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Rice farms contaminated with toxic heavy metals: The case of Agusan del Sur, Philippines

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Abstract

Rice plays a crucial role in food security, but its production faces threats from human-induced pollutants. In the studied area, rice paddies are irrigated with water from the Solibao River, which collects runoff from creeks contaminated with heavy metals due to artisanal and small-scale mining. Heavy metal levels in the paddy soils were analyzed using Direct Air-Acetylene Flame Atomic Absorption for lead (Pb) and Cold Vapor Atomic Absorption Spectroscopy for mercury (Hg). Among the three agricultural sites studied, the downstream site (Santa Cruz) showed heavy metal concentrations exceeding WHO limits for Pb (0.10 mg kg^{-1}) and Hg (0.08 mg kg^{-1}), with mean values of 38.6 mg kg^{-1} and 7.71 mg kg^{-1}, respectively. Environmental indices classified this site as æExtremely Contaminated" for Geo-Accumulation Index (Igeo), at æVery High Risk" for Ecological Risk Index (ER), and æVery High Contamination" for Contamination Factor (CF) for both Pb and Hg. Midstream and upstream sites generally had levels below detection limits but require further study for other heavy metal contaminants. The high heavy metal concentrations in downstream agricultural soils are likely due to unregulated waste disposal. This contamination poses significant environmental risks, impacting irrigation water quality and the safety of agricultural soils.

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Introduction

Throughout human history, there has been a symbiotic relationship between our societies heavy reliance on the benefits provided by the earth, as evident in our evolving ability to sustainably manage the soil (Brodt *et al.*, 2011). Crop cultivation, a hallmark of human civilization, epitomizes the connection between humans, the earth, and food sources, underscoring soil as the fundamental bedrock of agriculture (Parikh and James, 2012).

Farmers and ranchers are pivotal in producing the food and fibers essential for daily life and soil plays a critical role in the success of agricultural practices (Tahat *et al.*, 2020; Mehmet, 2020; Kicińska and Wikar, 2024). The nutrient content and overall health of the soil directly influence crop health (Morgan and Conolly, 2013), impacting the quality and abundance of food supplies (Silver *et al.*, 2021). As Sindelar (2015) notes, the healthiest soils yield the most nutritious and abundant food supplies, highlighting the crucial link between soil health and agricultural success. Between 1960 and 2015, agricultural production saw a more than threefold increase, partly due to the Green Revolution's productivity-enhancing technologies and expanded use of natural resources (FAO, 2017). This period also witnessed significant industrialization and globalization in food and agriculture (Anderson, 2010). Agriculture, a cornerstone of society, not only ensures food security but also significantly contributes to the economy as well as impacts the environment (Fogle and Kime, 2021; Kicińska and Wikar, 2021). In regions like Southern and Eastern Asia, wet-rice cultivation is prevalent, utilizing small, flooded fields that support the sustenance of much of the rural population (Lee *et al.*, 2021; Liu *et al.*, 2021; Britannica, 2023). Soil contamination has emerged as a global concern in recent decades due to rapid industrialization, urbanization, unregulated mining, emissions, uncontrolled wastewater discharge, sewage irrigation, and prolonged pesticide usage (Blachowski *et al.*, 2024). The issue of heavy metal contamination in agricultural soils has garnered international attention (Alloway, 2012; Guo *et al.,* 2014). These metals are naturally present in the environment but have accumulated in soils primarily due to human activities such as wastewater irrigation, unregulated fertilizer use, and airborne deposition from smelting and fossil fuel combustion (Guo *et al.*, 2020; Jendruś *et al.*, 2023). This contamination poses significant environmental and food safety risks (Hu *et al.*, 2016). China, one of the largest producers and consumers of metals, significantly contributes to heavy metal contamination in agricultural soils (Chen *et al.*, 2022). Accumulated heavy metals can degrade soil quality, hinder crop growth, and pose health risks through the food chain (Mouhsine *et al.*, 2012; Nabulo, 2010), thus, raising widespread public concern about food safety (Arao *et al.*, 2010; He *et al.*, 2013).

In the Philippines, rice is a staple food critical to daily life and occupies a substantial portion of arable land, whereas of 2021, constitute about 4.81 million hectares of land cultivated to æPalay” (*Orayza sativa*) in the Philippines (NNC, 2020; Gonzalez, 2020; DOST-PCAARRD, 2024). Ensuring a stable, adequate, and affordable rice supply is essential due to its social, cultural, economic, and political importance in the Philippines (Navata and Turingan, 2013; Mamiit *et al.*, 2021). However, heavy metal contamination in major rice-growing areas such as Zambales and Negros Occidental has been reported, with concentrations exceeding intervention values (Mangahud *et al.*, 2015). Sources of this contamination include mine tailings, contaminated irrigation water, farm chemicals, and animal defecation (Ramos and Manangkil, 2022). Given the potential health risks posed by heavy metal contamination, it is crucial to assess and address these hazards in rice-growing regions. Monitoring metal concentrations in soils and plants can indicate potential toxicity risks to consumers (Wei *et al.*, 2023), underscoring the need for ongoing research and intervention to ensure safe rice cultivation. This study aims (1) to investigate the presence of heavy metal pollutants on the rice paddy soils of Agusan Del Sur, (2) to determine the degree of heavy metal contamination using established soil environmental metrics, (3) to assess the transport of these pollutants to the rice paddy soils in the area and (4) to add existing data in terms of heavy metal contamination on rice paddies in the Philippines.

Materials and methods

Study area

The study was done in the Municipality of Rosario in the southern part of Agusan Del Sur, Caraga region in Northern Mindanao. It spans approximately 40,273 hectares and comprises eleven barangays which are mostly agricultural lands used for Palm and Coconut Tree Plantations, Root crops, Rice Paddies, etc. (RMPS, 2022).

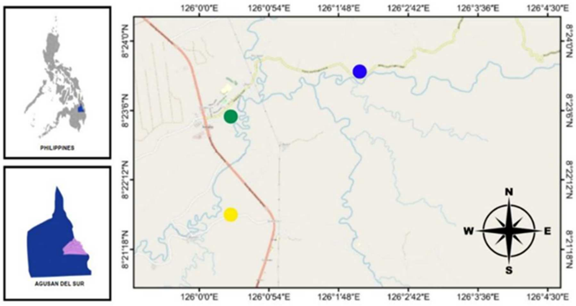

Fig. 1. The study area is situated in the Province of Agusan del Sur highlighted in blue and delineating the area of the Municipality of Rosario (Pink). The three study sites are identified as follows: Barangay Cabantao (Upstream, Blue), Barangay Poblacion (Midstream, Green), and Barangay Santa Cruz (Downstream, Yellow)

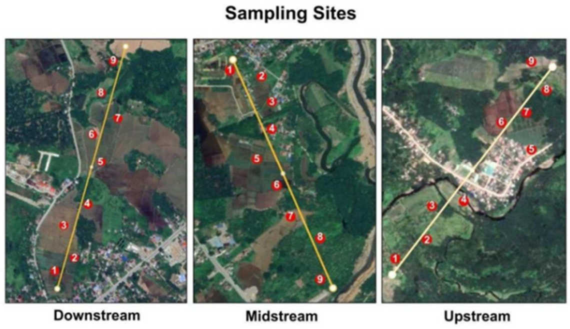

Fig. 2. The red dots on the map represent the sampling points taken from a one-kilometer stretch (indicated by the yellow line). The images used were captured using Google Map

In this study, the research area is a section of the Solibao River, as this river connects to the Economic Mining Zone Creeks, where Acopiado *et al.* (2020) found elevated levels of mercury in 2019 surpassing DENR standards. Solibao River is used as one of the water sources of irrigation for their rice paddies. The study focused on three riverine barangays along the river gradient as shown in Fig. 1: Sta. Cruz as the downstream site, Poblacion, as the midstream site, and Cabantao as the upstream site and sample points (within the 1 kilometer transect) are shown in Fig. 2 and the corresponding sample point coordinates.

Soil Sampling

Soil sampling were done in all three barangays of Rosario from August 7 to 14, 2023. Following minor adjustments, the approach outlined by Anwarul Hasan *et al.* (2022) was followed. Within each barangay, soil samples were collected in 1-foot depth using non-metallic shovel to avoid metal contamination. Within one-kilometer stretch of rice fields using random sampling at every 100 meters, one sample was gathered resulting in nine replicates per sampling location. Each sample weighed at least one kilogram, securely stored in labeled zip-lock bags for subsequent analysis.

Preparation of soil samples for heavy metal analysis

After collection, soil samples were dried at a temperature of 50°C for 24 hours to remove the moisture (Anwarul Hasan *et al.,* 2022). A 200-gram dried soil sample was then extracted from the dried soils after one day of drying, subsequently ground to pass through a 2 mm sieve using a pulverizer, with a resulting total of 27 dried and finely ground samples, meeting the minimum requirements for laboratory analysis. These samples were stored in smaller zip-lock bags and transported for mercury analysis using Cold Vapor Atomic Absorption Spectroscopy (USEPA Method 3050B) and for lead analysis using Direct Air-Acetylene Flame Spectroscopy (USEPA Method 7471B) (Soares *et al.*, 2015; Parikh and James, 2012).

Although environmental impact assessment studies usually employ threshold values established by national or international authorities, unfortunately, there are no formal sediment and soil quality recommendations in the Philippines (Domingo *et al.*, 2023). This study adopted the international quality requirements for agricultural soils published by the World Health Organization (Kinuthia *et al.,* 2020).

Environmental indices

Geo-accumulation index (Igeo)

Since its introduction by Müller (1969), the geological accumulation index (Igeo) has been extensively used in studies and initiatives pertaining to heavy metals (Ji *et al.*, 2008). The elevated concentrations of pollutants accumulating in the soil were determined by comparing the observed values with background or standard reference values (Abdullah *et al.*, 2020). The following formula was applied to calculate the Igeo of the analyzed soil:

$$\mathrm{Igeo} = \log2\left(\frac{\mathrm{Cn}}{1.5*\mathrm{Bn}}\right) \quad (1)$$

where Bn is the geological chemical background or standard value used by the WHO in agricultural land for lead (0.10 mg kg-1) and mercury (0.08 mg kg-1) and Cn is the observed concentration (mg kg-1) of each heavy metal in the soil. Igeo values were interpreted in Table 1.

Ecological risk index (ER)

The ER, which Hakanson (1980) established, was used to quantify the potential ecological danger related to the buildup of heavy metals in the soil. The properties of soil heavy metals and their environmental behavior are considered when evaluating the possible ecological danger associated with these metals (Zhao *et al.*, 2022). Furthermore, it considers the synergistic effects of various elements, pollution levels, and environmental associations with heavy metals (Liu *et al.*, 2021; Zhang *et al.*, 2021).

$$\mathrm{ER} = \mathrm{Tr} \times \mathrm{CF} \quad (2)$$

Calculation formula is where Tr is the toxicity coefficient of heavy metals Lead and Mercury are 5 and 40 respectively (Darko *et al.*, 2017) and CF is the contamination factor (Eq. 3) (Zhao *et al.*, 2022). Listed in Table 1 are the interpreted values of ER.

Contamination factor (CF)

Utilizing the Contamination Factor (CF), the level of sointamination was evaluated (Kowalska *et al.*, 2018; Sudarningsih, 2023). This index allows for the evaluation of soil contamination by considering the heavy metal content at the soil surface concerning pre-industrial reference levels (Kinthua *et al.*, 2020).

$$\mathrm{CF} = \frac{\mathrm{Cn\ (sample)}}{\mathrm{Cn\ (background)}} \quad (3)$$

Where Cn (background) is the baseline or background value (mg kg-1) of the heavy metal and Cn (sample) is the amount of concentration (mg kg-1) of each heavy metal identified in the sample agricultural soil while the assessment of values are listed in Table 1.

Table 1. Classification of indexes (Igeo, ER, and CF) with their corresponding evaluation

Igeo	ER	CF
Class 1: Igeo ≤ 0, Uncontaminated	LR: ER < 40, low risk	LC: CF < 1, low contamination
Class 2: 0 < Igeo ≤ 1, Uncontaminated to moderately contaminated	MR: 40 ≤ ER < 80, moderate risk	MC: 1 ≤ CF < 3, moderate contamination
Class 3: 1 < Igeo ≤ 2, Moderately contaminated	CR: 80 ≤ ER < 160, considerable risk	CC: 3 ≤ CF < 6, considerable contamination
Class 4: 2 < Igeo ≤ 3, Moderately to heavily contaminated	HR: 160 ≤ ER < 320, high risk	VHC: CF ≥ 6, very high contamination
Class 5: 3 < Igeo ≤ 4, Heavily contaminated	VHR: ER ≥ 320, very high risk	
Class 6: 4 < Igeo ≤ 5, Heavily to extremely contaminated		
Class 7: Igeo > 5, Extremely contaminated		

Data analysis

The plotting of sampling points and geological maps were created using QGIS 3.32. Descriptive Statistical analyses for the data and graphical representation of the results were performed using Excel 2019. Additionally, all sites with more than 50% of measurements below detection limits (<dl) were excluded from the graphical presentation.

Results and discussion

Heavy metal concentrations in rice paddy soils

A collection of a total of 27 samples from three different barangays: Santa Cruz, Poblacion, and Cabantao. Each sample was analyzed using Cold Vapor Atomic Absorption Spectroscopy for Mercury and Direct Air-Acetylene Flame for Lead, resulting in a total of 54 samples analyzed for both heavy metals. This study utilized the World Health Organization's (WHO) recommended values for heavy metals in soils used for agricultural practices, as cited by Kinuthia *et al.* (2020). The permissible values for Lead and Mercury in agricultural soils are 0.10 mg kg-1 and 0.08 mg kg-1, respectively.

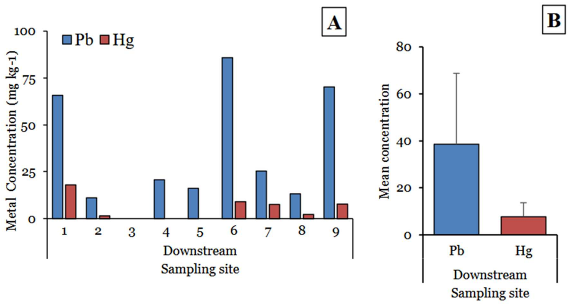

Fig. 3. A) Heavy metal concentrations (Pb and Hg) in the three sampling sites and B) mean and standard deviation concentration of downstream

Fig. 3 presents a graphical representation of the collected data, while Table 2 provides the laboratory results for Hg and Pb concentrations, indicating that all upstream samples fall below detectable levels for these heavy metals. Midstream samples show only 2 stations with Pb concentrations above detection limit readings S7 (1033 mg kg-1) and S9 (444 mg kg-1).

According to K.D. Villegas, (personal communication, 9 August 2023), these two sampling stations were the areas where the harvesters or automobile anchorages were placed whenever their harvest or plantation started. This probably account for the used (waste) oil from automobiles that include metals, organic and inorganic compounds such as oil additives, oxidation products, sediments, water, and metallic particles from worn gear (EEA, 2007; Ololade, 2014). This circumstance made these sampling stations highly contaminated with Pb as determined by laboratory results. Excluding these two contaminated sites because of its usage, in general, Midstreams paddy soils are all below detection limits. Downstream showed variations of Hg and Pb concentrations ranging from below the detection limit to a maximum of 85.9 mg kg-1 for Pb and 18.00 mg kg-1 for Hg. Comparing these results with the WHO recommended levels for lead and mercury in agricultural soils, the downstream site significantly exceeds the permissible limit for Pb and Hg across all sampled points, exhibiting fluctuating concentrations. The average lead concentration in downstream areas is 38.6 ± 30.2 mg kg-1, whereas the permissible limit for agricultural soils is 0.10 mg kg-1. Similarly, mercury concentrations in downstream stations are 7.71 ± 5.91 mg kg-1, compared to the permissible limit of 0.08 mg kg-1. Water sources for irrigation and cultivation are also indicated in Table 3.

Table 2. Analyzed Pb and Hg concentrations in all sampling poin

Stations	Downstream		Midstream		Upstream	
	Pb^{b}	Hg^{c}	Pb^{b}	Hg^{c}	Pb^{b}	Hg^{c}
	0.10^{a}	0.08^{a}	0.10^{a}	0.08^{a}	0.10^{a}	0.08^{a}
1	65.9	18.0	<dl	<dl	<dl	<dl
2	11.1	1.55	<dl	<dl	<dl	<dl
3	<dl	<dl	<dl	<dl	<dl	<dl
4	20.7	<dl	<dl	<dl	<dl	<dl
5	16.1	<dl	<dl	<dl	<dl	<dl
6	85.9	9.05	<dl	<dl	<dl	<dl
7	25.4	7.61	1033	<dl	<dl	<dl
8	13.2	2.31	<dl	<dl	<dl	<dl
9	70.3	7.72	444	<dl	<dl	<dl
Mean±SD	38.6±30.2	7.72±5.91	738±416	-	-	-

Detection Limit^{a}; <dl: below detection limit; - : no calculated data

Reference: USEPA Method 7471B^{b} and USEPA Method 3050B^{c}

Table 3. Different water sources used in Rice Paddy Soils within sampling sites

Stations	Water sources		
	River-Water	Rain-Water	Deep-Well
Downstream	✔	*	*
Midstream	*	✔	✔
Upstream	*	✔	✔

✔ Frequently used; * Occasionally used

These water sources are identified on the sites based on availability for the utilization of the farmers as mentioned by K.D. Villegas, (personal communication, 9 August 2023). Since river water receives pollutants primarily from human activity, identifying the source of contamination is crucial, in this case, artisanal and small-scale mining (Acopiado *et al.*, 2020). In downstream rice paddy soils, river-water is more frequently used for irrigation compared to upstream or midstream areas. In contrast, rice paddies in upstream and midstream regions primarily rely on rainfall and deep wells for their irrigation needs. Based on the results of this study, paddy soils in downstream locations exhibit the highest levels of contamination, attributed to regular utilization of river-water for irrigation and its associated transport of pollutants.

Table 4. Summary of related studies of heavy metals in paddy soils around the world

Location	Source	Mean concentration (mg kg-1)								Reference
		As	Cd	Cu	Cr	Hg	Pb	Zn	Ni	
Rosario, Agusan Del Sur, Philippines	Solibao River	-	-	-	-	1.74	66.2	-	-	This Study
Guilan Province, Iran	Zarjoub and Goharroud Rivers	12	-	47.4	124	-	72.3	136	48.3	Haghnazar *et al.* (2023)
Uttar Pradesh, India	Kali River	-	0.33	0.13	0.22	-	-	0.58	-	AL-Huqail *et al.* (2022)
Ondo State, Nigeria	Ogbese River	-	0.23	0.62	-	1.68	-	5.02	-	Adewumi and Lawal (2022)
Vietnam	Red River	21.9	0.56	72	64	-	48	160	38	Nguyen *et al.* (2020)a
	Houng River	13.6	0.25	27.1	-	-	29.7	83	28.5	Nguyen *et al.* (2020)b
	Mekong River Delta	12.6	0.27	30	-	-	28.6	90	36.3	
Tajan Watershed, Iran	Tajan River		0.7	25.4	108		0.6	52.3		Vatanpour *et al.* (2020)
Jiangsu Province, Zhejiang Shanghai Province, and Shanghai Province, China	Yangtze River Delta	7.267	0.356	41.0	72.91	0.146	31.6	117	-	Mao *et al.* (2019)
Yongshuyu Irrigation, North-east China	Songhua River	8.77	0.18	17.3	82.8	0.22	34.6	88.6	21.2	Cui *et al.* (2018)
Isfahan Province, Iran	Zayandeh Rood River	-	1.34	-	-	-	61.1	52.6	56.7	Rahimi *et al.* (2017)
Paramillo Massif, Columbia	Sinú River	-	0.41	38.9	-	0.07	27	70	29	Marrugo-Negrete *et al.* (2017)
Hubei Province, Hunan Province, and Jiangxi Province, China	Yangtze River Region	-	0.92	-	75.19	0.26	24.1	-		Liu *et al.* (2016)
Cabatuan, Isabela, Philippines	River Irrigated	9.6	<10.0	57.0	54.9	<7.0	>8.0	59.8	<50.0	Magahud *et al.* (2015)
San Miguel, Iloilo, Philippines	River Irrigated	<9.0	<10.0	46.8	82.9	<7.0	10.3	47.5	67.6	
Kabacan, North Cotabato, Philippines	River Irrigated	<9.0	<10.0	49.7	40.9	<7.0	15.6	51.6	<50.0	
Punjab Province, Pakistan	Ravi River	-	35.0	-	37.8	-	1065	-	85.8	Tariq and Rahid (2013)

Table 4 summarizes research on heavy metal concentrations in paddy soils worldwide, spanning continents such as South America, Africa, Asia, and the Middle East. Heavy metals, including As, Cd, Cu, Cr, Hg, Pb, Zn, and Ni. These metals have been measured in soils irrigated by rivers like China's Yangtze River Delta (Mao *et al*., 2019), the Zarjoub and Goharroud Rivers in Iran (Haghnazar *et al*., 2023), and the Solibao River in the Philippines (This study). Notably, Punjab Province, Pakistan (Tariq and Rahid, 2013), exhibited the highest lead (Pb) and cadmium (Cd) concentrations, with mean data of 1065 mg kg-1 and 35 mg kg-1, respectively. Lead (Pb) concentrations in Agusan Del Sur, Philippines, were 66.2 mg kg-1, while mercury (Hg) concentrations were significantly lower across all sites, peaking at 1.74 mg kg-1 (for <dl sample points; the value used for calculation was half of the Detection Limit). These findings highlight substantial variation in heavy metal pollution, influenced by regional industrial activities and agricultural practices. Specific environmental management measures are necessary to mitigate potential threats to food safety and human health.

Soil contamination assessments

Geo-accumulation index (Igeo)

The Igeo has been extensively employed in studies and projects focused on heavy metals (Ji *et al.*, 2008; Charzynski *et al.*, 2017). Using the given equation (Eq. 1) on solving Igeo, calculated values (Fig. 4) of the index with their corresponding æClass" are shown in Table 5.

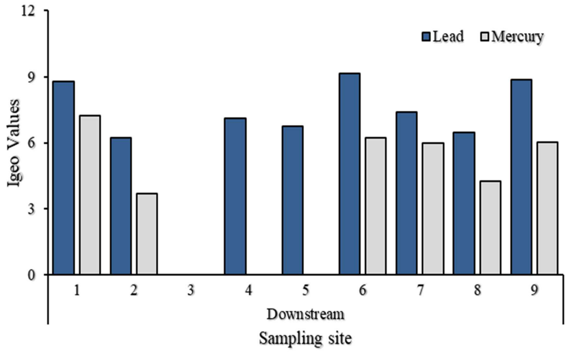

Fig. 4. Graphical representation of calculated geo-accumulation index (Igeo) values of Pb and Hg on each sampling point

Table 5. Geological accumulation index (I_{geo}) of lead and mercury in all sites

Samples	Downstream		Midstream		Upstream	
	Pb	Hg	Pb	Hg	Pb	Hg
1	Class 7	Class 7	-	-	-	-
2	Class 7	Class 5	-	-	-	-
3	-	-	-	-	-	-
4	Class 7	-	-	-	-	-
5	Class 7	-	-	-	-	-
6	Class 7	Class 7	-	-	-	-
7	Class 7	Class 7	Class 7	-	-	-
8	Class 7	Class 6	-	-	-	-
9	Class 7	Class 7	Class 7	-	-	-

- : no calculated data, Class 5: 3<Igeo≤4, Heavily contaminated; Class 6: 4<Igeo≤5, Heavily to extremely contaminated; Class 7: Igeo＜5, Extremely contaminated.

The majority of the samples with Pb traces exhibit Class 7 (Igeo＜5) distinction which is equal to æExtremely Contaminated" in the Downstream site; while Hg traces are observed on 6 out 9 samples ranging from Class 5 æHeavily Contaminated" (3 < Igeo ≤ 4) to Class 7 æExtremely Contaminated" (Igeo＜5) categories. However, only two samples, S7 and S9 exhibit the æExtremely Contaminated" class on the Midstream site due to vehicle anchorage, while the rest of midstream and all Upstream samples are below detection limit (<dl) for Lead. Likewise, for mercury for both mid to upstream sites. This is a probable indication that these heavy metals have low concentration in the area, low enough to not be detected. The Downstream site's total Pb distribution was found to be Class 7, indicating extreme contamination while Hg's distribution varies from Heavy to Extreme contamination. The below detection limit (<dl) results in Table 2 indicate that the sampling stations in upstream and midstream paddy soils exhibit minimal or

negligible contamination. This is likely due to the predominant use of rainwater and deep-well water for irrigation. "No data" (-) signifies that no assessment was conducted using Equation (1) to classify accumulation, as the results were below the detection limit (<dl).

Ecological risk index (ER)

The characteristics of these metals and their behavior in the environment are considered when assessing the ecological risk posed by soil contaminants (Zhao *et al.*, 2022). The analyzed soil yielded varying concentrations of Pb and Hg, which were used to assess the ER values.

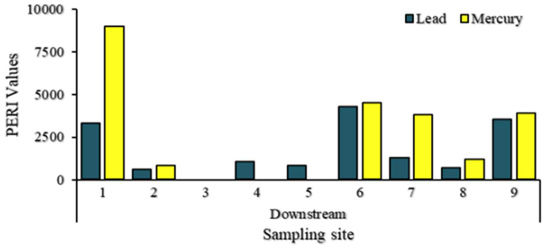

Fig. 5. Graphical representation of potential ecological risk index (PERI) values of Pb and Hg on each sampling point

These results are presented in Fig. 5. As indicated in Table 6, most of the Downstream samples showed a æVery High Risk” (VHR: ER ≥ 320) indication of the risk assessment in both Pb and Hg. Midstream's high Pb concentration on S7 and S9 is the result of vehicle anchorage during harvest season making these sample points much higher than the rest concerning Pb (EEA, 2007; Ololade, 2014). On the other hand, due to <dl, Pb and Hg's ER on this sampling stations cannot be calculated. While the Midstream and Upstream sites revealed "no calculated data" (-) regarding ecological risk, this should not be interpreted as an indication that heavy metals are entirely absent or incapable of posing environmental risks, particularly in soils. The "below detection limit" (<dl) results presented in Table 2 suggest that the levels of these heavy metals were very low to be detected by the analytical methods employed in this study. However, the fact that these metals were not detected does not necessarily mean they are absent or insignificant; rather, their levels were below the sensitivity threshold of the instruments used.

Table 6. Potential ecological risk index (PERI) of lead and mercury in all sites

Stations	Downstream		Midstream		Upstream	
	Pb	Hg	Pb	Hg	Pb	Hg
1	VHR	VHR	-	-	-	-
2	VHR	VHR	-	-	-	-
3	-	-	-	-	-	-
4	VHR	-	-	-	-	-
5	VHR	-	-	-	-	-
6	VHR	VHR	-	-	-	-
7	VHR	VHR	VHR	-	-	-
8	VHR	VHR	-	-	-	-
9	VHR	VHR	VHR	-	-	-

- : no calculated data
VHR: Er ≥ 320, very high risk

Contamination factor (CF)

CF is a soil assessment index which evaluates surface heavy metal levels relative to pre-industrial reference values. This metric revealed that among the studied sites, Downstream sampling points are all except for few sites (4 stations) categorized as with æVery High Contamination” (VHC: CF ≥ 6) in both Pb and Hg as shown in Table 7. Midstream Hg values rendered no data since the concentration is Below Detection Limit (<dl). As illustrated in Fig. 6 and Table 7, the calculated values were notably high, particularly for Pb compared to Hg. Furthermore, Pb concentrations indicated a 'Very High Contamination' classification at only two sampling points within the midstream site, likely attributed to their use as anchorage areas for vehicles or machinery involved in rice harvesting.

Table 7. Contamination factor (CF) of lead and mercury in all sites

Sampling points	Downstream		Midstream		Upstream	
	Pb	Hg	Pb	Hg	Pb	Hg
1	VHC	VHC	-	-	-	-
2	VHC	VHC	-	-	-	-
3	-	-	-	-	-	-
4	VHC	-	-	-	-	-
5	VHC	-	-	-	-	-
6	VHC	VHC	-	-	-	-
7	VHC	VHC	VHC	-	-	-
8	VHC	VHC	-	-	-	-
9	VHC	VHC	VHC	-	-	-

- : no calculated data

VHC: CF ≥ 6, very high contamination

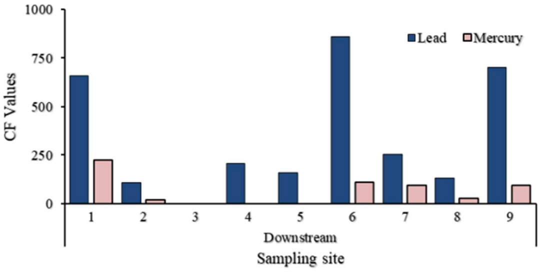

Fig. 6. Graphical representation of contamination factor (CF) values in each sampling point

Leakage of fuels for this equipment may cause this drastic change in Pb concentration since Pb is one of the elements found in fuels making midstream shows very high contamination results (Santos *et al.*, 2012).

For upstream on the other hand, both Pb and Hg showed no data since their concentration for detection is below the standard limit rendering no calculated data in all sampling sites.

Conclusion

The study identifies heavy metal contamination specifically at the downstream site in Santa Cruz, where it significantly impacts the agricultural soils. In contrast, upstream and midstream sampling points generally show lead (Pb) and mercury (Hg) levels below detection limits. The rice paddies in the downstream area exhibit the highest levels of lead and mercury contamination, primarily due to the creeks used for small-scale mineral processing within Santa Cruz's Economic Mining Zone (EMZ). These tributaries flow directly into the Solibao River, which subsequently carries the contamination to the downstream location studied. Environmental metrics classify the Downstream site as "Extremely Contaminated" using the Geo-accumulation Index a "Very High Risk" for Potential Ecological Risk Index and "Very High Contamination" from the Contamination Factor. Given the Solibao River's critical role in irrigation, extensive monitoring across all barangays that depend on it is essential to fully assess heavy metal contamination. Effective collaboration between government agencies particularly local government units and educational institutions is crucial for designing and implementing mitigation strategies to address the effect of these pollutants on the water bodies. Additionally, strict regulation of small-scale mining operations is imperative to prevent further environmental degradation.

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