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# Trace and Potentially Toxic Elements in Canned Tuna Marketed in Eastern Saudi Arabia: ICP-OES/LIBS Method Comparison and Dietary Exposure Assessment

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**ABSTRACT:** Canned tuna is nutritionally valuable but may contain trace elements introduced through the marine environment, processing, or packaging. This study quantified fourteen elements in 14 commercial canned-tuna products marketed in Dammam and Al Khobar, Eastern Saudi Arabia, using inductively coupled plasma optical emission spectrometry (ICP-OES) and orthogonal double-pulse laser-induced breakdown spectroscopy (ODP-LIBS). Scanning electron microscopy (SEM) and Fourier-transform infrared (FTIR) spectroscopy were used for complementary structural characterization. Brand-level ICP-OES concentrations (mean ± SD, mg/kg) included Pb 0.549 ± 0.530, Cd 0.095 ± 0.048, Hg 0.264 ± 0.155, and Al 84.736 ± 54.903. For contextual screening, eight of 14 samples contained Pb above 0.30 mg/kg, five contained Cd above 0.10 mg/kg, and all had Hg below 1.0 mg/kg; these comparators are used for screening rather than a formal Saudi regulatory compliance determination. Method comparison showed very high Pearson correlations for Zn, Pb, Al, Cd, Cr, Fe, Mg, Na, and Ca, but correlation did not imply interchangeability. Lin's concordance correlation coefficient was high for Pb (0.994), Al (0.996), Zn (0.989), Fe (0.972), Na (0.997), and Ca (0.960), but substantially lower for Hg (0.211), Ni (0.145), Cu (0.265), and Co (0.310), reflecting systematic element-specific bias in LIBS. Dietary exposure was recalculated using the manuscript's stated external scenario of 7.35 g tuna/week and 61.6 kg body weight. Mean weekly exposures were 0.0655 µg/kg bw for Pb, 0.0113 for Cd, 0.0315 for Hg, and 10.11 for Al. Under this low-consumption scenario, Hg represented approximately 1.97% of the JECFA

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methylmercury PTWI and Al approximately 0.51% of the JECFA aluminium PTWI; the current JECFA lead PTWI has been withdrawn. The results support continued monitoring of Pb and Cd concentrations in canned tuna and indicate that LIBS may be useful as a rapid screening tool for selected elements after matrix-specific validation, but it should not be considered analytically interchangeable with ICP-OES for all analytes.

## 1. INTRODUCTION

Fish and fishery products are important sources of high-quality protein, long-chain fatty acids, vitamins, and minerals. Tuna is consumed widely in fresh, frozen, and canned forms because of its nutritional value and shelf stability. At the same time, predatory marine fish can accumulate trace elements through water, diet, and trophic transfer, and additional contamination may arise during processing, canning, or storage. Consequently, surveillance of potentially toxic elements in tuna remains relevant to food safety and public health (Miedico et al., 2020; Norhazirah et al., 2020; Lehel et al., 2023; Oktariani et al., 2023).

The toxicological significance of individual elements differs. Lead (Pb) has no established safe exposure threshold for key neurodevelopmental effects, and the former JECFA provisional tolerable weekly intake (PTWI) was withdrawn. Cadmium (Cd) has a long biological half-life and is evaluated by JECFA against a provisional tolerable monthly intake (PTMI). Mercury in fish is of particular concern because much of the mercury in predatory fish may be present as methylmercury, a developmental neurotoxicant. Aluminium (Al), although not conventionally grouped with classic heavy metals, is also relevant to dietary exposure and has a health-based guidance value (JECFA, 2011a; JECFA, 2011b; JECFA, 2007). Essential elements such as Zn, Cu, Fe, Mn, and Mg are required physiologically but may also be undesirable at excessive concentrations.

Inductively coupled plasma optical emission spectrometry (ICP-OES) is widely used for multielement determination after sample digestion. Laser-induced breakdown spectroscopy (LIBS) offers rapid, multielement analysis with limited sample preparation and potential for high-throughput screening; however, matrix effects, surface heterogeneity, calibration strategy, and element-specific emission behavior can influence quantitative performance (Khalil et al., 2019; Khalil et al., 2022; Khalil et al., 2023). A high correlation between LIBS and ICP-OES therefore does not necessarily demonstrate analytical agreement or interchangeability.

The objectives of this study were to: (i) quantify trace and potentially toxic elements in commercial canned tuna marketed in the Eastern Province of Saudi Arabia; (ii) compare brand-level ICP-OES and ODP-LIBS measurements using correlation, concordance, paired-difference, and bias analyses; (iii) describe the relative elemental distribution among products; (iv) estimate dietary exposure using the consumption scenario reported in the source manuscript; and (v) provide complementary SEM and FTIR characterization of the tuna matrix.

## 2. MATERIALS AND METHODS

### 2.1. Study design and sample collection

Fourteen commercially available canned-tuna products were purchased from supermarkets in Dammam and Al Khobar, Eastern Province, Saudi Arabia. The source manuscript reports a sampling period extending from September 2024 to June 2026 and states that five cans were collected for each brand. Products included tuna packed in sunflower oil, vegetable oil, brine, or water. Because the source data tables provide one concentration value per brand for each analytical technique, the present statistical analysis treats the 14 brand-level values as the analytical units ($n = 14$). The exact procedure used to combine or summarize the five cans per brand should be confirmed before submission.

### 2.2. Reagents and sample preparation

Multielement standard solutions (1,000 mg/L; Sigma-Aldrich) were used for calibration. Laboratory glassware and volumetric equipment were soaked overnight in 10% (v/v) nitric acid and rinsed with deionized water before use. The packing medium was drained and the edible tuna portion was homogenized using stainless-steel cutters. Approximately 1–2 g of homogenized sample was treated with 1.0 mL $HNO_3$ (65%), 3.0 mL ultrapure water, and 1.0 mL $H_2O_2$ (35%) until a clear digest was obtained. Concentrations were expressed as mg/kg. The source manuscript also mentions an HCl:$HNO_3$ mixture elsewhere; the final protocol should be verified against the laboratory record before submission.

### 2.3. ICP-OES analysis

Elemental concentrations were determined using an iCAP 6300 Duo ICP-OES instrument (Thermo Fisher Scientific). Calibration curves were prepared from multielement standards and concentrations were derived from element-specific emission responses. The source manuscript reports triplicate instrumental analysis. Method blanks, certified-reference-material results, spike recovery, LOD/LOQ, precision, and measurement uncertainty were not provided in the submitted draft and should be inserted if available, because these parameters are important for analytical-method validation.

### 2.4. ODP-LIBS analysis

For orthogonal double-pulse LIBS (ODP-LIBS), dried tuna material was homogenized, mixed with 2 g KBr matrix, and compressed into pellets using a hydraulic press. The setup used two Q-switched Nd:YAG lasers in an orthogonal reheating configuration. The source manuscript reports laser wavelengths of 266 nm and 1064 nm, pulse energies of approximately 100 mJ, a repetition rate of 20 Hz, and an optimized detection delay of 200 ns. Emission was collected with an echelle spectrometer and ICCD detector over approximately 250–975 nm. Atomic and ionic lines were assigned using the NIST Atomic Spectra Database. Calibration-curve and integrated-intensity approaches were used for quantitative analysis. Because the original draft contains inconsistent calibration details for some elements, the final numerical calibration coefficients and LOD/LOQ values should be checked against the instrument output before journal submission.

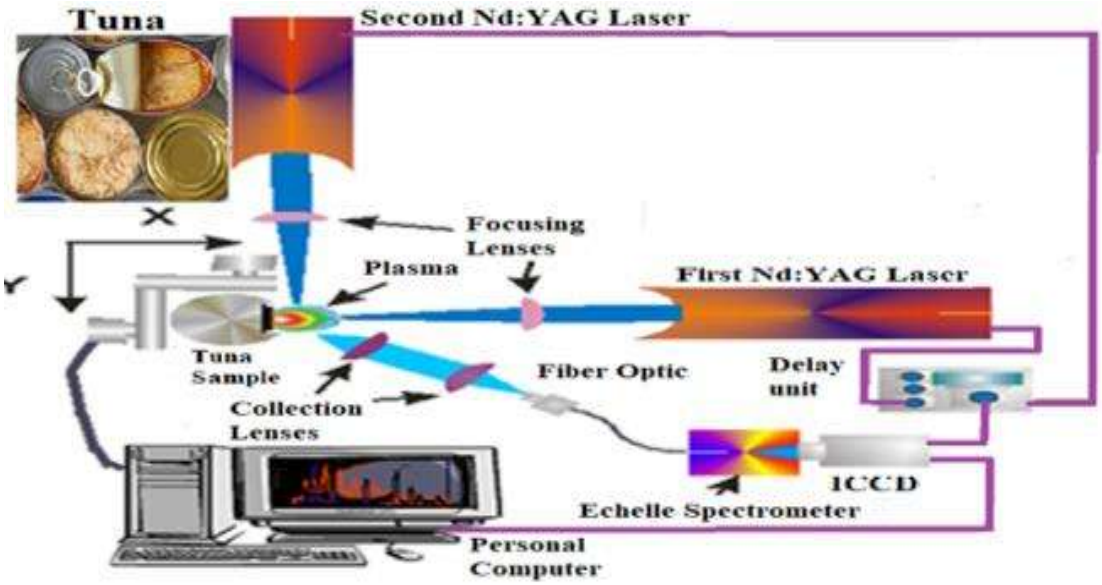



**Figure 1.** Schematic of the orthogonal double-pulse LIBS configuration used for tuna analysis (from the authors' source manuscript).

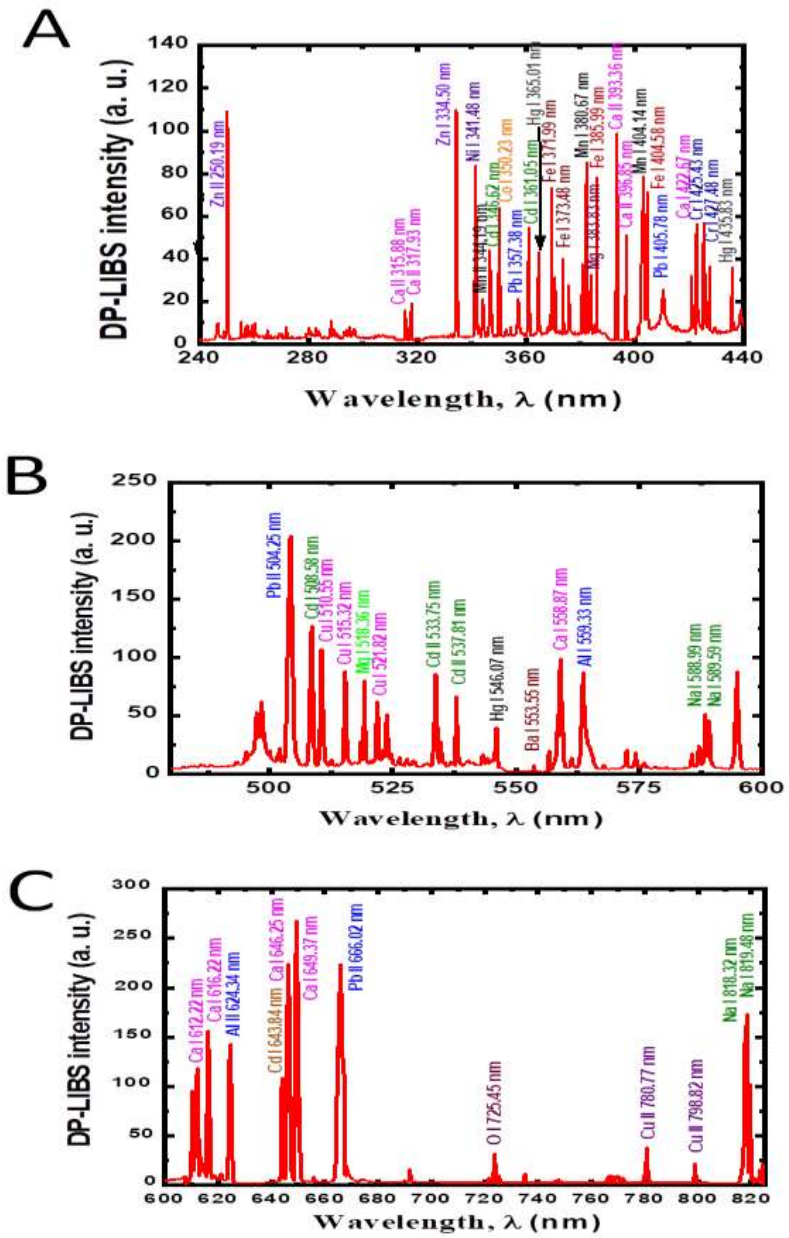



**Figure 2.** Representative ODP-LIBS spectra in three wavelength regions used for elemental-line identification.

### 2.5. Relative elemental distribution

For each element and analytical technique, the relative elemental distribution (RED%) was defined as the concentration in a given product divided by the sum of that element's concentrations across all 14 products, multiplied by 100: $RED_i,e = [C_i,e / \Sigma_k C_k,e] \times 100$. RED% is therefore a descriptive measure of the relative contribution of each product to the total measured concentration of a specific element; it is not a toxicological risk index.

### 2.6. SEM and FTIR characterization

Surface morphology was examined using an FEI INSPECT S50 scanning electron microscope (Brno, Czech Republic). Samples were gold-coated using a Quorum Q150R ES coater and imaged at multiple magnifications; representative images are shown at approximately ×500. FTIR spectra were recorded over approximately 4,500–400 $cm^{-1}$ to identify major protein and lipid functional groups, including amide and triglyceride-associated bands.

### 2.7. Dietary exposure and health-based comparison

Dietary exposure was recalculated from the ICP-OES concentrations because ICP-OES was the more completely described quantitative laboratory method in the source manuscript. The source manuscript adopted an external consumption scenario from Bae et al. (2023): weekly tuna intake (I) = 7.35 g/week and adult body weight (BW) = 61.6 kg. This scenario reflects Korean population data and should not be interpreted as a Saudi consumption estimate. Weekly exposure was calculated as: Exposure (μg/kg bw/week) = C (mg/kg) × I (kg/week) ÷ BW (kg) × 1,000.

Health-based guidance values were applied only where scientifically appropriate. For methylmercury, JECFA established a PTWI of 1.6 μg/kg bw/week. Because this study measured total Hg rather than methylmercury, comparison with the methylmercury PTWI was treated as a conservative screening scenario in which all measured Hg was assumed to be methylmercury. For aluminium, the JECFA PTWI is 2 mg/kg bw/week (2,000 μg/kg bw/week). For cadmium, the JECFA PTMI is 25 μg/kg bw/month; weekly exposure was converted to a monthly estimate using 4.345 weeks/month. JECFA withdrew the former lead PTWI and did not establish a replacement health-protective PTWI; therefore, a %PTWI was not calculated for Pb.

For concentration-level context, Pb and Hg were screened against the Saudi Food and Drug Authority finfish values of 0.30 mg/kg and 1.0 mg/kg, respectively, and Cd was compared with the 0.10 mg/kg maximum level for tuna in EU Regulation (EU) 2023/915. These are contextual comparators; a formal legal-compliance determination for canned tuna sold in Saudi Arabia should use the current applicable Saudi/GCC technical regulation (GSO 193:2021), product classification, and any processing-related provisions.

### 2.8. Statistical analysis

Statistical analyses were recalculated from the 14 brand-level concentrations reported in the source manuscript. Results are presented as mean ± standard deviation (SD), median, and range where appropriate. Agreement between ICP-OES and LIBS was evaluated using Pearson correlation (r), Lin's concordance correlation coefficient (CCC), the paired mean difference (ICP-OES − LIBS), and 95% limits of agreement (mean difference ± 1.96 SD of paired differences). Because n was small and several paired-difference distributions were non-normal, the Wilcoxon signed-rank test was used as a consistent paired comparison across elements. Two-sided $p < 0.05$ was considered statistically significant. Correlation was interpreted as similarity in rank/concentration trend, whereas CCC and paired bias were used to evaluate numerical agreement.

## 3. RESULTS AND DISCUSSION

### 3.1. Element concentrations

Substantial between-product variation was observed. ICP-OES mean concentrations (mg/kg) for the principal elements of public-health interest were Pb 0.549, Cd 0.0945, Hg 0.264, and Al 84.736. The maximum Pb concentration was 1.61 mg/kg (Sample 4), the maximum Cd concentration was 0.203 mg/kg (Sample 10), and the maximum Hg concentration was 0.45 mg/kg (Sample 6). All Hg values were below the 1.0 mg/kg contextual finfish/tuna comparator. Eight of 14 products had Pb concentrations above 0.30 mg/kg, and five of 14 had Cd concentrations above the 0.10 mg/kg tuna comparator. These comparisons identify products requiring regulatory verification but do not by themselves establish legal non-compliance under Saudi law.

**Table 1.** Summary of element concentrations measured by ICP-OES and LIBS (mg/kg; n = 14 brand-level values).

| Element | ICP-OES mean ± SD | ICP range | LIBS mean ± SD | LIBS range |
|---|---|---|---|---|
| Zn | 1.091 ± 0.389 | 0.610–2.040 | 1.036 ± 0.382 | 0.570–1.960 |
| Pb | 0.549 ± 0.530 | 0.000–1.610 | 0.499 ± 0.517 | 0.000–1.540 |
| Al | 84.736 ± 54.903 | 13.400–199.400 | 80.426 ± 56.404 | 0.960–198.800 |
| Cd | 0.095 ± 0.048 | 0.046–0.203 | 0.059 ± 0.059 | 0.013–0.201 |
| Co | 0.283 ± 0.072 | 0.170–0.460 | 0.192 ± 0.051 | 0.110–0.280 |

| Element | ICP-OES mean ± SD | ICP range | LIBS mean ± SD | LIBS range |
|---|---|---|---|---|
| Cr | 0.504 ± 0.378 | 0.050–1.120 | 0.360 ± 0.390 | 0.016–1.090 |
| Cu | 0.222 ± 0.132 | 0.060–0.400 | 0.088 ± 0.041 | 0.024–0.170 |
| Ni | 0.325 ± 0.227 | 0.080–0.770 | 0.175 ± 0.159 | 0.027–0.660 |
| Hg | 0.264 ± 0.155 | 0.010–0.450 | 0.080 ± 0.042 | 0.007–0.140 |
| Fe | 20.029 ± 13.358 | 2.320–47.830 | 17.104 ± 12.375 | 1.120–42.920 |
| Mg | 31.233 ± 7.694 | 22.850–51.230 | 27.552 ± 8.232 | 17.870–48.780 |
| Mn | 0.403 ± 0.208 | 0.089–0.897 | 0.178 ± 0.203 | 0.045–0.857 |
| Na | 981.786 ± 312.924 | 418.900–1510.000 | 960.636 ± 309.977 | 391.800–1494.100 |
| Ca | 37.809 ± 14.435 | 13.670–61.840 | 34.466 ± 13.181 | 15.570–57.340 |

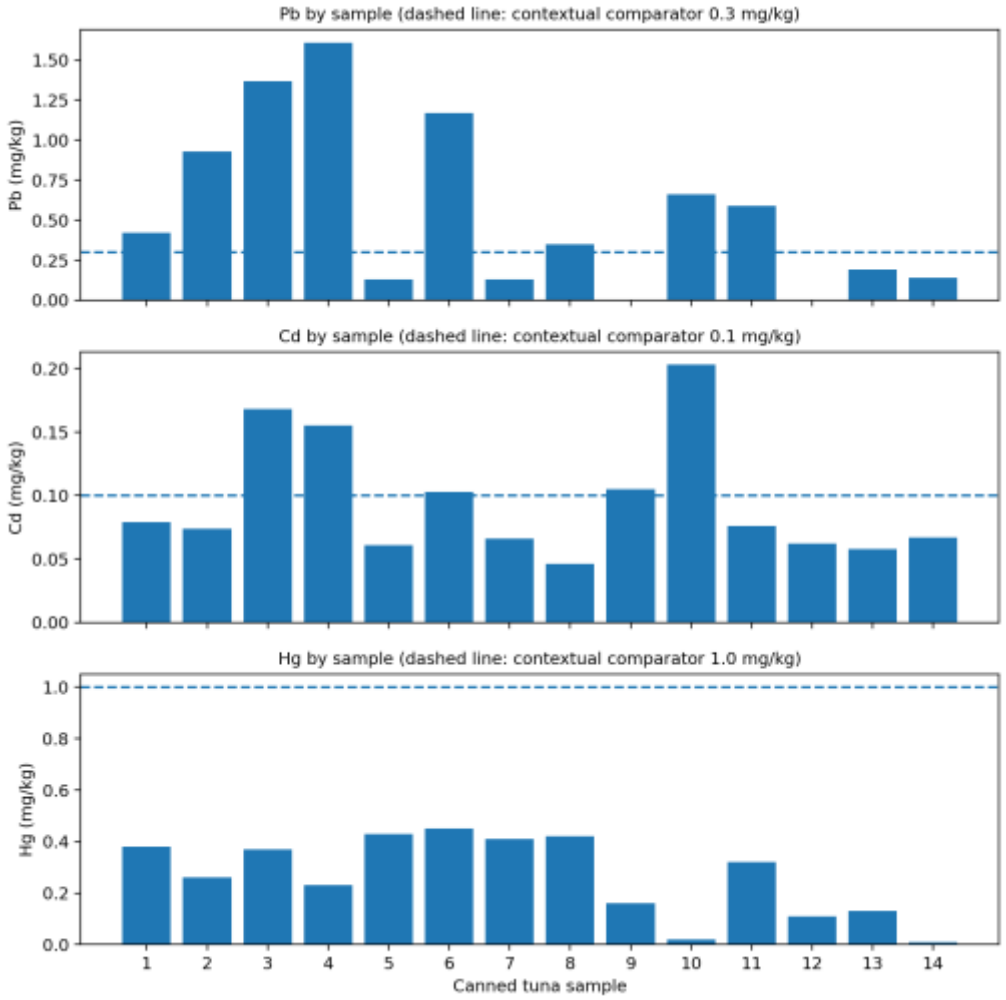



**Figure 3.** ICP-OES concentrations of Pb, Cd, and Hg across the 14 products. Dashed lines are contextual screening comparators (Pb 0.30 mg/kg; Cd 0.10 mg/kg for tuna; Hg 1.0 mg/kg) and are not a substitute for a formal Saudi regulatory-compliance assessment.

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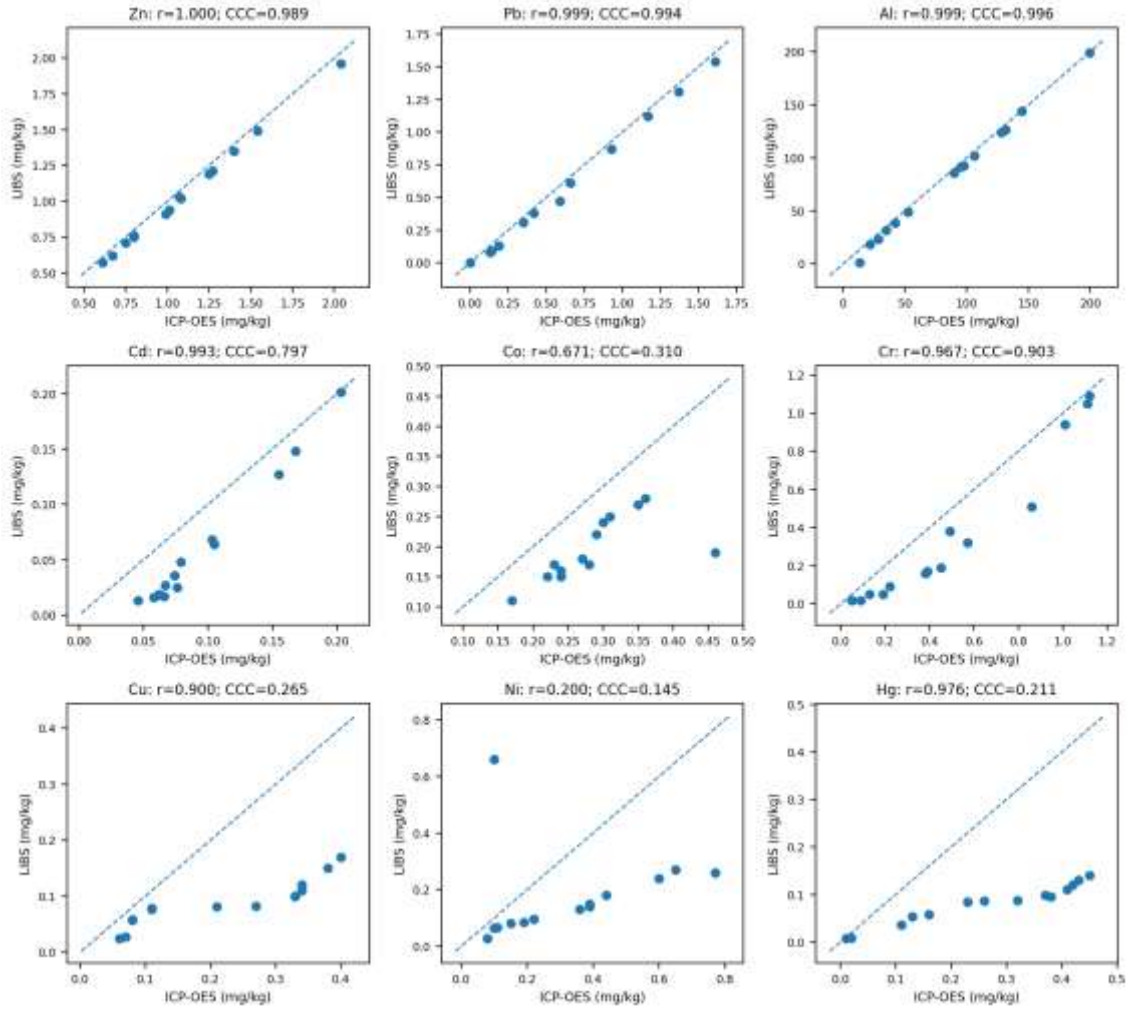



**Figure 4.** Brand-level ICP-OES versus LIBS concentrations for nine trace/potentially toxic elements. Dashed line = line of identity. High Pearson r does not necessarily imply high concordance.

### 3.3. Relative elemental distribution

RED% varied across products and differed between ICP-OES and LIBS for several elements. Because RED% is normalized within each element and analytical method, it is most appropriately interpreted as a descriptive distribution profile rather than as evidence that one method is more accurate or that a product is more toxic. The technique-dependent differences were greatest for elements showing larger method bias, consistent with the concordance results above.

### 3.4. Dietary exposure and risk characterization

Using the stated 7.35 g/week, 61.6 kg body-weight scenario, the recalculated exposures were orders of magnitude lower than those shown in the original draft because the original calculations contained unit and denominator inconsistencies. Mean weekly exposure was 0.0655 μg/kg bw for Pb, 0.0113 μg/kg bw for Cd, 0.0315 μg/kg bw for Hg, and 10.11 μg/kg bw for Al. For total Hg, the conservative assumption that all Hg was methylmercury produced a mean exposure equivalent to 1.97% of the JECFA methylmercury PTWI. Mean Al exposure represented 0.51% of the JECFA aluminium PTWI. Cadmium mean exposure corresponded to approximately 0.049 μg/kg bw/month, or 0.20% of the JECFA PTMI. No %PTWI was calculated for Pb because JECFA withdrew the former lead PTWI and did not establish a replacement value.

**Table 3.** Recalculated dietary exposure. *Exposure in μg/kg body weight/week using 7.35 g tuna/week and 61.6 kg body weight. Cd is compared on a monthly basis after multiplying weekly exposure by 4.345. The Hg comparison conservatively treats total Hg as methylmercury.

| Element | Mean C (mg/kg) | Range C | Mean exposure* | Exposure range* | Health-based reference | Mean % reference |
|---|---|---|---|---|---|---|
| Pb | 0.5493 | 0.0000–1.6100 | 0.0655 | 0.0000–0.1921 | No current PTWI | Not applicable |
| Cd | 0.0945 | 0.0460–0.2030 | 0.0113 | 0.0055–0.0242 | 25 μg/kg bw/month (JECFA PTMI) | 0.20% |
| Hg | 0.2643 | 0.0100–0.4500 | 0.0315 | 0.0012–0.0537 | 1.6 μg/kg bw/week (MeHg, JECFA) | 1.97% |
| Al | 84.7357 | 13.4000–199.4000 | 10.1105 | 1.5989–23.7920 | 2,000 μg/kg bw/week (JECFA) | 0.51% |

The low percentages above reflect the very low weekly tuna-intake assumption and should not be generalized to Saudi consumers, high-frequency tuna consumers, children, or pregnant women without population-specific intake and body-weight data. Concentration-based regulatory screening and exposure-based risk characterization answer different questions and should be interpreted separately.

### 3.5. SEM and FTIR characterization

SEM demonstrated heterogeneous muscle-surface architecture among products, including variable fiber organization, fissuring, and surface deposits. These images provide morphological context but do not establish a quantitative relationship with elemental concentrations. FTIR spectra showed the expected protein-associated amide bands and lipid-related absorption bands. Across the products, the principal tuna-matrix bands were broadly similar despite substantial variation in element concentrations; therefore, the FTIR findings should be interpreted as matrix characterization rather than evidence of elemental contamination or chemical 'integrity'.

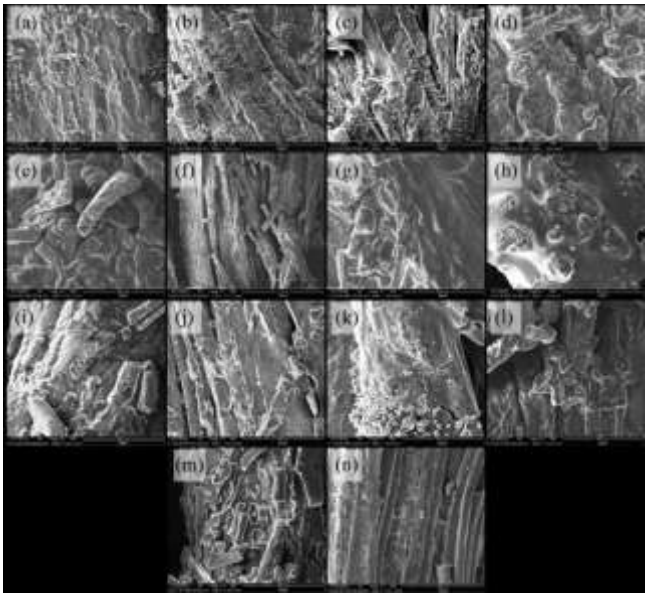


**Figure 5.** Representative SEM micrographs of the 14 canned-tuna products (a–n), as provided in the source manuscript. Scale bars approximately 300 μm.

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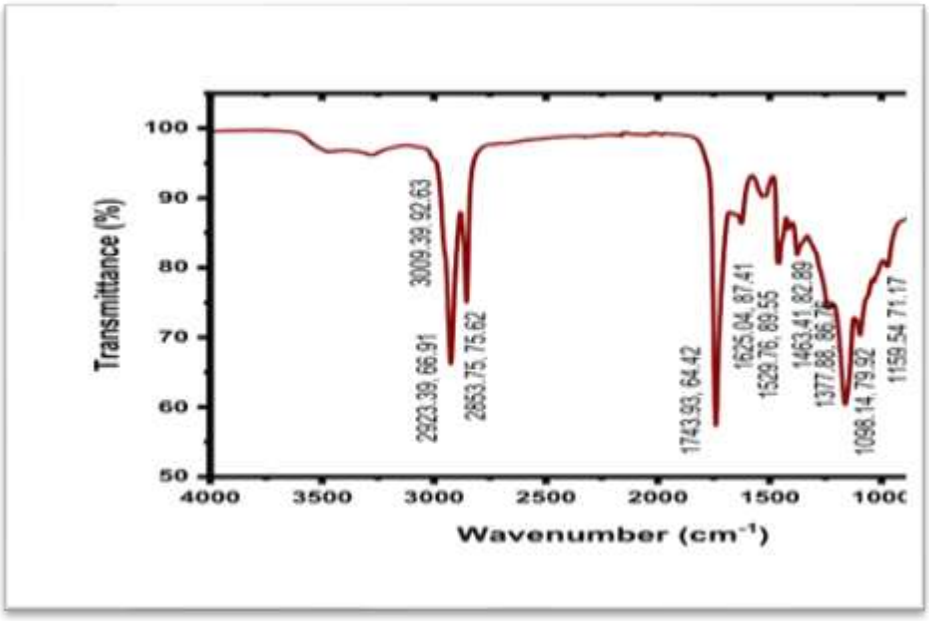



**Figure 6**. Representative FTIR spectrum from the source manuscript, showing major protein- and lipid-associated absorption bands.

**Table 4.** Principal FTIR bands reported in the tuna samples.

| Approximate wavenumber ($cm^{-1}$) | Assignment |
|---|---|
| 3009–3290 | =C–H cis stretching |
| 2922–2930 | $CH_2$ asymmetric stretching |
| 2852–2854 | $CH_2$ symmetric stretching |
| 1704–1749 | C=O stretching of triglycerides |
| 1622–1625 | Amide I: C=O stretching / hydrogen bonding |
| 1518–1530 | Amide II: C–N stretching and N–H bending |
| 1377–1378 | $CH_3$ symmetric bending |
| 1235–1236 | Amide III: C–N stretching and N–H bending |
| 1139–1162 | $CH_2$ bending |
| 1096–1099 | C–O stretching |
| 720–723 | Amide IV / $(CH_2)n$ rocking |

## 4. DISCUSSION

### 4.1. Element concentrations and food-safety context

The 14 canned-tuna products showed substantial variation in elemental composition. Pb and Cd warrant particular attention because several brand-level concentrations exceeded commonly used contextual maximum levels for fish or tuna. Eight products exceeded 0.30 mg/kg Pb, and five exceeded 0.10 mg/kg Cd. These observations are consistent with the wider literature showing that canned tuna can exhibit large between-product and between-region differences in Pb, Cd, and Hg concentrations

(Mahalakshmi et al., 2012; Miedico et al., 2020; Lehel et al., 2023; Kosker et al., 2023; Ulusoy, 2023). All total-Hg concentrations in the present dataset were below 1.0 mg/kg.

The Al concentrations were numerically much higher than the concentrations of most other trace elements. However, a large concentration value in mg/kg does not automatically mean that Al dominates health risk: risk depends on exposure, toxicological reference values, consumption, body weight, chemical form, and uncertainty. The original manuscript's conclusion that Al accounted for approximately 156% of a weekly tolerable intake was not supported by the stated intake/body-weight assumptions. After unit-correct recalculation, mean Al exposure under the adopted scenario was approximately 10.11 μg/kg bw/week, which is about 0.51% of the current JECFA PTWI of 2 mg/kg bw/week.

### 4.2. Performance of LIBS relative to ICP-OES

ODP-LIBS reproduced between-product concentration patterns very closely for several elements, as shown by the high Pearson correlations. Nevertheless, the concordance and bias analyses demonstrate that a screening method can correlate strongly with ICP-OES while still giving systematically different absolute concentrations. For Hg, for example, r was 0.976 but CCC was only 0.211 because LIBS values were consistently lower. The same issue was evident for Cu, Co, and Ni. Therefore, the manuscript no longer uses a bounded 'agreement percentage' formula that produced nonsensical negative values (for example, −460% for Ni); instead, it reports CCC and paired bias, which are more appropriate for assessing method agreement.

For Zn, Pb, Al, Fe, Na, and Ca, concordance was high, suggesting that LIBS may be useful for rapid screening when the method is calibrated for the specific tuna matrix. For Cd and Cr, the correlation was excellent but the magnitude of bias was larger. The weak Ni relationship indicates that analyte-specific spectral interference or matrix effects require further investigation. Before LIBS can be used as a replacement method, a full validation study should include certified reference materials, recovery, repeatability/reproducibility, LOD/LOQ, robustness, and predefined acceptance criteria.

### 4.3. Dietary exposure interpretation

The corrected dietary-exposure results differ materially from the original manuscript. Using 7.35 g tuna/week and 61.6 kg body weight, all calculated exposures were low relative to the applicable JECFA health-based guidance values for Al, Cd, and methylmercury. This finding is mathematically consistent with the very small tuna-intake assumption. The scenario originates from a Korean population study (Bae et al., 2023) and should be regarded as an external comparator rather than a Saudi dietary-exposure estimate. Saudi-specific tuna consumption distributions, age/sex strata, and high-consumer scenarios would be needed for a population-representative risk assessment.

Lead requires special handling because JECFA withdrew its previous PTWI after concluding that it was not health protective and that available dose–response data did not support a threshold for key effects. Consequently, reporting a Pb %PTWI using the obsolete 25 μg/kg bw/week value would be scientifically misleading. The concentration findings for Pb should instead be evaluated against the applicable regulatory maximum and, for exposure assessment, with contemporary benchmark-dose or margin-of-exposure approaches where appropriate.

The study measured total Hg rather than methylmercury. Because methylmercury is the primary mercury species of concern in tuna, the exposure comparison was deliberately conservative: it assumed that all measured Hg was methylmercury. Future studies should include mercury speciation, particularly if the study is intended to support consumer advice for pregnant women and children.

### 4.4. SEM, FTIR, and preservation medium

SEM and FTIR provide useful complementary information on matrix morphology and major chemical functional groups, but neither technique directly establishes the source of trace-element contamination. The original draft attributed differences in metal concentrations to the preservation medium (oil versus water) and storage duration; however, no statistical analysis linking preservative type or storage duration to metal concentrations was reported. That causal statement has therefore been removed. A future study could test this hypothesis prospectively by recording species, origin, can material, packing medium, manufacture date, storage duration, and batch, with sufficient replication for multivariable analysis.

### 4.5. Strengths and limitations

Strengths of the study include multielement analysis, use of two complementary spectroscopic techniques, and integration of SEM/FTIR characterization. The revised analysis also distinguishes correlation from analytical agreement and corrects the unit handling in the dietary-exposure calculations. Several limitations remain. First, the dataset contains only 14 brand-level values and does not provide can-level replicate data, limiting inference about within-brand variability. Second, tuna species, catch origin, manufacturing batch, and wet-/dry-weight reporting basis were not fully described. Third, analytical QA/QC information (LOD/LOQ, certified-reference-material recovery, blanks, and uncertainty) was not reported in the draft. Fourth, total Hg rather than methylmercury was measured, and arsenic speciation was not included. Fifth, the exposure scenario is based on Korean rather than Saudi consumption data. Finally, the cross-sectional design does not permit causal attribution of metal concentrations to packing medium, canning, or storage duration.

## 5. CONCLUSIONS

Commercial canned tuna marketed in Eastern Saudi Arabia showed marked between-product variation in trace-element concentrations. Under contextual concentration screening, Pb and Cd values in several products warrant regulatory verification, whereas all measured total-Hg concentrations were below 1.0 mg/kg. The corrected dietary-exposure analysis based on 7.35 g tuna/week and 61.6 kg body weight yielded low exposures relative to JECFA health-based guidance values for aluminium, cadmium, and methylmercury; however, this is an external low-consumption scenario and should not be interpreted as a Saudi population risk estimate. ICP-OES and LIBS showed strong concentration-trend correlations for many elements, but concordance and bias analyses demonstrated that LIBS is not analytically interchangeable with ICP-OES for all analytes, especially Hg, Ni, Cu, and Co. LIBS may nevertheless have value as a rapid screening technology after matrix-specific validation. Future work should include larger probability-based sampling, full analytical QA/QC, tuna species and origin, can- and packing-medium characteristics, mercury/arsenic speciation, and Saudi-specific dietary-consumption data.

## DECLARATIONS

### Author contributions

Ossama A. Labib: conceptualization, chemical and statistical analyses, writing – original draft.

Ahmed A. Khalil: LIBS analysis, methodology, writing – review and editing.

Khalid F. Salama: exposure and risk-assessment analysis, writing – review and editing.

Mahmoud M. Berekaa: writing – review and editing some points in the manuscript.

Mohammed T. Aljassim: Review the manuscript and rewriting the manuscript.

Abdulmalik S. Alsaif: Review the manuscript and rewriting the manuscript.

Salman A. AlQuwayi: Review the manuscript.

Mahmoud F. Alsharkawy: Review and editing.

Nuhu D. Mu'Azu: chemical analysis.

Sultan Akhtar Abdul Rashid: SEM analysis.

Muhammed Nawaz Noor Muhammed: FTIR analysis.

Author roles should be aligned with the target journal's Credit requirements before submission.

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The authors report that no external funding was received for this study.

### Conflict of interest

The authors declare no conflict of interest.

**Data availability**

The data supporting the findings of this study are available from the corresponding author on reasonable request. The numerical tables used for the statistical reanalysis are reproduced in the Supplementary Tables of this document.

**Ethics statement**

The study analysed commercially available food products and did not involve human participants or animals; institutional ethics approval was therefore not required.

**REFERENCES**

[1] Bae, S.-J., Shin, K.-S., Park, C., Baek, K., Son, S.-Y., & Sakong, J. (2023). Risk assessment of heavy metals in tuna from Japanese restaurants in the Republic of Korea. Annals of Occupational and Environmental Medicine, 35, e3. https://doi.org/10.35371/aoem.2023.35.e3

[2] European Commission. (2023). Commission Regulation (EU) 2023/915 on maximum levels for certain contaminants in food. Official Journal of the European Union.

[3] Gulf Cooperation Council Standardization Organization. (2021). GSO 193:2021: Contaminants and toxins in food and feed.

[4] Khalil, A. A. I., Hafez, A. A., Abd El-Alem, M. A., & Khalil, E. M. (2019). Characterization of a low-cost adsorbent material prepared from date palm kernel pits via DP-LIBS and ICP-OES spectroscopic techniques. Environmental Science and Pollution Research, 26, 20753–20768.

[5] Khalil, A. A. I., El-Deen, H. Z., & Hafez, A. I. (2022). Synthesis and characterisation of a low-cost sensor based on polymer nanocomposite for monitoring pollution and cross-validation using UV-LIPS. International Journal of Environmental Analytical Chemistry, 102(10), 2277–2304. https://doi.org/10.1080/03067319.2020.1753717

[6] Khalil, A. A. I., Labib, O. A., Mu'Azu, N. D., Chndrasekhararao, A. V., & Shemsi, A. M. (2023). Detection of micro-toxic heavy metals in commercial ink powder brands via orthogonal dual-pulse LIPS and ICP-OES. International Journal of Environmental Analytical Chemistry, 103, 8241–8265. https://doi.org/10.1080/03067319.2021.1983553

[7] Kosker, A. R., Gundogdu, S., Esatbeyoglu, T., Ayas, D., & Ozogul, F. (2023). Metal levels of canned fish sold in Türkiye: health risk assessment. Frontiers in Nutrition, 10, 1255857.

[8] Lehel, J., Papp, Z., Bartha, A., Palotás, P., Szabó, R., Budai, P., & Süth, M. (2023). Metal load of potentially toxic elements in tuna (Thunnus albacares): food safety aspects. Foods, 12(16), 3038.

[9] Mahalakshmi, M., Balakrishnan, S., Indira, K., & Srinivasan, M. (2012). Characteristic levels of heavy metals in canned tuna fish. Journal of Toxicology and Environmental Health Sciences, 4(2), 43–45.

[10] Miedico, O., Pompa, C., Moscatelli, S., Chiappinelli, A., Carosielli, L., & Chiaravalle, A. E. (2020). Lead, cadmium and mercury in canned and unprocessed tuna: six-years monitoring survey, comparison with previous studies and recommended tolerable limits. Journal of Food Composition and Analysis, 94, 103638.

[11] National Institute of Standards and Technology. Atomic Spectra Database. https://physics.nist.gov/asd

[12] Norhazirah, A. A., Shazili, N. A. M., Kamaruzzaman, Y., Sim, S. F., Ahmad, A., & Ong, M. C. (2020). Heavy metals in tuna species meat and potential consumer health risk: a review. IOP Conference Series: Earth and Environmental Science, 494, 012013.

[13] Oktariani, A. F., Sudaryatma, P. E., Ramona, Y., Wirasuta, I. M. G., Darmayasa, I. B. G., Wiradana, P. A., & Okabayashi, T. (2023). Heavy metals content in fresh tuna and swordfish caught from Indian and Pacific Oceans: health risk assessment of dietary exposure. Veterinary World, 16(4), 858–868.

[14] Saudi Food and Drug Authority. (2022). Aquaculture EU Manual 2022: chemical standards for shrimp and finfish products. SFDA, Kingdom of Saudi Arabia.

[15] Ulusoy, S. (2023). Determination of toxic metals in canned tuna sold in developed and developing countries: health risk assessment associated with human consumption. Marine Pollution Bulletin, 187, 114518.

[16] World Health Organization/JECFA. (2007). Methylmercury evaluation: PTWI 1.6 μg/kg body weight/week. JECFA database.

[17] World Health Organization/JECFA. (2011a). Lead evaluation: former PTWI withdrawn; no new health-protective PTWI established. 73rd JECFA meeting.

[18] World Health Organization/JECFA. (2011b). Aluminium-containing food additives: PTWI 2 mg/kg body weight/week. 74th JECFA meeting.
**[19]** World Health Organization/JECFA. (2021). Cadmium evaluation: PTMI 25 μg/kg body weight/month. JECFA database.

**SUPPLEMENTARY TABLES**

The following tables reproduce the brand-level concentration values used for the statistical reanalysis. They should be checked against the original laboratory spreadsheet before final submission.

**Supplementary Table S1.** ICP-OES concentrations of trace/potentially toxic elements (mg/kg).

| Sample | Zn | Pb | Al | Cd | Co | Cr | Cu | Ni | Hg |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 0.800 | 0.420 | 52.400 | 0.079 | 0.290 | 0.220 | 0.210 | 0.220 | 0.380 |
| 2 | 0.990 | 0.930 | 128.100 | 0.074 | 0.170 | 0.570 | 0.380 | 0.360 | 0.260 |
| 3 | 1.270 | 1.370 | 144.800 | 0.168 | 0.240 | 0.490 | 0.340 | 0.440 | 0.370 |
| 4 | 1.080 | 1.610 | 131.700 | 0.155 | 0.220 | 1.110 | 0.340 | 0.390 | 0.230 |
| 5 | 0.800 | 0.130 | 42.200 | 0.061 | 0.240 | 0.090 | 0.080 | 0.100 | 0.430 |
| 6 | 2.040 | 1.170 | 89.900 | 0.103 | 0.350 | 0.390 | 0.330 | 0.770 | 0.450 |
| 7 | 0.610 | 0.130 | 13.400 | 0.066 | 0.230 | 0.050 | 0.070 | 0.080 | 0.410 |
| 8 | 0.750 | 0.350 | 28.500 | 0.046 | 0.310 | 0.130 | 0.060 | 0.150 | 0.420 |
| 9 | 1.010 | 0.000 | 95.400 | 0.105 | 0.280 | 0.190 | 0.110 | 0.190 | 0.160 |
| 10 | 1.540 | 0.660 | 199.400 | 0.203 | 0.460 | 1.120 | 0.330 | 0.650 | 0.020 |
| 11 | 1.250 | 0.590 | 106.200 | 0.076 | 0.270 | 0.450 | 0.400 | 0.390 | 0.320 |
| 12 | 1.400 | 0.000 | 97.800 | 0.062 | 0.300 | 1.010 | 0.270 | 0.600 | 0.110 |
| 13 | 0.670 | 0.190 | 21.700 | 0.058 | 0.240 | 0.860 | 0.110 | 0.100 | 0.130 |
| 14 | 1.070 | 0.140 | 34.800 | 0.067 | 0.360 | 0.380 | 0.080 | 0.110 | 0.010 |

**Supplementary Table S2.** LIBS concentrations of trace/potentially toxic elements (mg/kg).

| Sample | Zn | Pb | Al | Cd | Co | Cr | Cu | Ni | Hg |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 0.760 | 0.380 | 48.700 | 0.048 | 0.220 | 0.090 | 0.081 | 0.096 | 0.095 |
| 2 | 0.910 | 0.870 | 123.800 | 0.036 | 0.110 | 0.320 | 0.150 | 0.130 | 0.086 |
| 3 | 1.210 | 1.310 | 143.900 | 0.148 | 0.150 | 0.380 | 0.120 | 0.180 | 0.098 |
| 4 | 1.020 | 1.540 | 126.500 | 0.127 | 0.150 | 1.050 | 0.110 | 0.140 | 0.084 |
| 5 | 0.750 | 0.080 | 38.600 | 0.018 | 0.160 | 0.018 | 0.058 | 0.065 | 0.130 |
| 6 | 1.960 | 1.120 | 85.600 | 0.068 | 0.270 | 0.170 | 0.100 | 0.260 | 0.140 |
| 7 | 0.570 | 0.080 | 0.960 | 0.017 | 0.170 | 0.016 | 0.027 | 0.027 | 0.110 |
| 8 | 0.710 | 0.310 | 23.500 | 0.013 | 0.250 | 0.049 | 0.024 | 0.081 | 0.120 |
| 9 | 0.940 | 0.000 | 91.500 | 0.064 | 0.170 | 0.050 | 0.078 | 0.084 | 0.058 |

| Sample | Zn | Pb | Al | Cd | Co | Cr | Cu | Ni | Hg |
|---|---|---|---|---|---|---|---|---|---|
| 10 | 1.490 | 0.610 | 198.800 | 0.201 | 0.190 | 1.090 | 0.100 | 0.270 | 0.009 |
| 11 | 1.190 | 0.470 | 101.700 | 0.025 | 0.180 | 0.190 | 0.170 | 0.150 | 0.087 |
| 12 | 1.350 | 0.000 | 92.600 | 0.019 | 0.240 | 0.940 | 0.082 | 0.240 | 0.036 |
| 13 | 0.620 | 0.130 | 18.400 | 0.016 | 0.150 | 0.510 | 0.077 | 0.660 | 0.054 |
| 14 | 1.030 | 0.090 | 31.400 | 0.027 | 0.280 | 0.160 | 0.057 | 0.067 | 0.007 |

**Supplementary Table S3.** Nutritionally relevant element concentrations by ICP-OES and LIBS

| Sample | Fe ICP | Mg ICP | Mn ICP | Na ICP | Ca ICP | Fe LIBS | Mg LIBS | Mn LIBS | Na LIBS | Ca LIBS |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 10.590 | 30.700 | 0.184 | 887.800 | 13.670 | 7.780 | 27.560 | 0.068 | 879.400 | 15.570 |
| 2 | 20.580 | 23.750 | 0.432 | 757.100 | 49.270 | 17.550 | 18.670 | 0.138 | 749.400 | 42.760 |
| 3 | 22.200 | 32.700 | 0.342 | 1086.000 | 29.360 | 19.430 | 28.570 | 0.116 | 1048.400 | 27.780 |
| 4 | 18.850 | 28.180 | 0.306 | 1105.500 | 43.630 | 15.770 | 24.680 | 0.105 | 1096.300 | 38.540 |
| 5 | 19.210 | 24.560 | 0.284 | 885.300 | 30.410 | 16.630 | 21.560 | 0.098 | 872.500 | 29.660 |
| 6 | 16.190 | 23.050 | 0.310 | 1439.800 | 61.840 | 13.540 | 18.630 | 0.109 | 1426.700 | 57.340 |
| 7 | 2.320 | 22.850 | 0.089 | 418.900 | 23.020 | 1.120 | 17.870 | 0.045 | 391.800 | 19.680 |
| 8 | 4.530 | 33.270 | 0.488 | 862.300 | 40.020 | 2.540 | 29.670 | 0.148 | 844.600 | 36.820 |
| 9 | 38.630 | 36.000 | 0.487 | 1061.800 | 58.880 | 33.890 | 32.680 | 0.147 | 1032.600 | 53.540 |
| 10 | 36.720 | 39.430 | 0.592 | 1510.000 | 37.620 | 32.650 | 35.720 | 0.165 | 1494.100 | 33.740 |
| 11 | 21.086 | 29.280 | 0.897 | 1285.300 | 54.560 | 18.650 | 25.890 | 0.857 | 1226.500 | 51.620 |
| 12 | 47.830 | 34.470 | 0.608 | 1089.800 | 25.450 | 42.920 | 31.760 | 0.281 | 1056.600 | 21.460 |
| 13 | 4.230 | 27.790 | 0.200 | 500.000 | 25.420 | 2.360 | 23.690 | 0.076 | 484.300 | 21.440 |
| 14 | 17.440 | 51.230 | 0.422 | 855.400 | 36.180 | 14.620 | 48.780 | 0.132 | 845.700 | 32.570 |