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Heavy Metals Accumulation in the Agricultural Soils around the Limestone-Mining Area of Gunungkidul Regency, Indonesia

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Abstract

The study area, situated in an agricultural zone near limestone mining activities, faces significant threats from heavy metal pollution. The study aims to assess the concentrations of heavy metals (Pb, Zn, Cu, Cd, Mg, and Cr) in agricultural soils surrounding limestone-mining areas and evaluate the extent of heavy metal pollution

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based on World Health Organization (WHO) guidelines. Ten soil samples were collected from agricultural fields, with an additional three taken from limestone-mining sites to compare heavy metal accumulation using opportunistic sampling techniques. Heavy metal concentrations in the limestone formation influenced the levels found in soil samples from MOS-01, MOS-02, MOS-03, MOS-04, MOS-06, MOS-09, MOS-10, MOS-11, MOS-12, and MOS-13. At MOS-05, MOS-07, and MOS-08 sampling sites, heavy metals in agricultural soil were impacted by concentrations from clastic rock formations. Mining activities and agricultural fertilizers collectively influenced heavy metal content in agricultural soil at MOS-01, MOS-02, and MOS-10 sampling sites. Meanwhile, agricultural fertilizers alone impacted heavy metal concentrations at MOS-03, MOS-04, MOS-05, MOS-06, MOS-07, MOS-08, and MOS-09 sampling sites. Several sampling locations showed heavy metal concentrations that exceeded WHO standards, particularly Zn at all sites except MOS-09 and MOS-13, and Cu at all sites except MOS-10 and MOS-13. These findings highlight significant environmental concerns and underscore the urgent need for mitigation strategies to safeguard agricultural productivity and human health in the affected areas.

Keywords: Soil pollution; agriculture; heavy metals; limestone mining

1. Introduction

Environmental contamination due to the direct disposal of heavy metals has become a serious issue in recent years (Tarawneh et al., 2021; Fang et al., 2022). Since various forms and amounts of heavy metals can be found in soil, it is important to monitor their levels. The types, concentrations, and relationships of heavy metals in soil have been investigated through field sampling and indoor chemical analysis techniques (Fu et al., 2019). Heavy metal accumulation is often associated with mining activities (Agarin et al., 2021; Senoro et al., 2023). A study by Nolos et al. (2022) revealed that the high concentration of heavy metals in the soil of an island province in the Philippines was attributed to nearby mine sites. A significant amount of waste material rich in metals is generated during mineral exploration. These materials remain in the environment and pose a threat to human health, often leading to severe physical and chemical degradation of soils. Contamination with hazardous elements such as Cd, Pb, and Zn is a serious concern (Yang et al., 2009), as they can accumulate in soils and waterways, posing environmental and public health risks. According to Penido et al. (2019), high levels of heavy metals in soils can degrade the soil ecosystem, affecting parameters such as pH, electrical conductivity, soil mineralogy, cation exchange capacity, and microbial and biological activities.

Gunungkidul is a regency in Daerah Istimewa Yogyakarta (DIY) Province, Indonesia. Located in the eastern part of the province, Gunungsewu Geopark is one of the oldest tropical karst landscapes, spanning over 120 kilometers and featuring diverse geographical features, from coastal areas to highland locales (Zamroni et al., 2022; Zamroni et al., 2023). Large-and-small-scale limestone-mining activities pose the greatest threat to preserving karst areas in this region, evident in the destruction of hillsides due to mining operations (Sari et al., 2020). The potential ecological hazards associated with heavy metal contamination from limestone-mining operations have been extensively documented globally (Ali et al., 2022; Luo et al., 2021; Sarireh et al., 2021; Xie et al., 2022). Following the mining and crushing of limestone, significant quantities of mine waste materials are dispersed near the mining sites (Mohd Isha et al., 2021). One of the most active limestone-mining areas is Semin District, Gunungkidul Regency, where sedimentary limestone mine wastes are prevalent.

In agricultural areas, soil heavy metal pollution is increasingly becoming a serious environmental hazard. Over the past 50 years, more than 0.8 million tons of Pb and 0.03 million tons of Cr have been released into the environment, primarily accumulating in soils and causing severe heavy metal contamination (Xiang et al., 2021). Due to their non-biodegradable nature, toxic heavy metals pose a significant concern. Moreover, crops can absorb these elements, potentially affecting food safety and quality (Yaseen and Al-Hawari, 2019). The persistence and toxicity of heavy metals make them particularly harmful. Soil acts as a reservoir for heavy metals through processes such as sorption, precipitation, and complexation. The accumulation of hazardous substances in agricultural soils, located close to human populations, is worrisome. Heavy metals can enter the human body through the food chain, inhalation, ingestion, and skin contact (Khudhur et al., 2018).

In Indonesia, rice cultivation plays a crucial role in ensuring food security. To enhance soil quality, ensure the safety and quality of agricultural products, and safeguard human health, it is essential to establish a plan for controlling soil pollution (Kang et al., 2020). This study follows up on research by Zamroni et al. (2022), which investigated the geochemical characteristics of surface water in the study area. According to Indonesian government regulations, the quality of surface water in the research area was deemed suitable for irrigation. In this context, understanding the accumulation of soil heavy metals, including contamination levels and associated hazards in agricultural areas, is crucial. The present study aims to determine the concentrations of heavy metals (Pb, Zn, Cu, Cd, Mg, and Cr) in agricultural soils surrounding limestone-mining areas in Gunungkidul Regency. Additionally, it seeks to evaluate the extent of heavy metal pollution in agricultural soils in Gunungkidul Regency using guidelines established by the World Health Organization (WHO).

2. Geology of the Study Area

The study area is located within the Surakarta-Giritontro Quadrangle of Java's regional geological map (Figure 1). The predominant structural trends in the area are northeast-southwest and northwest-southeast (Sutarto et al., 2020). Several faults have been identified based on their northwest-southeast orientation, intersecting the Semilir Formation volcanic rock unit and the Wonosari Formation limestone unit. Recent studies have characterized these faults as thrust faults extending continuously to the southeast (Prasetyadi et al., 2011). The exposed formations in the study area, arranged from oldest to youngest, include the Mandalika Formation, Semilir Formation, Wonosari-Punung Formation, and Alluvium Formation (Surono et al., 1992). The Mandalika Formation, formed from late Oligocene to early Miocene magmatic activity, consists of tuff, basalt, andesite, and andesite breccias. Extensive areas are covered with breccia and lava deposits (Idrus et al., 2021; Susilo et al., 2021). The lithology of the Semilir Formation comprises tufaceous sandstone, lapilli tuff, sandstone, tuff, claystone, siltstone, and shale. This formation, dating to the Early Miocene, was deposited by turbidite currents in a deepwater environment influenced by gravity flows (Rahmad et al., 2017). The abundance of tuff and pumice in the Semilir Formation suggests it was formed during a significant volcanic eruption (Ardine et al., 2022). The Wonosari-Punung Formation, described by Fawzy Ismullah M. and Altin Massinai (2018), includes limestone, conglomerate limestone, marble-tuff limestone, siltstone, tuff, and sandstone. The geochemical composition of the Wonosari-Punung limestones indicates influence from hydrothermal fluid activity, post-depositional diagenetic processes, and a minor contribution of terrigenous material (Atmoko et al., 2018). Lastly, the Alluvium Formation consists of clay, silt, sand, and gravel, formed along rivers due to denudation processes on steep and extremely steep terrain (Saputra et al., 2016).

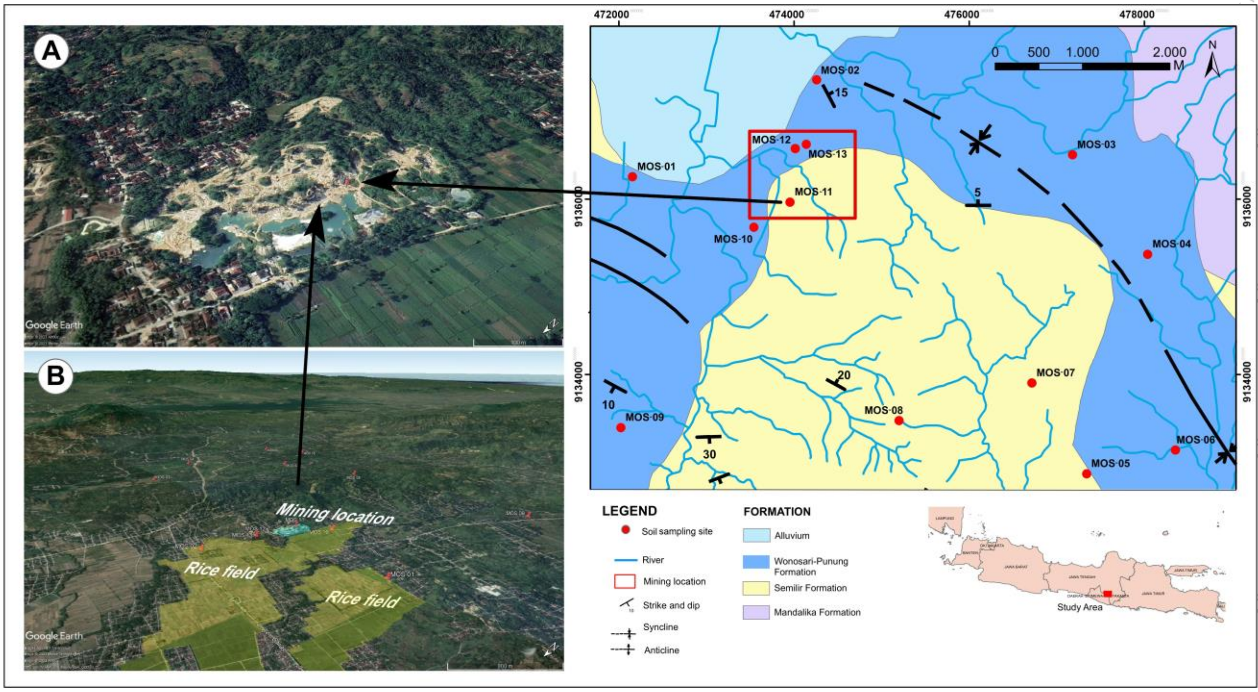

Figure 1. Geological map of the study area (A) Mining location, and (B) Mining location and rice fields around the study site (Modified from Surono et al., 1992).

3. Materials & Methods

In July 2023 (dry season), sampling was conducted in Semin District, Gunungkidul Regency, Daerah Istimewa Yogyakarta Province, Indonesia (Figure 1). The study area is characterized by limestone mining activities where locals use rudimentary mining equipment. Mining operations have been ongoing in the area since the 1990s, covering approximately 1.5 square kilometers of land dedicated to limestone extraction. Sampling points in this study were categorized into two zones: agricultural fields and mining sites. Ten soil samples were collected from agricultural fields near the limestone mining area, while three samples were taken directly from the limestone mining site to compare levels of heavy metal accumulation. An opportunistic sampling approach was employed based on accessibility, with proper consent obtained from relevant authorities or property owners (Bora et al., 2023). At each sampling location, soil samples were collected from the top 0–50 cm layer and placed into brand-new plastic zipper bags. The samples were kept chilled before analysis (Prartono et al., 2016).

Each sample's pH was measured using a pH meter. Concentrations of lead (Pb), zinc (Zn), copper (Cu), cadmium (Cd), magnesium (Mg), and chromium (Cr) were determined using an atomic absorption spectrophotometer (AAS) at the Balai Besar Teknik Kesehatan Lingkungan dan Pengendalian Penyakit (BBTKLPP), also known as the Center for Environmental Health and Disease Control Engineering, in Yogyakarta, Indonesia. The analysis followed the US EPA SW-846 7000B method for flame atomic absorption spectroscopy, utilizing a Varian SpectraAA atomic absorption spectrophotometer (United States Environmental Protection Agency, 2007). The World Health Organization (WHO, 1996) has established maximum permissible levels for heavy metals in soil, as indicated in Table 1. To assess potential risks, a risk assessment was conducted by comparing the measured concentrations of heavy metals in the soil (mg/kg) with these maximum permissible limits.

Table 1. The maximum permissible levels for heavy metals in soil (WHO, 1996)

Element	**Maximum permissible levels in soil (mg/kg)**
Pb	85
Zn	50
Cu	36
Cd	0.8
Mg	No guideline value set
Cr	100

4. Results and Discussion

4.1 Possible Source of Heavy Metals Accumulation

Table 2 presents the results of the analysis of heavy metal concentrations in agricultural soils within the study area. The elevation of each sampling site in the

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limestone-mining region (MOS-11, MOS-12, and MOS-13) was determined using a Shuttle Radar Topography Mission (SRTM) image. Figure 2 shows the SRTM image of the study area, categorizing sampling sites into two groups based on elevation relative to the limestone-mining area: those with elevations lower than or equal to the mining area (MOS-01, MOS-02, and MOS-10), and those with elevations higher than the mining area (MOS-03, MOS-04, MOS-05, MOS-06, MOS-07, MOS-08, and MOS-09). The elevation plays a significant role in determining the origin of heavy metal pollution. Areas with elevations equal to or lower than the limestone-mining area are influenced by pollution originating from mining activities, geological conditions, and human activities such as the use of chemical fertilizers. Conversely, areas with elevations higher than the limestone-mining area are primarily affected by geological factors and chemical fertilizers, without direct exposure to sediment from the mining area through rainwater runoff and airborne soil transport.

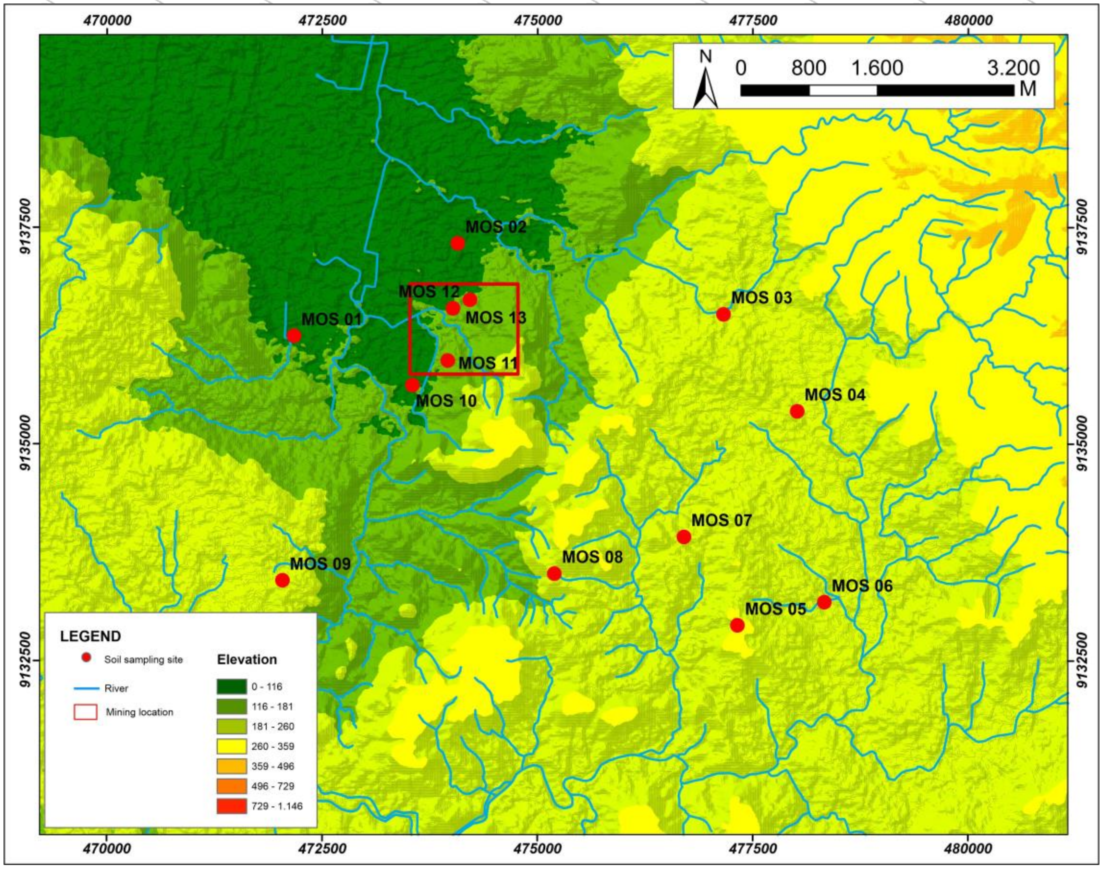

Figure 2. The Shuttle Radar Topography Mission (SRTM) of the study area.

Table 2. Heavy metal concentrations in agricultural soils in the study area.

Location	**Coordinate**		**Land use type***	**pH**	**Pb (mg/kg)**	**Zn (mg/kg)**	**Cu (mg/kg)**	**Cd (mg/kg)**	**Mg (mg/kg)**	**Cr (mg/kg)**
	Easting	**Northing**								
MOS-01	472173.00	9136244.00	AA	6.62	<3.251	55.401	44.151	<0.848	4,826.87	29.505
MOS-02	474077.00	9137311.00	AA	6.48	<3.251	57.505	55.795	<0.848	5,703.45	19.667

MOS-03	477162.00	9136494.00	AA	6.72	5.510	53.403	69.297	<0.848	2,002.62	20.344
MOS-04	478016.00	9135375.00	AA	6.67	<3.251	54.994	52.896	<0.848	2,813.77	16.163
MOS-05	477325.00	9132905.00	AA	5.26	<3.251	82.949	52.653	<0.848	2,588.77	22.566
MOS-06	478332.00	9133172.00	AA	5.5	3.373	55.238	54.184	<0.848	1,935.44	14.547
MOS-07	476703.00	9133926.00	AA	5.71	<3.251	52.208	50.489	<0.848	3,130.32	9.668
MOS-08	475198.00	9133502.00	AA	5.63	<3.251	68.501	60.865	<0.848	3,237.43	7.635
MOS-09	472042.00	9133422.00	AA	5.78	<3.251	43.077	39.132	<0.848	1,583.46	11.730
MOS-10	473550.00	9135676.00	AA	5.57	<3.251	59.788	33.455	<0.848	3,753.49	13.598
MOS-11	473959.00	9135959.00	MA	5.97	<3.251	73.265	110.238	<0.848	4,103.30	21.775
MOS-12	474018.00	9136562.00	MA	6.54	<3.251	67.106	52.433	<0.848	397.67	21.577
MOS-13	474018.00	9136562.00	MA	6.37	<3.251	42.662	32.257	<0.848	4,145.52	18.105

*AA: Agricultural Area, MA: Mining Area

4.2 The Relationship between pH and Heavy Metal Concentrations

In the study area, the pH values range from 5.26 to 6.72. Typically, pH in limestone-mining areas tends to be alkaline (Akande and Ifelola, 2011), but the measured values in this study are acidic to close to neutral. This acidity or near-neutrality is likely influenced by leaching processes involving other materials, including heavy metal concentrations in top soils and shales. Studies conducted across various contexts (agricultural, urban, and transitional land-use zones) have shown that heavy metals are more mobile in acidic soils compared to alkaline soils. The solubility of heavy metals decreases as pH increases, leading to more common heavy metal accumulation in alkaline environments. Conversely, heavy metal contamination can elevate soil pH levels (Kazlauskaitė-Jadzevičė et al., 2014; Sintorini et al., 2021).

In Microsoft Excel, a simple linear regression was performed to examine the relationship between pH and heavy metals (Zn, Mg, Cu, and Cr). Notably, Pb and Cd were excluded from the analysis as their values were below the detection limit. Figure 3 displays the results of the regression analysis between pH and the aforementioned heavy metals. A negative correlation was observed between pH and the concentrations of Zn, Mg, Cu, and Cr, with corresponding R-squared (R^2) values of 0.1327, 0.0179, 0.0021, and 0.2465, respectively. While previous studies have often reported significant associations between pH and heavy metal levels in soils, the findings of this analysis suggest otherwise due to limited supporting data. The lack of a substantial relationship between pH and heavy metals could be attributed to variations in pollution sources, soil types, and fertilizer applications across the sampled area (Ma et al., 2015).

Higher pH values are typically observed in sampling sites near mining areas, likely influenced by contact with alkaline limestone and the accumulation of heavy metals from anthropogenic activities, thereby increasing heavy metal concentrations in soils. Alkaline soils also tend to contain clay minerals with high cation exchange capacity (CEC), enabling them to adsorb and retain metal ions, contributing to their accumulation in the soil (Anjolaiya, 2015).

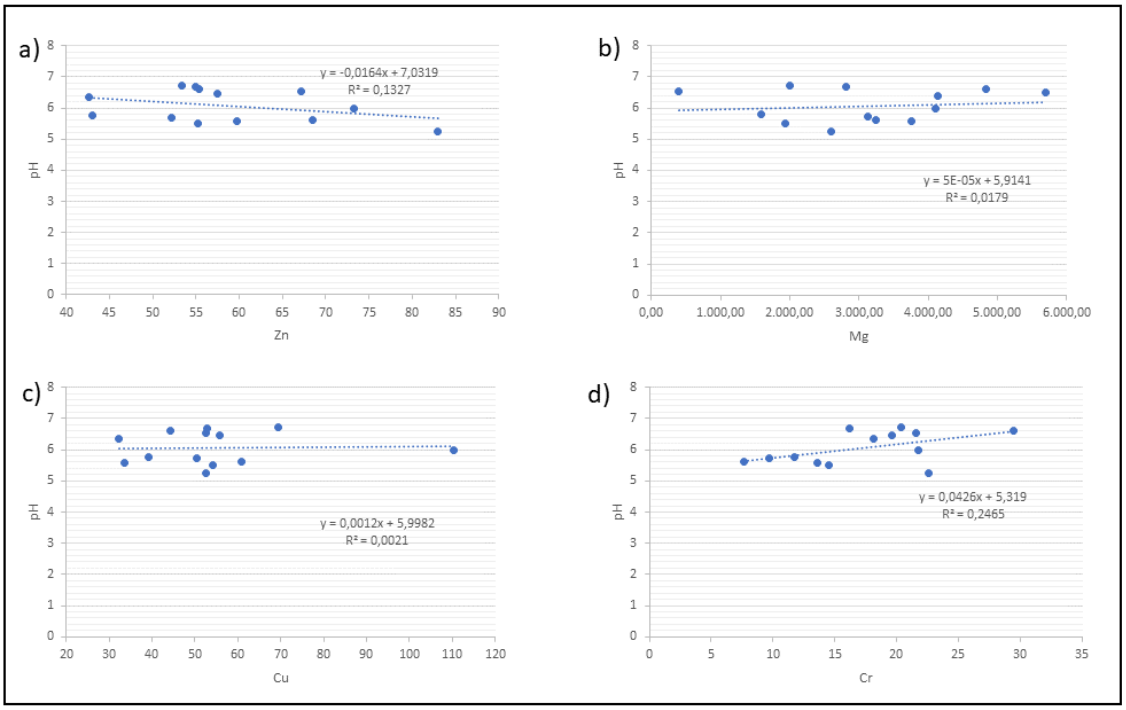

Figure 3. The regression analysis between pH and heavy metals; a) pH vs Zn, b) pH vs Mg, c) pH vs Cu, and d) pH vs Cr.

4.3 Heavy Metal Concentrations in Agricultural Soils

In the geological setting of the study area, sampling sites are situated within two formations: the Wonosari-Punung Formation (MOS-01, MOS-02, MOS-03, MOS-04, MOS-06, MOS-09, MOS-10, MOS-12, and MOS-13) and the Semilir Formation (MOS-05, MOS-07, and MOS-08). Given MOS-11's location in the Semilir Formation but near the Wonosari-Punung Formation, the assumption is that this specific location is considered part of the Wonosari-Punung Formation due to its association with soil sampling at a limestone mining site. The geological setting discussion focuses on the relationship between the lithology of these formations and the concentrations of heavy metals in the study area. The Wonosari-Punung Formation consists of limestone, conglomerate limestone, marble-tuff limestone, tuff, siltstone, and sandstone. On the other hand, the Semilir Formation is composed of tufaceous sandstone, lapilli tuff, sandstone, tuff, claystone, siltstone, and shale.

The sampling sites MOS-01, MOS-02, MOS-03, MOS-04, MOS-06, MOS-09, MOS-10, MOS-11, MOS-12, and MOS-13 are situated within the limestone formation, where weathering processes of the limestone lithology predominantly influence heavy metal concentrations. Regarding soil metals, Pb is known for its stability and low mobility in non-acidic soils (Elnazer et al., 2015). This stability is reflected in the consistently low Pb values observed across all sampling sites. In nature, Pb is commonly found in the form of galena, a compound containing sulfur. The paragenetic stages during formation influence the Pb isotope ratios found in galena, which typically reflect the original Pb isotope composition of hydrothermal fluids (Hu et al., 2022). In the parent limestones, Zn exists in three forms: Zn associated with pyrite and calcite sphalerite grains, Zn bound to goethite within inherited phosphate nodules, and Zn attached to phyllosilicates. During pedogenesis (soil formation), processes such as eluviation, two stages of redox reactions, and carbonate dissolution contribute to the redistribution of Zn. The breakdown of carbonates in limestones releases Zn previously bound to calcite into the soil solution. As a result, Zn concentrations in soil often exceed those in the parent limestones due to residual enrichment (Laveuf et al., 2009). At most sampling sites, Zn concentrations are high; this enrichment contribution is likely attributed to hydrothermal inputs, which are considered the primary source of elevated Zn concentrations in limestone at these sites (Jacquat et al., 2011). The geochemical composition of the Wonosari-Punung limestones indicates that hydrothermal fluid activity, a minor contribution of terrigenous material, and post-depositional diagenetic processes played significant roles in the deposition of rare earth elements. Additionally, hydrothermal fluids have influenced the enrichment of Cr concentrations in this formation (Atmoko et al., 2018). The Wonosari-Punung Formation also contains mineralized porphyry with lower-grade Cu adjacent to ore-grade primary Cu within the limestone. During the Miocene epoch, numerous dioritic rocks intruded into the Wonosari-Punung Formation. This formation predominantly comprises Quaternary sediments and volcanic products from nearby active volcanoes (Idrus et al., 2023).

The concentrations of Cd in soils are primarily determined by factors such as soil type, geological age, rock type, and geomorphic characteristics. Specifically, in karst areas like the Wonosari-Punung Formation within the Wonosari karst, carbonatite weathering, and deposition processes contribute significantly to Cd concentrations (Zhao et al., 2020). The Wonosari karst is a vital component of the Gunungsewu karst megasystem in Gunungkidul Regency (Damayantia et al., 2021). The levels of Mg observed can be attributed to the presence of high-Mg lava during the formation of limestones, rather than diagenesis processes (Cutillas-Barreiro et al., 2016). This is supported by the occurrence of volcanic rocks such as tuff, marble tuff, and conglomerate, which are in contact with limestone within the Wonosari-Punung Formation.

The explanation above pertains to the heavy metals contained in the parent limestone. However, several sampling sites in the study area have heavy metal contents that exceed WHO standard limits (Table 1), specifically Zn at all sampling sites except MOS-09 and MOS-13, and Cu at all sampling sites except MOS-10 and MOS-13. This indicates that anthropogenic factors have contributed to the increase in heavy metal concentrations at those sampling sites. Natural weathering of parent materials contributes to the presence of heavy metals in soils, human activities have significantly augmented metal reservoirs in the soil system since the early 1900s. The intensity of human activity can disrupt the biogeochemical cycles of heavy metals in terrestrial ecosystems (Asih et al., 2022; Putra et al., 2023). Excavation activities in the limestone-mining disturb the natural soil layers, bringing heavy metals closer to the surface, particularly Zn and Cu, the soil surrounding limestone quarries often exhibits severe pollution levels (Mulwa et al., 2012; Wang et al., 2021). Run-off from rainwater, erosion, and airborne transport contribute to spreading these contaminants, affecting nearby areas, especially those at or below the elevation of the limestone mining sites, such as MOS-01, MOS-02, and MOS-10. Agricultural activities, notably in rice fields within the study area, also contribute to the high concentrations of heavy metals observed at various sampling sites, regardless of their elevation relative to the limestone mining areas. The primary sources of heavy metals in agriculture are fertilizers and pesticides. Both organic and inorganic fertilizers contribute to the accumulation of heavy metals in soil. Prolonged use of fertilizers increases the potential for accumulation of metals such as copper Cu, Zn, and Cd in agricultural soils. Synthetic magnesium sulfate, often used in fertilizers, contributes to the elevated Mg levels observed in the study area (Azzouzi et al., 2016). Inorganic fertilizers such as phosphate fertilizers, liming materials, and biofertilizers are major contributors to heavy metal release into agricultural soils, where they can be absorbed by plants and subsequently enter the food chain, affecting humans and animals (Alengebawy et al., 2021).

Compared to clastic rocks, soils derived from carbonate rocks exhibit significantly higher levels of heavy metals. This phenomenon can be attributed to several factors: the formation of clay minerals, high initial concentrations of heavy metals in carbonate rocks, and secondary enrichment processes during weathering and soil formation. Background concentrations of heavy metals in carbonate rocks often exceed crustal abundance estimates, particularly noticeable for Cd in limestone. As carbonate rocks weather, they release heavy metals into the soil, resulting in parent materials with higher concentrations of heavy metals than the original bedrock (Zhang et al., 2020). The accumulation of heavy metals in topsoils primarily depends on ongoing weathering of the soil's parent material, regardless of external inputs. However, sampling sites such as MOS-05, MOS-07, and MOS-08 also exhibit elevated heavy metal concentrations comparable to those found in limestone formations. This indicates that high concentrations are not solely due to the weathering of clastic rocks in the Semilir Formation but are exacerbated by agricultural practices, particularly the use of fertilizers, at sites higher in elevation than the mining areas. Figure 4 illustrates a schematic representation of the study's findings.

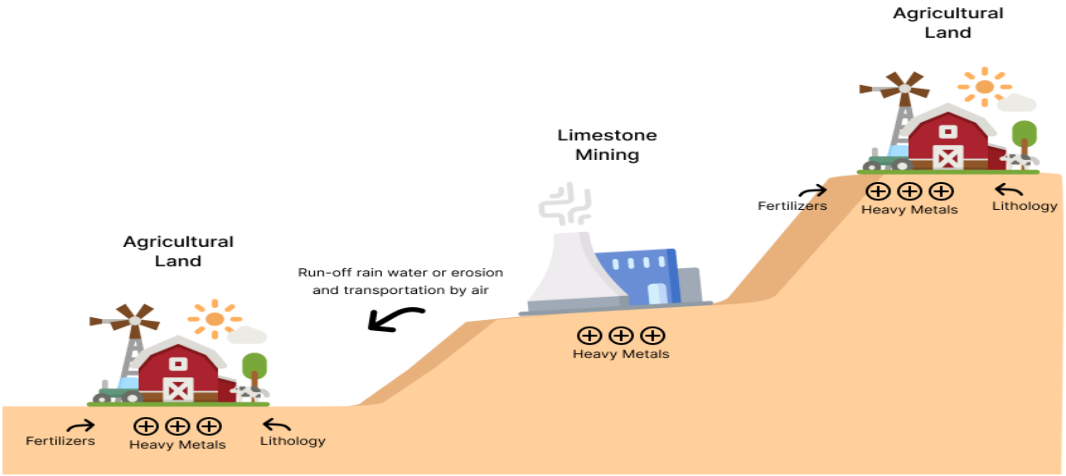

Figure 4. The sketch of heavy metal contamination in the agricultural soil in the study area (Icon made by www.flaticon.com).

4.4 Comparison with Sediment Quality Standard

The sediment quality standards in the study area are based on the maximum permissible levels of heavy metals in the soil as defined by the WHO (Table 1). According to the heavy metal concentrations observed in agricultural soils within the study area, several sampling sites have heavy metal contents that exceed WHO standard limits (Table 1), specifically Zn at all sampling sites except MOS-09 and MOS-13, and Cu at all sampling sites except MOS-10 and MOS-13. Zn plays crucial roles as a catalytic, structural, and regulatory cofactor in numerous enzyme processes in plants. It is essential for glucose metabolism, protein synthesis, and growth hormone production such as indoleacetic acid, maintaining cell membrane integrity. Plants experiencing acute Zn deficiency exhibit symptoms like stunted growth, leaf chlorosis, shortened internodes and petioles, and clustering of small, deformed leaves at the top (a typical dicotyledon rosette symptom). Even without apparent deficiency symptoms, moderately Zn-deficient soils can lower crop yields and quality (Montalvo et al., 2016). Water-soluble Zn in soils can contaminate groundwater, posing risks due to its accumulation in plants beyond their physiological needs. While Zn is essential, excessive amounts can be phytotoxic, adversely affecting crop yields and soil fertility. Soil concentrations of total Zn ranging from 70 to 400 mg/kg are considered critical, with toxicity observed at higher levels. Excessive Zn can also pose health risks to humans, potentially causing poisoning (Bentum et al., 2011). Cu is another essential micronutrient for plants, but its excessive presence in soil can lead to detrimental effects. Cu toxicity disrupts cellular processes, causing protein denaturation and membrane damage in bacteria, and inhibits the growth and function of microbial communities, even at low concentrations like 1% CuO (Alengebawy et al., 2021). Additionally, Cu toxicity can affect gene expression, neuronal activity, and lipid metabolism, and potentially influence tumor cell resistance to chemotherapy (Cai et al., 2019). Given these implications, the elevated concentrations of Zn and Cu highlight a significant environmental concern that necessitates mitigation strategies to prevent further contamination of agricultural soils and safeguard water sources used by the community.

Mitigation is key to addressing environmental issues caused by heavy metal contamination from mining activities and associated health risks linked to industrial expansion (Prasetya et al., 2021; Zamroni et al., 2020). Government regulators and mining companies must take decisive action. Strict enforcement of environmental regulations, particularly regarding waste discharge, and effective control of pollution sources are essential strategies to mitigate soil heavy metal pollution. Many small-scale mining operations significantly harm the environment due to inefficient mining practices and outdated technology. Therefore, supporting sustainable integrated approaches—such as legislation, education, and financial incentives for adopting appropriate pollution control technologies—is crucial for communities affected by small-scale mining. In Indonesia, the enforcement of environmental rules is often lax, leading to relatively low rates of environmental restoration, despite legal requirements for all mining companies to participate in such efforts. Furthermore, cleaning up heavy metal-contaminated soils is costly and technically challenging. Phytoremediation presents a more affordable and efficient alternative to soil replacement and leaching techniques. Instead of solely focusing on agriculture and forestry for economic gain, diversifying restoration efforts to include wildlife habitats and nurseries is essential. Priority should be given to controlling key pollutants that pose significant risks to human health. Special attention must also be paid to protecting vulnerable groups, particularly children living near mining areas. Specific measures, such as restricting outdoor activities, can help reduce soil ingestion rates among children in proximity to mining zones (Li et al., 2014; Rachmawati and Zamroni, 2020; Kurniati et al., 2023; Nolos et al., 2023).

5. Conclusions

Heavy metal concentrations (Pb, Zn, Cu, Cd, Mg, and Cr) in the study area were influenced by geological factors and anthropogenic activities. Geological factors refer to the weathered rock lithology, the parent materials for agricultural soil, while anthropogenic activities are dominated by farm fertilizer and limestone mining. Heavy metal concentrations in the limestone formation influenced the heavy metal content in soil at sampling sites of MOS-01, MOS-02, MOS-03, MOS-04, MOS-06, MOS-09, MOS-10, MOS-11, MOS 12, and MOS-13. In contrast, heavy metal concentrations in the clastic rock formation influenced the heavy metal content in agricultural soil at MOS-05, MOS-07, and MOS-08 sampling sites. Heavy metals from mining activities and agricultural fertilizers influenced the heavy metal content in agricultural soil at sampling sites of MOS-01, MOS-02, and MOS-10, while the concentration of heavy metals at sampling sites of MOS-03, MOS-04, MOS-05, MOS06, MOS-07, MOS-08, and MOS-09 was only influenced by agricultural fertilizers. Several sampling sites have heavy metal contents that exceed WHO standard limits, specifically Zn at all sampling sites except MOS-09 and MOS-13, and Cu at all sampling sites except MOS-10 and MOS-13. Government authorities and mining firms must take significant action to address the heavy metal pollution caused by mining operations and the attendant health concerns connected with industrial development.

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References

Agarin, C. J. M., Mascareñas, D. R., Nolos, R., Chan, E., & Senoro, D. B. (2021). Transition metals in freshwater crustaceans, tilapia, and inland water: Hazardous to the population of the small island province. *Toxics*, *9*(4), 71.

Akande, J. M., & Ifelola, E. O. (2011). Analysis of soil, water and dust during limestone mining and processing. *Miner Wealth*, *157*, 14-24.

Alengebawy, A., Abdelkhalek, S. T., Qureshi, S. R., & Wang, M. Q. (2021). Heavy metals and pesticides toxicity in agricultural soil and plants: Ecological risks and human health implications. *Toxics*, *9*(3), 42.

Ali, M. M., Rahman, S., Islam, M. S., Rakib, M. R. J., Hossen, S., Rahman, M. Z., ... & Phoungthong, K. (2022). Distribution of heavy metals in water and sediment of an urban river in a developing country: a probabilistic risk assessment. *International journal of sediment research*, *37*(2), 173-187.

Anjolaiya, O. (2015). Sorption behaviour of metal contaminants in clay minerals, soils and matrices: understanding the influence of organic matter, pH, ionic strength and mineralogy (Doctoral dissertation, Loughborough University).

Ardine, J. E., Nugroho, M. O. B., Maulana, M. I., Nugroho, A. N. K., & Hisan, N. K.

(2022). Deep Marine Reservoir Analog From Semilir Formation Outcrop Data in Ngoro-Oro Area, Gunungkidul, Indonesia.

Asih, A.S., Zamroni, A., Alwi, W., Sagala, S.T., & Putra, A.S. (2022). Assessment of Heavy Metal Concentrations in Seawater in the Coastal Areas around Daerah Istimewa Yogyakarta Province, Indonesia. The Iraqi Geological Journal, 55 (1B), 14-22.

Atmoko, D. D., Titisari, A. D., & Idrus, A. (2018). Geochemical Characteristics of Limestone of Wonosari-Punung Formation, Gunungkidul Regency, Yogyakarta, Indonesia. *Indonesian Journal on Geoscience*, *5*(2).

Azzouzi, H., Ouzaouit, K., Aboulaich, A., Dali, Y., Kaddami, A., & Akalay, I. (2016). Managem products potentially used in fertilizers industry. *Procedia Engineering*, *138*, 302-307.

Bentum, J. K., Adotey, J. P. K., Koka, J., Koranteng-Addo, E. J., Yeboah, A., & Boamponsem, L. K. (2011). Assessment of lead, copper and zinc contamination of soil from University of Cape Coast School of Agricultural farmland, Ghana. *International journal of biological and chemical sciences*, *5*(4), 1703-1711.

Bora, F. D., Babeș, A. C., Călugăr, A., Jitea, M. I., Hoble, A., Filimon, R. V., ... & Bunea, C. I. (2023). Unravelling Heavy Metal Dynamics in Soil and Honey: A Case Study from Maramureș Region, Romania. *Foods*, *12*(19), 3577.

Cai, L. M., Wang, Q. S., Luo, J., Chen, L. G., Zhu, R. L., Wang, S., & Tang, C. H. (2019). Heavy metal contamination and health risk assessment for children near a large Cu-smelter in central China. *Science of the Total Environment*, *650*, 725-733.

Cutillas-Barreiro, L., Pérez-Rodríguez, P., Gómez-Armesto, A., Fernández-Sanjurjo, M. J., Álvarez-Rodríguez, E., Núñez-Delgado, A., ... & Nóvoa-Muñoz, J. C. (2016). Lithological and land-use based assessment of heavy metal pollution in soils surrounding a cement plant in SW Europe. *Science of the total environment*, *562*, 179-190.

Damayantia, A., Riadinia, F., & Pamungkasa, F. D. (2021). Potential Areas of Land Subsidence in Karst Landscape: Case Study in Ponjong and Semanu District, Gunungkidul Regency, Yogyakarta, Indonesia. *International Journal on Advanced Science, Engineering and Information Technology*, *11*(2), 712-719.

Elnazer, A. A., Salman, S. A., Seleem, E. M., & Abu El Ella, E. M. (2015). Assessment of some heavy metals pollution and bioavailability in roadside soil of Alexandria-Marsa Matruh Highway, Egypt. *International Journal of Ecology*, *2015*.

Fang, H., Wang, X., Xia, D., Zhu, J., Yu, W., Su, Y., ... & Qiu, J. (2022). Improvement of Ecological Risk Considering Heavy Metal in Soil and Groundwater Surrounding Electroplating Factories. *Processes*, *10*(7), 1267.

Fawzy Ismullah M, M., & Altin Massinai, M. (2018, March). Shallow Depth Study Using Gravity & Magnetics Data in Central Java-Yogyakarta. In *Journal of Physics Conference Series* (Vol. 979, No. 1, p. 012046).

Fu, P., Yang, K., & Feng, F. (2019). Study on heavy metal in soil based on spectral second-order differential Gabor transform. *Journal of the Indian Society of Remote Sensing*, *47*, 629-638.

Hu, Y., Ye, L., Huang, Z., Wei, C., Wu, T., Xiang, Z., ... & Li, Z. (2022). Genetic model for early Cambrian reef limestone-hosted Pb-Zn deposits in the world-class Huayuan orefield, South China: New insights from mineralogy, fluorite geochemistry and sulfides in situ S-Pb isotopes. *Ore Geology Reviews*, *141*, 104682.

Idrus, A., Dana, C.D., Setijadji, L.D., Sutarto, Ernowo, Sakellaris, G.A., & van Leeuwen, T. (2023). Nature of magma and ore-forming conditions at the Randu Kuning porphyry Cu-Au deposit, Indonesia: a comparative study with other Cu-Au deposits in the region. *International Geology Review*, pp.1-19.

Idrus, A., Masti, S. D., & Azizi, R. R. (2021, March). Determination of slope susceptibility in hydrothermally altered rocks region with a case study in wonotirto district, blitar regency, east java province, indonesia. In *IOP Conference Series: Earth and Environmental Science* (Vol. 683, No. 1, p. 012058). IOP Publishing.

Jacquat, O., Rambeau, C., Voegelin, A., Efimenko, N., Villard, A., Föllmi, K. B., & Kretzschmar, R. (2011). Origin of high Zn contents in Jurassic limestone of the Jura mountain range and the Burgundy: evidence from Zn speciation and distribution. *Swiss Journal of Geosciences*, *104*(3), 409-424.

Kang, Z., Wang, S., Qin, J., Wu, R., & Li, H. (2020). Pollution characteristics and ecological risk assessment of heavy metals in paddy fields of Fujian province, China. *Scientific reports*, *10*(1), 12244.

Kazlauskaitė-Jadzevičė, A., Volungevičius, J., Gregorauskienė, V., & Marcinkonis, S. (2014). The role of pH in heavy metal contamination of urban soil. *Journal of Environmental Engineering and Landscape Management*, *22*(4), 311-318.

Khudhur, N. S., Khudhur, S. M., & Ahmad, I. N. (2018). An Assessment of heavy metal soil contamination in a Steel Factory and the surrounding area in Erbil City. *Jordan Journal of Earth and Environmental Sciences*, *9*(1), 1-11.

Kurniati, A.C., Putri, W.E.C., Zamroni, A., Sagala, S.T., & Rachmawati, Y. (2023, June). How to educate children in the mining areas: A concept to implement environmental education for elementary students in Indonesia. In *AIP Conference Proceedings* (Vol. 2598, No. 1). AIP Publishing.

Laveuf, C., Cornu, S., Baize, D., Hardy, M., Josière, O., Drouin, S., ... & Juillot, F. (2009). Zinc redistribution in a soil developed from limestone during pedogenesis. *Pedosphere*, *19*(3), 292-304.

Li, Z., Ma, Z., van der Kuijp, T. J., Yuan, Z., & Huang, L. (2014). A review of soil heavy metal pollution from mines in China: pollution and health risk assessment. *Science of the total environment*, *468*, 843-853.

Luo, P., Xu, C., Kang, S., Huo, A., Lyu, J., Zhou, M., & Nover, D. (2021). Heavy metals in water and surface sediments of the Fenghe River Basin, China: Assessment and source analysis. *Water Science and Technology*, *84*(10-11), 3072-3090.

Ma, L., Sun, J., Yang, Z., & Wang, L. (2015). Heavy metal contamination of agricultural soils affected by mining activities around the Ganxi River in Chenzhou, Southern China. *Environmental monitoring and assessment*, *187*, 1-9.

Mohd Isha, N. S., Mohd Kusin, F., Ahmad Kamal, N. M., Syed Hasan, S. N. M., & Molahid, V. L. M. (2021). Geochemical and mineralogical assessment of sedimentary limestone mine waste and potential for mineral carbonation. *Environmental Geochemistry and Health*, *43*, 2065-2080.

Montalvo, D., Degryse, F., Da Silva, R. C., Baird, R., & McLaughlin, M. J. (2016). Agronomic effectiveness of zinc sources as micronutrient fertilizer. *Advances in agronomy*, *139*, 215-267.

Mulwa, B. M., Maina, D. M., & Patel, J. P. (2012). Multielemental analysis of limestone and soil samples of Kitui South (Kenya) limestone deposits. *International Journal of Fundamental Physical Sciences (IJFPS)*, *2*(4), 48-51.

Nolos, R. C., Agarin, C. J. M., Domino, M. Y. R., Bonifacio, P. B., Chan, E. B., Mascareñas, D. R., & Senoro, D. B. (2022). Health Risks due to metal concentrations in soil and vegetables from the six municipalities of the Island Province in the Philippines. *International Journal of Environmental Research and Public Health*, *19*(3), 1587.

Nolos, R. C., Zamroni, A., & Evina, K. F. P. (2023). Drivers of Deforestation And Forest Degradation In Palawan, Philippines: An Analysis Using Social-Ecological Systems (SES) And Institutional Analysis And Development (IAD) Approaches. *GEOGRAPHY, ENVIRONMENT, SUSTAINABILITY*, *15*(4), 44-56.

Penido, E. S., Martins, G. C., Mendes, T. B. M., Melo, L. C. A., do Rosário Guimarães, I., & Guilherme, L. R. G. (2019). Combining biochar and sewage sludge for immobilization of heavy metals in mining soils. *Ecotoxicology and Environmental Safety*, *172*, 326-333.

Prartono, T., Sanusi, H. S., & Nurjaya, I. W. (2016). Seasonal distribution and geochemical fractionation of heavy metals from surface sediment in a tropical estuary of Jeneberang River, Indonesia. *Marine pollution bulletin*, *111*(1-2), 456-

462.

Prasetya, H. N. E., Aditama, T., Sastrawiguna, G. I., Rizqi, A. F., & Zamroni, A. (2021, June). Analytical landslides prone area by using Sentinel-2 Satellite Imagery and geological data in Google Earth Engine (a case study of Cinomati Street, Bantul Regency, Daerah Istimewa Yogyakarta Province, Indonesia). In *IOP Conference Series: Earth and Environmental Science* (Vol. 782, No. 2, p. 022025). IOP Publishing.

Prasetyadi, C., Sudarno, I., Indranadi, V. B., & Surono, S. (2011). Pola dan Genesa Struktur Geologi Pegunungan Selatan, Provinsi Daerah Istimewa Yogyakarta dan Provinsi Jawa Tengah. *Jurnal Geologi dan Sumberdaya Mineral*, *21*(2), 91-107.

Putra, A. S., Zamroni, A., Asih, A. S., Sagala, S. T., & Tingson, K. N. (2023). Heavy Metals in Surface Sediments of the Coastal Area Around Daerah Istimewa Yogyakarta, Indonesia: Their Relations to Land-Use Types. *The Iraqi Geological Journal*, 156-168.

Rachmawati, Y., & Zamroni, A. (2020). How Indonesian Governments Care for Local People's Education in the Mining Area: Experiences from other Countries. *Psychology and Education Journal*, *57*(9), 5924-5934.

Rahmad, B., Hananto, H., Nugroho, T., Pramono, S. H., & Sumantri, A. Shale Hydrocarbon Potential of Semilir Formation in Buyutan, Klaten, Central Java, Indonesia.

Saputra, A., Gomez, C., Hadmoko, D. S., & Sartohadi, J. (2016). Coseismic landslide susceptibility assessment using geographic information system. *Geoenvironmental*

Disasters, *3*, 1-16.

Sari, A.S., Bahagiarti, S., Suharsono, S., & Prasetyadi, C. (2020). Groundwater quality in Ponjong Karst, Gunungkidul Regency, Special Region of Yogyakarta. *Journal of Earth and Marine Technology (JEMT)*, *1*(1), pp.7-11.

Sarireh, M., Ghrair, A. M., Alsaqoor, S., & Alahmer, A. (2021). Evaluation of the Use of Volcanic Tuff in concrete block production. *Jordan Journal of Earth and Environmental Sciences (JJEES)*, *16*.

Senoro, D. B., Plasus, M. M. G., Gorospe, A. F. B., Nolos, R. C., Baaco, A. T., & Lin, C. (2023). Metals and Metalloid Concentrations in Fish, Its Spatial Distribution in PPC, Philippines and the Attributable Risks. *Toxics*, *11*(7), 621.

Sintorini, M. M., Widyatmoko, H., Sinaga, E., & Aliyah, N. (2021, April). Effect of pH on metal mobility in the soil. In *IOP Conference Series: Earth and Environmental Science* (Vol. 737, No. 1, p. 012071). IOP Publishing.

Surono, Toha, B, & Sudarno, I. (1992). Peta Geologi Lembar Surakarta Giritontro, Jawa, Skala 1:100.000 (Bandung: Pusat Penelitian dan Pengembangan Geologi).

Susilo, A., Haji, A. T. S., Suharto, B., Suyadnya, I. W., Pramais, C. W., & Rahman, A. H. (2021, February). Inventory and identification of geodiversity to support geotourism in the Lenggoksono bay area of South Malang, Indonesia. In *Journal of Physics: Conference Series* (Vol. 1816, No. 1, p. 012111). IOP Publishing.

Sutarto, S., Idrus, A., Harjoko, A., Setijadji, L. D., Meyer, F. M., & Sindern, S. (2020, July). Mineralization style of the Randu Kuning porphyry Cu-Au and intermediate sulphidation epithermal Au-base metals deposits at Selogiri area, Central Java

Indonesia. In *AIP Conference Proceedings* (Vol. 2245, No. 1). AIP Publishing.

Tarawneh, K., Eleyan, I., Alalwan, R., Sallam, S., & Hammad, S. (2021). Assessment of heavy metals contamination levels in surfaces soil in Baqa'a area, Jordan. *Jordan Journal of Earth & Environmental Sciences*, *12*(4).

United States Environmental Protection Agency – US EPA. (2007). Method 7000B (SW-846): Flame Atomic Absorption Spectrophotometry, Revision 2. Washington: US EPA.

Wang, Z., Bao, J., Wang, T., Moryani, H. T., Kang, W., Zheng, J., ... & Xiao, W. (2021). Hazardous heavy metals accumulation and health risk assessment of different vegetable species in contaminated soils from a typical mining city, central China. *International Journal of Environmental Research and Public Health*, *18*(5), 2617.

World Health Organization (WHO). (1996). Permissible limits of heavy metals in soil and plants. *Geneva, Switzerland*.

Xiang, M., Li, Y., Yang, J., Lei, K., Li, Y., Li, F., ... & Cao, Y. (2021). Heavy metal contamination risk assessment and correlation analysis of heavy metal contents in soil and crops. *Environmental Pollution*, *278*, 116911.

Xie, F., Yu, M., Yuan, Q., Meng, Y., Qie, Y., Shang, Z., ... & Zhang, D. (2022). Spatial distribution, pollution assessment, and source identification of heavy metals in the Yellow River. *Journal of Hazardous Materials*, *436*, 129309.

Yang, P., Mao, R., Shao, H., & Gao, Y. (2009). An investigation on the distribution of eight hazardous heavy metals in the suburban farmland of China. *Journal of* *hazardous materials*, *167*(1-3), 1246-1251.

Yaseen, I. B., & Al-Hawari, Z. (2019). Assessment of Metal Pollution of the Surface Sediments along the Wadi Al Rayyan area, Jordan. *Jordan Journal of Earth & Environmental Sciences*, 75.

Zamroni, A., Kurniati, A. C., & Prasetya, H. N. E. (2020). The assessment of landslides disaster mitigation in Java Island, Indonesia: a review. *Journal of Geoscience, Engineering, Environment, and Technology*, *5*(3), 124-128.

Zamroni, A., Trisnaning, P. T., Prasetya, H. N. E., Sagala, S. T., & Putra, A. S. (2022). Geochemical Characteristics and Evaluation of the Groundwater and Surface Water in Limestone Mining Area around Gunungkidul Regency, Indonesia. *The Iraqi Geological Journal*, 189-198.

Zamroni, A., Trisnaning, P. T., & Widiatmoko, F. R. (2023, February). Karst landscapes in Indonesia: Potential disaster and mitigation. In *AIP Conference Proceedings* (Vol. 2482, No. 1). AIP Publishing.

Zhang, J., Yang, R., Li, Y. C., Peng, Y., Wen, X., & Ni, X. (2020). Distribution, accumulation, and potential risks of heavy metals in soil and tea leaves from geologically different plantations. *Ecotoxicology and Environmental Safety*, *195*, 110475.

Zhao, Y., Deng, Q., Lin, Q., Zeng, C., & Zhong, C. (2020). Cadmium source identification in soils and high-risk regions predicted by geographical detector method. *Environmental Pollution*, *263*, 114338.