Risk assessment of heavy metal contamination in agricultural sites and river sediments within the vicinity of an operational Gold Mine in Vatukoula, Fiji

Ivan Diarra (✉ Ivand@sprep.org)
The University of the South Pacific https://orcid.org/0000-0003-1565-0295

Research Article

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Abstract

A comprehensive study was conducted to explore the concentration and distribution of heavy metals in farm soils and river sediments around a gold mining area in Fiji with particular emphasis on ecological and human health risks. Representative samples were acquired from farm sites in Matanagata Village and the Nasivi river, both situated around the Vatukoula Gold Mine Limited (VGML), the largest operational gold mine in Fiji. Following *aqua regia* digestion and analysis by AAS, the average soil concentrations for Cu (110.4 mg kg^{-1}), Cr (136.2 mg kg^{-1}) and Cd (1.7 mg kg^{-1}), and sediment concentrations for Pb (69.31 mg kg^{-1}), Cd (1.82 mg kg^{-1}), Cu (88.95 mg kg^{-1}) and Cr (143.12 mg kg^{-1}) were found to exceed the recommended guideline values. Based on the geo–accumulation index (I_{geo}) and enrichments factor (EF), the farm soils were moderately contaminated with Cd while the sediments showed moderate to significant contamination with Pb, Ni and Cr. Ecological risk assessment confirmed moderate to considerable ecological risk in the metal–contaminated samples, with Cd and Pb generally presenting greater risk compared to other metals. Multivariate analyses including principal component analysis pointed to gold mining activities as a potential source for heavy metals in the area. Furthermore, human health risk assessment (HRA) indicated that while adults faced no significant carcinogenic or non–carcinogenic risks from metal exposure (HI < 1), children were at more risk from Co, Mn, Cr and Fe exposure, as well as potential carcinogenic risk from Cd (ILCR = 1.46E–04).

1.0. Introduction

The unprecedented rates of urbanization and industrialization have been largely cited as significant factors behind the pollution and contamination of the biosphere, atmosphere and hydrosphere. The proliferation of inorganic contaminants, particularly heavy metals in soils, sediments, agricultural resources, and marine environments, has become a major issue of global proportions with even small developing countries such as Fiji unspared (Diarra and Prasad, 2020). In Fiji, numerous studies conducted on soil, sediments and dust samples have confirmed the presence of these toxic heavy metals in urban and industrial areas as well as marine environments, with concentrations often exceeding ecotoxicity thresholds and established sediment quality guidelines (SQG) (Maata and Singh, 2008; Chandra et al., 2016; Maeaba et al., 2019). These have been largely attributed to anthropogenic activities including food processing and bottling plants, metal fabrication and construction, textile, battery and paint manufacturing plants, petroleum storage, as well as effluents released from the Kinoya Waste-Water Treatment Plant (KWWTP) (Arikibe and Prasad, 2020; Pratap et al., 2020). Although less studied, mining has been cited as a significant source of recalcitrant pollutants especially heavy metal(loid)s (Lin et al., 2005; J. Zhou et al., 2018). Globally, several studies have reported increased heavy metal concentrations and ecological risks in areas associated with mining activities (Ngole–Jeme and Fantke, 2017; Oyebamiji et al., 2018; Sungur et al., 2020).

The situation of Fiji along the Pacific and Indo–Australian Plate boundary is suggestive of it having major potential for porphyry copper–gold, and epithermal gold mineralization. Mineral deposits in the country consist of manganese ores; numerous kinds of massive sulfide; disseminated porphyry–type copper–gold deposits; residual deposits such as iron sands and bauxite; epithermal–telethermal gold–telluride–silver deposits; and veins, skarns, limestone replacements related to plutonism (Colley and Greenbaum, 1980). While several metalliferous mines have been established since the early 1900s, most have been abandoned with only a few currently operational. Most of these mines are situated in mountainous regions and headwaters of major rivers where several varieties of root crops and vegetables are grown. The mining and quarrying scene in the country has been dominated by gold production with notable production of cement, bauxite, limestone, and silver– which account for about 1.9% of GDP and constitute the third largest export industry. Gold mining is associated with the production of large quantities of mine waste (mine tailings) during beneficiation – a process which physically separates and concentrates the ore mineral(s) mostly using physical and chemical techniques (Lottermoser, 2010). In fact, estimates suggest that about 99% of extracted ore during gold mining are deposited back into the environment as tailings (Adler and Rascher, 2007). Reports suggest that mine tailings have been produced since the 1920s through the mining of a gold–telluride ore containing minor arsenopyrite at the Vatukoula Gold Mine Limited (VGML), the largest and longest operational mine in Fiji (Anderson and Eaton, 1990). Though tailing dams have been erected to collect and arrest the release of mine tailings, wastewater and solid waste into the neighbouring environment, incidents of waste discharge have been documented. Of note was a collapse along one of the tailings pipeline (Toko tailings pipeline) in 2006, resulting in the exposure of residential compounds and the surrounding community with mine waste (Emperor Mines Ltd., 2006). In addition, recurring cyclones and flooding during the rainy season can raise the water level by five to ten meters and transport vast amounts of sediments resulting in the inundation of lower streams and farmland areas with mine tailings (Ackley, 2008). These have led to concerns over the possible contamination of nearby agricultural sites and natural water resources (rivers and streams) with recalcitrant toxicants such as heavy metals. High concentrations of As (6.6 mg L^{-1}) have been detected in the Nasivi River system (Singh and Mosley, 2003), located downstream of the VGML tailing ponds, far exceeding the 10 µg L^{-1} guidelines for drinking water set by the USEPA and the WHO (US EPA, 2015; WHO, 2017). Furthermore, communities surrounding the tailings dams have been documented using the tailings as 'soil' for crop cultivation (Ko et al., 2008), presenting serious health risks to nearby residents and effects on local agriculture through the bioaccumulation, biomagnification and trophic transfer of such hazardous heavy metals in the food chain. In fact, a recent retrospective cohort study by Matakarawa (2018) identified dust emissions from gold mining activities at the VGML as the single independent risk factor for acute upper respiratory tract infection (AURI) in the region.

Consequently, raising awareness on the possible ecological and health risks posed by the storage, transportation and handling of mine tailings is invaluable for residents. Nonetheless, investigations into the environmental extent of heavy metal contamination in Fiji have focused on urban areas, thus, there is a scarcity of literature on the levels and effects of these pollutants in agricultural and rural settings, particularly those situated around mines. In addition, although most developed countries have enacted strict regulations to monitor and curtail the storage and disposal of tailings, such regulations are often non-existent and/or hardly enforced in the developing world (Carvalho, 2017). Hence, geochemical studies of metal concentrations in soil and sediments located around the VGML, their mobility and potential ecological risks, is imperative towards developing long term monitoring and evaluation programs. A first of its kind conducted at the VGML, this study was designed to determine the composition of metals and the extent of contamination in farm soils and surface sediments associated with gold mining activities. In addition, the potential ecological and human health risks from heavy metal exposure are evaluated.

2.0. Materials And Methods

2.1. Study area

The Vatukoula Gold Mine Limited (VGML), formerly Emperor Gold Mine Ltd, is located within the Tavua Basin, situated within the Tavua Volcano, the largest of a series of tertiary shoshonitic shield volcanoes which occur within a northeast–trending extensional fault zone across the northern portion of Viti Levu, Fiji's largest island (Anderson and Eaton, 1990). Vatukoula, with an estimated population of 5,580 (Fiji Bureau of Statistics, 2018), lies within the 140 km^2 Nasivi Catchment, which is drained by the Nasivi River (Sinclair Knight Merz Pty Ltd., 1994). The major land uses of the catchment include mining, sugar cane cultivation, pine plantations on upper ridges, and livestock grazing (goats, cattle, and poultry). The Nasivi River flows through the mangroves of the Tavua Delta and discharges into the Pacific Ocean through two primary channels, the Nasivi and the Nasiriti (Sinclair Knight Merz Pty Ltd., 1994).

Historically, the VGML is considered the most productive of Fiji's precious metal mines, which have the distinction of being the world's farthest from any continental land mass (Smith et al., 2008). The mine spreads across part of the western margin of the Tavua Caldera, marked by a clustered gravity low, with a capacity to treat over 500,000 tons of ore per annum (AMC, 2011). The VGML is a multi–shaft underground mine, with average gold grading of 7–11 g ton^{-1}. The gold recovery process begins with the crushing and grinding of ore and the removal of the resulting primary slime through screening and rake classification. Next, the bulk gold–telluride/pyrite concentrate and primary slime are sent through separate flotation circuits and then recombined after achieving a specified level of concentration (Sinclair Knight Merz Pty Ltd., 1994). The combined flotation concentrates then undergo roasting and cyanidation. Tailings are subsequently pumped off for disposal into five tailings dams distributed around the Vatukoula region.

2.2. Study sites and sample acquisition

The study site is the village of Matanagata located downstream from the tailing dams of the VGML (Fig. 1). During sampling, farms were cultivated with root crops (Taro and Tapioca) as well as various vegetables, thus, the accessibility of the sites played a major role in sample collection. To ensure representativeness, a composite sampling scheme was employed to retrieve surface soil samples (≤ 20 cm) from farm sites located within the vicinity of the VGML. At each site, at least ten samples were collected from a 10 x 10 m^2 plot and homogenized into a single composite sample. To prevent cross contamination, a plastic scoop was used for soil collection and thoroughly cleaned between each sample collection. In addition, sediment samples from the Nasivi river were also retrieved randomly following the methods outlined by the Australian and New Zealand Guidelines for Fresh and Marine Water Quality (Australian Government, 2020). Three representative sediment samples were each collected upstream, midstream and downstream of the river, constituting a total of nine sediment samples. All retrieved samples were placed in clean Ziploc plastic bags and clearly labelled with GPS coordinates and sampling date and time.

2.3. Soil and sediment laboratory characterization

Following air drying at room temperature, the soil and sediment samples were disaggregated in a porcelain mortar and pestle and passed through a 2 mm sieve in preparation for physico–chemical analysis. Soil particle size distribution was estimated using the graduated cylinder method and classified based on the USDA soil texture classification triangle and Shepard's sediment classification system, respectively. Soil pH was determined by diluting samples in deionized water (DW) at a ratio of 1:1 (50 g of soil in 50 mL of water) and measuring with a calibrated pH meter (Eutech instruments pH 700). Similarly, soil electrical conductivity (EC) was also determined using a 1:1 soil and DW ratio and measuring with conductivity meter (Eutech instruments CON 700). Water holding capacity of the soil was determined saturating the soil in water and calculating the soil weight before and after saturation. Soil organic matter (SOM) was determined by weight loss on ignition (WLOI) (Hoogsteen et al., 2018).

2.4. Soil elemental analysis

Soils and sediments were digested according to a modification of the *aqua regia* procedure outlined by ISO 11466:1995 (ISO, 2007). Around 1.000 g of soil and sediment samples were accurately weighed in triplicates and placed in 250 mL Pyrex beakers. After the addition of 10 mL of a (3:1, v/v) mixture of HCl (36%) and HNO_3 (68%), the suspension was covered with a watch glass and gradually heated to 150°C on a hotplate (LABEC, Australia). 5 mL aliquots of *aqua regia* were continuously supplemented until a clear colorless endpoint was reached. The samples were digested until ~ 1 mL of acid remained. After cooling, the digest was filtered through a Whatman 42 filter paper into a 100 mL volumetric flask, and made to the mark with Ultra–Millipore DW. Digested samples were stored in polyethylene bottles at 4°C until analysis. Elemental concentrations were determined using a flame atomic absorption spectrometer (FAAS) (PerkinElmer PinAAcle 500) after calibration with a series of five working standards prepared by serial dilutions of stock solutions.

2.5. Quality control

All glassware used were vigorously washed in acid baths containing 10% HNO_3 and rinsed in deionized water (DW) before and after each use. To reduce contamination and increase reliability, analytical grade reagents and chemicals and ultra–Millipore DW (Millipore 18.2 MΩ·cm at 25°C) were used for all analyses. For repeatability, all analyses were conducted in triplicates and coefficient of variation was kept at ≤ 15%. For reproducibility, a certified reference material for trace metal(loid)s in sandy loam soils (CRM023–50G) from Sigma Aldrich, was digested in quintuplets following the exact procedure for samples, and analyzed. The percent recovery of elements is presented in Table 1 and fell within the 80–120% range recommended by the Association of Analytical Communities (AOAC) Guidelines (Horwitz, 2002). Validation of the AAS was carried out using method validation parameters including limit of detection (LOD) and limit of quantification (LOQ) expressed by Eqs. (1) and (2), where X_{bl} is the mean of 10 calibration blanks and S_{bl} is the standard deviation (Shrivastava and Gupta, 2011). The LOD and LOQ values for heavy metals in this study are provided in Supplementary Table S1.

$$LOD = X_{bl} + 3S_{bl} \quad (1)$$

$$LOQ = X_{bl} + 10S_{bl} \quad (2)$$

2.6. Geochemical pollution assessment

The heavy metal(loid) concentrations obtained were compared to their corresponding Maximum Permissible Concentrations (MPC) established by international bodies such as the World Health Organization (WHO), Canadian Environmental Quality Guidelines (CEQG) and the Dutch Target Value (DTV), to make informed decisions about the soil quality. The MPC is the concentration of a substance in air, water, soil or sediment that should protect all species in ecosystems from adverse effects of that substance (Crommentuijn et al., 2000).

2.6.1. Contamination degree (CD)

The degree of contamination (CD) is the sum of all contamination factors (CFs) for a particular site and aims to provide a measure of the degree of overall contamination. The CD is expressed as shown in Eq. (3), where n is the number of metal(loid)s and C_f^i is the CF (Hakanson, 1980). The CD is also divided into four classes.

$$CD = \sum_{(i=1)}^{n} C_f^i \quad (3)$$

2.6.2. Pollution load index (PLI)

PLI is used to determine the magnitude of heavy metal contamination in soils. It is a potent tool in heavy metal pollution evaluation (Tomlinson et al., 1980). The PLIs are calculated for all the metal(loid)s. PLI is expressed as in Eq. (4), where Cf_1 is the CF of each metal, and n is the number of metals.

$$PLI = (Cf_1 \times Cf_2 \times Cf_3 \ldots\ldots \times Cf_n)^{1/n} \quad (4)$$

2.6.3. Geoaccumulation index (I_{geo})

Another potent tool developed by Müller (1969) is the I_{geo} which allows the assessment of soil contamination with heavy metal based on its contents in A or O horizons referenced to a specified background value. I_{geo} is expressed as follows:

$$I_{geo} = log_2 \frac{C_x}{1.5 \times B_x} \quad (5)$$

where C_x is the metal concentration, B_x is the metal geochemical background value, and the constant 1.5 is used to represent the natural fluctuations and minor anthropogenic influences. The I_{geo} was distinguished into seven classes as shown in Table 1.

2.6.4. Enrichment factor (EF)

EF is a measure of the possible impact of anthropogenic activity on the concentration of heavy metals in soil using normalizer elements characterized by low variability of occurrence. Normalizer elements are usually Fe, Al, Ca, Ti, Sc or Mn. For this study, Fe was used as a reference element. EF is calculated using the following formula (Sutherland, 2000):

$$EF = \frac{\left[\frac{C_x}{C_{ref}}\right]}{\left[\frac{B_x}{B_{ref}}\right]} sample \quad (6)$$

C_x is the content of the examined element in the examined environment, C_{ref} is the content of the examined element in the reference environment, B_x is the content of the reference element in the examined environment, in this case Fe, and B_{ref} is the content of the reference element in the reference environment. The classifications for the enrichment factor are provided in Table 1.

2.6.5. Ecological risk index (ERI)

The ERI is used to evaluate heavy metal pollution in soil to associate ecological and environmental effects with their toxicology and the toxic–response factor (T_r^i) of Cu, Zn, Cd, Cr, Ni and Pb is 5, 1, 30, 2, 5 and 5 (mg g^{-1}), respectively (Hakanson, 1980). ERI is expressed using Eq. (7), where T_r^i is the toxic–response factor for a given substance and C_f^i is the CF.

$$E_r^i = T_r^i \times C_f^i \quad (7)$$

Potential ecological risk index (PERI) is employed to determine the semi–quantitative evaluation of regional pollution level. It can be expressed as follows (Hakanson, 1980):

$$PERI = \sum_{(i=1)}^{n} E_r^i \quad (8)$$

where n is the number of heavy metals and E_r^i is the single index of the ecological risk factor. The classifications for degree of heavy metal(loid) assessment by ERI and PERI are both shown in Table 1.

2.7. Human health risk assessment

To evaluate the health risks associated with human exposure to heavy metals at the VGML, a health risk assessment (HRA) was conducted (Li et al., 2014). Heavy metal exposure in human occurs through three major pathways, viz.; i) oral ingestion of heavy metal particles, ii) inhalation of heavy metal particles, and iii) dermal absorption of heavy metal particles on exposed skin (Qu et al., 2012). Hence, the risk assessment process is critical and is comprised of four major elements; hazard identification, exposure assessment, dose–response assessment, and risk characterization (Fowle and Dearfield, 2000; Kumar et al., 2019). Exposure assessment measures the intensity, frequency and duration of human exposure to a particular contaminant. Precisely, exposure assessment can be conducted by calculating the chronic daily intake (CDI) (mg kg^{-1} day^{-1}) of heavy metals through different exposure pathways on both adults and children – separated due to their behavioural and physiological differences (Miller et al., 2016). The CDI values from heavy metal exposure for different pathways were estimated using Eqs. (9), (10) and (11) obtained from the USEPA (USEPA, 1989).

$$\mathrm{CDI}_{\mathrm{ingest}} = \frac{\mathrm{C}_x \times \mathrm{IngR} \times \mathrm{EF} \times \mathrm{ED}}{\mathrm{BW} \times \mathrm{AT}} \times \mathrm{CF} \quad (9)$$

$$\mathrm{CDI}_{\mathrm{inhale}} = \frac{\mathrm{C}_x \times \mathrm{InhR} \times \mathrm{EF} \times \mathrm{ED}}{\mathrm{PEF} \times \mathrm{BW} \times \mathrm{AT}} \quad (10)$$

$$\mathrm{CDI}_{\mathrm{dermal}} = \frac{\mathrm{C}_x \times \mathrm{SA} \times \mathrm{AF}_{soil} \times \mathrm{ABS} \times \mathrm{EF} \times \mathrm{ED}}{\mathrm{BW} \times \mathrm{AT}} \times \mathrm{CF} \quad (11)$$

where C_x is the metal concentration in the sample; IngR represents the ingestion rate; EF is the exposure frequency; ED is the exposure duration; BW refers to the average body weight of the receptor; AT is the averaging time; CF is the unit conversion factor; the InhR is the inhalation rate; PEF is the particulate emission factor; SA is the surface area of the exposed skin; AF_{soil} is the soil adherence factor; and ABS is the dermal absorption factor. The exposure factors and their respective values used in the determination of the of CDI have been provided in Supplementary Table S2 (USEPA, 1989, 2010).

To conduct a full hazard assessment, the hazard quotient (HQ) was developed by comparing the CDI with the reference dose (RfD) as shown in Eq. (12), while the hazard Index (HI) was estimated by summing up all the HQs as expressed in Eq. (13). The RfD in the equation refers to reference dose for each metal provided by the US Environmental Protection Agency (USEPA, 2014; Kamunda et al., 2016) and are presented in Table 4.

$$\mathrm{HQ} = \frac{\mathrm{CDI}}{\mathrm{RfD}} \quad (12)$$

$$HI = \sum \mathrm{HQ} = HQ_{ing} + HQ_{inh} + HQ_{derm} \quad (13)$$

Lastly, the carcinogenic risks were determined to assess the probability of an individual developing cancer over a lifetime as a result of exposure to a carcinogenic metal. The cancer risks for metals from each exposure pathway was estimated by using the CDI and the cancer slope factor (CSF) as shown in Eq. (14) (USEPA, 1989). The incremental lifetime cancer risk (ILCR) risk, which is the average contribution of the individual heavy metals to cancer risks from all pathways was calculated using Eq. (15). The respective reference dose and CSF values for each metal are presented in Supplementary Table S3.

$$\mathrm{Cancerrisk} = \mathrm{CDI} \times \mathrm{CSF} \quad (14)$$

$$\sum \mathrm{CancerRisk} = \mathrm{ILCR} = \mathrm{Cancerrisk}_{\mathrm{ing}} + \mathrm{Cancerrisk}_{\mathrm{inh}} + \mathrm{Cancerrisk}_{\mathrm{derm}} \quad (15)$$

2.8. Statistical analysis

All data were processed in Microsoft Excel 2016 and statistically analyzed in IBM SPSS 25. Descriptive statistics was used to analyze the mean of the data obtained from three replicate analyses of the samples. A Pearson correlation matrix (PCM) was also performed to observe the mutual correlations between soil parameters and metal concentrations at the VGML. Additionally, to distinguish the potential sources of heavy metals, a principal component analysis (PCA) was conducted using factor extraction with an eigenvalue ⩾ 1 in XLSTAT Excel plugin.

3.0. Results And Discussion

3.1. Physico–chemical properties of soil and sediment samples

Several physicochemical parameters and statistics for the studied soils and sediments are provided in Table 2. The mean pH in the farm soils (FS) samples and river sediments (RS) were determined to be 6.85 and 7.47, respectively. Although both substrates were found to be in the neutral pH range, the RS typically had higher pH values (≥ 7.0) while the FSs were typically below 7.0. While the average silt fraction was typically higher in the FS (above 40%) than in the RS (below 20%), on average, the RS were comprised of more sand fraction (76%) than the FS (53%). In all samples, the clay content was below 40%, but still significantly higher in the FS than in RS ($p < 0.05$). The highest soil organic matter (SOM) content was observed at site FS1 with 10.4%. The highest SOM in RS was observed at site RS4 (1.98%) while the lowest was recorded at sites RS1 and RS5 (0.8%). FS markedly exceeded RS in terms of SOM. Electrical conductivity (EC) values for FS averaged around 518 µS cm^{-1} while for RS, this value dropped to 238 µS cm^{-1}. The EC values are indicative of the levels of dissolved salts and nutrients in the substrates and hence, points to higher levels of nutrients in the soil over the sediments. This is further highlighted by the higher abundance of macronutrients (Mg, K and Ca) in the FS compared to the RS.

3.2. Heavy metal concentrations in farm soils and river sediments

Metal concentrations in 20 farm soil samples (FS1–FS20) from Matanagata village are shown in Table 6. Metal concentrations followed the order Fe (5.11%) > Mn (503.8 mg kg^{-1}) > Cr (136.2 mg kg^{-1}) > Cu (110.4 mg kg^{-1}) > Zn (80 mg kg^{-1}) > Ni (57.2 mg kg^{-1}) > Pb (45.4 mg kg^{-1}) > Co (35.4 mg kg^{-1}) > Cd (1.7 mg

kg^{-1}). The concentrations of the studied metals showed little variations at all sites except for Pb, Cu, and Zn. The highest Zn concentration (116.85 mg kg^{-1}) and Mn concentration (544.9 mg kg^{-1}) were observed at site FS7 while the highest values for Ni and Cu (63.5 and 131.2 mg kg^{-1}) were both observed at site FS12. The highest concentration of Pb (63.64 mg kg^{-1}) was recorded at site FS20. An increasing trend in soil Pb concentration was observed moving downstream away from the mine with the farm sites further downstream (FS13–FS20) having the highest levels of Pb. However, the opposite case was noted for Zn and Fe, as soil concentrations generally decreased with distance from the mine site pointing to possible enrichment from the mine. The highest concentrations of Cd, Cr, Mn and Fe were also observed in farm sites with closest proximity to the mine tailings.

The concentration of heavy metals in Nasivi river sediments are summarized in Table 3 and designated RS1 to RS9. The range of metals in the sediments was: Pb (59.3–77.6 mg kg^{-1}), Zn (53.9–80.7 mg kg^{-1}), Cd (1.6–2.1 mg kg^{-1}), Ni (40.4–62.6 mg kg^{-1}), Cu (59.1–123.2 mg kg^{-1}), Cr (91.2–205.9 mg kg^{-1}), Mn (416.0–643.5 mg kg^{-1}), Co (24.5–42.7 mg kg^{-1}), Fe (3.84–5.58%). For all metals except Mn, the highest average concentrations were found in the midstream section of the Nasivi river, closest to the mine tailing dams. The highest concentrations of Zn, Cd, Ni, Cu, and Co were all observed at Site RS24, while the highest Fe and Cr concentrations were found at site RS25. Metal concentrations at sites sampled upstream before the mine generally had lower metal concentrations compared to sites midstream and downstream. This was confirmed by statistical analyses which revealed that heavy metal contamination differed between the upstream and both the midstream and the downstream sections of the river ($P < 0.05$). Site RS27, located downstream from the VGML, was found to contain the lowest concentration of Zn, Cd, Ni, Cr, Co and Fe amongst all sites. This decrease in metal concentration downstream may be due to 'dilution' by local sediment supply, chemical sorption, dissolution of contaminants and/or contaminant uptake by biota (Hudson-Edwards et al., 2008).

3.4. Comparison of soil and sediment metal concentrations at Vatukoula with international standards and background concentrations.

Table 4 presents the metal concentrations from FS in comparison to standard guidelines and permissible limits established by international bodies including the WHO Maximum Permissible Concentration (MPC), Canadian Agricultural Soil Quality Criteria (CASQC), Dutch Target Value (DTV) and background metal concentrations for global soils obtained from (Kabata–Pendias, 2010). Pb, Mn and Zn concentrations in all studied soils were found to be below the 100 mg kg^{-1} permissible limit set by the WHO and also below the CASQC and DTV. However, although Cd values were below the WHO limit (3 mg kg^{-1}), it exceeded both the CASQC (1.4 mg kg^{-1}) and DTV (0.8 mg kg^{-1}) guidelines by 24.3% and 117.5%, respectively. For Co, the average concentration was above the WHO MPC (30 mg kg^{-1}) but below the CASQC (40 mg kg^{-1}). Mean concentrations of Pb, Cd, Ni, Cu, Cr, Co and Fe were found to be 68%, 14.3%, 324.4%, 97%, 183.8%, 130.8%, 3%, 18% and 89.3% above background levels, respectively. The average Cu (110 mg kg^{-1}) and Cr (136 mg kg^{-1}) concentrations in soil were both found to exceed all three guidelines as well as the natural background levels for global soils, elucidating possible enrichment from the mine (Kabata–Pendias, 2010). Although both Cu and Cr are considered essential micronutrients, they have been widely reported to display toxicity at levels that exceed cellular homeostatic control capacity (Sheehan et al., 1991; Stern, 2010). In fact some scientists regard Cu as the most toxic essential element (Hunter, 2015), while Cr, particularly in its hexavalent state (Cr[VI]), has been classified as a human carcinogen by the WHO.

On the other hand, Nasivi river sediments had higher average values for Pb, Cd and Cr compared to the FS, while the concentrations of Zn, Ni, Cu, Co, and Fe were generally lower. For reference, sediment concentrations were compared against Canadian Freshwater Sediment Quality Criteria (CFSQC) and the Australian and New Zealand Environment and Conservation Council (ANZECC) guidelines as shown in Table 4. Average sediment concentrations of all metals except Zn, Mn, Co and Fe, were found to greatly exceed both CFSQC and ANZECC guidelines. Particularly notable were the concentrations of Pb, Cd, Cu and Cr which exceeded CFSQC limits by 98%, 203%, 149.2% and 283.7%, respectively and ANZECC limits by 38.6%, 21.3%, 36.9%, 78.9%. For Ni, although no established CFSQC limit exists, the observed values exceeded the ANZECC guidelines by 136.5%. While the Nasivi river isn't utilized as a drinking water source by the residents, livestock have been reported to drink from the river and these moderate levels may pose adverse risks. To properly contextualize the results, the baseline metal concentrations reported for the relatively 'pristine' Great Astrolabe reef in Fiji (Morrison et al., 1997), were used as local background values and compared with this study. All metals concentrations from the Nasivi RS greatly exceeded the concentrations reported for the Astrolabe reef. Concentrations of Pb, Zn, Cd, Ni, Cu, Cr, Mn, and Co in Nasivi sediments were 812%, 137%, 90%, 471%, 201%, 616%, 145% and 279% higher than respective concentrations reported in the Great Astrolabe reef sediments (Morrison et al., 1997). Particularly concerning were the high relative difference in Pb, Ni and Cr concentrations at both sites. This strongly points to possible contamination of the sediments with heavy metals emanating from the mine tailing dams.

3.5. Comparison of Vatukoula soil and sediment heavy metal concentrations with similar sites locally and globally.

The concentrations for heavy metals in FS near the VGML are compared with those in similar areas locally and globally as shown in Table 5. Metal concentrations in Matanagata village soils were generally lower than the levels reported for road side soils in Fiji's capital, Suva (Maeaba et al., 2019). However, the mean concentration of Ni, Cr, Co and Fe observed in this study exceeded those in Suva roadside soils. Similarly, the levels of Pb, Cu and Cr were greater than values reported in agricultural soils from the Avliyana antimonite mineralization area in Torul, Turkey (Sungur et al., 2020) and concentrations in paddy fields adjacent to the Co Dinh chromite mine, the largest mine in Vietnam (Kien et al., 2010). For sediments, it was observed that the concentrations of Pb, Zn, Cd and Cu from the Nasivi river were lower than the respective concentrations reported for the Suva Harbor in Fiji (Maata and Singh, 2008). While metal concentrations from this study were far below those reported for the Molonglo river in Australia (Marasinghe Wadige et al., 2016), they exceeded those reported for the Ipojuca river in Brazil (Silva et al., 2019)and the Jequetepeque River Basin in Peru (Yacoub et al., 2012).

3.6. Geochemical pollution assessment

3.6.1. Contamination Degree (CD) and Pollution Load Index (PLI)

The results for contamination degree (CD) and pollution load index (PLI) are presented in Fig. 3. Based on the results from the CD, it was clear that the FS all had CD values above 16, delineating these sites as having high degree of contamination. Most concerning was the CD values for the RS which were found to be above 32, making these sites very highly contaminated. Noteworthy were sites RS4 and RS8 which possessed the highest CD values amongst all sites. However, based on PLI analyses, all FS were considered unpolluted in regards to metals. In contrast, the RS were considered moderately polluted at sites RS1 and RS7, strongly polluted at site RS4, and significantly polluted at all other sites.

3.6.2. Geoaccumulation Index (I_{geo})

A close observation of Fig. 4A shows that there was little variation in the range of I_{geo} values obtained for the FS. Amongst all heavy metal contaminants in this study, Cd had the highest I_{geo} values in soil. All the FS were considered moderately polluted with Cd with an average I_{geo} value of 1.5. Similarly, the I_{geo} values for Cu fell in the $1 \leq I_{geo} < 2$ class indicating moderate Cu pollution. For Zn, Mn and Co, I_{geo} values for the FS were found to be in the unpolluted class ($I_{geo} \leq 0$), suggesting that these metals were not in excess of background levels. Similarly, the FS were considered unpolluted to moderately polluted with Pb, Ni and Fe ($0 \leq I_{geo} < 1$). In contrast, the RS showed higher levels of contamination compared to the FS (Fig. 4B). The average I_{geo} values for Pb in sediments was 2.6 and fell in the moderately to strongly contaminated class ($I_{geo} \leq 3$). This suggests that the Pb concentrations in the river system is an area of concern and may manifest toxicity. Similarly, the I_{geo} values for Cr and Ni in the sediments fell in moderately to heavily polluted class ($2 \leq I_{geo} < 3$). I_{geo} values for Zn, Cd, Mn and Fe in the sediments were all ≤ 1, indicating no pollution while values for Co and Cu suggested moderate pollution. It is interesting to note that while Pb, Zn, Ni and Co were classified as unpolluted in FS, the I_{geo} levels in the sediments were much higher. This is indicative of possible heavy metal enrichment of the river system through flooding and leaching from the mine tailings.

3.6.3. Enrichment factor

The enrichment factors for the studied metals were determined to comment on the extent of contamination due to anthropogenic activities. The EF for each heavy metal was calculated relative to the background values after normalization with the element Fe and shown in Fig. 5. In FS, EF values for all metals except Cd were < 2 suggesting minimal enrichment of these elements. This indicates that the concentration of these elements in the FS are primarily of geogenic origin with little to no input from mining. As for Cd, the EF values observed for FS was > 2 indicating moderate enrichment likely from the VGML. In the sediments, there was higher enrichment of heavy metals compared to the soils. EF values for Zn, Cd, Cu, Mn, Co were typically < 2 and were considered minimally enriched. Additionally, the sediments were considered moderately enriched in terms of Ni and Cr which both had EF values in the $2 \leq EF < 5$ class. As for Pb, EF values revealed that the RS were significantly enriched with this metal. According to (Liu et al., 2016), an EF between 0.05–1.50 point to a natural origin for the heavy metal concentration, while an EF > 1.50 indicates possible enrichment from non–crustal materials, particularly anthropogenic sources. On this basis, it is safe to assume that Cd, Cu, Cr, Ni and Pb levels were likely enriched from mining activities at the VGML.

3.6.4. Ecological risk index

The ERI and PERI were introduced to determine the semi–quantitative evaluation of regional pollution level, according to the toxicity of heavy metals and the response of the environment. The ERI values for heavy metals in the FS were; Pb (4.81–11.79), Zn (0.91–1.67), Cd (94.70–144.50), Cu (11.71–16.87), Ni (8.13–10.95) Mn (0.91–1.12), Co (21.36–27.44) and Cr (3.40–6.13), while in RS the range were; Pb (40.58–52.89), Zn (1.83–2.73), Cd (48.99–65.46), Cu (9.98–20.80), Ni (23.20–35.99) Mn (2.01–3.11), Co (14.17–24.73) and Cr (9.12–20.59), respectively. In the FS, all metals except Cd presented low ecological risk (ERI < 40). ERI values for Cd indicated considerable ecological risks. However, in the RS, only Pb and Cd were found to present moderate ecological risks ($40 \leq ER < 80$) while other metals presented low risks (ERI < 40). Generally, Pb and Cd were the main contributors to the potential ecological risk in the RS. Several studies have suggested that mining activities generate Cd contamination which can seriously threaten the growth of marine life and human health due to its intense biotoxicity and high bioaccumulation potential (Liu et al., 2019; Zhou et al., 2018).

3.7. Human health risk assessment

As widely emphasized, the accrual of heavy metals in the tissues of biological organisms can lead to toxicity and induce several disorders. Heavy metals do not only compete with essential elements due to their chemical similarities but they also interact with several divalent transporters which affects various physiologic functions including cardiovascular, neural, hematopoietic, immunological, and gastrointestinal systems, as well as a possible role in kidney dysfunction, anaemia, liver toxicity, cancer, and Alzheimer's disease (Tchounwou et al., 2012; Jaishankar et al., 2014; Rehman et al., 2017). Therefore, the carcinogenic and non–carcinogenic health risk associated with heavy metal exposure from the three pathways (ingestion, inhalation and dermal contact) on adults and children were quantified using the chronic daily intake (CDI) and the hazard index (HI).

3.7.1. Non–carcinogenic risks

The non–carcinogenic risks associated with heavy metal exposure for both adults and children are presented in Table 6. The HI values for non–carcinogenic risks were higher for children when compared to adults. The HI values for adults were in the range of 4.21E–04 to 1.37E–01 while for children, the values ranged from 3.73E–03 to 2.19E + 00. For both adults and children, the HI values for heavy metals were found to be in the order of Co > Mn > Cr > Fe > Co > Pb > Cd > Ni > Cu > Zn. Heavy metals with HI values exceeding one (HI > 1) strongly suggest that the metal may induce non–carcinogenic effects. In the present study, the calculated adult HI values for all metals were below one (HI < 1) suggesting minimal non–carcinogenic risks for adults from exposure to metals in the area. However, it was observed that HI values for children, particularly for Co (2.19E + 00), Mn (2.19E + 00), Cr (1.42E + 00) and Fe (1.17E + 00) were all above one (HI > 1). These high values observed for children in the area indicates that heavy metal pollution, particularly Co, Mn, Cr and Fe, may pose some adverse health risks to children living in the area. For reference, Naz et al. (2016) reported elevated carcinogenic risks due to high levels of Fe, Mn, and Cr in drinking water near the Sukinda chromite mine in India. Mn is mainly neurotoxic and increased levels have been linked with neurodevelopmental effects in children from across the world (Grandjean and Landrigan, 2014; Coetzee et al., 2016). An assessment of children living in a Mn–mining region of Ukraine also

observed impaired growth and rickets–like skeletal deformities in 33% of children (Duka et al., 2011). Similarly, high doses of cobalt may affect the heart, lungs, blood and thyroid (Paustenbach et al., 2013; Leyssens et al., 2017; Banza Lubaba Nkulu et al., 2018).

3.7.2. Carcinogenic risks

Heavy metals such as Pb, Cd, Cr, and Ni are considered category 1 heavy metals according to the International Agency for Research on Cancer (IARC, 1980). The carcinogenic risks (incremental lifetime cancer risk) associated with exposure to these heavy metals from different exposure pathways are provided in Table 7. The obtained results showed that the ILCR values ranged from 6.40E–07 to 1.58E–05 in adults and 5.90E–06 to 1.46E–04 in children. According to US–EPA recommendations, cancer risks exceeding 1 in 10,000 exposure (ILCR > 1.00E – 04) are deemed unacceptable, while risks below 1 chance in 1,000,000 lifetime exposure (ILCR < 1.00E – 06) are not expected to pose significant health effects, and risks between 1.00E – 04 and 1.00E – 06 are generally considered acceptable depending on the circumstances of exposure (Fryer et al., 2006; USEPA, 2014). While ILCR values for Pb, Cr and Ni for both adults and children were found to be well within the USEPA threshold risk limit (ILCR > 1.00E – 04), we observed that Cd posed the highest potential carcinogenic risk especially in children (ILCR = 1.46E–04). The ILCR values for heavy metals in decreasing order was Cd > Ni > Cr > Pb. For both adult and children, the ingestion route was found to be the largest contributor to ILCR. This emphasizes the need for constant monitoring of Cd in the soils and sediments surrounding the mine. Several studies have reported the presence of elevated Cd levels in farm soils and sediments located near mines and the adverse health risks (Galunin et al., 2014; Mohammed and Abdu, 2014; Zhou et al., 2018). Generally, the above results indicate that children have a slightly higher likelihood of experiencing adverse health effects due to Cd exposure around the Vatukoula area.

3.8. Apportionment of heavy metal sources

A Pearson correlation matrix (PCM) was performed to determine the relationships between soil physico–chemical parameters and heavy metals as shown in Table 8. The silt and clay fractions of the soils showed moderate but negative correlations with Pb and weak positive correlations with the metals Ni, Co and Fe, while for Zn, the soil fractions were moderately positively correlated. Clay particles usually have affinity for metal cations due to the negative charges and are thought to adsorb metal ions through both ion exchange and specific adsorption (Rieuwerts et al., 1998; Bradl, 2004). Soil pH showed a moderate positive correlation with Pb; however, metals such as Ni, Cu, Co and Fe were all showed weak negative correlations with the pH. This is in contrast with most studies which established that the adsorption and mobility of cationic metals increased linearly with pH (Harter, 1983; McLean and Bledsoe, 1992; Barrow and Whelan, 1998); however, it has been reported that the retention of the metals did not significantly increase until the pH was greater than 7 (Harter, 1983). As for soil EC and WHC, we observed that both variables presented a moderately positive correlation with Ni, Cu and Co, while for Pb, the correlation was inverse. Similarly, SOM and CEC presented a moderately positive correlation with Zn, Ni, Cu, Co and Fe while inversely correlated with Pb and Cd. Amongst heavy metals, a particularly strong positive correlation was observed between Co, Fe and Ni. In addition, Fe was inversely correlated with Pb but positively correlated with Zn, and Cr. With regards to Mn, Pb, and Cd, these metals did not particularly show meaningful correlations with other metals in the study.

A principal component analysis (PCA) was used to deduce the sources and major contributors to metal pollution in the soils and sediments around the Vatukoula mine. Based on the PCA analysis, three significant principal components (PCs) (eigenvalues ≥ 1) were identified, accounting for approximately 77.52% of the total percent variability as shown in Table 9 and Fig. 7. This strongly indicates that several controlling factors or sources were responsible for the heavy metal concentrations in the soil and sediments around the VGML. PC1 accounted for 41.26% of the total variance and was explained by the high loading for Co (0.489) and Ni (0.492), which was consistent with the high correlation among these metals (r = 0.888). Moreover, Cu, Zn and Fe were also added into PC1 considering their close correlations with Co and Ni. Based on the low concentrations of these metals observed in this study, it is inferred that PC1 components are likely derived from natural sources. The metal relationships obtained from the PCA is corroborated by the correlation results (Table 8) in which Zn, Ni, Co and Fe presented moderate to strong positive correlations thus, indicating their common geogenic/natural sources. PC2 accounted for 20.05% of the total variance associated with Pb, Cd and Cr. Considering the fact that Pb has been associated with mining activities (Ogola et al., 2002; Rabiu et al., 2019), this suggests that metals associated with this component are likely sourced from the nearby mine. PC3, which comprised 15.86% of the contribution, had loadings of Cu (0.478), Mn (0.546), Fe (–0.461) and Cr (–0.355).

4.0. Conclusion

The present study was designed to explore the heavy metal concentrations in farm soils from Matanagata village and river sediments from the Nasivi River system owing to their proximity to the Vatukoula Gold Mine in Fiji. From the present observation, it has been established that heavy metals particularly, Pb, Cr, Cu and Cd had concentrations which were above international guidelines and also exceeded background values for Fiji. Pollution assessment, conducted with single and multi–element indices including geoaccumulation index and contamination degree, revealed moderate enrichment and possible contamination of the studied sites. Although metal concentrations in soils revealed moderate contamination, river sediments showed moderate, and in some cases, heavy contamination. The current results suggest that there is moderate enrichment of heavy metals particularly Pb, Cr, Ni and Cu from the VGML and the tailing dams. Ecological risk assessment revealed that Cd concentration presented considerable and moderate risks in the farm soils and river sediments, respectively, due to its high toxicity and potential for bioaccumulation. Furthermore, health risk assessment showed that adults were not in danger of carcinogenic and non–carcinogenic health risks from exposure to the metal contaminated soil (HI < 1). However, children were found to be at risk for adverse health risks from Co (2.19E + 00), Mn (2.19E + 00), Cr (1.42E + 00) and Fe (1.17E + 00), and potential carcinogenic risk from Cd (ILCR = 1.46E–04). While the current study is preliminary, robust studies are recommended to evaluate the bioaccumulation of heavy metals particularly in food crops and river species in the area to explore the risks from consumption. Additionally, continuous monitoring of metal concentrations, particularly Pb, Cu, Cd, and Cr is necessary to explore seasonal and long–term variations in metal concentrations and sediment fluxes.

Declarations

Competing Interests

The authors have no relevant financial or non-financial interests to disclose

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Data availability

The datasets generated during and/or analyzed during the current study are available from the corresponding author on reasonable request.

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Tables

Table 1
Classifications for geochemical indices; CD, PLI, Igeo, EF, ER and PERI.

CD	Classification	PLI	Classification	Igeo	classification	EF	Classification	ERI	Classification	PERI	Classification
8	Moderate contamination	4	Moderately polluted	Igeo < 0	Unpolluted	EF < 0	Deficiency to minimal enrichment	ER < 40	Low risk	PERI < 50	Low risk
16	High contamination	6	Significantly polluted	0 ≤ Igeo < 1	Unpolluted to moderately polluted	2 ≤ EF < 5	Moderate enrichment	40 ≤ ER < 80	Moderate risk	50 ≤ PERI < 200	Moderate risk
32	Very high contamination	8	Strongly polluted	1 ≤ Igeo < 2	Moderately polluted	5 ≤ EF < 20	Significant enrichment	80 ≤ ER < 160	Considerable risk	200 ≤ PERI < 300	Considerable risk
		10	Extremely polluted	2 ≤ Igeo < 3	Moderately to heavily polluted	20 ≤ EF < 40	Very high enrichment	160 ≤ ER < 320	High risk	PERI > 300	High risk
				3 ≤ Igeo ≤ 4	Heavily polluted	EF > 40	Extremely high enrichment	ER > 320	Very high risk		
				4 ≤ Igeo < 5	Heavily to extremely polluted						
				Igeo > 6	Extremely polluted						

Table 2
Statistical summary of major soil physico–chemical parameters

Parameters	Farm soils (n = 20)					River sediments (n = 9)				
	Min	Max	Mean	Median	Std	Min	Max	Mean	Median	Std
pH	6.46	7.88	6.85	6.83	0.28	6.99	7.98	7.47	7.44	0.33
EC (µS cm^{-1})	280.00	857.50	518.00	506.75	152.07	107.85	574.00	238.63	234.50	140.52
WHC (mL L^{-1})	6.40	18.98	10.60	2.93	10.52	6.00	8.32	6.95	0.88	6.48
TOM (%)	1.19	10.37	5.23	5.08	2.39	0.80	1.98	1.43	1.49	0.46
TOC (%)	0.69	6.01	3.03	2.95	1.38	0.46	1.15	0.83	0.87	0.26
PD (g cm^{-3})	1.77	3.70	2.42	2.32	0.47	2.57	2.97	2.74	2.70	0.17
Na (mg kg^{-1})	504	1,176	843	840	165	721	1,635	1,174	1,119	276
Mg (mg kg^{-1})	5,035	11,235	8,118	8,189	1,839	1,267	9,168	5,971	6,332	2,338
K (mg kg^{-1})	1,350	2,184	1,603	1,542	225	972	1,959	1,383	1,295	339
Ca (mg kg^{-1})	8,062	30,643	11,009	10,031	4,726	5,989	11,456	9,072	9,541	1,946

EC– Electrical conductivity; PD– particle density; TOC– Total organic carbon; TOM– Total organic matter; WHC– water holding capacity;

Table 3
Statistical summary of heavy metal concentrations in farm soils and river sediments from Vatukoula.

Metal	Min	Max	Mean	Median	Std	SEM	Kurtosis	Skewness	CI (95%)	
									LB	UB
	Farm Soils (mg kg^{-1}, n = 20)									
Pb	25.95	63.64	45.41	47.02	11.19	2.50	−0.95	−0.33	40.17	50.65
Zn	64.02	116.85	80.03	78.40	11.44	2.56	4.91	1.67	74.68	85.38
Cd	1.29	1.97	1.74	1.77	0.18	0.04	1.96	−1.38	1.66	1.83
Ni	47.18	63.49	57.15	57.77	4.69	1.05	−0.43	−0.68	54.95	59.35
Cu	91.08	131.24	110.37	109.29	13.12	2.93	−1.39	0.09	104.23	116.51
Cr	100.37	180.90	136.21	137.03	22.78	5.09	−0.80	0.06	125.55	146.87
Mn	442.05	544.94	503.83	508.19	24.70	5.52	1.19	−0.95	492.27	515.39
Co	29.90	38.41	35.36	36.43	2.62	0.59	−0.62	−0.71	34.14	36.59
Fe (%)	4.27	5.85	5.11	5.06	0.46	0.10	−0.74	0.04	4.89	5.32
	River Sediments (mg kg^{-1}, n = 9)									
Pb	59.25	77.57	69.31	68.59	6.65	2.22	−1.54	−0.09	64.20	74.43
Zn	53.85	80.68	69.82	73.57	9.53	3.18	−0.97	−0.74	62.49	77.14
Cd	1.57	2.09	1.82	1.82	0.15	0.05	0.59	0.26	1.70	1.93
Ni	40.37	62.62	49.67	49.51	6.78	2.26	0.84	0.43	44.46	54.88
Cu	59.08	123.15	88.95	87.62	20.36	6.79	−0.70	0.19	73.30	104.61
Cr	91.20	205.87	143.12	135.97	34.34	11.45	0.17	0.45	116.72	169.52
Mn	416.02	643.49	506.75	501.35	73.26	24.42	−0.11	0.74	450.43	563.06
Co	24.49	42.73	32.71	32.76	5.68	1.89	0.13	0.09	28.34	37.08
Fe (%)	3.84	5.58	4.72	4.77	0.63	0.21	−1.13	0.07	4.24	5.21

All metal data are expressed in mg kg^{-1} except Fe, which is expressed in %.

CI– Confidence interval

Std– Standard deviation

SEM– Standard error of the mean

Table 4
Metal concentrations from Vatukoula compared with established soil and sediment quality guidelines

Metals	Soil values (mg kg^{-1})					Sediment values (mg kg^{-1})			
	This study	WHO MPC[a]	CASQC[b]	Dutch Target Value[c]	Background concentration[d]	This study	CFSQC[b]	ANZEC DGV[e]	Background concentration[f]
Pb	45.41	100	70	85	27	69.31	35	50	7.3
Zn	80.03	200	250	140	70	69.82	123	200	29.5
Cd	1.74	3	1.4	0.8	0.41	1.82	0.6	1.5	0.96
Ni	57.15	75	45	35	29	49.67	–	21	8.7
Cu	110.37	100	63	36	38.9	88.95	35.7	65	29.6
Cr	136.21	100	64	100	59	143.12	37.3	80	20
Mn	503.83	1500	–	–	488	506.75	–	1500	207.2
Co	35.36	30	40	–	30	32.71	–	50	8.64
Fe (%)	5.11	–	–	–	2.7	4.72	–	–	–

[a]WHO Maximum Permissible Concentration.

[b]Canadian Environmental Quality Guidelines (CEQG).

[c]Dutch Soil Quality Criteria (Denneman and Robberse, 1990).

[d]Global background soil heavy metal concentrations (Kabata–Pendias, 2010).

[e]Australian and New Zealand sediment default guideline values.

[f]sediment heavy metal concentrations reported for the Great Astrolabe reef, Fiji (Morrison et al., 1997).

Table 5
Metal concentrations in soils and sediments compared with values from other parts of Fiji and mining areas around the world.

Location	Soil metal concentrations (mg kg^{-1})									Reference
	Pb	Zn	Cd	Ni	Cu	Cr	Mn	Co	Fe (%)	
Vatukoula, Fiji	25.95–63.94	64.02–116.85	1.29–1.97	47.18–63.49	91.08–131.24	100.37–180.90	442.05–544.94	29.90–38.41	4.27–5.85	This study
Suva, Fiji	59.3	507	3.1	32.4	265.7	34.0	–	33.2	3.95	(Maeaba et al., 2019)
Torul, Turkey	27.38–33.16	42.04–55.50	1.23–1.45	41.50–72.00	31.71–41.84	47.80–65.25	–	–	–	(Sungur et al., 2020)
Central Spis, Slovakia	30.1–503.5	148.9–1697.8	1.12–7.4	17.9–342.3	17.3–1273.7	22.2–331.9	–	8.55–30.2	–	(Demková et al., 2017)
Co Dinh Mine, Vietnam	Nd–1.08	–	–	0.06–32.3	0.01–0.58	0.06–13.2	–	Nd–3.06	–	(Kien et al., 2010)
Iludun–Oro, Nigeria	0–687	7–222	–	1.6–93.1	8.8–145	1.4–81	0.01–0.11	–	1.64–8.87	(Oyebamiji et al., 2018)
	Sediment metal concentrations (mg kg^{-1})									
Nasivi River, Fiji	59.25–77.57	53.08–80.68	1.57–2.09	40.37–62.62	59.08–123.15	91.20–205.87	416.02–643.49	24.49–42.73	3.48–5.58	This study
Suva Harbor, Fiji	22–93.5	40.2–269	–	–	21.4–143.0	–	–	–	1.40–4.87	(Maata and Singh, 2008)
Raohe Basin, China	39.63	32.31	0.51	31.03	197.21	35.26	–	–	–	(Wei et al., 2019)
Molonglo River, Australia	23–1796	697–6818	0.13–8.7	–	10–628	–	–	–	–	(Marasinghe Wadige et al., 2016)
Jequetepeque River Basin, Peru	62.6	241.6	7.4	10.3	91.7	5.2	1841	–	1.58%	(Yacoub et al., 2012)
Ipojuca River, Brazil	36.27	63.27	0.16	3.01	4.42	9.10	–	–	0.11%	(Silva et al., 2019)

Table 6
Chronic daily intake (CDI), hazard quotient (HQ) and cumulative hazard index (HI) for non–carcinogenic risk.

Metals	Adults							Children						
	CDI_{ing}	CDI_{inh}	CDI_{derm}	HQ_{ing}	HQ_{inh}	HQ_{derm}	HI	CDI_{ing}	CDI_{inh}	CDI_{derm}	HQ_{ing}	HQ_{inh}	HQ_{derm}	HI
Pb	7.24E−05	1.06E−08	2.89E−06	2.07E−02	3.02E−06	5.50E−03	2.62E−02	6.75E−04	2.48E−08	1.89E−05	1.93E−01	7.05E−06	3.60E−02	2.29E−01
Zn	1.05E−04	1.55E−08	4.20E−06	3.51E−04	5.16E−08	7.00E−05	4.21E−04	9.83E−04	3.61E−08	2.75E−05	3.28E−03	1.20E−07	4.59E−04	3.73E−03
Cd	2.42E−06	3.56E−10	9.65E−08	2.42E−03	3.56E−05	9.65E−03	1.21E−02	2.26E−05	8.30E−10	6.32E−07	2.26E−02	8.30E−05	6.32E−02	8.58E−02
Ni	7.51E−05	1.10E−08	3.00E−06	3.76E−03	5.36E−07	5.55E−04	4.31E−03	7.01E−04	2.58E−08	1.96E−05	3.51E−02	1.25E−06	3.63E−03	3.87E−02
Cu	1.42E−04	2.09E−08	5.67E−06	3.83E−03	5.20E−06	4.72E−04	4.31E−03	1.33E−03	4.88E−08	3.71E−05	3.57E−02	1.21E−05	3.09E−03	3.89E−02
Cr	1.90E−04	2.79E−08	7.56E−06	6.32E−02	9.75E−04	1.26E−01	1.90E−01	1.77E−03	6.50E−08	4.95E−05	5.90E−01	2.27E−03	8.26E−01	1.42E + 00
Mn	6.91E−04	1.02E−07	2.76E−05	1.98E−01	2.03E−03	5.25E−02	2.52E−01	6.45E−03	2.37E−07	1.81E−04	1.84E + 00	4.75E−03	3.44E−01	2.19E + 00
Co	4.73E−05	6.96E−09	1.89E−06	2.37E−03	1.22E−03	3.31E−01	3.35E−01	4.42E−04	1.62E−08	1.24E−05	2.21E−02	2.85E−03	2.17E + 00	2.19E + 00
Fe	6.83E−02	1.00E−05	2.73E−03	9.76E−02	1.44E−05	3.90E−02	1.37E−01	6.38E−01	2.34E−05	1.79E−02	9.11E−01	3.35E−05	2.55E−01	1.17E + 00

Table 7
Carcinogenic risk for different exposure pathways for adults and children.

Metals	Adults				Children			
	CR_{ing}	CR_{inh}	CR_{derm}	ILCR	CR_{ing}	CR_{inh}	CR_{derm}	ILCR
Pb	6.15E−07	9.05E−11	2.45E−08	6.40E−07	5.74E−06	2.11E−10	1.61E−07	5.90E−06
Cd	1.52E−05	2.24E−09	6.08E−07	1.58E−05	1.42E−04	5.23E−09	3.98E−06	1.46E−04
Cr	9.48E−05	1.39E−08	3.78E−06	9.86E−05	8.84E−04	3.25E−08	2.48E−05	9.09E−04
Ni	6.83E−05	1.01E−08	2.73E−06	7.11E−05	6.38E−04	2.35E−08	1.79E−05	6.56E−04

Table 8
Pearson correlation matrix showing the relationships between soil parameters and heavy metal concentration

	%sand	%silt	%clay	pH	EC	WHC %	SOM	PD	CEC	Pb	Zn	Cd	Ni	Cu	Cr
%sand	1														
%silt	−.97**	1													
%clay	−.47*	.35	1												
pH	.38	−.10	−.41*	1											
EC	−.54**	.39*	.56**	−.635**	1										
WHC %	−.56**	.57**	.60**	−.584**	.866**	1									
SOM	−.62**	.55**	.67**	−.664**	.828**	.928**	1								
PD	.35	−.30	−.62**	.347	−.467*	−.552**	−.557**	1							
CEC	−.61**	.51**	.93**	−.543**	.737**	.817**	.893**	−.659**	1						
Pb	.39	−.39*	−.46*	.690**	−.583**	−.713**	−.729**	.473*	−.625**	1					
Zn	−.49*	.61**	.51**	−.063	.331	.522**	.445*	−.454*	.553**	−.311	1				
Cd	.15	−.19	−.32	.235	−.163	−.295	−.545**	.259	−.455*	.385*	−.030	1			
Ni	−.34	.39*	.48**	−.413*	.558**	.521**	.477*	−.566**	.534**	−.301	.640**	.202	1		
Cu	−.39	.08	.40*	−.435*	.593**	.364	.447*	−.415*	.466*	−.216	.317	.128	.656**	1	
Cr	.17	.15	−.05	.180	−.159	−.064	−.150	.061	−.098	.340	.220	.326	.407*	−.161	1
Mn	−.03	.07	.21	.002	.208	.174	.230	−.400*	.253	.110	.353	−.096	.280	.315	−.14
Co	−.32	.33	.39*	−.336	.499**	.497**	.411*	−.486*	.445*	−.140	.571**	.246	.888**	.591**	.490
Fe	−.33	.44*	.45*	−.436*	.461*	.637**	.533**	−.491**	.525**	−.51**	.500**	−.130	.616**	.121	.449

Table 9
Principal component analysis for selected heavy metals in farm soils and river sediments from Vatukoula, Fiji.

Components	Initial eigenvalues			Heavy metals	Component matrix				
	Total	Variability (%)	Cumulative %		PC1	PC2	PC3	PC4	PC5
PC1	3.713	41.261	41.261	Pb	−0.178	0.569	0.291	0.322	−0.206
PC2	1.804	20.046	61.307	Zn	0.388	−0.120	0.002	0.289	0.719
PC3	1.427	15.856	77.163	Cd	0.071	0.551	0.212	−0.426	0.482
PC4	0.943	10.477	87.640	Ni	0.492	0.042	0.065	−0.131	−0.059
PC5	0.505	5.610	93.250	Cu	0.314	−0.139	0.478	−0.429	−0.297
PC6	0.368	4.089	97.339	Cr	0.217	0.542	−0.355	0.224	−0.160
PC7	0.156	1.728	99.067	Mn	0.174	−0.127	0.546	0.609	−0.045
PC8	0.058	0.643	99.711	Co	0.489	0.142	0.035	−0.033	−0.243
PC9	0.026	0.289	100.000	Fe	0.393	−0.084	−0.461	0.092	−0.170
				Eigenvalue	3.713	1.804	1.427	0.943	0.505
				Variability (%)	41.26	20.05	15.86	10.48	5.61
				Cumulative %	41.26	61.31	77.16	87.64	93.25

Figures

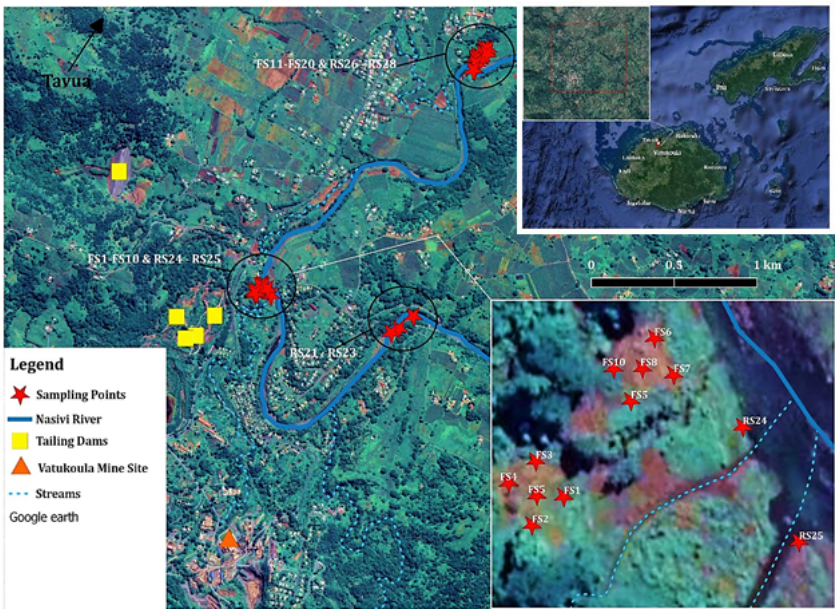

Figure 1

A map of Fiji (inset) showing the study area and the sampling points.

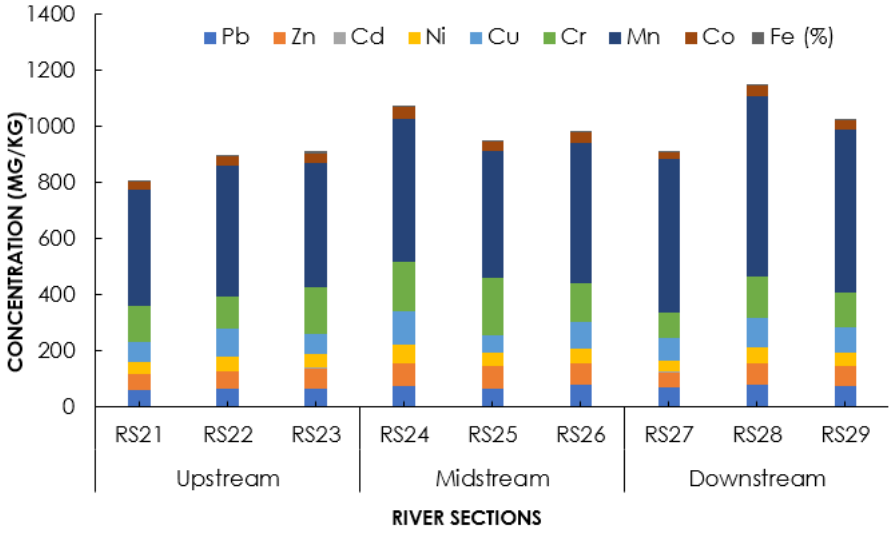

Figure 2

Sediment heavy metal concentrations at different sections of the Nasivi river. The midstream sediments were located in close proximity to the mine tailing dams.

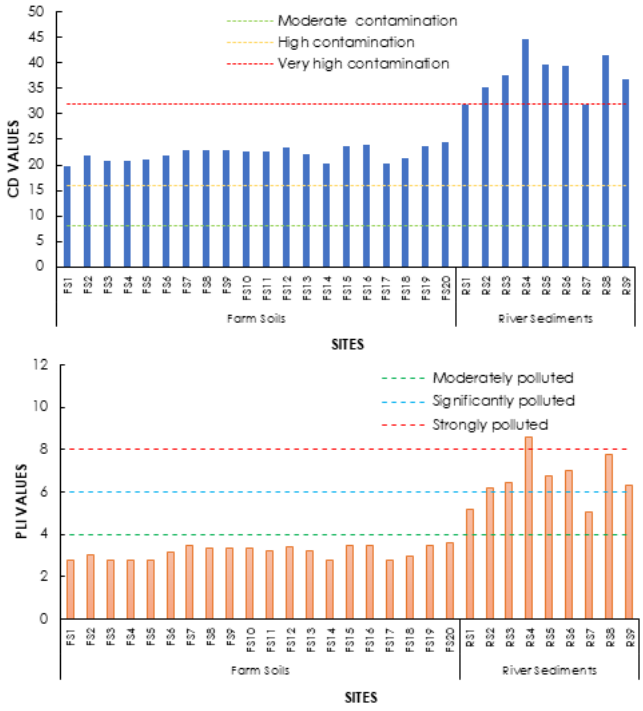

Figure 3

Contamination degree (CD) and pollution load index (PLI) values for heavy metals at Vatukoula.

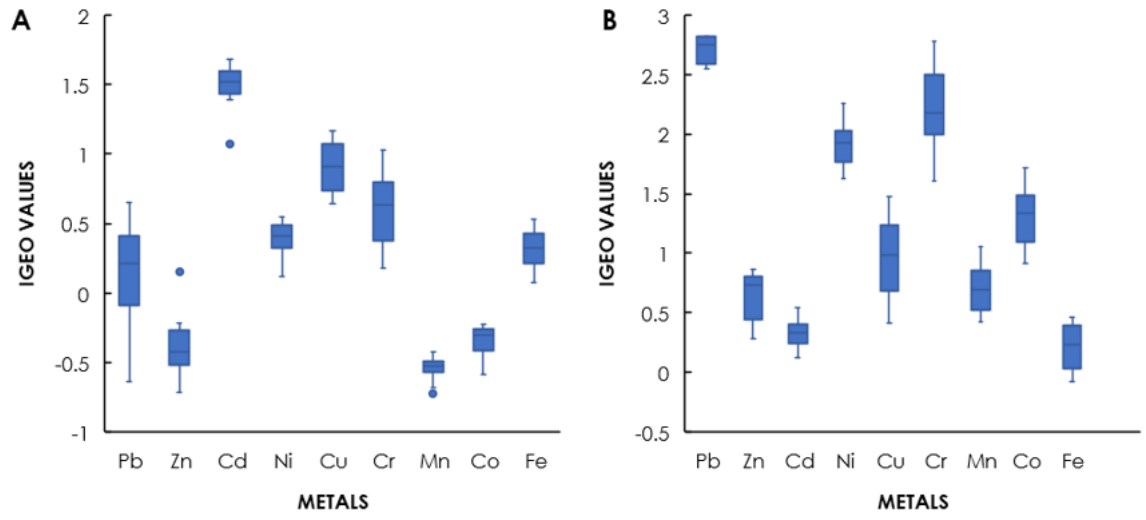

Figure 4

Geoaccumulation index (I_{geo}) values for heavy metals in (A) Farm soils and (B) River sediments.

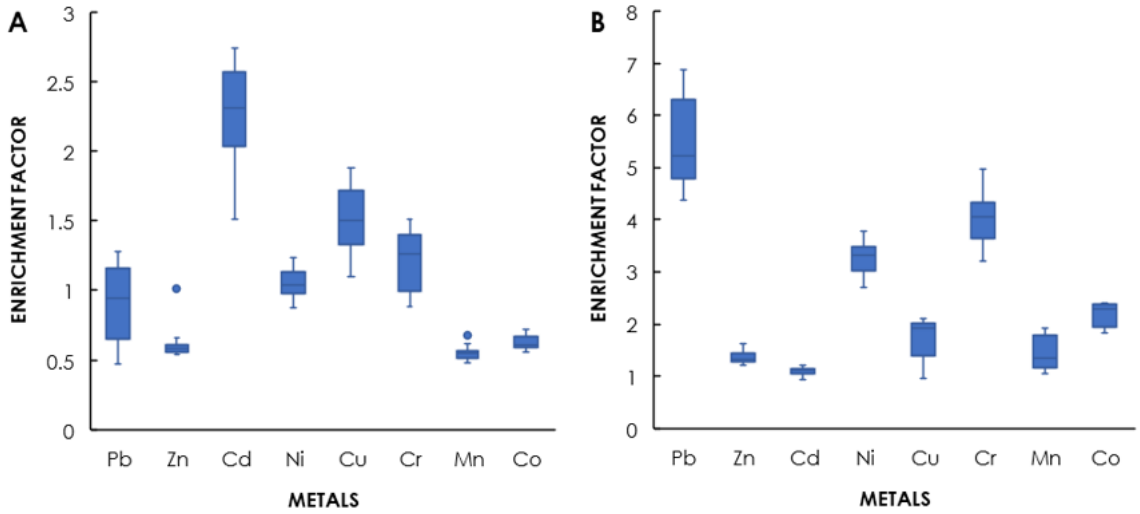

Figure 5

Enrichment Factor (EF) values for heavy metals in (A) Farm soils and (B) River sediments.

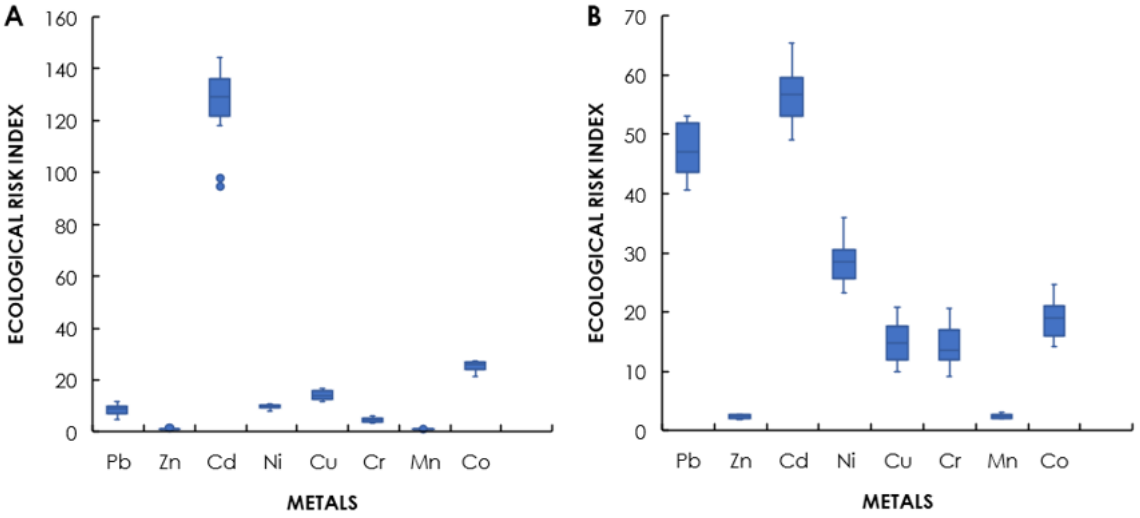

Figure 6

Ecological risk index (ERI) values for heavy metals in (A) Farm soils and (B) River sediments.

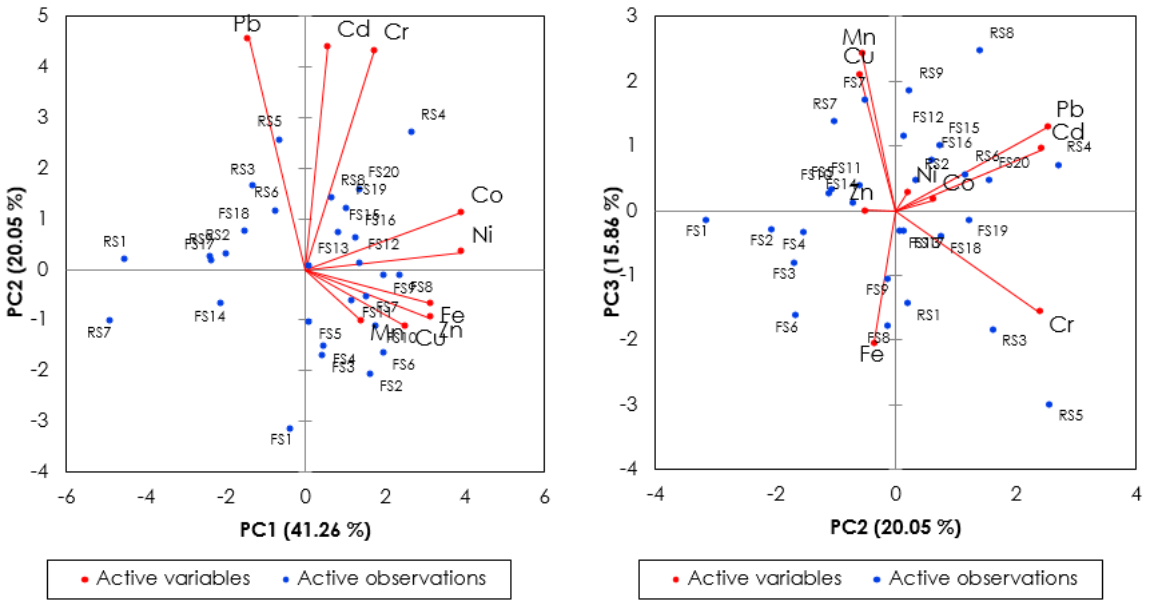

Figure 7

Biplots for the principal component analysis showing the sources of variation and partitioning for heavy metals in the soils and sediments from Vatukoula. Red lines represent environmental parameters, and blue dots represents sampling points.

Supplementary Files

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