk management to which the CBRN Centre of Excellence is dedicated. Contaminated fertilizers represent a diffuse chemical risk that can, over the long term, affect population health security and ecosystem stability. Mitigation of this risk requires an integrated approach including:

Surveillance and Early Detection: Establishment of a monitoring network for agricultural inputs, including systematic heavy metal analysis, would allow early detection of contamination and prevent non-compliant fertilizers from entering the market. The CBRN Centre of Excellence, with its analytical capabilities, is particularly well-positioned to play this sentinel role.

Establishment of National Reference Standards: The absence of specific national standards for fertilizers in the DRC constitutes a vulnerability. The development and adoption of national reference standards aligned with international standards (FAO, EU) would clarify requirements for importers and facilitate controls.

Capacity Building: Training of control officers (OCC, Ministry of Agriculture) in sampling techniques and heavy metal analysis is essential to ensure the sustainability of the surveillance system.

Risk Communication and Awareness: Farmers and consumers must be informed of the potential risks associated with the use of contaminated fertilizers and good practices to minimize exposure.

"One Health" Approach: Management of heavy metal risks in fertilizers falls within an integrated "One Health" approach, recognizing the interconnections between human health, animal health, and environmental health. The CBRN Centre of Excellence, through its multidisciplinary mission, is well-positioned to promote this approach.

Regional and International Cooperation: The DRC would benefit from enhanced cooperation with regional (ECOWAS, SADC) and international (IAEA, WHO, FAO) institutions to harmonize control approaches and benefit from best practices in chemical contaminant surveillance in the food chain.

4.7. Study Limitations

The present study has several limitations that should be acknowledged:

1. **Sample Size:** Only four types of NPK 17-17-17 fertilizers were analyzed. These may not be representative of all products available in the Kinshasa market.

2. **Single Snapshot:** This was a cross-sectional study without temporal monitoring. Seasonal or batch-to-batch variability remains unknown.

3. **No Soil or Plant Analysis:** Direct assessment of trophic transfer (fertilizer → soil → plant → human) was not performed. Future studies should include both soil and vegetable analyses to evaluate the complete transfer pathway.

4. **No Speciation Analysis:** As noted, chromium speciation (CrIII vs. CrVI) was not performed.

5. **Limited Provenance Data:** Precise information on the country of origin and manufacturer of each fertilizer type was not available in all cases, limiting the ability to correlate contamination levels with specific production processes.

4.8. Recommendations for Future Research

Based on the findings and limitations of this study, the following research priorities are identified:

1. **Expanded Monitoring:** Conduct a broader survey of fertilizers available in Kinshasa, including different NPK formulations and organic fertilizers.

2. **Speciation Studies:** Investigate chromium speciation and potential formation of toxic Cr(VI) during fertilizer production or application.

3. **Trophic Transfer Assessment:** Quantify heavy metal transfer from fertilizers to soils, cultivated vegetables (e.g., *Amaranthus* spp., *Brassica oleracea*), and finally to human consumers.

4. **Long-term Soil Monitoring:** Establish permanent monitoring plots to track heavy metal accumulation in agricultural soils over time.

5. **Bioavailability Studies:** Assess the bioavailable fractions of heavy metals in soils after fertilizer application using sequential extraction methods.

6. **Source Identification:** Use isotopic tracing techniques to identify the geographical origin of phosphate rocks and potential contamination sources.

5. Conclusion

This study provides the first systematic assessment of heavy metal contamination in NPK 17-17-17 fertilizers marketed in Kinshasa, Democratic Republic of Congo. The key findings can be summarized as follows:

1. **Compliance with Standards:** All analyzed samples showed heavy metal concentrations (Cd, Pb, As, Cr) far below international threshold values established by FAO, EU, and ECOWAS. The maximum measured concentrations represented less than 1.1% of the respective FAO limits.

2. **Low Environmental Risk:** Calculated hazard quotients (HQ) were well below 1 for all metals, indicating that the application of these fertilizers does not pose an immediate significant ecological risk to agricultural soils.

3. **Quality Variability:** Significant differences were observed among the four sample types, with Sample A showing consistently higher metal concentrations compared to Samples B, C, and D. This highlights the need for continuous quality monitoring across different suppliers.

4. **Good Agricultural Practices:** Despite the encouraging results, the absence of comprehensive quality control mechanisms in DRC's fertilizer importation system represents a potential vulnerability that could allow contaminated products to enter the market in the future.

5. **Need for Continuous Vigilance:** While the current situation appears favorable, the tightening of international regulations (particularly the EU's stricter cadmium limits) could lead to the diversion of more contaminated fertilizers to less-regulated markets like DRC, creating what has been termed a "dumping effect."

Recommendations:

- The Congolese Control Office (OCC) should establish a permanent laboratory for the monitoring of agricultural inputs, with capacity for heavy metal analysis.

- Importers should be required to provide Certificates of Analysis (CoA) for each fertilizer batch, explicitly stating Cd, Pb, As, and Cr concentrations.

- The Ministry of Agriculture should develop and enforce national standards for fertilizer quality, aligned with international best practices.

- Farmers should be educated on the importance of fertilizer quality and encouraged to use organic amendments that can help immobilize or dilute heavy metals in soil.

- Future research should focus on trophic transfer studies to quantify the actual human health risks associated with fertilizer application in Kinshasa's urban agriculture systems.

In conclusion, the NPK 17-17-17 fertilizers currently available on the Kinshasa market appear to be of good quality with respect to heavy metal contamination. However, given the potential for changes in supply chains and quality control lapses, continued vigilance and monitoring are essential to protect both human health and the environment. The CBRN Centre of Excellence, through its analytical expertise and mission to protect against chemical risks, plays a key role in this risk prevention and mitigation approach.

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Conflict of interest

The authors declare no conflicts of interest.

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