Soil contamination by trace elements in the food chain: experiences in different mining and urban scenarios

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IRNAS

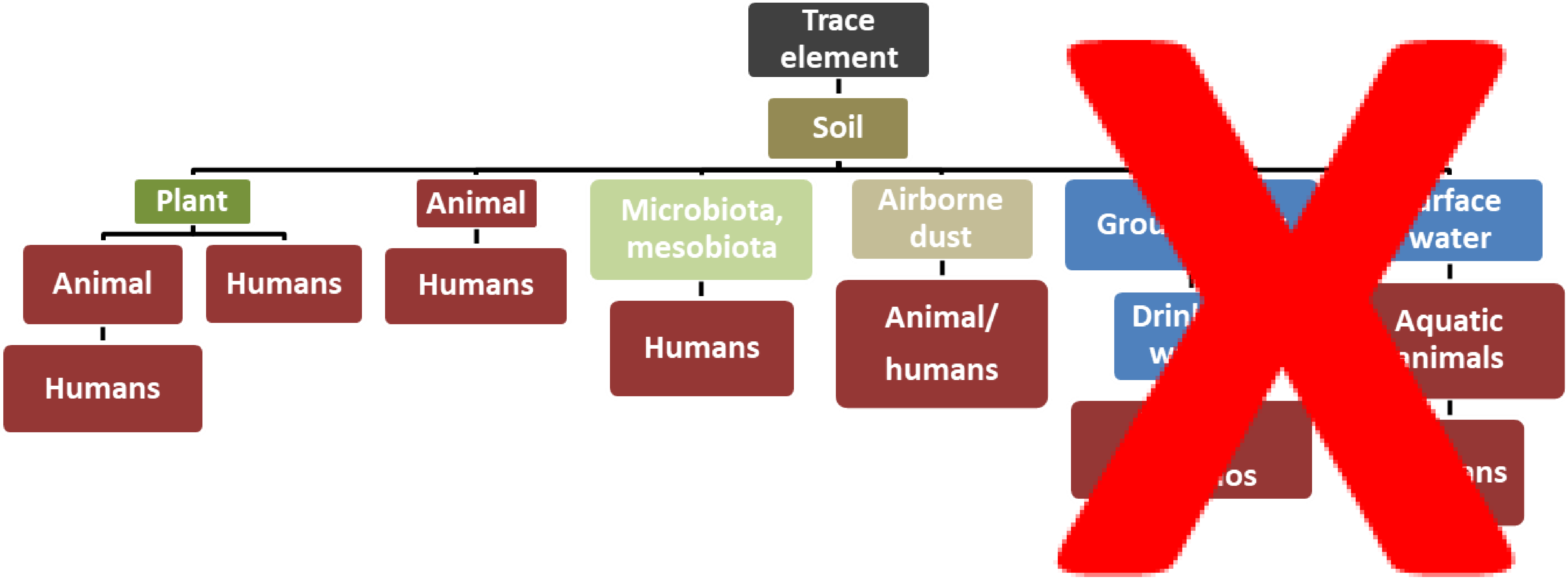
SUITMA 13
PISA 2025

Trace elements

Essential TE are vital for the metabolism of plants and animals. They play **specific, irreplaceable biochemical roles** and include elements like **B, Co, Cu, Fe, Mn, Mo, and Zn**. These are also called **micronutrients** because they are required in **small amounts** for organisms to complete their life cycles. However, they can become **toxic at high concentrations**

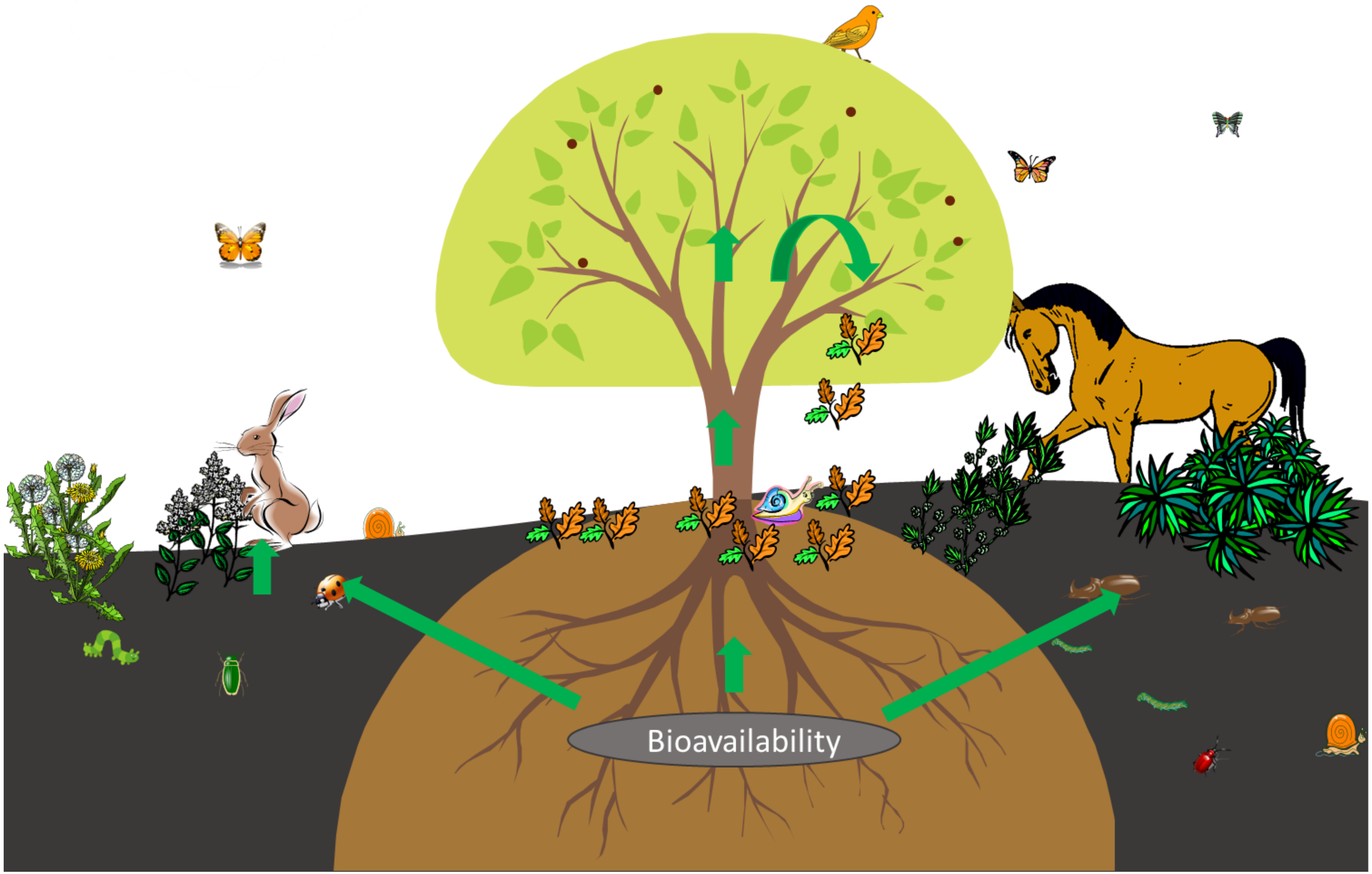
Non essential TE such us **As, Cd, Pb, Tl, Sb, Bi, and Hg.** They do not have a known biological function and are always **toxic at moderately high concentrations.**

Transfer of trace elements through the food chain



Potential pathways for the transfer of trace elements through the food chain—from soil to humans (adapted from Kabata-Pendias & Mukherjee, 2007).

BIOAVAILABILITY OF TRACE ELEMENTS IN SOILS



- TE in soil does **not necessarily imply a risk** to living organisms.
- TE becomes **harmful** if it is absorbed by an organism at levels **above a critical threshold.**
- **TE must be in a bioavailable** form—that is, in a chemical form that is accessible and **assimilable by organisms**. Depends on soil pH, OM, Texture….
- Important: oxidation states.

BIOACCUMULATION OF TRACE ELEMENTS IN TERRESTRIAL ENVIRONMENTS

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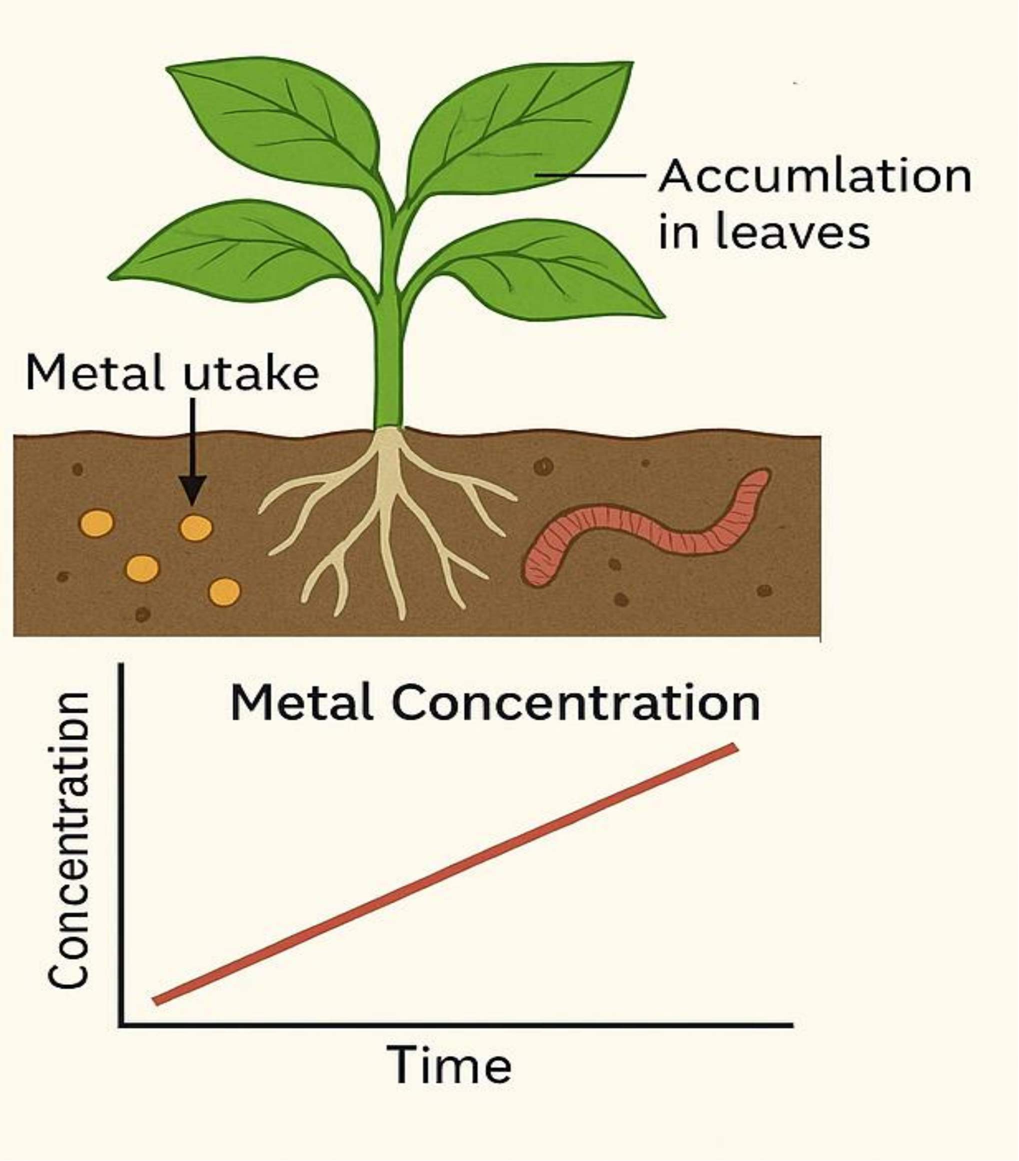
- Bioaccumulation refers to gradual build up of TE (e.g. Cd, Pb, Hg) in tissues of living organisms over time, due to direct exposure from soil, water or air.

- Occurs when organisms absorb TE faster than they can excrete them.

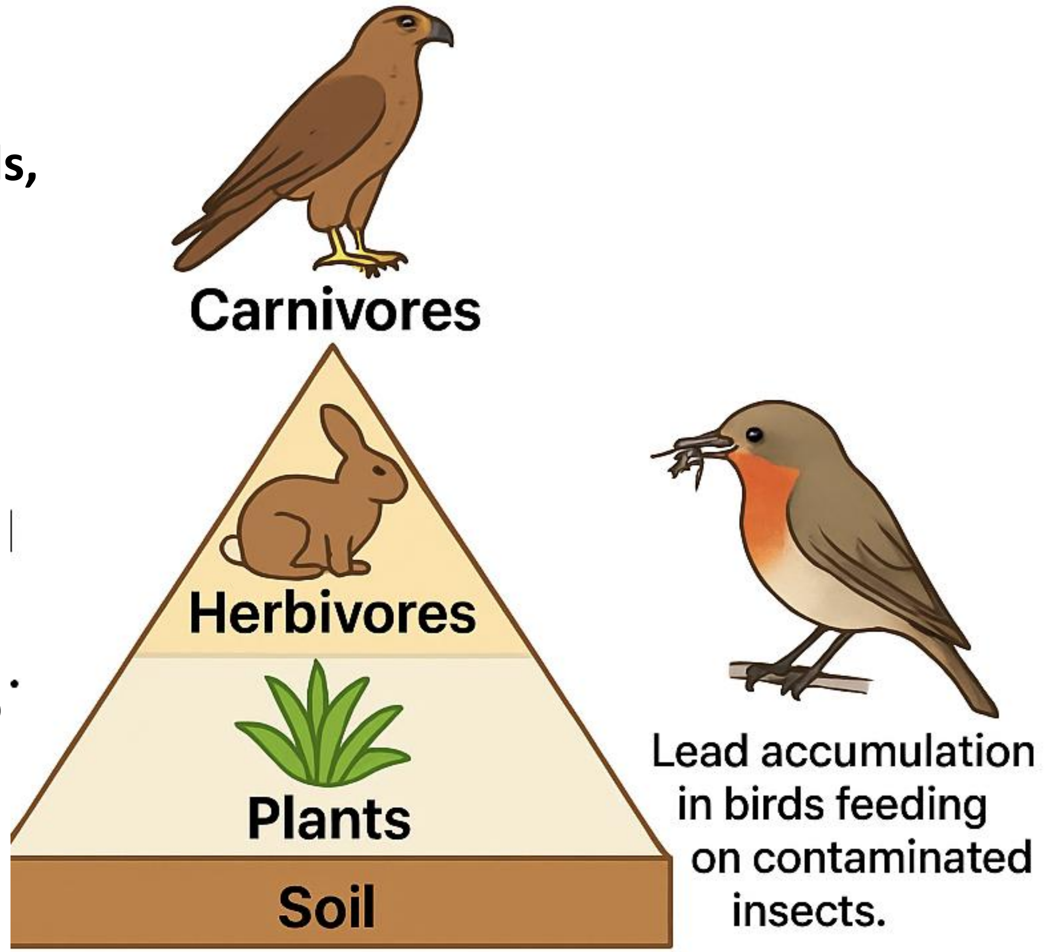
- Common soil invertebrates (e.g. earthworms), plants and small mammals.

- This process is directly influence by TE bioavailability (soil pH) and organism physiology.



BIOMAGNIFICATION OF TRACE ELEMENTS IN TERRESTRIAL ENVIRONMENTS

- Biomagnification refers to the progressive increase in TE concentrations across successive trophic levels, from soil organisms to higher-order predators
- TE accumulated in plants and invertebrates are transferred to herbivores and the to carnivores
- Top predators (e.g. birds of prey) show the highest concentrations
- TE such as Hg and Cd are particularly susceptible to bioaccumulation and exhibit high toxicity in biological systems



Overview of Case Studies

- Case Study: Horse Grazing
- Case study of Snails
- Case study of mushrooms

Risks to agricultural plots near mining zones:
The case study of Tharsis village orchards

Risk urban gardens: Case study Miraflores Park

Case study of the Guadiamar Green Corridor (GGC)

Corredor Verde del Guadiamar

The Aználcollar mine accident

Aznalcóllar mine is Located in the eastern most area of the Iberian Pyrite Belt.
Mining tradition since Roman times."

On April 25, 1998, the containment wall of the “Los Frailes” tailing pond broke.

Around **5 million cubic meters of toxic sludge and acidic water** were spilled and spread along the Agrio and Guadiamar rivers.

Extension the mine spill mine

Spill Volume

- ✓ sludge 2 × 10^6 m^3
- ✓ water: 3-4 × 10^6 m^3

25 × 10^6 m^3 stayed in the tailings pond

A strip approximately 300 meters wide and 40 kilometers long was covered by a layer (2–30 cm) of black sludge

In certain areas, the sludge reached depths of up to 3 meters.

Composition of the sludge

Elementt	Sluge (mg kg^{-1})	No contaminated soil
As	1028-4022 (2878)	0.1-40
Cd	15.1-36.4 (25.0)	0.01-2
Cu	715-2035 (1552)	2-250
Pb	3664-9692 (7888)	2-300
Zn	4424-10950 (7096)	1-900

Soil remediation measures

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Removal of the superficial sludge layer + the upper 10–20 cm of soil

Addition of amendments: limestone, compost, and manure, followed by ploughing

Afforestation of the contaminated area with native plant species

Corredor Verde del Guadiamar

Before Today

Worldwide success in remediating areas affected by trace element contamination.

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Review

Soil-plant relationships and contamination by trace elements: A review of twenty years of experimentation and monitoring after the Aznalcóllar (SW Spain) mine accident

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Evolution of TE in remediated soils in the GGC

Year		As	Cd	Cu	Pb	Zn
Affected soils mg kg^{-1}						
2002	Mean	**153**	**4.44**	**155**	**321**	**462**
	Range	*11.7-595*	*1.23-7.67*	*12.7-443*	*8-1556*	*40-936*
2005	Mean	**155**	**1.44**	**115**	**218**	**475**
	Range	*59-408*	*0.45-3.11*	*65.8-198*	*75-630*	*190-798*
2014	Mean	**127**	**1.79**	**135**	**387**	**525**
	Range	*15.3-793*	*0.28-9.35*	*28.5-428*	*22.8-3032*	*117-3413*
Un-affected soils mg kg^{-1}						
1998	Mean	**18.9**	**0.33**	**30.9**	**38.2**	**109**
	Range	*8.37-38.5*	*0.12-1.06*	*12.3-85.0*	*19.5-86.3*	*53.9-271*

The data are indicative only (variability of soil samplings), but suggest that no widespread soil deterioration in the GGC.

Transfer of trace elements to fauna in the Guadiamar Green Corridor (GGC).

Studies related to the effects of pollution from the Aznalcóllar mining accident that impacted both wildlife and humans

Fauna category ,	References
1. Zooplankton	Prat et al. (1999)
2. Nematodes	Peña-Santiago et al. (2005)
3. Mollusks and crustaceans	Alcorco et al. (2006), Blasco et al. (1999), Drake et al. (1999), Madejón et al. (2013), Martín et al. (2004), Prat et al. (1999), Romero-Ruiz et al. (2003), Sánchez-López et al. (2004), Suñer et al. (1999)
4. Insects	Cárdenas and Hidalgo (2006), Ferreras-Romero et al. (2003), Luque et al. (2007), Prat et al. (1999), Solá et al. (2004), Solá and Prat (2006).
5. Fish	De Miguel et al. (2013), Drake et al. (2005), Moreno-Rojas et al. (2005)
6. Reptiles	Fletcher et al. (2006), Márquez-Ferrando et al. (2009)
7. Birds	Baos et al. (2006, 2012), Baos et al., (2024), Benito et al. (1999), Gil-Jiménez et al. (2017), Gómez et al. (2004), Hernández et al. (1999), Martínez-Haro et al. (2013), Mateo et al. (2006), Meharg et al. (2002), Pastor et al. (2001, 2004), Taggart et al. (2006)
8. Mammals (mice and shrews)	Bonilla-Valverde et al. (2004), Festa et al. (2003), López-Barea et al. (2005), Mateos et al. (2008), Ruiz-Laguna et al. (2001), Sánchez-Chardi (2007), Sánchez-Chardi et al. (2009), Tanzanella et al. (2001)
9. Mammals (horses)	Madejón et al. (2009)
10. Humans	Gil et al. (2006)

All hunting and collecting plants or animals in the GGC is forbidden!

Case Study: Horse Grazing in the GGC

Madejon et al., 2009

Case Study: Horse Grazing in the GGC

This study was conducted eight years after the accident, in 2007

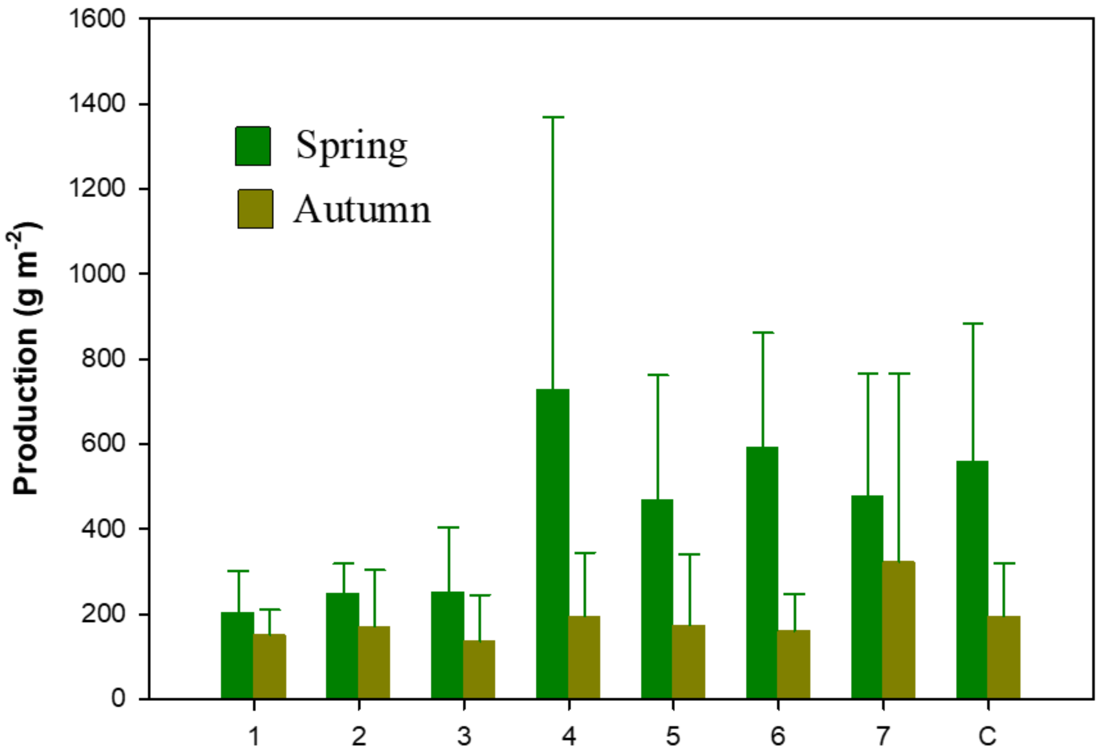
This study was conducted at three levels: soil, plant, and animal.

To assess the accumulation of trace elements (TEs) in horses, we analyzed feces and mane hair.

Biomass of the pasture

Two samplings : Spring and Autumn

Seven contaminated sites and one control site were included in the study

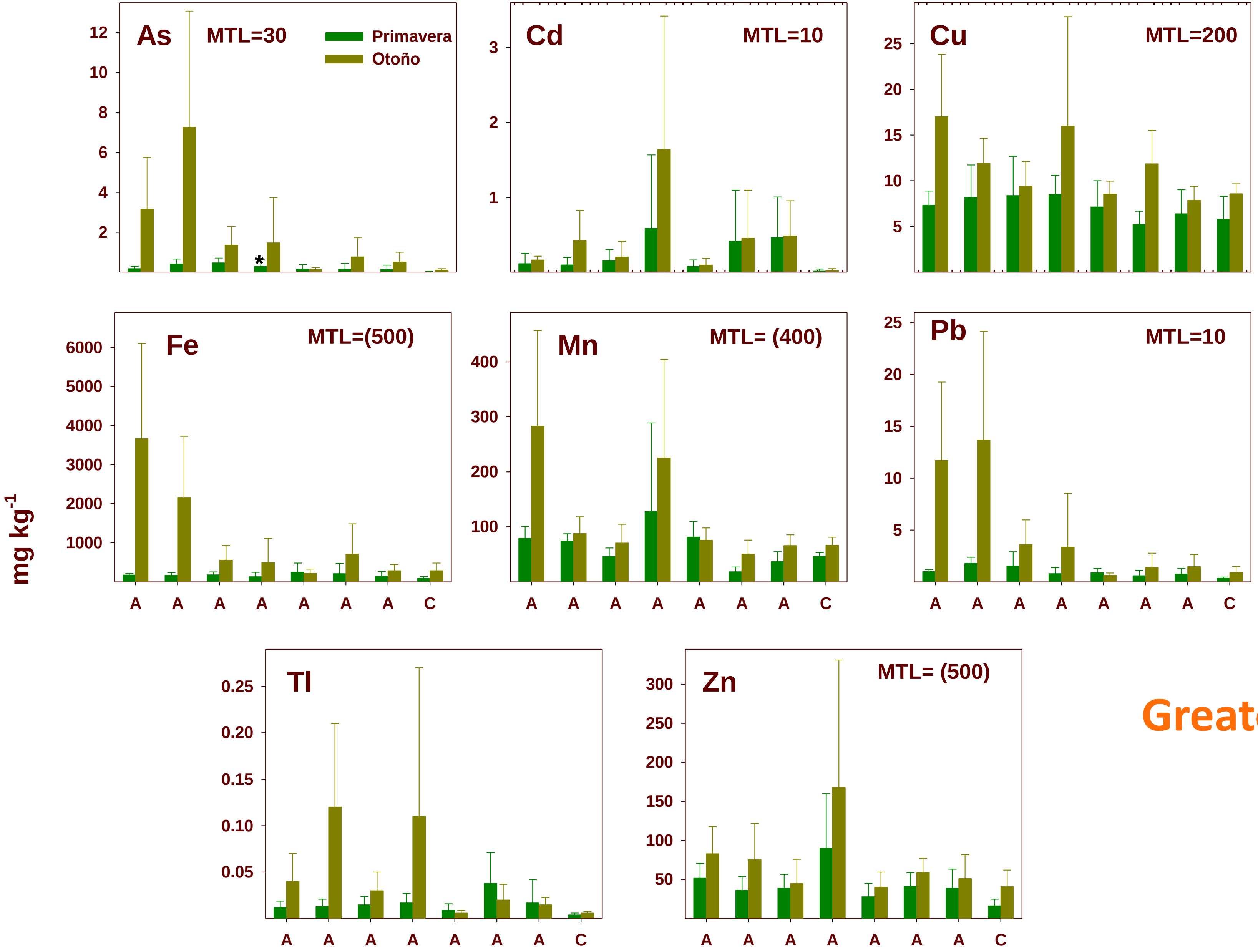


Soil contamination in the GGC did not affect pasture production or its floral composition

LOWER BIOMASS IN AUTUMN

Madejon et al., 2009

Trace element accumulation in the pastures of the GGC



Plant material analyzed without washing to assess the actual contamination of TE in the grass and their potential toxic impact when consumed as forage

Greater risk in short grass (autumn): soil consumption

Trace element concentration in horses faeces

The elemental composition in faeces can reflect changes in diet

Faeces were washed to avoid soil contamination

Essential elements	Soil	Cu	Fe	Mn	Zn
			mg kg^{-1}		
	GGC	34.9±23.9	1914±774*	187± 64.5*	142±60.3
	Control	19.4±8.81	914±78.8	90.6± 6.75	68.7±19.0

No Essential	Soil	As	Cd	Pb	Tl
			mg kg^{-1}		
	GGC	4.93±3.69*	0.78±0.57	13.8± 12.6	0.13±0.11
	Control	0.58±0.08	0.15±0.13	2.02± 0.37	0.02±0.001

- Greater differences between control and contaminated samples in non-essential elements.
- Preferential excretion of non-essential elements

The absorption of essential elements is regulated by homeostatic mechanisms which control their accumulation. However, non-essential elements tend to be preferentially excreted by horses.

Trace element concentration in horses hair

Hair proposed for biomonitoring of trace elements. Metabolically active fiber during growth, and its composition reflects the individual's health and nutritional status.

[a] Reference range of trace elements in mane hair of healthy race horses (Asano et al. 2002)

Essential elements	Soil	Cu	Fe mg kg^{-1}	Mn	Zn
	GGC	14.7±7.74*	334±151*	14.1±7.53*	185±23.8
	Control	9.84±0.71	21.7±3.57	4.29±1.04	208±6.82
Reference range [a]		5.9	22.4	5.00	102

The hair samples were washed washing with acetone, and distilled water

No Essential	Soil	As	Cd mg kg^{-1}	Pb	Tl
	GGC	0.85±0.49*	0.20	1.34±0.66*	0.015±0.01*
	Control	0.19±0.12	0.01	0.37±0.02	0.001±0.001
Reference range [a]		1.11	0.20	0.77	-

TE in horse hair in GGC were in the range for healthy horses; No evidence that supports a toxic risk to horses grazing this region.

Using horses as ecological management tools to help prevent and control wildfires and recreational purposes.

Horses are forbidden for human consumption

Case study: Snails as indicators of trace elements and risk for human in the GGC

Potential of the snail to accumulate TE

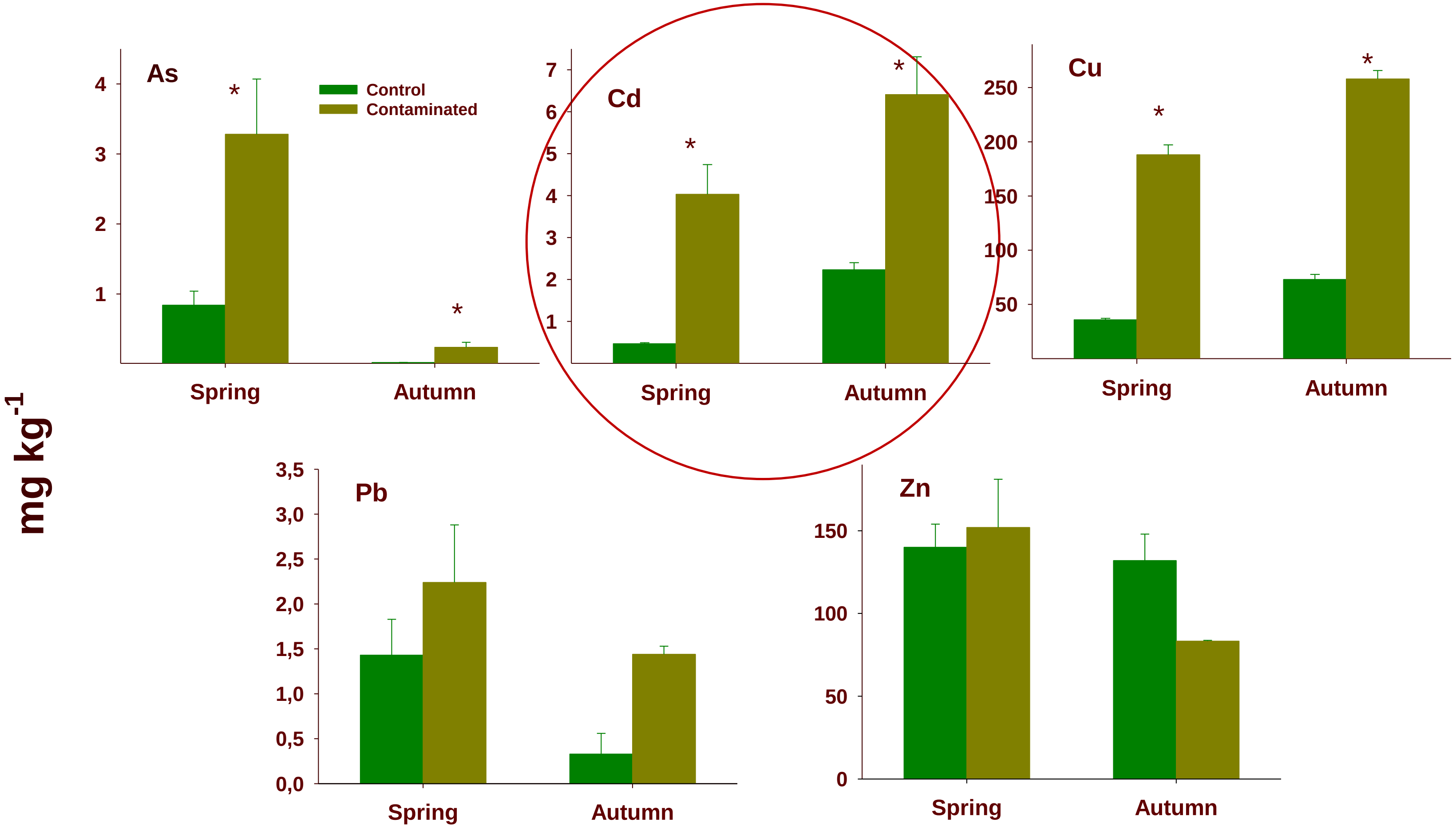
Potential risk for its consumption

Sampling:
Collected in spring and autumn 2010 in contaminated zones and a control site in the GGC

Methodology
Unpurged snails: Frozen immediately at −80 °C to reflect real environmental exposure (as consumed by predators).
Purged snails: Starved for 48 h and washed to simulate human consumption practices, then frozen.

Madejón et al., 2013

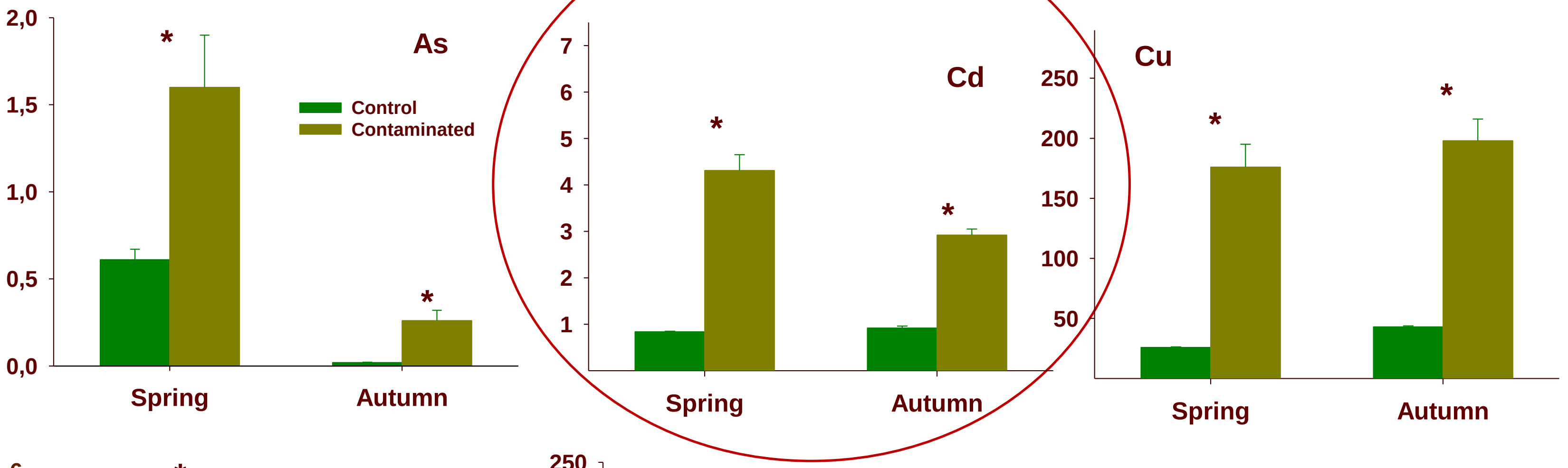
Indicators and potential risks associated with their consumption by animals (unpurged)



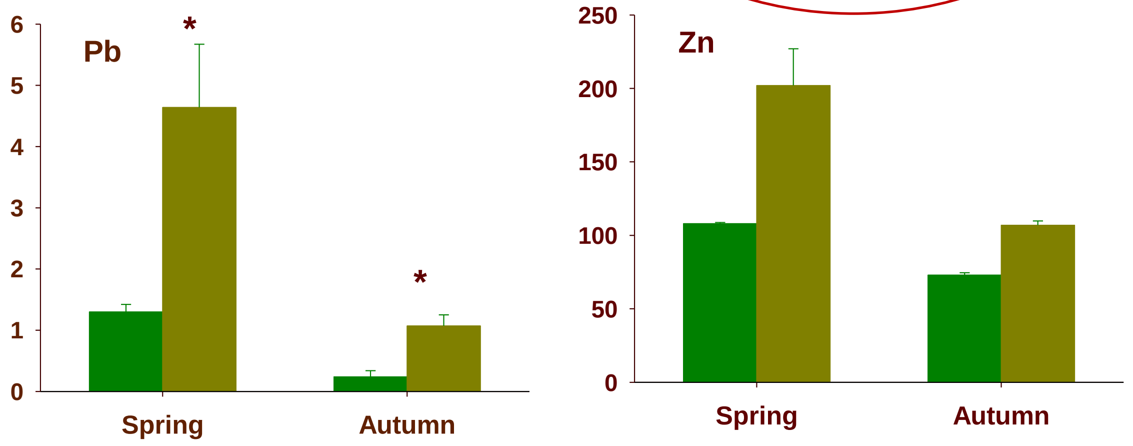
Significant differences were found in As, Cd, and Cu, suggesting potential accumulation of TE in snail tissues

Potential bioaccumulation of Cd

Potential Risk for human consumption (purged snails)



- **As:** Spring levels: sometimes exceeding typical food limits.



- **Cd:** Above maximum Cd levels of 1 mg kg^{-1} FW for bivalve mollusks. **Cd represents a risk for human consumption**

- **Pb :** values close to EU safety threshold.

Snail bodies showed TE concentrations that may pose health risks.
Highest values recorded in **spring**, when snails are most consumed.

It is advised to avoid collecting snails for human consumption due to potential health risks

Case study of mushrooms in the GGC

Mushrooms tend to accumulate high concentrations TE

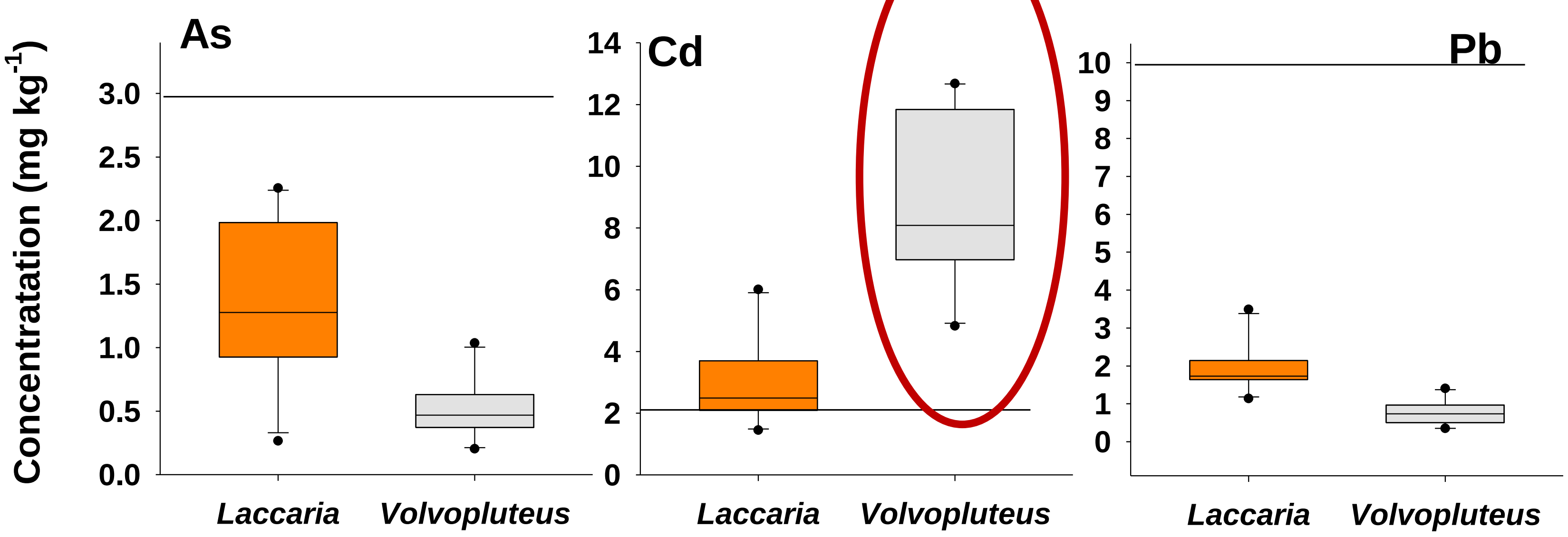
Evaluate potential health risks for animals and humans from mushroom consumption

•No prior chemical composition studies exist for mushrooms in the GGC.

•Sampling: December 2016

- *Laccaria laccata* (ectomycorrhizal)

- *Volvopluteus gloiocephalus* (saprotrophic)

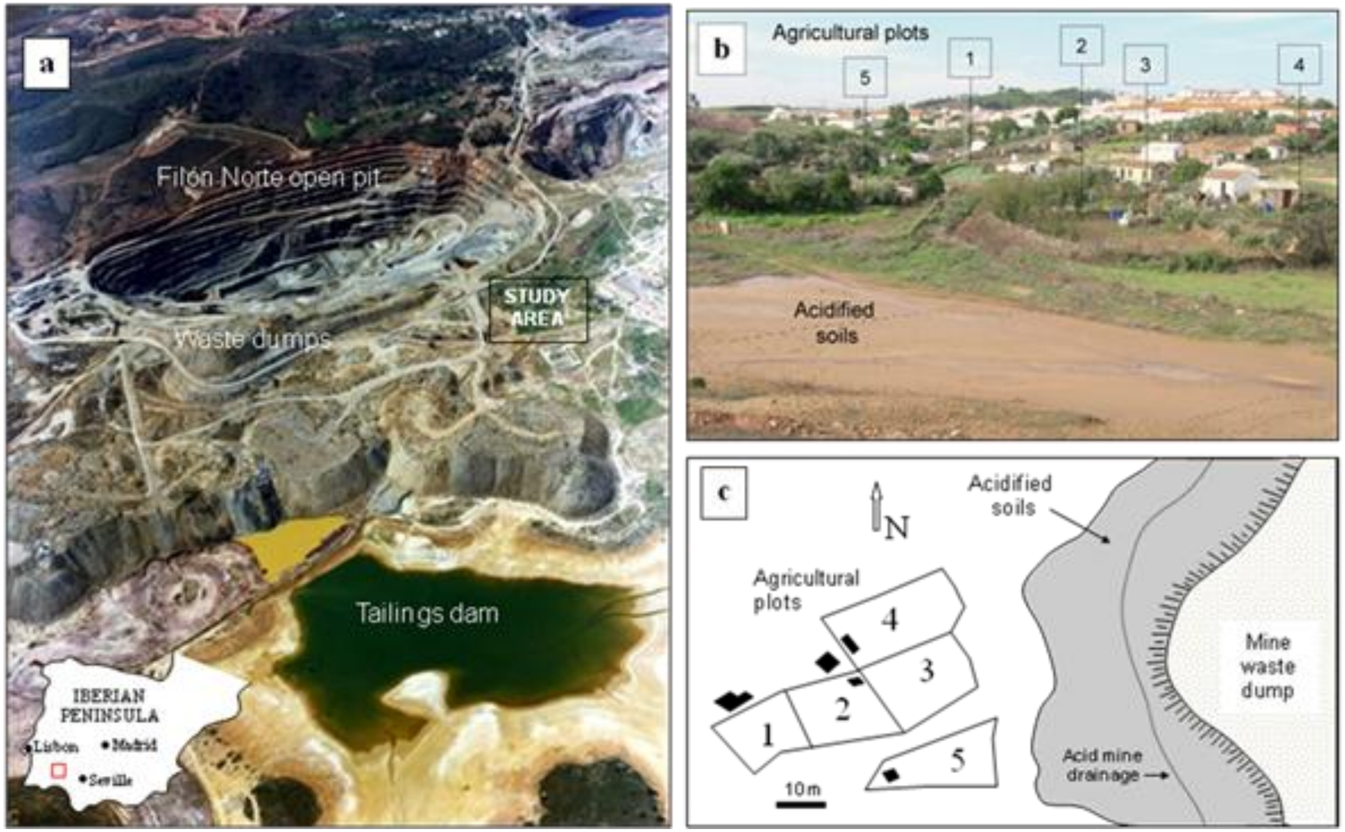


As and Pb levels safe consumption limits

High Cd concentrations, especially in Volvopluteus , above legal limits for human consumption .
Cd concentrations of up to **13 mg/kg — unacceptable in any type of food**.

Animal consumption is unpredictable and uncontrollable, reinforcing the need for **long-term monitoring** of wildlife health in the GGC.

Case study : Agricultural plots located near mining areas



Past mining activities caused marginal areas unsuitable for commercial agriculture. However, traditional small-scale farming still persists in limited arable zones near mining villages.

- Periodic flooding by acid waters from nearby sulfidic waste dumps and mine workings.

- These conditions pose risks for soil health and increase the potential for TE transfer from soil to plants.

Madejón et al., 2011

Traditional Soil Amendments and Cropping Practices in contaminated soils

- Farmers routinely apply lime to correct acidity and add animal manure to improve fertility.
- These practices have been consistently used for over 25 years.

Treatment $CuSO_4$:Fungicide and bactericide

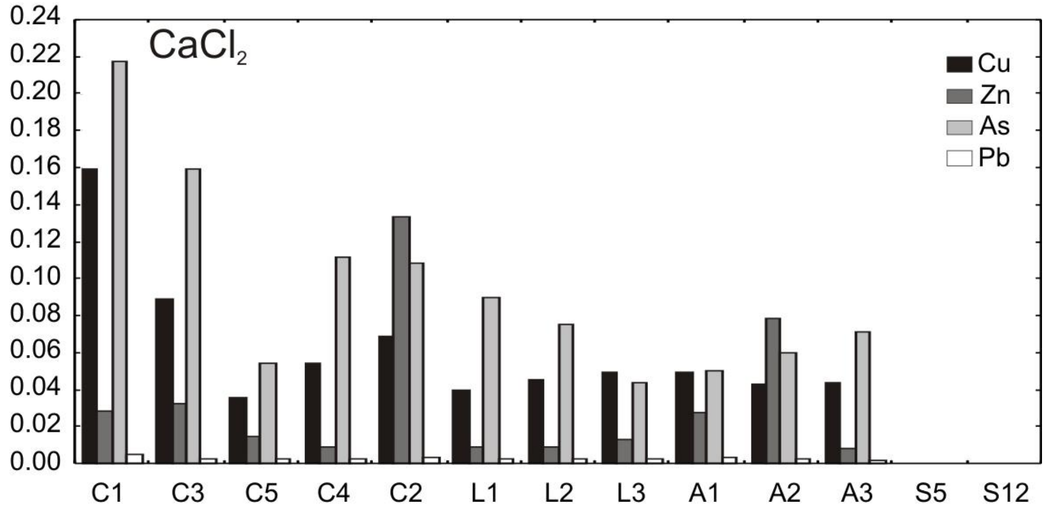
Traditional Soil Amendments and Cropping Practices

Total trace element concentrations in soil expressed as mean values ± sd (mg kg^{-1})

Plot (n)	As	Cu	Pb	Zn
1	203 ± 26.7	326 ± 51.4	864 ± 74.3	314 ± 25.1
2	332 ± 70.9	486 ± 84.6	1281 ± 241	499 ± 39.9
3	469 ± 85.1	603 ± 20.2	1715 ± 274	570 ± 15.7
4	575	692	2395	593
5	621	752	2260	589
Regional background*	25	32	38	76
Normal levels in agricultural soils**	n.d.	13	16	47
Threshold values for agricultural soils of Andalusia***	20	100	200	300

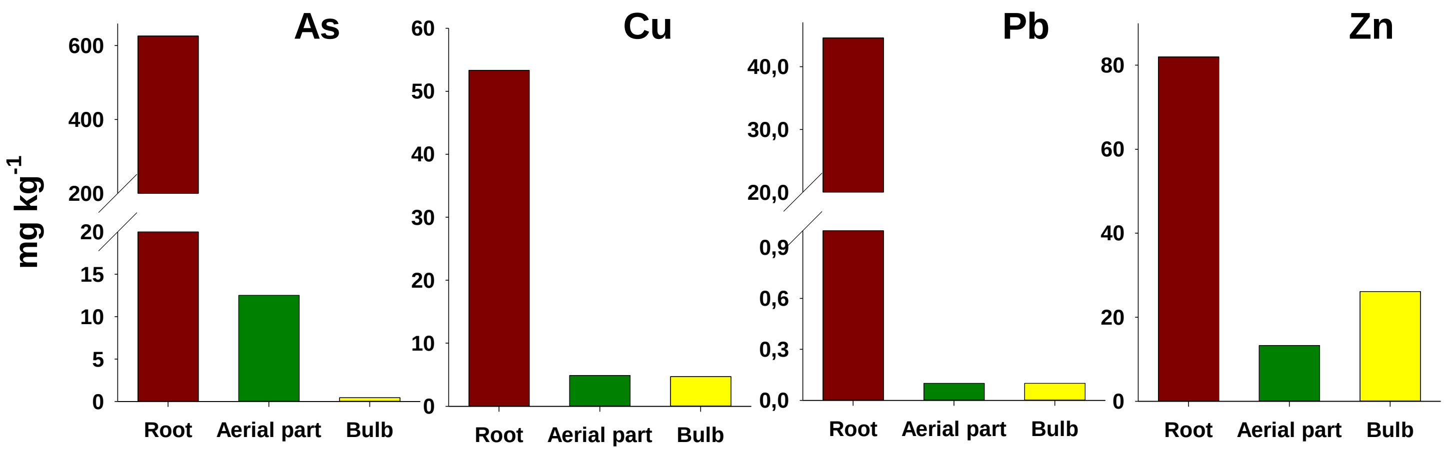
* Galán et al., (2008); ** López-Arias and Grau-Corbí, (2004); *** Aguilar et al., (1999)

% Available fraction



Very low percentage of TE availability < than 0.5 %

ONIONS RESULTS



Higher concentration s in roots >aerial part>bulb (except Zn)

Plant species	Organ	As	Cu	Pb	Zn
Ripe Onion	Bulbs	**0.31 (0.1-1.2)**	**4.15 (2.9-5.0)**	**0.33 (0.1-0.83)**	**23.9 (14.9-29.1)**
Onion bulbs*		-	4.0-6.0	1.1-2.0	22-32
Young Onion	Bulbs	**8.81 (1.95-23.5)**	**13.3 (9.0-18.0)**	**2.65 (3.01-8.3)**	**62.4 (34.9-101)**
Normal levels **		0.0001-0.46	0.04-2.4	0.0004-0.8	0.5-118
Statutory limits**		1.00	-	1.00	

* Possible background values compiled by Kabata-Pendias and Mukherjee (2007); **Normal levels in vegetables Szefer and Nriagu, (2007); *** Davies and White (1981).

As: young bulbs concentrations up to 23.5 mg kg^{-1}, exceeding statutory limits. In mature bulbs concentrations decreased: dilution effect from biomass increase.
Pb: young bulbs reached 8 mg kg^{-1} but dropped below statutory limits in mature bulbs.
Cu : exceeded normal plant concentrations in young and dropped to background vales. Cu treatments!
Zn: Fine

POTATOES RESULTS

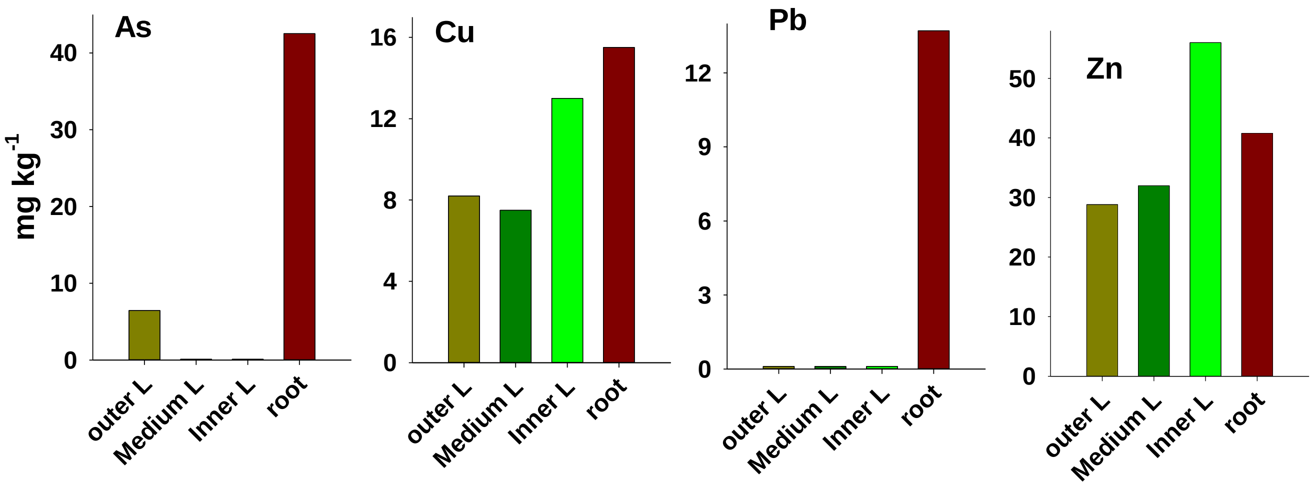
Plant species	Organ	As	Cu	Pb	Zn
Potato (n=5)	Peel	0.1	11.5 (8.9-12.6)	0.1	21.1 (19.2-24.0)
	Tuber	**0.1**	**10.3 (8.2-12.0)**	**0.1**	**25.0 (20.8-28.8)**
Potato tubers*		-	3.0-6.6	0.5	10-26
Normal levels in vegetables**		0.0001-0.46	0.04-2.4	0.0004-0.8	0.5-118
Statutory limits**		1.00	-	1.00	

* Possible background values compiled by Kabata-Pendias and Mukherjee (2007); **Normal levels in vegetables Szefer and Nriagu, (2007); *** Davies and White (1981).

As and Pb : Negligible concentrations (0.1 mg kg^{-1}), with no contamination detected in tubers.

Elevated Cu levels may be linked to foliar absorption of Cu-based agrochemicals used locally.

LEAFY VEGETABLES RESULTS



As: As levels within statutory limits in edible leaves. Highest As in non-edible parts (roots and outer leaves).

Pb: below statutory limits in leaves.

Cu and Zn: normal ranges; Highest concentrations found in inner leaves, unlike As and Pb.

As and Pb : In the range of statutory limits. Cu above normal levels

Plant species	Organ	As	Cu	Pb	Zn
Chard (plot 1)	**Leaves**	**0.45 (0.20-0.70)**	**14.8 (13.6-15.9)**	**0.90 (0.75-1.1)**	**43.9 (41.4-46.4)**
Chard (plot 2)	**Leaves**	**1.07 (0.77-1.30)**	**18.4 (16.0-19.9)**	**1.50 (1.2-1.76)**	**79.8 (54.2-110)**
Normal levels in vegetables**		0.0001-0.46	0.04-2.4	0.0004-0.8	0.5-118
Statutory limits**		1.00	-	1.00	

It is important to consider that the low risk to human health observed in this case study cannot be generalized to other contexts. Washing vegetables thoroughly before consumption is essential

Case study : Urban and peri-urban community gardens: Urban agriculture (UA)

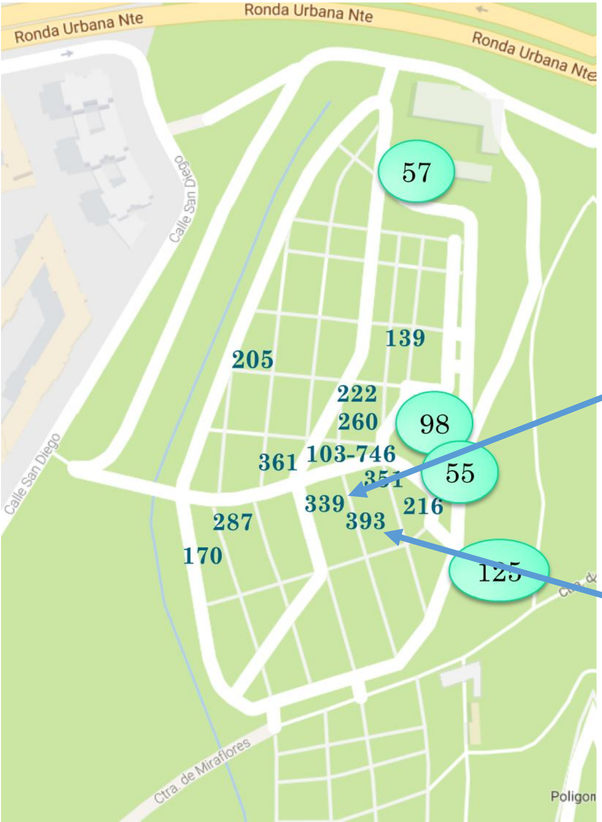
In Spain, there are about 20,000 urban gardens.

Urban agriculture is practiced not only for subsistence, but also for social and environmental purposes, and for the health benefits associated with both the practice and the consumption of its products

López et al., 2019

Urban Gardens of Miraflores Park in Seville

SOILS



Pb concentrations at different depths in two lots:

20-40 cm: 512 mg kg^{-1}
0-100cm: 393 mg kg^{-1}

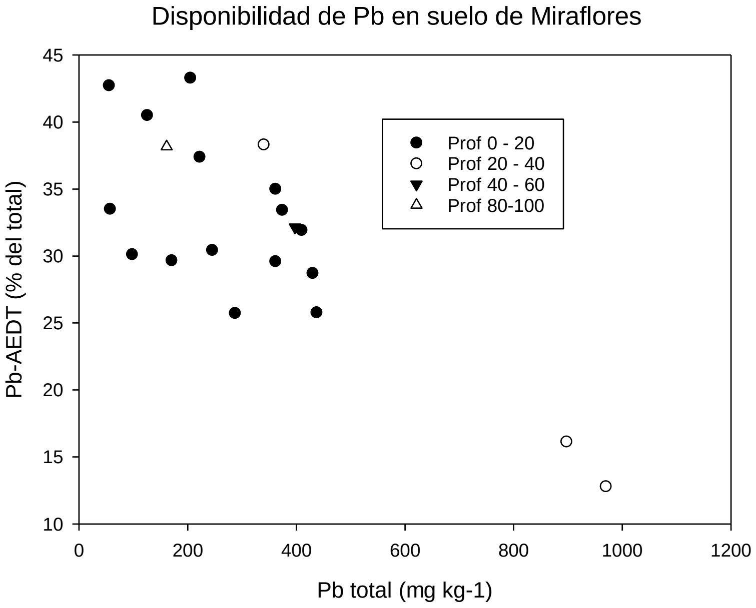
20-40 cm: 601 (329-970) mg kg^{-1}
0-100 cm: 350 mg kg^{-1}

Concentrations at 0-15 cm

	Pb (mg kg^{-1})	Cu (mg kg^{-1})	Zn (mg kg^{-1})
Mean	**308.5**	116.6	168.2
Mín	103.9	73.5	120.1
Máx	746.2	222.9	222.6

Above the Generic Reference Level for agricultural soils

Origin: This soil was once used to dump waste for construction. The Pb found here likely comes from old white paint from that was discarded (**$PbCO_3$**).

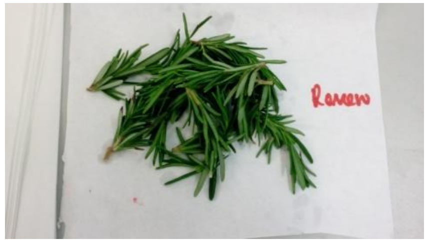


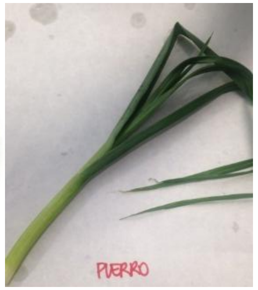
Lead availability:

The form in which Pb is found is highly available (chemical criterion). Its availability decreases as the total content in the soil increases.

Pb carbonate is the most soluble Pb compound in the soil environment, releasing small particles of Pb as the Pb-based paint weathers in the soil.

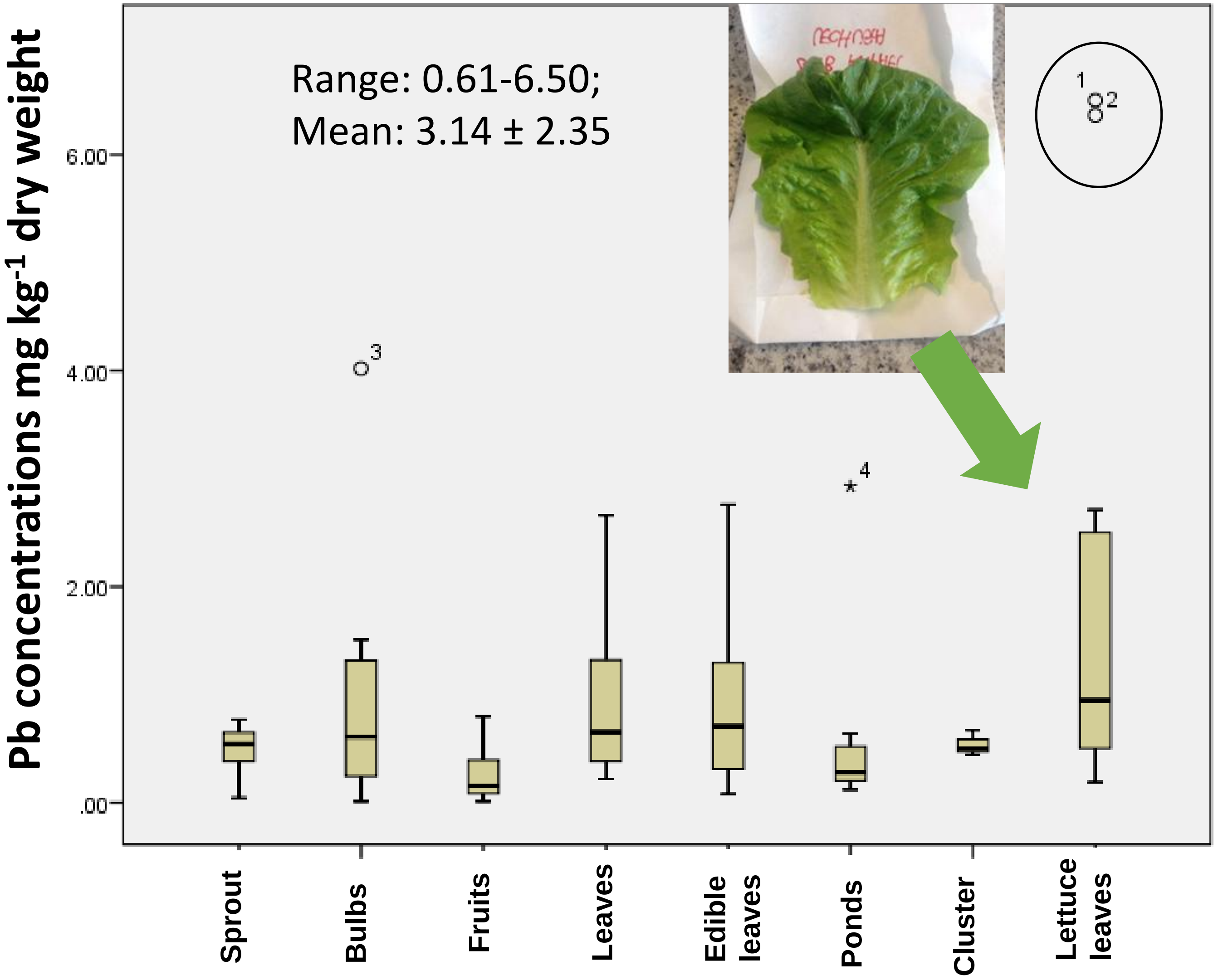
Objective : Study the content of Pb and TE in different types of vegetables and plant parts grown in the gardens of “Parque de Miraflores” in Seville.



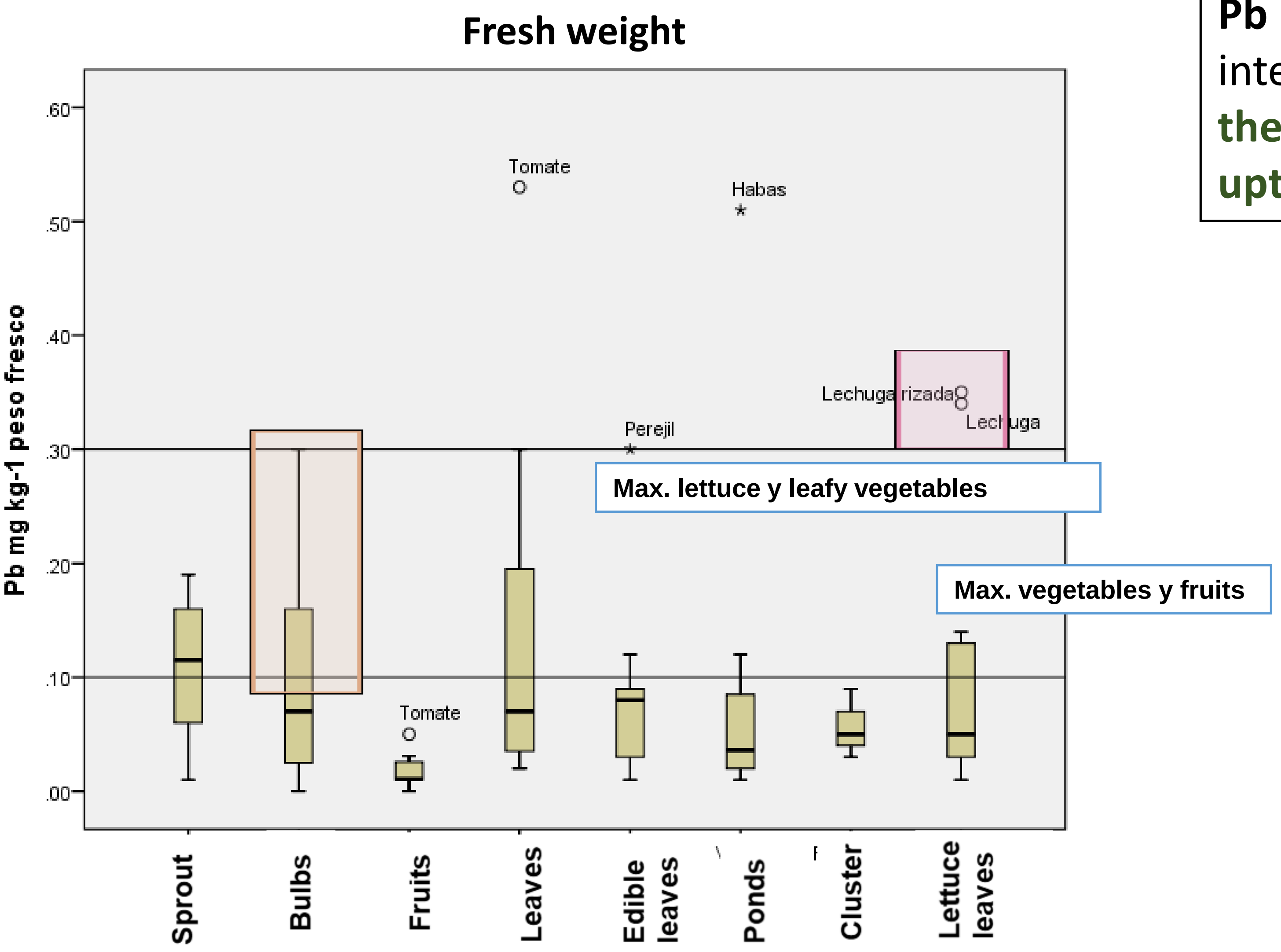


Lead concentrations in different vegetables and part (dry weight)

- **Fruits**: Tomato, loquat
- **Pons** Broad beans, green beans, peas
- **Clusters**: Broccoli, Romanesco, cauliflower
- **Sprouts**: Lavender, rosemary, myrtle
- **Bulbs**: Leek, onion, red beet, carrot, radish, potato
- **Edible leaves**: Swiss chard, parsley



Pb concentrations on fresh weight



Maximum permitted levels by European Community legislation (European Commission 2006b) : Leafy vegetables and lettuce 0.30 mg kg^{-1}

Pb is a challenge in this garden, requiring intervention. **Soil organic matter can reduce the amount of lead available for plant uptake**.

Growers often skip rinsing vegetables, believing they're pesticide-free, and prepare them directly in the garden, increasing soil contact. This practice, in Mediterranean climates with dry, dusty conditions, raises health risks—especially from Pb pollution. **Long-term exposure is a concern since community gardeners typically consume their own produce over many years.**

Take home messages

- **Historical land use analysis:** Investigating previous land uses is essential for identifying sources of contamination and detecting soils with elevated trace element concentrations.

- **Persistence of trace elements**: Trace elements can persist in soils for extended periods, necessitating **long-term monitoring of soils, plants, and other biota to detect potential accumulation effects within these systems**.

- **Soil management strategies**: Applying organic matter and lime helps maintain neutral soil pH and reduces the **bioavailability of TEs**. However, **crops cultivated in contaminated soils should be excluded from human food.**

- **Exposure assessment**: Differentiating between acute (occasional) and chronic (long-term) exposure is essential for accurate risk evaluation.

- **Site-specific research** necessity: Due to variability in soil properties, climate, crop types, and local biodiversity, research findings are often not directly transferable between regions.

Acknowledgment

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Thanks!!!