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SOIL NICKEL CONCENTRATION IN A DELTA NEAR A LARGE SCALE MINE IN SURIGAO DEL NORTE, PHILIPPINES

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Abstract
Soil deposits in Kinalablaban delta located within a large-scale nickel mining company in Cagdianao, Surigao del Norte, were examined to assess the level of nickel in the soil. The spatial distribution of nickel was determined in the established zones. The analysis of nickel concentration was performed using the Flame Atomic Spectrophotometer. The soil has a very high nickel content, ranging from 2281.34 ± 122.34 to 11090.09 ± 2450.60ppm. The soil was also characterized to be slightly acidic (6.44) to strongly alkaline (8.89). The area was dominated by fine sand for about 39% of all the sediment grain size composition, with a bulk density ranging from 0.51-1.67g/cm^3 indicating a suitable soil for plant growth. Due to the very high nickel content, the area is already contaminated with this heavy metal and should be subjected to remediation and restoration. Consequently, for an effective site restoration, bioremediation using plant species that could accumulate nickel could be applied to cope with the local conditions of soil having a high nickel content.
Keywords: *Heavy metal; Nickel mining; Riparian; Soil quality; Wetland*

Introduction

A river delta is formed when soil and sediments carried by the water from the uplands are deposited at the mouth of the river before it empties into the sea. Most deltas are classified as wetlands due to the presence of water, either permanently or temporarily. Wetlands are ecosystems that serve a critical role in filtering silt, sediment, and pollutants, hence enhancing water quality. Wetlands are also geochemical traps and act as "green filters" for terrestrial pollutants [1]. It is also a haven for many floral and faunal species since it serves as a habitat, nursery, and feeding ground for juvenile organisms as well as a source of food. This is why wetlands are now legally protected, not only because society perceived them to be valuable due to their ecological services but also because population pressure has depleted their ecological and economic value [2].

Within the vicinity of a large-scale nickel mine is the outlet of Kinalablaban River, which leads straight to Hinadkaban Bay, where sediments from the mine industry are deposited. The area forms a delta and wetland at the same time, creating a diverse and ecologically important ecosystem. During a severe rain or wet season, coastal waters around mining areas turn reddish and become very turbid, probably due to the lateritic soil from the upland mined areas that drained into the sea. Turbid coastal waters near mining areas pose a threat to marine ecosystems because silt reduces the quality of water and its suitability for use. This scenario has always been an issue since some mitigation measures by surrounding mining companies are insufficient

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to remedy the problem. The Mines and Geosciences Bureau (MGB) of the Department of Environment and Natural Resources (DENR) requires every mining company to establish a settling pond where water containing silt and sediment will settle. However, it still did not address the issue of coastal siltation and sedimentation.

The presence of vegetation in Kinalablaban Delta functions as silt and sediment barrier, which is one method of preventing sedimentation in coastal areas. These vegetations slows down the sediment transport by weakening the bed shear stress and plants can adsorbed the fine particles, reducing water turbidity [3].

Vegetated areas of channels and wetlands are used to trap suspended sediment in the water [4], thereby reducing the silt and sediment that go directly to the sea. Since the study site is adjacent to a nickel mining industry, a certain amount of nickel has accumulated in the delta over time. While nickel is a nutritionally essential trace metal for at least several animal species, microorganisms, and plants, toxicity symptoms can occur when too little or too much nickel is taken up. Nickel is generally distributed uniformly through the soil profile but typically accumulates at the surface from deposition by natural or anthropogenic activities. If the deposition of nickel in the surface soil of deltas is high, it may influence to adjacent ecosystems and organisms thriving in the area. According to *Sheoran and Sheoran* [5], wetlands absorb and bind heavy metals, causing them to slowly concentrate in sedimentary deposits. This could result heavy metal accumulation in the food chain [6–7].

With this, the concentration of nickel in the entire delta of Kinalablaban was determined, along with soil pH, bulk density, and sediment types that are deposited in the area.

The result of this study is helpful to nearby mining companies since it can contribute to their environmental management plan by coming up with a strategy to minimize sedimentation and mitigating high nickel deposits in the delta. This could also shed light and help them draw a conclusion so that necessary management and precautionary measures could be implemented to either maintain or enhance biodiversity in the area. This study is also useful for concerned local and national government agencies since it can provide baseline information and improve their policies regarding mitigating pollution brought about by large-scale mining companies. Also, the government can help monitor compliance with regulations and take necessary actions if needed. Research institutions can also benefit from this study because it can pave the way for other research that is still needed to better understand the nature of the wetlands.

Experimental part

Study Area

The study was conducted in a delta that serves as the catchment basin for sediments from the Kinalablaban River and two minor rivers (Fig. 1). The study area is within the vicinity of a large-scale nickel mining company. The Kinalablaban River is the biggest of the three tributaries that leads straight to the sea. Since the area is large, zoning was established, and the sampling points were grouped according to zones. Zone one was in the riparian area; zone two was located in area with abundant vegetation; and zone three was in the coastal area (Fig. 2).

Soil Sample Collection

Using a stainless-steel spade, surface soil samples were taken from the study area at 20 cm depth within the designated sampling points in the various zones. Three replicates per sampling point were collected. There were 22 sampling points established in the whole area. For the bulk density, soil samples were collected using the soil core sampler. The collected samples were packed in polyethylene bags, properly labelled, and transported to the laboratory for further analysis.

Laboratory Analysis

Sediment Grain Size Analysis

Sediments that were collected from the study site were oven dried in an electric oven at 105°C for 48h. Sediment grain sizes were determined by sieve method. A total of 20g of dried sand-rich sediment were sieved using a mesh size of 150μm to get rid of mud from the sediments. Particles coarser than 150μm were collected and dried in an electric oven at 105°C for 24h, and then they were gently pounded with fingers. The particles passed through a series of sieves using a Tyler sieve shaker with mesh sizes of 1.4, 0.6, 0.425, 0.300, 0.212, and 0.15mm. The particles that were retained on each sieve were weighed and converted into a percentage of the total sediment sample.

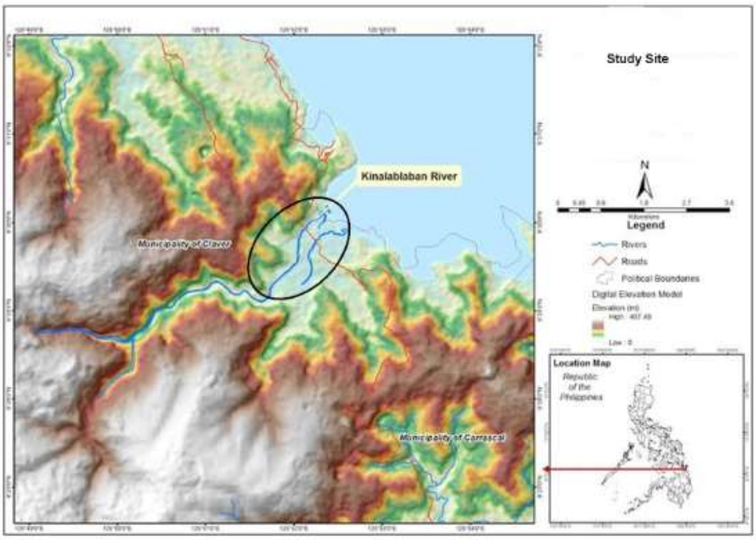

Fig. 1. Map of the Kinalablaban Delta in Cagdianao, Claver, and Surigao del Norte.

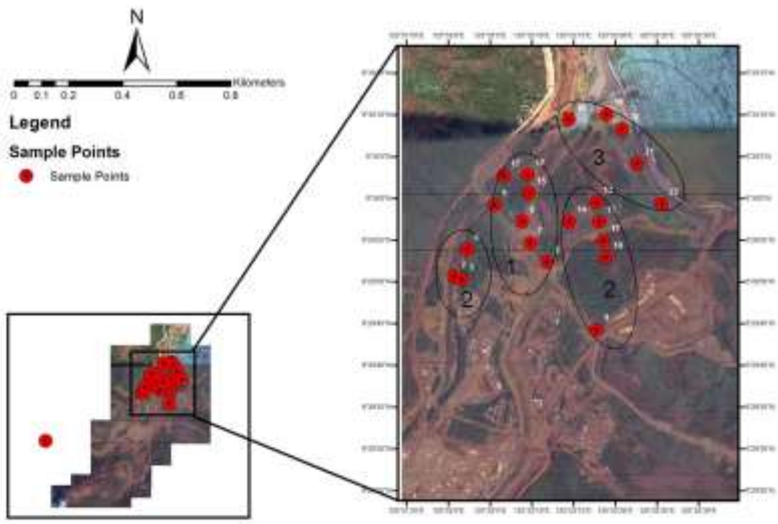

Fig. 2. Map of the Kinalablaban Delta indicating the sampling points in Cagdianao, Claver, and Surigao del Norte (1-Riparian, 2-Vegetated Area, 3-Coastal)

Bulk Density

Soil samples collected were air-dried, while rocks and roots were removed from the samples. The soil samples were then oven dried at 105°C for 72 hours, and a constant weight was recorded using the analytical balance. Since the presence of rocks and roots can affect the bulk density of the soil, the volume of the rocks and roots was determined using volume displacement through a graduated cylinder. The volume of the soil was calculated by determining the volume of the core sampler used during the gathering of the soil sample. The following formula was used to calculate bulk density:

Soil bulk density (g/cm^3) = oven dry weight of soil (g)/Total volume of soil (cm^3)

Soil pH

Soil pH was determined potentiometrically at a soil to water ratio of 1:2.5 [8]. Twenty grams of air-dried soil (< 2mm) were added with 50mL of distilled water to achieve the 1:2.5 ratio. The solution was stirred and allowed to stand for 30 minutes. The pH was then determined using the HACH portable multi-parameter water checker.

Nickel

Nickel in the soil samples was analysed using the standard method of the US Environmental Protection Agency [9]. The method involved the digestion of samples using hydrochloric acid with repeated additions of nitric acid and hydrogen peroxide. The final digested sample was filtered (Whatman No. 41) and diluted to 100 ml volume in a volumetric flask. Samples were then quantified using the Flame Atomic Absorption Spectrophotometer.

Results and discussion

Soil pH

The soil pH level of the Kinalablaban delta ranges from 6.4–8.89, indicating that soil deposits in the delta are weakly acidic to strongly alkaline (Fig. 3). The pH range is typical for most soils in the Philippines. The variation of pH across the entire delta could be due to the production of humus and organic acids by the vegetation, or it could also be due to the inherent variability of the soil. Soil pH management can be used in soil conservation because it is a low-cost strategy for remediating nickel-contaminated areas [10].

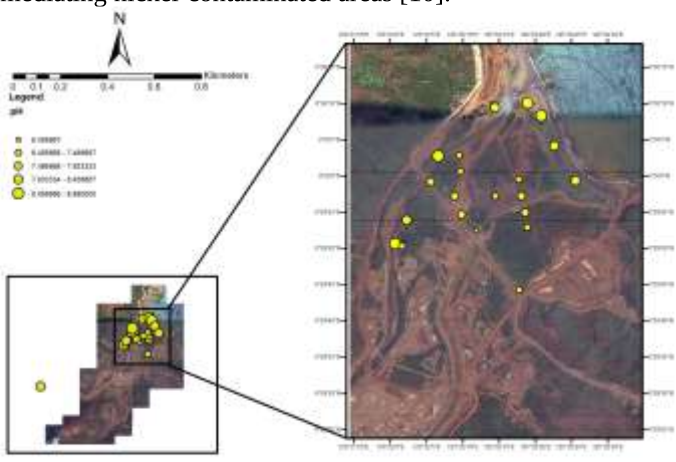

Fig. 3. Soil pH across Kinalablaban Delta in Cagdianao, Surigao del Norte

Bulk Density

The soil bulk density in Kinalablaban Delta ranges from 0.59 to 1.71g/cm^3 (Table 1), indicating that the values are not too compact and are adequate for root penetration. Bulk density did not exceed the recommended value of 1.8 g/cm^3, because beyond this value, penetration of plant roots is restricted, which may limit plant growth and affect the diversity of the entire delta. The coastal zone area has the highest bulk density mean value of 1.32±32 g/cm^3, and riparian areas have the lowest bulk density of 0.82±0.17g/cm^3. The concentration of sand was found to have a more direct effect on soil bulk density than other soil properties [11]. It indicates that the concentration of sand is a relevant soil property that affected bulk density in soils since the coastal area has the highest sand content of the three zones. According to *J. Beniston* [12], soil bulk densities influence heavy metal accumulation

Table 1. Means of Nickel, pH, and Bulk Density Across Different Zonations in the Kinalablaban Delta in Cagdianao, Claver, Surigao del Norte

Zones	Nickel (mg/kg)	pH	Bulk Density (g/cm^3)
Riparian	8,448.03[a]	7.57[a]	0.82[a]
Vegetated	7,201.69[a]	7.59[a]	0.97[a]
Coastal	2,662.78[b]	8.58[b]	1.32[b]

[a and b] Different letters denote significant differences across zones ($p < 0.05$)

Sediment Grain Size

Surface sediments for the whole area are largely composed of five particle sizes: very fine sand, fine sand, coarse sand, medium sand, and very coarse sand (Fig. 4). Very fine sand dominates the area for about 37%, and silt has the lowest percentage composition for about 1%. The distinct segregation of individual grain size fractions in response to changing energy levels during transport sheds some light on the transport-deposition relationship. Sediment mixing between different source populations during transport is a common phenomenon even in tidal environments [13]. The finest sediments occur mostly at the high waterline, while in the middle part of a tidal flat, fine sandy muds can be found. The riparian and vegetated areas are dominated by very fine sand, while the coastal zone is dominated by medium sand. Sandy tidal flats are dominated by hydrodynamic factors and morphologic settings that affect bed sediments and directional sediment transport; thus, the rate of wave energy and tidal currents must affect tidal flat sedimentation [14].

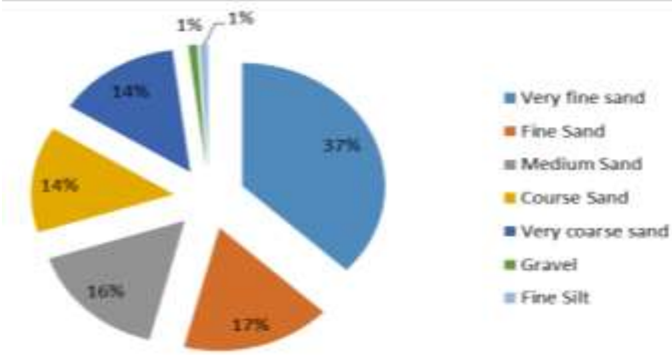

Fig. 4. Percent composition of sediments in the Kinalablaban Delta

Nickel Concentration in Sediments of the Kinalablaban Delta

Nickel concentration for the entire delta is very high since values range from 2,281± 122.34 to 11,090.09±2455.60mg/kg (Fig. 5). The high concentration of nickel in the study site could be attributed to the nature of the parent material and soil in the upland that is currently subjected to nickel mining. It could also be attributable to the sediments deposited throughout the delta, which could be coming from saprolitic soil from the uplands. A significant concentration of nickel in different layers of saprolite in a lateritic soil profile, ranging from 2335mg/kg in a serpentinite rock to 6829mg/kg in the upper saprolite [15]. Nickel also had excessively high concentrations (5000mg/kg) found in the soils formed from an ultrabasic igneous rock [16]. The nickel content is also high in the saprolitic samples (16,775–25,577mg/kg) of an ultramafic complex of Barro Alto (BA) in Goiás State, Brazil, due to the residual concentration of nickel and nickel leaching from the upper horizons [17]. Ultramafic rocks and the soils have elevated concentrations of nickel, which range from 1300–3900mg/kg Ni for surface soil samples derived from such rocks found in the Sierra Nevada and Coast Range [18]. High nickel concentrations in recent (post-Roman) overbank and deltaic deposits supplied by the Po River exceeded the Italian threshold limits of 120mg/kg [19]. The study site is adjacent to a nickel mining industry, and hence, there is a tendency that nickel from saprolitic soil becomes part of runoff during heavy rains and that nickel has been deposited and accumulated in the delta over time. Wetlands absorb and bind heavy metals, causing them to slowly accumulate in sedimentary deposits [5]. The elevated concentration of nickel could also be attributed to fine soil sediments. The clayey loam texture of the mangrove sediments, with a relatively high silt and clay fraction, is known to bind heavy metals [20]. *S.M. Saifullah et al.* [21] also found a greater proportion of nickel deposited in sediments in a mangrove ecosystem.

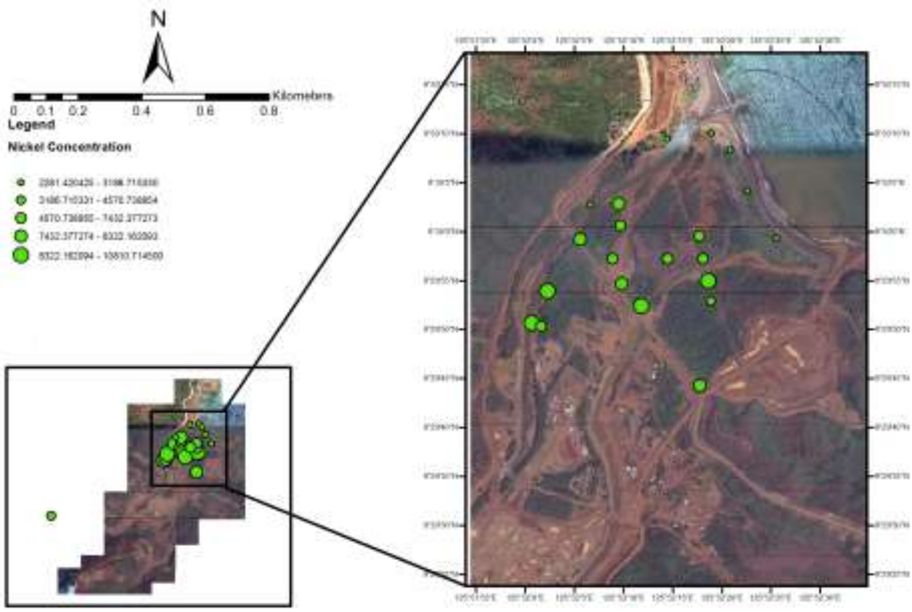

Fig. 5. Concentration of nickel across the Kinalablaban Delta in Cagdianao, Surigao del Norte

Mining activities was considered the most important source zones of zinc and nickel in the Yangtze River's main channel of the [22], which could have been exacerbated by soil erosion as well. With the very high concentration of nickel in the soil, it is reasonable to say that it is already contaminated with this heavy metal and that the soil requires remediation. The USEPA limits the amount of nickel in soil that must be cleaned to 1600mg/kg. Bioremediation technique, which employs organisms to accumulate heavy metals in their bodies, can be used to remove heavy metals from ecosystems. There are already known nickel hyperaccumulator plants, which can be used to progressively absorb the nickel if planted throughout the Kinalablaban delta. It could also be observed that sampling points with higher nickel concentrations were generally in the riparian area (zone 1) and gradually decreased as they approach the coast (zone 3). The riparian soils are stream-deposited material, hence, the high nickel content in the riparian area could be attributed to nickel-rich upland sediments. The nickel isotope range in rivers was found to be significantly heavier than the range of nickel for silicate rocks in terrestrial areas [23], indicating a larger concentration of the heavier nickel isotope than the uplands. This can then contribute to the heavy dissolved riverine Ni load [17].

Riparian soils have the potential to be more minerally diverse than their upland equivalents. The flushing of organic litter and various minerals from riparian areas by water is complemented by periodic sediment deposition in riparian areas by streams during floods. The maximum allowable Ni concentration in soil is 36 ppm and quantities beyond this is deemed harmful.

Spatial Variation of pH, Bulk Density, and Nickel

Soil pH ranged from moderately acidic to strongly alkaline across the delta, with zone 3 being significantly different from other two zones (Table 1). The main factor influencing nickel solubility, mobility, and sorption is soil pH [24-25]. As a result, soils with high nickel content have lower pH, while soils with low nickel content tend to become alkaline.

The bulk density is significantly different between zones 1 and 3. The sediment grain size composition of the different zones influences soil bulk density; the higher the sand concentration in the soil or sediment, the higher the bulk density.

Nickel concentrations in the three zones were beyond the maximum concentration standards imposed by the USEPA to avoid acute toxicity to plants and other soil microorganisms. Despite the fact that metal concentrations were high in zones 1 and 2, no significant differences were observed in these two zones, however, zone 3 was significantly different from the other two zones. The coastal area has the lowest nickel concentrations as compared to riparian and vegetative areas. Washing the sediment with water has been claimed to remove a portion of the heavy metal contamination [26-27].

Conclusions

The grain size distribution in the area is dominated by fine sand. Despite the high nickel content, soil pH and bulk density are adequate for the establishment of some plant species.

The concentration of nickel in the region exceeds the US EPA's heavy metal standard. The soil needs to be remediated, which might be accomplished using bioremediation technology, which enables organisms to absorb the high concentration of heavy into their system.

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