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Determination of lead and cadmium in water of the Mezquital Valley

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Abstract

The Mezquital Valley, in the state of Hidalgo, has historically used wastewater from Mexico City for agricultural irrigation, which has favored local production, but has also generated environmental and health risks due to the presence of heavy metals with bioaccumulation capacity. The purpose of this research was to determine the levels of lead and cadmium in samples of wastewater, natural water, and drinking water from seven municipalities in the region. The determinations were made by flame atomic absorption spectrophotometry, following the NMX-AA-051-SCFI-2001 standard. The results showed that wastewater exceeded the permissible limits by 26% for Pb and 30% for cadmium. In natural water and drinking water, the excess was 70% and 100%, respectively, according to NOM-127-SSA1-2021 and NOM-001-SEMARNAT-2021. These findings highlight the need to establish continuous and specialized monitoring of heavy metals in water, in order to protect public health and promote safer use of water resources.

Keywords:

heavy metals, organic matter, public health.

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Introduction

The use of wastewater in the Mezquital Valley region of the state of Hidalgo has boosted agricultural development by providing wastewater to the following irrigation districts: 003-Tula, 100-Alfajayucan, and 112-Ajacuba, since the construction of the large drainage canal in 1856, thus allowing crop production (García, 2019; Rosas and García, 2024).

This practice has enriched soils with organic matter, favoring crop growth (Guédron *et al*., 2014); nevertheless, it has generated contamination of water sources, soil degradation, and exposure to toxic substances (González *et al*., 2015; Hernández *et al*., 2016; Leeser *et al*., 2018; Luneberg *et al*., 2018; Chamizo *et al*., 2020), leading to environmental and public health problems.

Among the most dangerous pollutants are heavy metals, due to their high mobility in the environment and their capacity for bioaccumulation (Garduño *et al*., 2023). Prolonged exposure to lead (Pb) and cadmium (Cd) represents a serious health risk, with permissible limits of 0.2 mg L^{-1} for Pb and Cd in wastewater and 0.01 mg L^{-1} and 0.005 mg L^{-1} for Pb and Cd, respectively, for human use and consumption, according to (NOM-001-SEMARNAT-2021; NOM-127-SSA1-2021; SCFI, 2022 a, b).

Heavy metals generate metal-specific free radicals that cause oxidative stress in cells, which causes DNA damage, inactivation of enzymatic proteins, protein aggregation, conformational changes that affect their structure, function, and cause cell damage (Wu *et al*., 2016), which is reflected in chronic systemic effects and increased incidence of cancer when found in high concentrations in drinking water (Contreras *et al*., 2017; Izquierdo *et al*., 2022).

Despite the environmental and public health impact, heavy metal pollution in the Mezquital Valley has been little analyzed, being one of the most environmentally affected regions in Mexico. This study aimed to measure the levels of lead and cadmium in different water sources in the Mezquital Valley, Hidalgo, to determine if they exceed the permissible limits established by Mexican regulations.

Specifically, it was sought to quantify the concentrations of these metals in wastewater, natural water, and drinking water in the region, as well as to statistically compare the levels between the different types of water sources to identify risk areas. The hypothesis stated that these concentrations exceeded the normative values, which represented a potential risk to public health and the environment, derived from the prolonged use of wastewater in agricultural activities.

Materials and methods

The water analysis was carried out at the Technological University of the Mezquital Valley. A total of 29 samples of wastewater were collected from irrigation canals, dams and rivers; in the case of purified and drinking water, six samples were obtained from springs, four from wells and 16 from drinking sources; in total, there were 54 samples from the state of Hidalgo and one from the State of Mexico as a control (Table 1).

Table 1. Samples of wastewater, natural water, and drinking water collected in the state of Hidalgo.

Code	Origin	Location	Altitude (masl)	Code	Origin	Location	Altitude (masl)
CPT1	Canal	Tecozautla	1 733	PMI1	Dam	El Maye, Ixmiquilpan	1 720
CPN1	Canal	Pueblo Nuevo, Ixmiquilpan	1 781	MTA	Spring	Arbolado, Tasquillo	1 704
CLJI	Canal	La Joya, Ixmiquilpan	1 772	MFI	Spring	El Fitzi, Ixmiquilpan	1 798
CSM1	Canal	San Miguel, Ixmiquilpan	1 714	MPA	Spring	Panales, Ixmiquilpan	1 780

Code	Origin	Location	Altitude (masl)	Code	Origin	Location	Altitude (masl)
CLSS	Canal	Lagunilla, San Salvador	1 979	MLR	Spring	Remedios, Ixmiquilpan	1 767
CPT2	Canal	Pañhe, Tecozautla	1 733	MAN1	Spring	Remedios, Ixmiquilpan	1 757
CPN2	Canal	Pueblo Nuevo, Ixmiquilpan	1 781	MAN2	Spring	Remedios, Ixmiquilpan	1 762
CBI1	Canal	Bangandho, Ixmiquilpan	1 795	PLRI	Well	Reforma, Ixmiquilpan	1 738
CNI1	Canal	El Nith, Ixmiquilpan	1 751	PXZ	Well	Xindho, Zimapan	1 779
CMLI	Canal	Media Luna, Ixmiquilpan	1 738	PJEM*	Well	Santa Ana, Jilotzingo	2 739
CSM2	Canal	San Miguel, Ixmiquilpan	1 714	CNI2	Well	Panales, Ixmiquilpan	1 751
COBI	Canal	La Otra Banda, Ixmiquilpan	1 738	RSNI	Drinking	Sn Nicolás, Ixmiquilpan	1 719
CTA1	Canal	Tasquillo	1 704	PBAI	Drinking	Bangando, Ixmiquilpan	1 795
CXA1	Canal	San Nicolás, Atotonilco	2 012	PEC	Drinking	El Carrizal, Ixmiquilpan	1 774
CPN3	Canal	Pueblo Nuevo, Ixmiquilpan	1 781	PLJI	Drinking	La Joya, Ixmiquilpan	1 772
CPI1	Canal	Portezuelo, Ixmiquilpan	1 784	PUTV	Drinking	UTVM, Ixmiquilpan	1 772
CDI1	Canal	El Deca, Ixmiquilpan	1 762	PVII	Drinking	Villagrán, Santiago de A.	1 941
CXA2	Canal	Xathé, Atotonilco el Grande	2 049	PLEC	Drinking	La Vega, Alfajayucan	1 848
CLOI	Canal	Loma del Oro, Ixmiquilpan	1 738	PEVI	Drinking	El Valante, Ixmiquilpan	1 731
CLRI	Canal	La Reforma, Ixmiquilpan	1 738	PMBI	Drinking	Maguey B., Ixmiquilpan	1 798
CVSA	Canal	Villagrán, Santiago de A.	1 941	PBSS	Drinking	Bóxtha, San Salvador	1 979
CMBI	Canal	Maguey Blanco, Ixmiquilpan	1 798	PENI	Drinking	El Nith, Ixmiquilpan	1 751
CSM3	Canal	San Miguel, Ixmiquilpan	1 714	PRPA	Drinking	Panales, Ixmiquilpan	1 780
CCAI	Canal	Capula, Ixmiquilpan	1 757	PRMA	Drinking	El Maye, Ixmiquilpan	1 720
RTI1	River	Tula	1 773	PLRE	Drinking	La Reforma, Ixmiquilpan	1 738
RMJ	River	Moctezuma, Jacala	1 360	PRPO	Drinking	Portezuelo, Ixmiquilpan	1 784
CPAI	Canal	Panales, Ixmiquilpan	1 780	PRAL	Drinking	Alfajayucan	1 871
PHZ	Dam	Hidroeléctrica, Zimapan	1 779				

*= sample collected in the State of Mexico.

Sampling was carried out following NMX-AA-003-1980 (SCFI, 1980). A volume of 500 ml of each sample was collected in polyethylene containers. They were preserved by adding nitric acid up to a pH of 2 and refrigerated at 4 °C for no more than six months.

Total metals were determined by the flame method with an atomic absorption spectrophotometer (model Buck Scientific AAS VGP 216, UAS.), in triplicate, according to NMX-AA-051-SCFI-2001 (SCFI, 2001). Digestion was carried out on a heating plate, and homogenization was performed to verify that there were no solids adhering to the bottom; then, a 50 ml aliquot was taken and transferred to a beaker.

Three milliliters of concentrated nitric acid were added, and it was heated on an evaporation dish, avoiding boiling, until 2 to 5 ml were obtained, and then left to cool. Five milliliters of concentrated nitric acid were added, and it was covered with a watch glass and placed on the plate, raising the temperature until the reflux of vapors; once digestion was completed, it was removed and left to cool.

For every 100 ml of final solution volume, 10 ml of hydrochloric acid (1:1) and 15 ml of water were added. Subsequently, the sample was heated for 15 min without reaching the boiling point and brought up to 100 ml. To take readings, the spectrophotometer was calibrated in accordance with paragraph 9.3 of the NMX-AA-051-SCFI-2001 standard; finally, the calculations were carried out according to equation 1 of the line, and the coefficient of determination, R^2, had values of 0.985 for Pb and 0.973 for Cd.

Equation 1. $y= mX+b$. Where: y= absorbance of the processed sample; m= slope (absorptivity coefficient) and b= ordered to the origin.

Statistical analysis

The values of Pb and Cd concentrations of the sampling sites were used to perform an analysis of variance (Anova) and a post-hoc analysis to make multiple comparisons between means; Scheffe’s multiple range test was used, with $\alpha= 0.05$, to indicate statistical significance due to the homogeneity of variances; the above was performed with SPSS Statistics, Version 25.

Results and discussion

Calibration curves. Standard solutions were prepared with known concentrations of Pb: 0.01, 0.05, 0.1, 0.2, 0.3 and 0.5 mg ml^{-1} and Cd: 0.005, 0.01, 0.05, 0.1, 0.15, and 0.3 mg ml^{-1}, including a blank as a reference. The measurements were made by atomic absorption spectroscopy, at wavelengths of 283.3 nm for Pb and 326.1 nm for Cd, with a bandwidth of 0.1 nm. Acetylene was used as fuel and nitrous oxide as a carrier gas, optimizing the atomization of the analytes (Figure 1).

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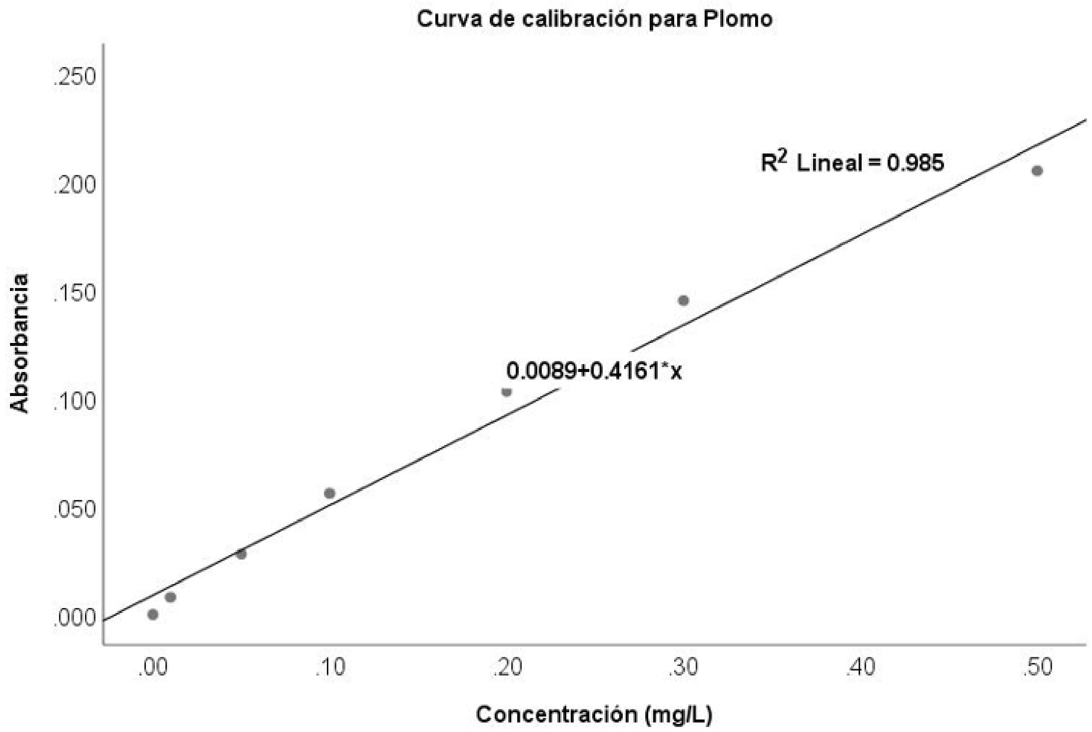
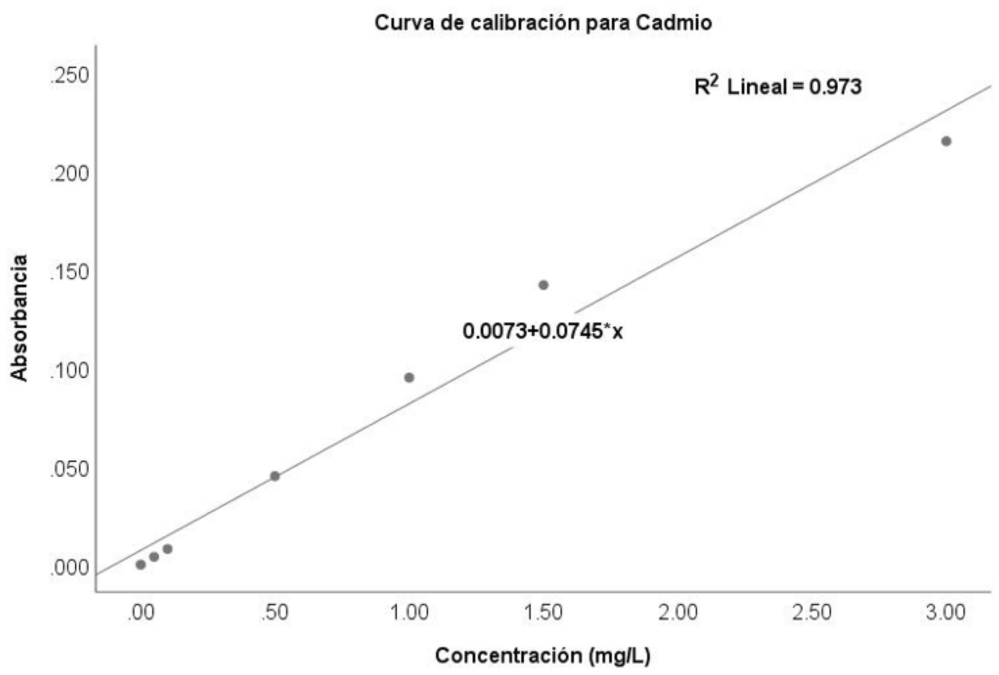
Figure 1. Calibration curve for Pb.



Concentrations of Pb and Cd in wastewater. Analysis of wastewater samples revealed that 26% of them exceeded the permissible Pb limits, which are set at 0.2 mg L^{-1}, with concentrations ranging from 0.017 mg L^{-1} to 0.466 mg L^{-1} (Figure 2).

Figure 2. Calibration curve for Cd.



In the case of Cd, 30% of the samples exceeded this limit, registering concentrations between 0.009 mg L^{-1} and 0.774 mg L^{-1}. The values obtained for both metals showed statistically significant differences (p= 0) in all the analyses of variance performed, under homogeneous conditions (Table 2). Similar results were reported by Oloruntoba *et al*. (2022), who identified high concentrations of Pb and Cd in wastewater.

Table 2. Pb and Cd concentrations in wastewater, natural water, and drinking water.

Code	Lead (mg L^{-1})	Cadmium (mg L^{-1})	Code	Lead (mg L^{-1})	Cadmium (mg L^{-1})
CPT1^{1}	0.046 ±0.006^{a-b}	0.184 ±0.006^{f}	PMI1^{1}	0.111 ±0.003^{c-f}	0.077 ±0.002^{a-d}
CPN1^{1}	0.029 ±0.002^{a-b}	0.077 ±0.007^{a-d}	MTA^{2}	0.022 ±0.021^{a-b}	0.009 ±0.002^{a}
CLJI^{1}	0.056 ±0.008^{a-c}	0.023 ±0.023^{a-b}	MFI^{2}	0.007 ±0.017^{a}	0.023 ±0.001^{a}
CSM1^{1}	0.226 ±0.031^{g}	0.64 ±0.012^{j}	MPA^{2}	0.015±0.006^{a-b}	0.036 ±0.006^{a-b}
CLSS^{1}	0.329 ±0.017^{h}	0.6 ±0.011^{j}	MLR^{2}	0.005 ±0.003^{a}	0.05 ±0.003^{a-b}
CPT2^{1}	0.048 ±0.008^{a-b}	0.077 ±0.004^{a-d}	MAN1^{2}	0.031 ±0.005^{a-b}	0.009 ±0.001^{a}
CPN2^{1}	0.303 ±0.009^{h}	0.05 ±0.005^{a-c}	MAN2^{2}	0.147 ±0.007^{a-c}	0.023 ±0.005^{a}
CBI1^{1}	0.128 ±0.007^{e-f}	0.063 ±0.005^{a-c}	PLRI^{2}	0.029 ±0.006^{a-b}	0.009 ±0.001^{a}
CNI1^{1}	0.048 ±0.003^{a-b}	0.09 ±0.003^{b-e}	PXZ^{2}	0.113 ±0.002^{c}	0.506 ±0.024^{e-f}
CMLI^{1}	0.152 ±0.009^{f}	0.009 ±0.001^{a}	PJEM^{2}	0.178 ±0.007^{d}	0.372 ±0.021^{c-d}
CSM2^{1}	0.113 ±0.002^{c-f}	0.506 ±0.02^{i}	CNI2^{2}	0.012 ±0.002^{a}	0.063 ±0.009^{a-b}
COBI^{1}	0.466 ±0.03^{i}	0.774 ±0.024^{k}	RSNI^{2}	0.329 ±0.03^{e}	0.466 ±0.015^{e-f}
CTA1^{1}	0.329 ±0.01^{h}	0.466 ±0.047^{i}	PBAI^{2}	0.005 ±0.001^{a}	0.533 ±0.008^{f-g}
CXA1^{1}	0.063 ±0.002^{a-d}	0.023 ±0.004^{a-b}	PEC^{2}	0.149 ±0.009^{c-d}	0.452 ±0.036^{d-f}
CPN3^{1}	0.082 ±0.003^{b-e}	0.009 ±0.003^{a}	PLJI^{2}	0.017 ±0.003^{a-b}	0.6 ±0.049^{g}
CPI1^{1}	0.111 ±0.002^{c-f}	0.05 ±0.009^{a-c}	PUTV^{2}	0.015 ±0.002^{a-b}	0.426 ±0.009^{c-d}
CDI1^{1}	0.029 ±0.004^{a-b}	0.023 ±0.004^{a-b}	PVII^{2}	0.022 ±0.008^{ab}	0.493 ±0.008^{e-f}

Code	Lead (mg L^{-1})	Cadmium (mg L^{-1})	Code	Lead (mg L^{-1})	Cadmium (mg L^{-1})
CXA2^1	0.017 ±0.006^a	0.009 ±0.003^a	PLEC^2	0.056 ±0.007^b	0.479 ±0.011$^{e\text{-}f}$
CLOI^1	0.034 ±0.005$^{a\text{-}b}$	0.036 ±0.005$^{a\text{-}c}$	PEVI^2	0.015 ±0.004$^{a\text{-}b}$	0.452 ±0.003$^{d\text{-}f}$
CLRI^1	0.07 ±0.01$^{a\text{-}d}$	0.103 ±0.004$^{a\text{-}e}$	PMBI^2	0.022 ±0.013$^{a\text{-}b}$	0.09 ±0.001$^{a\text{-}b}$
CVSA^1	0.039 ±0.003$^{b\text{-}e}$	0.157 ±0.014$^{c\text{-}f}$	PBSS^2	0.012 ±0.001^a	0.077 ±0.003$^{a\text{-}b}$
CMBI^1	0.08 ±0.003$^{e\text{-}f}$	0.077 ±0.008$^{a\text{-}d}$	PENI^2	0.015 ±0.003$^{a\text{-}b}$	0.023 ±0.001^a
CSM3^1	0.13 ±0.002$^{g\text{-}h}$	0.063 ±0.003$^{a\text{-}c}$	PRPA^2	0.005 ±0.002^a	0.332 ±0.002^c
CCAI^1	0.274 ±0.01$^{d\text{-}f}$	0.278 ±0.01^g	PRMA^2	0.007 ±0.002^a	0.533 ±0.017$^{f\text{-}g}$
RTI1^1	0.118 ±0.011$^{a\text{-}b}$	0.358±0.017^h	PLRE^2	0.024 ±0.007$^{a\text{-}b}$	0.009 ±0.004^a
RMJ^1	0.082 ±0.004$^{b\text{-}e}$	0.144 ±0.014$^{d\text{-}f}$	PRPO^2	0.027 ±0.005$^{a\text{-}b}$	0.117 ±0.002^a
CPAI^1	0.303 ±0.003^h	0.144 ±0.02^{def}	PRAL^2	0.017 ±0.001$^{a\text{-}b}$	0.774 ±0.029^h
PHZ^1	0.113 ±0.002$^{c\text{-}f}$	0.506 ±0.0251			
$\overline{x}$ ±SD	0.135 ±0.004	0.194 ±0.008	$\overline{x}$ ±SD	0.049 ±0.003	0.268 ±0.009
CV (%)	2.92	3.9	CV (%)	5.75	3.46

Results expressed as mean ± standard deviation; different letters in the same column indicate significant differences with p= 0.05. $\overline{x}$= mean; SD= standard deviation; CV= coefficient of variation; ^{1}= wastewater; $^{2=}$ natural and drinking waters.

Likewise, Kinuthia *et al*. (2020) documented that Pb levels in wastewater used for agricultural irrigation exceeded the limits set by the World Health Organization (WHO) and the US. Environmental Protection Agency (EPA). In more than 30% of the studies reviewed, concentrations of heavy metals, such as chromium (Cr), cadmium (Cd), lead (Pb), copper (Cu), and zinc (Zn), have been identified above the permissible limits established by current environmental regulations.

This situation highlights the urgent need to adequately treat wastewater tributaries before they are discharged into surface water bodies, in order to prevent contamination of groundwater aquifers (Arti and Mehra, 2023). In the Mezquital Valley region, the use of wastewater for agricultural irrigation is a common practice. Various studies have shown that the heavy metals present in these waters can be absorbed by plants.

In this sense, Lara *et al*. (2015) reported the presence of Cd and Pb in corn, alfalfa, and sunflower crops, with concentrations ranging from 0.001 to 0.096 mg kg^{-1} for Cd and from 0.05 to 0.613 mg kg^{-1} for Pb. The concentrations of Pb and Cd recorded in samples of natural and drinking water exceeded the permissible limits in 70% and 100% of cases, respectively. In addition, statistical differences were observed between the values obtained (Table 2, Figure 3 and Figure 4).

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Figure 3. Graph of Pb and Cd concentrations in wastewater.

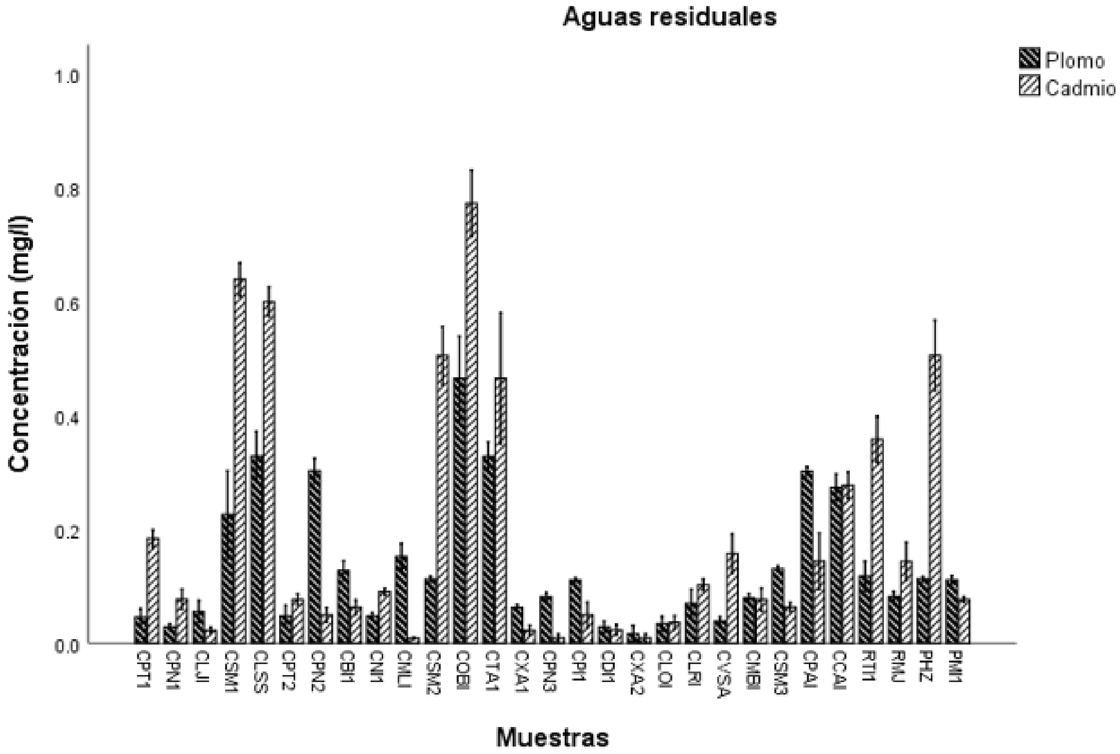

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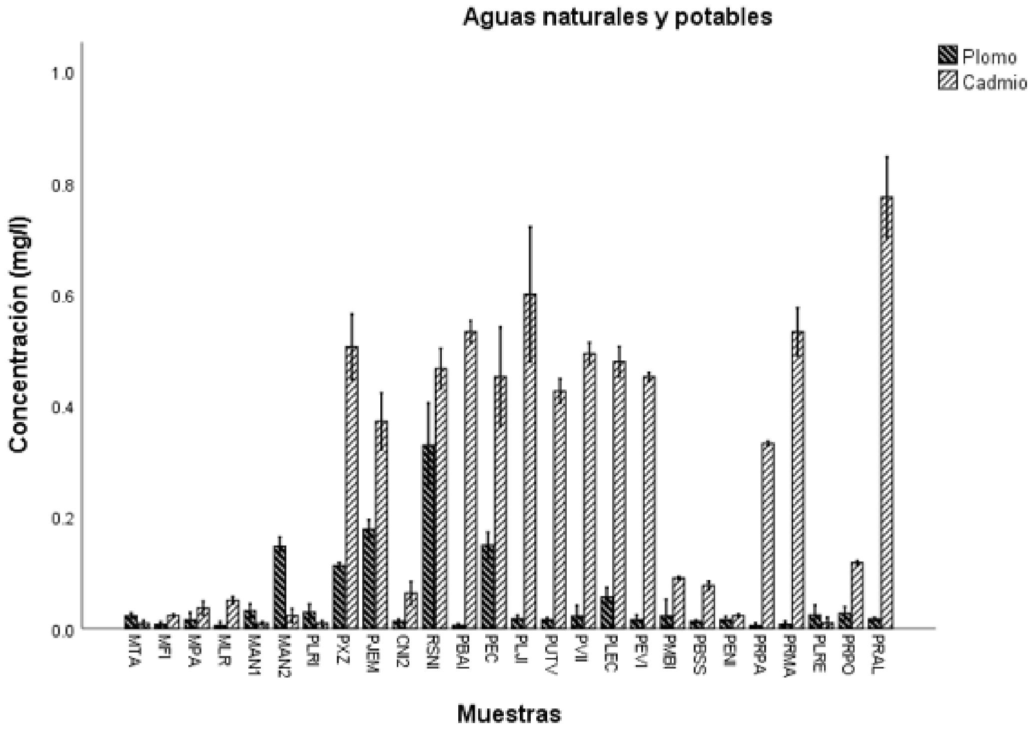
Figure 4. Graph of Pb and Cd concentrations in natural and drinking water.



These findings coincide with what was reported by Balli and Leghouch (2018); Oloruntoba *et al*. (2022), who documented elevated concentrations of Pb and Cd in drinking water from wells and springs. In both studies, the levels detected exceed the values established by the World Health Organization (WHO) for water suitable for human consumption, which represents a potential risk to public health.

In this regard, Sansom *et al*. (2019) reported that 30.8% of the households analyzed had Pb concentrations in drinking water between 0.6 and 2.4 g L^{-1}, exceeding the permissible limits and evidencing the need to protect public health. Groundwater contamination by heavy metals, whether due to geogenic or anthropogenic causes, poses a significant risk to human health, primarily through the intake of contaminated water (Oloruntoba *et al*., 2022).

Improving their quality before consumption is essential; however, treatment plants do not generate immediate effects due to the accumulation of organic matter, microorganisms, and heavy metals. In the Mezquital Valley, wastewater used for irrigation also recharges aquifers, contaminating drinking water sources. Globally, more than 20% of available freshwater no longer meets demand, and it is estimated that half of the population will face severe scarcity (Mancosu *et al*., 2015).

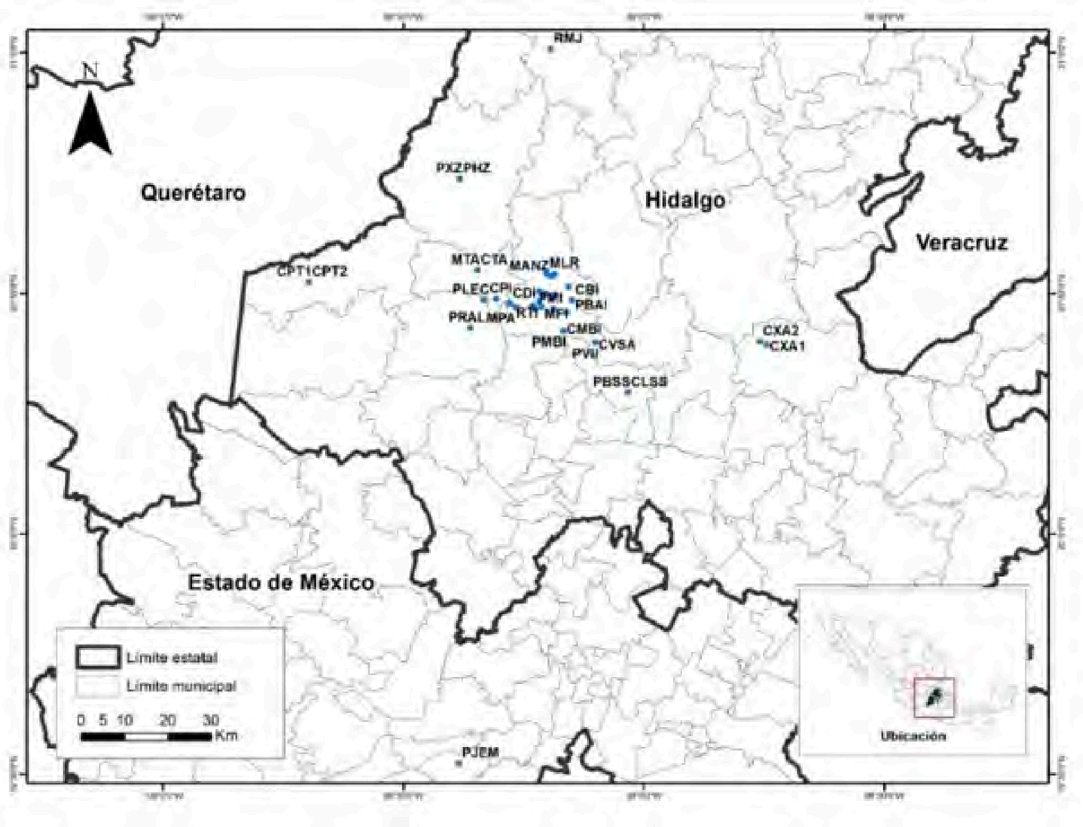
This highlights the urgency of comprehensive management and continuous monitoring of tributaries (Chamizo *et al*., 2020), given the cumulative toxicity in living organisms and its relationship with diseases, such as cancer (Arti and Mehra, 2023). Water is the main route of human exposure to heavy metals. Cd generates oxidative stress and damage to lungs, kidneys, and bones, and is considered carcinogenic (Bernhoft, 2013; Rinaldi *et al*., 2017). Pb, on the other hand, affects the nervous system, blood pressure and cognitive development, especially in children (Gidlow, 2004).

In the Mezquital Valley, water pollution is the result of the historical use of untreated wastewater for agricultural irrigation, the dumping of urban and industrial waste, as well as the runoff of agrochemicals from cultivated soils. This contaminated recharge of aquifers compromises the sources of supply.

The results obtained in this study open the door to the development of complementary research that includes physicochemical and microbiological parameters, which are fundamental for decision-making in the design of public policies and intervention strategies. The use of wastewater should be subject to strict surveillance, always prioritizing human safety (Vázquez *et al*., 2020).

According to the sampling area (Figure 5), no direct relationship was observed between the concentration of Pb and Cd and the proximity to the discharge points. Although a decrease was expected in more remote areas, the results do not reflect this trend, suggesting a more complex dispersion of pollutants.

Figure 5. Map of sampling sites for wastewater, drinking water, and purified water.



Conclusions

The water analysis carried out in the Mezquital Valley region, in the state of Hidalgo, showed that the concentrations of Pb and Cd exceed the permissible limits established by current Mexican regulations. In wastewater, the levels of Pb and Cd exceed these limits by 26% and 30%, respectively. In the case of natural and drinking water, concentrations exceed the normative values by 70% for Pb and up to 100% for Cd. These results reflect the consequences of more than a century of continuous wastewater use for agricultural irrigation in the region.

Given this situation, it is essential to strengthen and give continuity to scientific studies aimed at the periodic and specific evaluation of pollutants in bodies of water. It is also essential to implement comprehensive strategies for the proper management of waste and the efficient treatment of water, with a view to its safe reuse in agriculture. To achieve this, it is crucial to foster collaboration between the different sectors: academic, governmental, industrial, and social, promoting an interdisciplinary approach that guarantees the protection of public health, food security, and environmental sustainability in the region.

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