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# Levels of toxic metals in Dutch cucumbers biofortified (Fe–Zn) with chemically-modified spent coffee grounds

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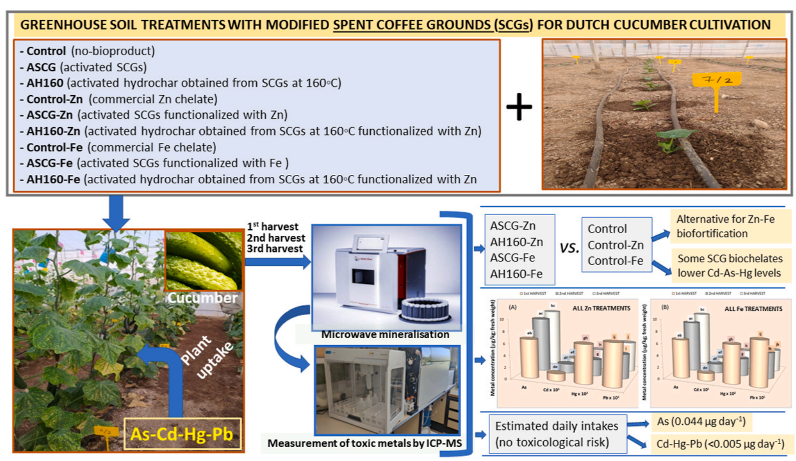
## HIGHLIGHTS

- Some biochelates of spent coffee grounds (SCGs) are alternative to Fe and Zn chelates.
- The four SCGs biochelates decreased the Cd concentrations in cucumber vs. control.
- Some SCGs biochelates decrease Hg and As levels cucumbers vs. commercial chelates.
- In successive harvests, As and Cd accumulate while Hg and Pb decrease in cucumbers.
- None of the estimated intakes of toxic metals poses any risk to human health.

## GRAPHICAL ABSTRACT

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## ABSTRACT

Spent coffee grounds (SCGs) are a form of biowaste that can be reused in agronomic biofortification with Zn and Fe to enhance environmental sustainability. Various chemical treatments of SCGs have been explored to reduce their known phytotoxicity. The aim of this study was to evaluate how different chemically modified SCGs used as soil amendments for iron (Fe) and zinc (Zn) biofortification of Dutch cucumbers under greenhouse conditions influence the accumulation of arsenic (As), cadmium (Cd), mercury (Hg), and lead (Pb). Cucumbers grown with SCGs activated with sodium hydroxide (NaOH) (ASCG) and all SCG-based biochelates showed reduced Cd concentrations compared to the control group ($p < 0.05$). Activated hydrochar derived from SCGs and

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functionalized with Fe (biochelate: AH160-Fe; 0.027 ± 0.019 μg $kg^{-1}$, fresh weight, f.w), or ASCG functionalized with Zn (biochelate: ASCG-Zn; 0.033 ± 0.025 μg $kg^{-1}$), reduced Hg levels relative to the control (0.050 ± 0.035 μg $kg^{-1}$; $p < 0.05$). Activated hydrochar produced from SCGs heated at 160 °C (AH160) decreased As concentrations (7.69 ± 1.41 μg $kg^{-1}$) compared to commercial Zn and Fe chelates (control-Zn: 9.57 ± 1.70 μg $kg^{-1}$ and control-Fe: 8.28 ± 1.38 μg $kg^{-1}$, respectively; $p < 0.05$). AH160 functionalized with Zn (biochelate AH160-Zn) and Fe (biochelate AH160-Fe) reduced As and Hg concentrations (8.51 ± 2.34 and 0.027 ± 0.019 μg $kg^{-1}$, respectively) compared to control-Zn and control-Fe (9.57 ± 1.70 and 0.049 ± 0.041 μg $kg^{-1}$, respectively; $p < 0.05$). Cucumbers harvested at later stages exhibited higher As and Cd levels, in contrast to Hg and Pb, which decreased over time. In conclusion, the four biochelates (ASCG-Zn, AH160-Zn, ASCG-Fe, and AH160-Fe) reduced Cd bioavailability in cucumbers (0.120, 0.126, 0.122, and 0.136 μg $kg^{-1}$, respectively), with ASCG-Zn and ASCG-Fe showing the most significant effect compared to the control (0.156 μg $kg^{-1}$). The tested biochelates present a promising alternative to commercial Zn and Fe chelates, enabling biofortification while simultaneously lowering Cd, Hg, and As levels. In subsequent harvests, As and Cd levels tend to increase, whereas Hg and Pb levels decrease. None of the estimated daily intakes of the analyzed toxic metals (0.0439, 0.0007, 0.0002, and 0.0027 μg $day^{-1}$ for As, Cd, Hg, and Pb, respectively) pose a risk to human health.

## 1. Introduction

Spent coffee grounds (SCGs) are a type of biowaste generated in large quantities during the coffee brewing process at both household and industrial levels, with global production estimated at approximately 6–8 million tons annually (Bevilacqua et al., 2023). SCGs contribute significantly to the carbon footprint and pose environmental concerns, particularly due to their direct application to croplands as organic amendments (Patrignani et al., 2025). Although SCGs can enhance soil organic matter, some of their components—such as polyphenolic compounds, caffeine, and melanoidins—have been shown to exert phytotoxic effects, reducing crop biomass (Cervera-Mata et al., 2019). For this reason, alternative reuse strategies involving treatment of SCGs are being investigated to mitigate these phytotoxic effects (Cervera-Mata et al., 2020).

Recently, SCGs have been studied as a potential alternative to commercial Zn and Fe chelates for crop biofortification (Cervera-Mata et al., 2021; Navajas-Porras et al., 2024a, 2024b). It has been demonstrated that activation of SCGs with NaOH or hydrothermal carbonization, followed by functionalization with Fe or Zn, can facilitate the production of Fe and Zn biochelates, offering a viable alternative to commercial chelates for biofortifying cucumbers under greenhouse conditions (Navajas-Porras et al., 2024a, 2024b).

Other studies have explored the potential of chemically modified SCGs in the bioremediation of toxic trace metals (As, Cd, Hg, and Pb) in crops grown on highly contaminated soils (Kim et al., 2014). For instance, magnetic biochar derived from SCGs has been proposed for $Cd^{2+}$ remediation (Hussain et al., 2020). Similarly, Chwastowski et al. (2020) found that fresh and pyrolyzed SCGs act as efficient adsorbents for removing $Cd^{2+}$ and $Pb^{2+}$ from aqueous solutions.

The mobilization of arsenic (As) from soils has been associated with dissolved organic matter and Fe oxides, and it is known that organic matter can enhance As leaching from mineral surfaces (Aftabtalab et al., 2022). Biochar derived from SCGs, due to its dissolved organic carbon content, has been shown to promote As mobilization in contaminated soils (Kim et al., 2018). Additionally, post-calcined SCG biochar decorated with a double-layered magnesium/aluminum hydroxide has been identified as a promising adsorbent for $As^{5+}$ in water matrices (Shin et al., 2024).

Cadmium (Cd) is highly bioavailable to plants and tends to accumulate in soil due to the continuous input of industrial waste, municipal sludge, and phosphate fertilizers, even without causing phytotoxic effects (Huang et al., 2003). Only a small fraction of Cd is removed via crop uptake (Nicholson et al., 1994), resulting in its progressive accumulation and potential health risks.

Mercury (Hg) induces oxidative stress in cucumber seeds, leading to plant damage and reduced growth (Cargnelutti et al., 2006). However, Zn has been reported to mitigate Hg toxicity in rice, likely due to a Zn–Hg antagonistic interaction (Li et al., 2024a). Therefore, Zn supplementation may serve a dual role: enhancing Zn content in crops and reducing Hg toxicity (Li et al., 2024a).

Regarding lead (Pb), SCGs have been shown to efficiently remove Pb from drinking and industrial waters (Lavecchia et al., 2016). Moreover, Kim et al. (2023) improved Pb adsorption using an electrochemical activation method for SCG biochar, enhancing the material's surface hydroxyl and carboxyl groups. Cucumber peel has also demonstrated Pb adsorption capacity, attributed to its carboxyl and phosphate groups (Basu et al., 2017), and this adsorption appears to be enhanced in the presence of Cd.

Heavy metals are soil pollutants that accumulate in plants and animals, ultimately entering the human food chain (Liang et al., 2019). Factors such as soil pH and organic content are critical in determining metal uptake by plants (Wu et al., 2018), along with ionic strength and dissolved organic carbon (Lara-Ramos et al., 2023).

Toxic metal concentrations were determined using Inductively Coupled Plasma–Mass Spectrometry (ICP-MS/MS), a technique that, along with ICP–Optical Emission Spectrometry (ICP-OES), is highly sensitive and time-efficient (Kargarghomsheh et al., 2024). Sample preparation involved microwave-assisted acid digestion, one of the most accurate and practical methods available (Moazzen et al., 2025).

A major limitation of previous studies conducted by our research group on SCG treatments to reduce phytotoxicity, and their activation and/or functionalization with Zn and Fe as soil amendments, is that they were conducted under controlled laboratory conditions in a bioclimatic chamber, and focused on baby lettuce, a crop unsuitable for assessing successive harvests (Cervera-Mata et al., 2019, 2020, 2021). Two subsequent studies tested the biofortification potential of Zn and Fe biochelates as alternatives to commercial chelates in cucumbers grown in greenhouses (Navajas-Porras et al., 2024a, 2024b), but they did not evaluate the impact on toxic metal accumulation or the potential dietary risk to consumers—key aspects addressed in the current study.

To date, no studies have evaluated the use of SCGs subjected to different activation and functionalization processes with Fe and Zn on the concentration of toxic trace metals (As, Cd, Hg, and Pb) in Dutch cucumbers cultivated under greenhouse conditions. It remains unknown whether the previously observed biofortification effects on Fe and Zn influence the final content of these toxic metals, or whether this effect changes across successive harvests throughout the plant's biological cycle (Navajas-Porras et al., 2024a, 2024b). In summary, this study aimed to evaluate the influence of chemically treated SCGs on the bioavailability of As, Cd, Hg, and Pb and their evolution in successive harvests of Dutch cucumbers, compared to a control group (no bioproduct added) and two additional groups supplemented with commercial Fe and Zn chelates. Additionally, the study sought to estimate the daily dietary intake of these toxic trace metals and determine their contribution to the provisional tolerable weekly intake (PTWI), in order to assess the potential health risks associated with cucumber consumption.

## 2. Materials and methods

### 2.1. SCG bioproducts, commercial Zn and Fe chelates, and control group

Spent coffee grounds (SCGs) were obtained from the cafeteria of the Faculty of Pharmacy (University of Granada). They were spread in a thin layer and dried at room temperature (18–21 °C) for 7 days to eliminate residual moisture.

To obtain the different bioproducts from SCGs, various treatments were applied, resulting in six experimental groups (Table 1): two activation treatments (SCGs activated with NaOH: ASCG; hydrochar derived from SCGs at 160 °C: AH160), two activation and Zn-functionalization treatments referred to as biochelates (Zn-functionalized activated SCGs: ASCG-Zn; Zn-functionalized hydrochar from SCGs at 160 °C: AH160-Zn), and two Fe-functionalized biochelates (Fe-functionalized activated SCGs: ASCG-Fe; Fe-functionalized hydrochar from SCGs at 160 °C: AH160-Fe) (Navajas-Porras et al., 2024a, 2024b).

Additionally, two treatments with commercial chelates—Zn-EDTA (control-Zn) and Fe-EDDHA (control-Fe)—commonly used in agriculture for crop biofortification were included (Table 1). A control group was also established using greenhouse soil without the addition of SCG bioproducts or commercial chelates (Table 1).

### 2.2. Reagents

The following reagents were used: 69 % nitric acid ($HNO_3$, TraceSELECT, Honeywell Fluka, France), 30 % hydrogen peroxide ($H_2O_2$, Merck Suprapur, Darmstadt, Germany), 36.5–38 % hydrochloric acid (HCl, Baker Instra-Analyzed®, PA, USA), and Milli-Q water (15.0 mΩ cm; Elix® 15, Merck Millipore, France).

For metal quantification, a multielement ICP calibration standard (As, Cd, Pb at 10 mg $L^{-1}$ in 2 % $HNO_3$; Reagecon, Ireland) and a mercury standard solution (Hg at 10 mg $L^{-1}$ in 2 % $HNO_3$; Reagecon, Ireland) were used. Internal standardization was performed with an Internal Standard Kit (Ge, Ir, Rh, Sc at 20 mg $L^{-1}$ in 2 % $HNO_3$; ISC Science, Spain). An ICP-MS tuning solution (Ce, Co, Li, Tl, Y at 10 mg $L^{-1}$ in 2 % $HNO_3$; Agilent Technologies, USA) was also used.

The commercial Zn and Fe chelates were EDTA-Zn (14 % w/w) and EDDHA-Fe (6 % w/w) (Trade Corporation International, S.A.U., Madrid, Spain).

**Table 1**
Description of soil treatments applied in the greenhouse experiment for Zn and Fe biofortification.

| Soil treatments for Zn biofortification | | | |
|---|---|---|---|
| Soil treatments for Zn biofortification | Characteristics | Soil treatments for Fe biofortification | Characteristics |
| Control | No bio-product applied | Control | No bio-product applied |
| Control-Zn | Commercial Zn chelate (EDTA-Zn, 14 % w $w^{-1}$) | Control-Fe | Commercial Fe chelate (EDDHA-Fe, 6 % w $w^{-1}$) |
| ASCGs | Activated spent coffee grounds (SCGs) | ASCGs | Activated spent coffee grounds (SCGs) |
| AH160 | Activated hydrochar from SCGs obtained at 160 °C | AH160 | Activated hydrochar from SCGs obtained at 160 °C |
| ASCG-Zn | Activated SCGs functionalized with Zn | ASCG-Fe | Activated SCGs functionalized with Fe |
| AH160-Zn | Activated hydrochar from SCGs at 160 °C functionalized with Zn | AH160-Fe | Activated hydrochar from SCGs at 160 °C functionalized with Fe |

Certified reference materials used for method validation were “Bovine muscle powder No. 8414” and “Apple leaves No. 1515” (NIST, Gaithersburg, MD, USA).

### 2.3. Greenhouse experiment and crop maintenance

Greenhouse cultivation conditions for Dutch cucumbers are described in detail elsewhere (Navajas-Porras et al., 2024a). SCG bioproducts (ASCG, AH160, ASCG-Zn, AH160-Zn, ASCG-Fe, and AH160-Fe) were applied at a rate of 0.2 % to prevent phytotoxicity (Uchimiya et al., 2020).

Three additional treatments were established: a control (no amendment) and two treatments with commercial Zn or Fe chelates at 10 mg $kg^{-1}$ soil (control-Zn and control-Fe) (Navajas-Porras et al., 2024a, 2024b). Crop maintenance conditions were identical to those described in previous work (Navajas-Porras et al., 2024a).

### 2.4. Plant sampling, processing, and trace metal determination

Cucumbers were harvested after 105 days of cultivation. Three harvests were conducted over the plant’s biological cycle. Fruits were washed, chopped, and dried in aluminum trays at room temperature for 48 h, then oven-dried at 50 °C for 72 h. After drying, samples were weighed (dry weight), milled, and stored at room temperature until analysis.

For trace metal analysis, 0.200 g of dried, homogenized sample was weighed (Ohaus PA224C, Switzerland) in borosilicate tubes. Each tube received 3 mL $HNO_3$ (69 %), 0.5 mL $H_2O_2$ (30 %), and 0.5 mL Milli-Q water. An additional 3 mL of 11.5 % $HNO_3$ was added to Teflon cups (Microwave digester: Multiwave 5000, Rotor 24HVT50, Anton Paar, Austria). Digestion was performed using a time–temperature program (20 min, 150–185 °C) (Navajas-Porras et al., 2024a).

After digestion, samples were diluted to 50 mL with Milli-Q water. As, Cd, Hg, and Pb concentrations were determined via ICP-MS/MS (Agilent 8900 Triple Quadrupole, Agilent Technologies Inc., Santa Clara, CA, USA). All samples were analyzed in triplicate with three blanks included. Final results were expressed as μg $kg^{-1}$ fresh weight (f. w.).

The ICP-MS/MS experimental conditions used for the determination of the toxic trace metals analyzed were as follows. Regarding instrument configuration, a MicroMist nebulizer, an integrated sample introduction system (ISIS), an SPS4 autosampler, aqueous solution plasma ignition mode, and x-lens ion lenses were employed. Argon gas (grade 6) was used as the carrier gas for the auxiliary, nebulizer, and plasma flows, under the optimal operating parameters of the RF generator (power: 1550 W). In this study, the flow rates of the nebulizer, auxiliary, and plasma gases were 1.01, 0.9, and 15.0 L $min^{-1}$, respectively. Sample stabilization, rinsing, and uptake times were set to 2 min and 58 s. The helium flow rate in the collision/reaction cell was 4.5 mL $min^{-1}$. The nebulizer pump speed was set to 0.10 rps, and the spray chamber (S/C) temperature was maintained at 2 °C. For the final determination of toxic metals, calibration curves were constructed using multielement standard solutions (for As, Cd, and Pb) and a separate Hg ICP standard, prepared by serial dilutions. A standard internal solution kit was used at a concentration of 400 μg $L^{-1}$ in 2 % $HNO_3$.

### 2.5. Quality assurance and quality control

Detection limits (LOD) were 0.06, 0.05, 0.09, and 0.07 μg $L^{-1}$ for As, Cd, Hg, and Pb, respectively. For method accuracy (n = 10), concentrations of As, Cd, Hg, and Pb in NIST 8414 and NIST 1515 were: 0.009 ± 0.001, 0.006 ± 0.002, 0.014 ± 0.005, and 0.41 ± 0.08 μg $g^{-1}$, and 0.0370 ± 0.002, 0.0130 ± 0.0020, and 0.0410 ± 0.0018 μg $g^{-1}$, respectively, compared with certified values of 0.009 ± 0.003, 0.005 ± 0.003, 0.013 ± 0.011, 0.38 ± 0.24 and 0.0380 ± 0.0070, 0.0132 ± 0.0015, 0.0432 ± 0.0018, 0.470 ± 0.024 μg $g^{-1}$, showing no significant differences ($p > 0.05$). Recovery values ranged from 95.8 % to 104.5 %. The mean coefficient of variation was 6.83 ± 3.2 %.

### 2.6. Estimated toxic metal intake and health risk assessment

Estimated daily intake (EDI; μg $day^{-1}$) was calculated using:

$$EDI = C \times CDI$$

where C is the metal concentration (μg $g^{-1}$, f.w.), and CDI is cucumber daily intake (5.2 g $day^{-1}$; Mercasa, 2023).

Estimated weekly intake (EWI; μg $kg^{-1}$ bw $week^{-1}$) was calculated as:

$$EWI = (EDI \times 7) / ABW$$

where ABW is average adult body weight in Spain (63 kg for women, 77.5 kg for men; El Mundo, 2024).

Health risk was assessed using the percentage of Provisional Tolerable Weekly Intake (%PTWI):

$$\%PTWI = (EWI / PTWI) \times 100$$

PTWIs: As = 15, Cd = 7, Hg = 5, Pb = 25 μg $kg^{-1}$ bw $week^{-1}$ (EFSA, 2009a, 2009b, 2010, 2012).

Estimated intake per cucumber serving size: (EICSS,μg) was also calculated:

EICSS = C x CSS

Where CSS is the cucumber serving size (150–200 g; Sociedad Española de Nutrición Comunitaria, 2003).

### 2.7. Statistical analysis

Data normality was assessed via the Kolmogorov–Smirnov test, and homoscedasticity with the Levene test. Parametric data were analyzed using the Student's t-test, and non-parametric data with the Kruskal–Wallis test. Correlations among metal concentrations in cucumbers were assessed using Pearson's or Spearman's correlation coefficients, depending on distribution. Statistical significance was set at $p < 0.05$, and SPSS 26.0 for Windows (IBM SPSS Inc., USA) was used for data analysis.

## 3. Results and discussion

In this section, the effects of adding different bioproducts to the soil (compared to controls) on the content of various heavy metals in harvested Dutch cucumbers are described and discussed. Additionally, the influence of different harvest times is also addressed.

### 3.1. Effects on As content

Regarding the levels of As in greenhouse-grown cucumbers (Fig. 1A), control-Zn (9.57 ± 1.70 μg kg⁻1) led to the highest As accumulation ($p < 0.05$). Previous work reported that Zn uptake efficiency by cucumbers is higher when using Zn biochelates (ASCG-Zn and AH160-Zn; $p < 0.05$) compared to control-Zn (Navajas-Porras et al., 2024a). Therefore, to obtain cucumbers that are both low in As and biofortified with Zn, AH160-Zn is recommended (8.51 ± 2.34 μg $kg^{-1}$; Fig. 1A). It was also observed that ASCG, AH160, and AH160-Zn reduced As content compared to the Zn-control, likely due to the adsorptive capacity of activated and/or functionalized SCGs, which could limit As availability in the soil and thus its uptake by cucumber plants. In line with this, Kim et al. (2018) reported that SCG biochar facilitates As mobilization from highly contaminated soils, supporting our findings. Similarly, post-calcination of SCG biochar has been shown to enhance $As^{5+}$ adsorption in aqueous matrices (Shin et al., 2024). Additionally, high

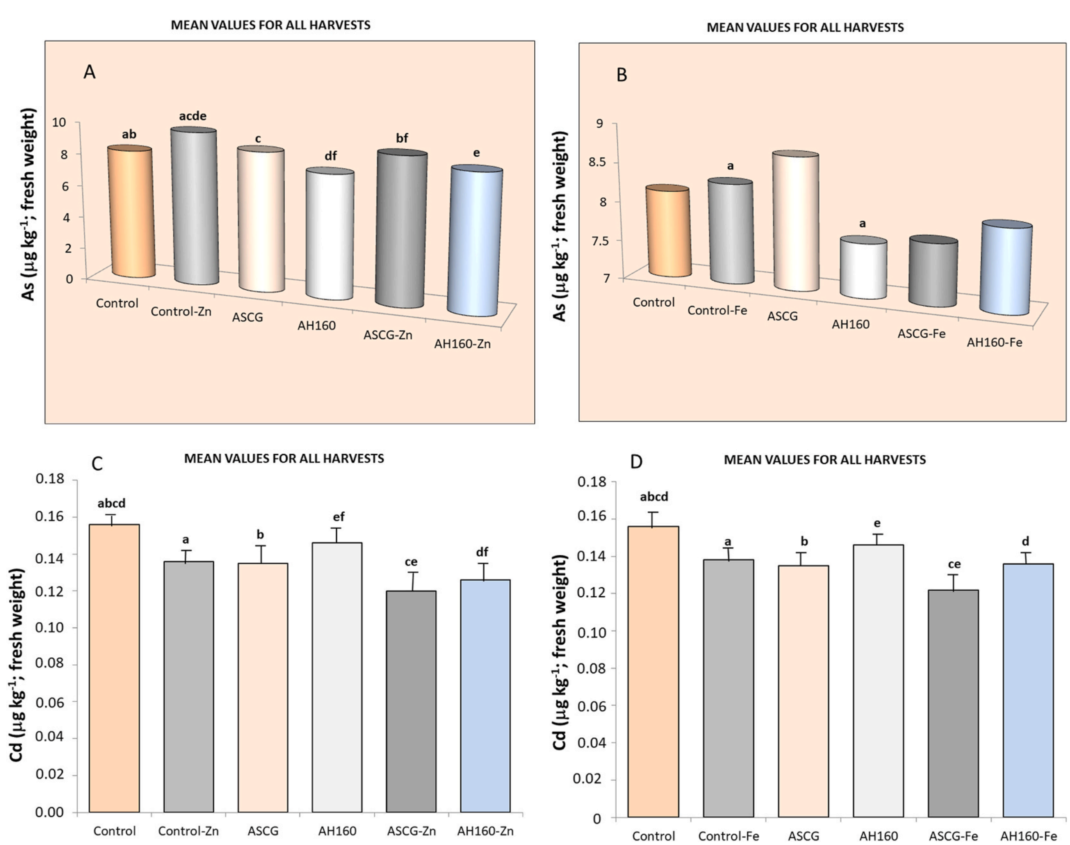


**Fig. 1.** Mean concentrations of As and Cd in cucumbers grown under greenhouse conditions across all experimental groups included in Zn (A, C) and Fe (B, D) biofortification, respectively. Equal letters on the bars in each figure indicate statistically significant differences among the experimental groups ($p < 0.05$).

levels of dissolved organic matter are known to promote As mobilization from soils (Aftabtalab et al., 2022). In our study, the addition of chemically modified SCGs as soil amendments led to low As mobilization, likely aided by the low organic matter content of the greenhouse soil (1.35 %) (Navajas-Porras et al., 2024a). However, we could not determine whether chemically modified SCGs promoted As accumulation in other parts of the cucumber plant (e.g., root, leaf, or stem), which requires further investigation.

Caution is warranted regarding the combined toxicity of As and Zn, especially in acidic soils, due to their potential synergistic effects on plant growth (Kader et al., 2017). A positive correlation between As and Zn concentrations was also observed in cucumbers grown under greenhouse conditions, albeit at low levels (Table 2).

Conversely, cucumbers grown with ASCG-Fe and AH160-Fe showed no significant differences in As levels compared to those grown with control-Fe (8.28 ± 1.38 μg kg-1; Fig. 1B). The control-Fe group only showed higher As content than the AH160 treatment (7.69 ± 1.41 μg $kg^{-1}$). Therefore, AH160-Fe is recommended for Fe biofortification (Navajas-Porras et al., 2024b), as it does not increase As levels. Likewise, AH160 alone should be considered, as it decreases As content relative to the Fe-control, and exhibits the second-highest Fe utilization efficiency in cucumbers (Navajas-Porras et al., 2024b).

As previously noted, further studies are needed to determine whether As accumulated in non-edible plant tissues or was taken up by soil microbiota. The role of soil microbes (bacteria and fungi) in reducing heavy metal bioavailability in rice—and their potential in other crops—has been demonstrated (Gerényi et al., 2017). Interestingly, we observed a negative linear correlation between As and Fe concentrations (Table 2). Similarly, Tian et al. (2020) reported that cucumber plants developed resistance to As toxicity when Fe ascorbate was added to the nutrient solution.

The mean As content in cucumbers from this study (8.43 ± 2.07 μg $kg^{-1}$) is lower than those reported in China (380 ± 46 μg $kg^{-1}$, d.w.; Song et al., 2019) and Iran (57.8 ± 65.6 μg $kg^{-1}$ in fermented pickled cucumbers, Jannat et al., 2021, and 33.6 ± 18.1 μg $kg^{-1}$, Ghalhari et al., 2024).

### 3.2. Effects on Cd content

Generally, Cd removal from agricultural soils is limited (Nicholson et al., 1994; Huang et al., 2003), consistent with the low mean Cd concentrations found in our cucumbers (0.136 ± 0.045 μg $kg^{-1}$). Cd accumulation is typically lower in cucumber fruit compared to roots, stems, or leaves (Mao et al., 2021). However, Nicholson et al. (1994) reported significant Cd accumulation in both cucumber plants and fruits.

In our study, Cd levels in the control group (0.156 ± 0.049 μg $kg^{-1}$) were significantly higher than in cucumbers treated with ASCG, the four biochelates (ASCG-Zn: 0.120 ± 0.045 μg $kg^{-1}$, AH160-Zn: 0.126 ± 0.030 μg $kg^{-1}$; ASCG-Fe: 0.121 ± 0.025 μg $kg^{-1}$; and AH160-Fe: 0.136 ± 0.045 μg $kg^{-1}$), or the control-Zn and control-Fe (Fig. 1C and D; $p < 0.05$). These findings support Hussain et al. (2020), who indicated that magnetic SCG biochar is an effective $Cd^{2+}$ adsorbent. Other studies also support the use of fresh or pyrolyzed SCGs as highly efficient $Cd^{2+}$ adsorbents (Cervera-Mata et al., 2019; Kim and Kim, 2020; Chwastowski et al., 2020). The low Cd levels found in cucumbers grown in SCG-amended soils (except AH160) may be attributed to: i) the adsorptive capacity of chemically modified SCGs; ii) the direct addition of Zn and Fe in the biochelates (0.2 % w $w^{-1}$), which may also explain why cucumbers grown with commercial Zn and Fe chelates (10 mg $kg^{-1}$) had lower Cd levels than the control group. Antagonistic interactions between Cd and Zn are well-documented, leading to reduced Cd availability in crops like wheat and rice (Sarwar et al., 2015; Yang et al., 2020). For Fe, its use as fertilizer not only promotes growth but also reduces Cd toxicity, especially in rice (Liu et al., 2017). Nevertheless, we observed a positive linear correlation between Cd and Zn, and between Cd and Fe concentrations in cucumbers across all treatments (Table 2).

A noteworthy finding is that all SCG biochelates reduced Cd uptake while enabling Zn or Fe biofortification (Navajas-Porras et al., 2024a, 2024b), highlighting their potential as alternatives to commercial chelates.

The mean Cd content in cucumbers from this study (0.136 ± 0.045 μg $kg^{-1}$) is lower than values reported in Spain (Tarragona: 5.00 ± 2.00 and 105 ± 103 μg $kg^{-1}$, Bosque et al., 1990), Egypt (44.0 ± 3.00 μg $kg^{-1}$, Mansour et al., 2009), Nigeria (471 μg $kg^{-1}$, Fadina et al., 2021), and Iran (57.80 ± 65.60 μg $kg^{-1}$ in fermented cucumbers, Jannat et al., 2021, and 35.22 ± 18.67 μg $kg^{-1}$, Ghalhari et al., 2024).

### 3.3. Effects on Hg content

In Dutch cucumbers, control plants (0.050 ± 0.035 μg $kg^{-1}$) exhibited significantly higher Hg levels than those grown with ASCG (0.036 ± 0.027 μg $kg^{-1}$; Fig. 2A and B), ASCG-Zn (0.033 ± 0.025 μg $kg^{-1}$; Fig. 2A), and AH160-Fe (0.027 ± 0.019 μg $kg^{-1}$; Fig. 2B) ($p < 0.05$). Thus, ASCG-Zn and AH160-Fe biochelates are promising options for minimizing Hg accumulation while supporting Zn and Fe biofortification (Navajas-Porras et al., 2024a, 2024b).

It is important to note that the Hg in cucumbers is inorganic, with lower human toxicity than methylmercury.

A negative correlation was observed between Hg and both As and Zn, while positive correlations were found with Pb and Fe (Table 2). Elemental interactions are known to be complex and influence the uptake of toxic trace metals in crops (Adamczyk-Szabela et al., 2020). In particular, the negative correlation between Hg and Zn observed here may be due to Zn's protective role against Hg toxicity, as reported in rice (Li et al., 2024a), which may also apply to Dutch cucumbers.

The mean Hg level in this study (0.041 ± 0.029 μg $kg^{-1}$) is lower than those found in China: 0.870 ± 0.240 μg $kg^{-1}$ in grocery samples and 9.870 ± 0.110 to 38.45 ± 1.40 μg $kg^{-1}$ near coal-fired power plants (Li et al., 2017).

**Table 2**
Pearson's or Spearman's linear correlation coefficients (r) and significance levels (p-values) between toxic trace metals (As, Cd, Hg, and Pb) and micronutrients (Zn and Fe) in Dutch cucumber samples from all treatments.

| Metal | As | | Cd | | Hg | | Pb | |
|---|---|---|---|---|---|---|---|---|
| | r | p | r | p* | r | p* | r | p* |
| As | | | 0.102 | 0.030 | −0.356 | <0.001 | −0.356 | <0.001 |
| Cd | 0.102 | 0.030 | – | – | – | ns | – | ns |
| Hg | −0.356 | <0.001 | – | ns | – | – | 0.438 | <0.001 |
| Pb | −0.356 | <0.001 | – | ns | 0.438 | <0.001 | – | – |
| Zn | 0.319 | <0.001 | 0.367 | <0.001 | −0.277 | <0.001 | – | ns |
| Fe | −0.113 | 0.025 | 0.200 | <0.001 | 0.152 | 0.003 | 0.369 | <0.001 |

*p values lower than 0.05 denotes the existence of a statistically significant correlation between metals. ns: not significant.

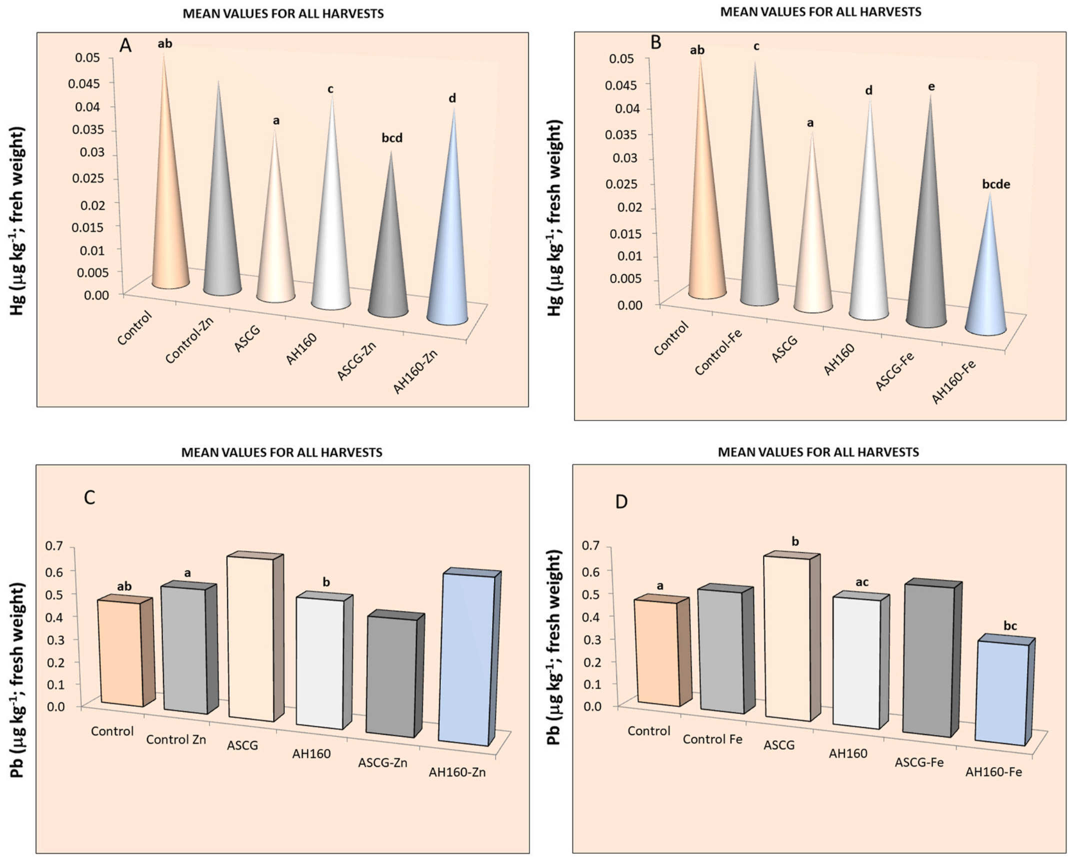


**Fig. 2.** Mean concentrations of Hg and Pb in cucumbers grown under greenhouse conditions across all experimental groups included in Zn (A, C) and Fe (B, D) biofortification, respectively. Equal letters on the bars in each figure indicate statistically significant differences among the experimental groups ($p < 0.05$).

### 3.4. Effects on Pb content

Cucumbers in the control group (0.458 ± 0.278 µg $kg^{-1}$ had significantly lower Pb levels than those in the control-Zn (0.542 ± 0.244 µg $kg^{-1}$; Fig. 2C) and AH160 (0.541 ± 0.249 µg $kg^{-1}$; Fig. 2C and D) groups ($p < 0.05$). Soil amendment with ASCG or AH160 increased Pb content in cucumbers, an effect that disappeared when SCGs were functionalized with Zn or Fe. Therefore, to avoid increasing Pb content while promoting Zn or Fe biofortification, the use of ASCG-Zn, AH160-Zn, ASCG-Fe, or AH160-Fe is recommended (Navajas-Porras et al., 2024a, 2024b), since control-Zn and activated SCGs were associated with increased Pb accumulation compared to the control.

Fresh SCGs have been used successfully to adsorb Pb in water (Li et al., 2024b), and similar results were obtained using SCG biochar (Chwastowski et al., 2020). Electrochemical activation of SCG biochar increases –COOH and –OH groups, enhancing Pb adsorption in wastewater (Kim et al., 2023). However, in our study, ASCG and AH160 increased Pb accumulation, suggesting Pb retention by SCGs may not have occurred. Basu et al. (2017) also noted that Pb preferentially accumulates in cucumber skin, due to its carboxyl and phosphate group content.

No linear correlation was found between Pb and Cd (Table 2), although in star grass, soil Pb increased bioavailable Cd (Madyiwa et al., 2004). Other authors suggested that Pb competes with Cd for adsorption sites on soil organic matter, with Pb having higher affinity, reducing Cd binding (Li et al., 2024b). In contrast, in our study, ASCG and AH160 increased soil organic matter, which was associated with increased Pb and decreased Cd content in cucumbers (in ASCG, ASCG-Zn, AH160-Zn, ASCG-Fe, AH160-Fe treatments). These findings suggest a different Pb–Cd interaction mechanism in SCG systems than previously described, a discrepancy that requires further study.

The mean Pb content in this study (0.511 ± 0.392 µg $kg^{-1}$) was higher than in Bosnia Herzegovina or Nigeria (not detected) (Murtić and Zahirović, 2019; Fadina et al., 2021; respectively), and lower than in Spain (Tarragona): 78.0 ± 98.0 and 64.0 ± 48.0 µg $kg^{-1}$ (Bosque et al., 1990), Egypt (: 260 µg $kg^{-1}$; Mansour et al., 2009), Nigeria (13.2 and 9.81 µg $kg^{-1}$) in washed and unwashed cucumbers (Igwegbe et al., 2013), Iran (113.5 ± 74.6 µg $kg^{-1}$ in pickled cucumbers, Jannat et al., 2021; 33.8 ± 6.27 µg $kg^{-1}$, Ghalhari et al., 2024), and Malaysia (30–120 µg $kg^{-1}$, Yap et al., 2024).

### 3.5. Impact of harvesting on toxic trace metal content

Previous studies have shown that the use of chemically modified SCGs not only facilitates their reuse (Cervera-Mata et al., 2020, 2021) but also enables agronomic biofortification with Zn (Navajas-Porras et al., 2024a) and Fe (Navajas-Porras et al., 2024b) in cucumbers grown under greenhouse conditions.

An interesting finding of the present study is that, when considering all treatments together (Fig. 3A and B) or separately (Fig. 4A and B for As; Fig. 4C and D for Cd; Fig. 4E and F for Hg; and Fig. 4G and H for Pb), the mean concentrations of toxic trace metals in Dutch cucumbers varied across the three successive harvests during the plant's biological cycle ($p < 0.05$).

Notably, As and Cd levels increased over time ($p < 0.05$), a relevant and previously unreported observation. This suggests that in soils heavily contaminated with these metals, later harvests may result in higher As and Cd accumulation in the edible portion ($p < 0.05$).

In contrast, Hg and Pb levels were highest in the first harvest, then decreased in the subsequent ones. Therefore, in soils with elevated Hg and Pb contamination, the first harvest may pose the greatest toxicological risk to consumers.

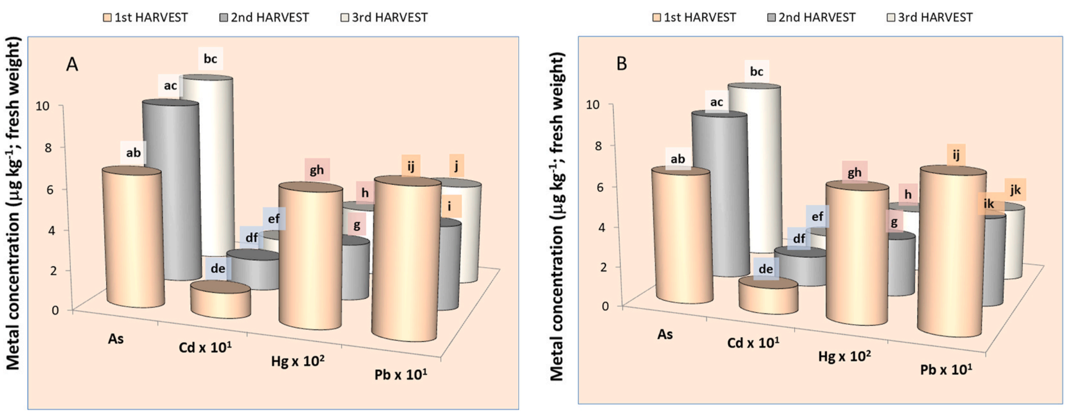


**Fig. 3.** Mean concentrations of As, Cd, Hg, and Pb in cucumbers grown under greenhouse conditions across successive harvests, considering all experimental groups together, for (A) Zn and (B) Fe biofortification. Equal letters on the bars in each figure indicate statistically significant differences among harvests ($p < 0.05$).

The observed influence of harvest time on heavy metal content in cucumbers may be explained by several factors. First, metal concentrations in soil could change due to extraction by plants and the effect of incorporated bioproducts. Second, plant age may affect nutrient absorption, as observed with other essential elements such as nitrogen and potassium. Therefore, more mechanistic studies are required to validate these hypotheses.

### *3.6. Estimation of dietary exposure to toxic metals in cucumbers and health risk assessment*

In the present study, we found that neither the intake per serving nor the EDI of toxic trace metals in cucumbers pose a health risk to humans (Table 3). The highest values were observed for As, with an EDI of 0.044 µg day$^{-1}$ and an EWI of 0.004 µg kg$^{-1}$ bw for adult men and 0.005 µg kg$^{-1}$ bw for adult women (Table 3). Additionally, the %PTWI covered was less than 0.04 % for women.

For Cd, Hg, and Pb, the %PTWI coverage was below 0.002 %, indicating that the weekly intake per kg of body weight of toxic metals from cucumber consumption is negligible. These values are well below the toxicity thresholds established by EFSA for As, inorganic Hg, and methyl-Hg (EFSA, 2009a, 2012).

Similarly, Pb toxicity from cucumbers appears negligible, even though EFSA was unable to establish a PTWI for Pb due to its potential risks (EFSA, 2010). For Cd, EFSA set a tolerable weekly intake of 2.5 µg kg$^{-1}$ bw, from which an internal dose threshold was also derived (EFSA, 2009b).

It is important to note that these estimates are based solely on cucumber consumption, and future studies should include all dietary sources to provide more comprehensive exposure assessments for specific populations.

Comparing our results with previous studies, the EDI of Cd (0.001 µg day$^{-1}$) in our cucumbers is lower than that reported in Nigeria for control group samples (0.200 µg day$^{-1}$; Fadina et al., 2021). Similarly, the EDI for Pb (0.003 µg day$^{-1}$) in our study is lower than values reported for cucumbers from peninsular Malaysia (0.200–0.740 µg kg$^{-1}$ day$^{-1}$ for adults and 0.310–1.18 µg kg$^{-1}$ day$^{-1}$ for children; Yap et al., 2024).

Finally, in contrast to the findings of the present study, Ghalhari et al. (2024) reported a health risk index for children based on the As content in cucumbers. They suggested that this risk could be mitigated by reducing soil As levels using remediation techniques, monitoring soil As concentrations, and implementing organic farming practices that avoid the use of fertilizers and pesticides (Ghalhari et al., 2024). Likewise, a study conducted in China found that the total probable weekly intake of Hg (4.36 µg kg$^{-1}$ wk$^{-1}$) was several times higher than the tolerable limit, indicating significant toxicity concerns (Li et al., 2017).

## 4. Conclusions

In general, SCG-derived biochelates are effective in decreasing the uptake of toxic elements (by limiting their availability in the soil) while enabling the biofortification of Dutch cucumbers with Fe or Zn. In the case of As, the most effective products for simultaneous biofortification and As reduction were AH160-Zn and AH160-Fe. For Cd, all four SCG biochelates tested reduced Cd uptake in cucumbers, while also contributing to Zn or Fe enrichment. Cucumbers grown with ASCG, ASCG-Zn, and AH160-Fe accumulated lower Hg levels, while being enriched in Zn and Fe. To avoid increasing Pb content in cucumbers while achieving biofortification with Zn or Fe, ASCG-Zn, AH160-Zn, ASCG-Fe, and AH160-Fe are recommended, since commercial Zn chelates and unmodified activated SCGs were associated with increased Pb levels. On the other hand, across the three successive harvests, As and Cd levels increased, whereas Hg and Pb levels decreased in Dutch cucumbers.

Finally, neither the intake per serving nor the estimated daily intake of As, Cd, Hg, or Pb from the analyzed cucumbers poses toxicity concerns for adults. These findings reinforce the potential of chemically modified SCGs as organic soil amendments, as they reduce heavy metal accumulation while offering a sustainable alternative to commercial Zn and Fe chelates. This approach supports a circular economy strategy and enhances environmental sustainability.

One of the main limitations of the present study lies in the complexity of incorporating the activated and functionalized SCGs (bioproducts) into greenhouse soils. To achieve this, holes measuring 20 cm in depth and 15 cm in diameter were dug, and the extracted soil (4 kg) was mixed in a concrete mixer with the bioproduct to obtain a homogeneous mixture with a final concentration of 0.2 %. For future studies, it would be advisable to design pelletized forms of the bioproducts that could be directly incorporated into greenhouse soils, allowing them to gradually dissolve with irrigation water as a precursor to plant absorption.

## CRediT authorship contribution statement

**Miguel Navarro-Moreno:** Methodology, Investigation, Formal analysis, Data curation. **Ana Cervera-Mata:** Methodology, Investigation. **Alejandro Fernández-Arteaga:** Methodology, Investigation, Conceptualization. **Silvia Pastoriza:** Methodology, Investigation. **Leslie Lara-Ramos:** Methodology, Investigation, Data curation. **Gabriel Delgado:** Writing – review & editing, Writing – original draft, Conceptualization. **Miguel Navarro-Alarcón:** Writing – review & editing, Writing – original draft, Visualization, Supervision, Software, Formal analysis, Data curation, Conceptualization. **José Ángel Rufián-Henares:** Writing – review & editing, Writing – original draft,

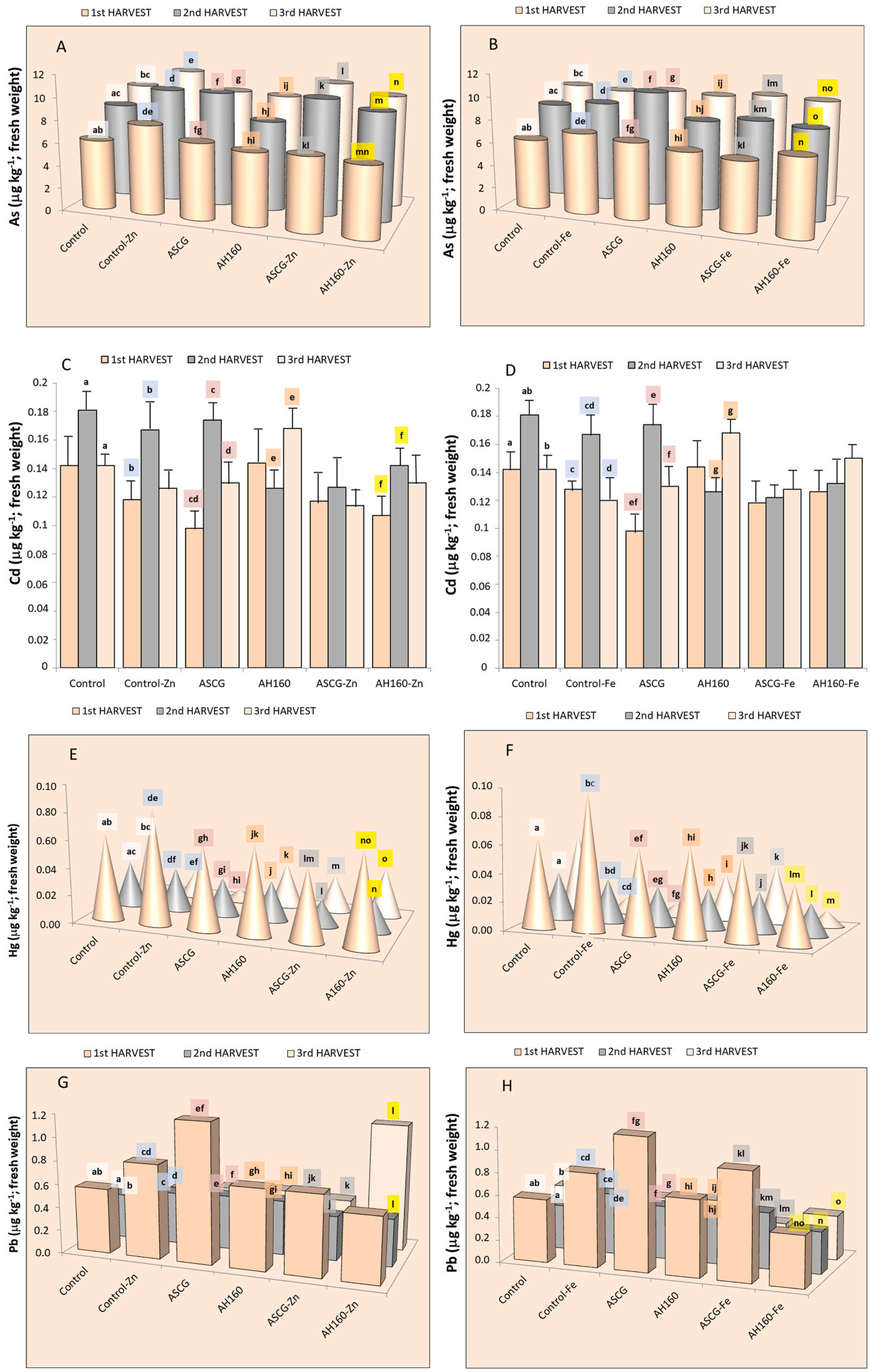


**Fig. 4.** Mean concentrations of toxic trace metals in cucumbers grown under greenhouse conditions across successive harvests, for all experimental groups under Zn and Fe biofortification: (A–B) As, (C–D) Cd, (E–F) Hg, and (G–H) Pb, respectively. Equal letters on the bars in each figure indicate statistically significant differences among harvests for the same experimental group ($p < 0.05$).

**Table 3**
Mean concentrations and estimated dietary intake of toxic metals from Dutch cucumbers. Health risk assessment based on serving size, average daily cucumber consumption in the Spanish population, and mean body weight of adult males and females in Spain.

| Metal | Metal concentration (μg $kg^{-1}$, f.w.) | Serving size intake (μg $serving^{-1}$) | EDI (μg $day^{-1}$) | EWI (μg $kg^{-1}$ bw $week^{-1}$) for males/females | PTWI (μg $kg^{-1}$ bw $wk^{-1}$) | %PTWI (for males and females) |
|---|---|---|---|---|---|---|
| As | 8.429 ± 2.067 | 1.47 | 0.04387 | 0.00396/0.00485 | 15 | 0.02641/0.03224 |
| Cd | 0.136 ± 0.045 | 0.03 | 0.00071 | 0.00006/0.00008 | 7 | 0.00091/0.00111 |
| Hg | 0.041 ± 0.029 | 0.01 | 0.00021 | 0.00002/0.00002 | 5 | 0.00038/0.00046 |
| Pb | 0.511 ± 0.392 | 0.09 | 0.00266 | 0.00024/0.00029 | 25 | 0.00096/0.00117 |

Validation, Supervision, Resources, Project administration, Funding acquisition, Conceptualization.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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## Data availability

Data will be made available on request.

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