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Rapid site assessment in a small island of the Philippines contaminated with mine tailings using ground and areal technique: The environmental quality after twenty years

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Abstract. This paper illustrates the impacts of mining disaster after more than 20 years. A two – day rapid assessment was carried out at Mogpog and Boac River catchment in Marinduque Island in March 2019. The target site included Maguilaguila Pit that connects the river catchment and formerly used as mining wastes pit. This is to understand the impacts of 1993 and 1996 mining disasters in the Boac-Mogpog river basin at Marinduque, Philippines. The island of Marinduque has been considered as among the top ten most vulnerable islands in the country due to its environmental condition and geographical location which affected the island demography. The island has suffered the impacts of one of the country's biggest mining disasters. The instruments used to conduct rapid site assessment were SciAps X-300 Handheld X-ray Fluorescence (XRF), Unmanned Air Vehicle (UAV) Model DJI Mavic Air, Google Earth, Hannah Multiparameter HI 9811-5 with HI 1285-5 probe and HI 70007, 70031, 70032 and 700661 solutions. The DJI Mavic Air captured images of Mogpog and Boac River catchment which helped direct the research team to take the right sampling locations. The DJI Mavic Air captured site images of the two rivers as dead rivers and use as land transportation route during dry season. The Google Earth captured the historical images of the target areas. The recorded data showed that the pit and nearby river water is acidic with pH equivalent to 2.9 and 4.1, respectively. The range of concentration of total dissolved solids in Mogpog and Boac river water was 100 – 1360 and 160 – 1150 ppm, respectively. The recorded concentration of iron near the pit was 125,587 ppm, and chromium concentration range was 80 – 99 ppm. The concentration of copper and manganese in the sediments was 5 and 158 times higher (respectively) than the 1998 detected concentrations. Based on the recorded data and images, the Maguilaguila pit, Boac and Mogpog River catchment need immediate attention. It



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could be concluded that based on the recent assessment results, leaks at the pit are likely. Also, the combination of areal-aerial and ground technique produced two – day rapid site assessment for areas contaminated by mine tailings. The information could aid in preparing prompt action and setting strategies that are helpful in carrying out risk reduction programs in the island.

1. Introduction

Marinduque Island is a small island province in the southern part of Luzon in the Philippines. This country has vast mineral resources. The Mines and Geosciences Bureau (MGB) reported in 2017 that the overall projected production for metallic minerals in the country was PhP109.45 billion. Marinduque was known to possess one of the biggest copper stocks in the Philippines. Mining processes extricating copper commenced in Marinduque during the period of 1969 - 1996 [1]. An earth dam was constructed in the mountainous headwaters of the Mogpog River in 1991. The dam was made-up to hold silt, from a waste dump for the new San Antonio Mine Pit, out of the Mogpog River. The dam was ruptured in 1993, flooding downstream villages. The town of Mogpog was seriously damaged, causing significant losses to structural properties, agriculture and public health. The 23 km Mogpog River was severely affected by the toxic waste from the dam [2]. Three years later, in 1996, one of the world's mining disaster happened, Tapan Pit ruptured and tailings were seen in adjacent area contaminating the 27 km Boac River of Marinduque island. Five villages had to be displaced and about 20,000 people were evacuated [3]. The volume of tailings that went out into the marine environment was estimated to be 180,000 to 260,000 cubic meters [4]. Most of the tailings material has stored in the proximate – shore environment near the western coast of the island. Nineteen sediments cores recorded high concentrations of Cu (706 – 3,080 ppm) and Mn (445 – 1,060 ppm) [4]. Sediments with heavy metals can move beyond 20 km from their origins, distressing water ecosystems. Two mine pits (San Antonio and Tapan) filled with water and two rivers with very limited water were observed in March 2019. Hence, this rapid assessment was conducted to understand the impacts of 1993 and 1996 mining disasters in the Boac-Mogpog river basin after more than 20 years. Integration of in-situ detection, aerial spotting, areal-data mapping and deterministic modeling technique was considered useful in rapid assessment.

2. Materials and methods

Below describes the study area and the integrated techniques employed during data collection and data analysis.

2.1 Description of study area and sampling points

The focus area of the study in March 2019 was the Boac-Mogpog river basin in Marinduque, Philippines (figure 1a). Boac River is within a watershed area of 214 km² while Mogpog River is in a watershed area of 58 km². Eight selected sites (figure 1b) were identified in the municipalities of Mogpog and Boac. These eight sites were: (a) Brgy. Hinapulan, (b) Puting Buhangin, (c) Former Marcopper Pit, San Antonio (d) Bocboc, (e) Butansapa, (f) Bantay, (g) Balimbing, and (h) Tabi. Thirty two (32), twenty one (21), and thirteen (13) sediment, surface and groundwater sampling locations (figure 2) respectively were chosen within the identified eight sites.

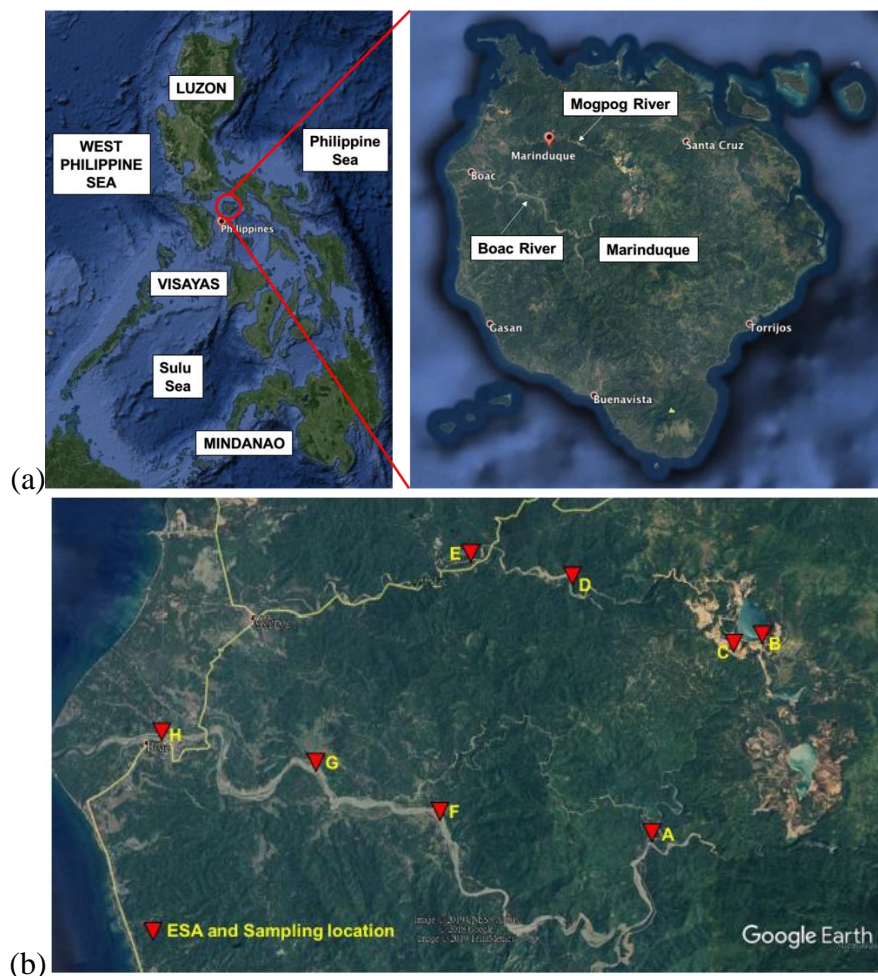


Figure 1. Targeted 8 sites for 32 sampling locations.

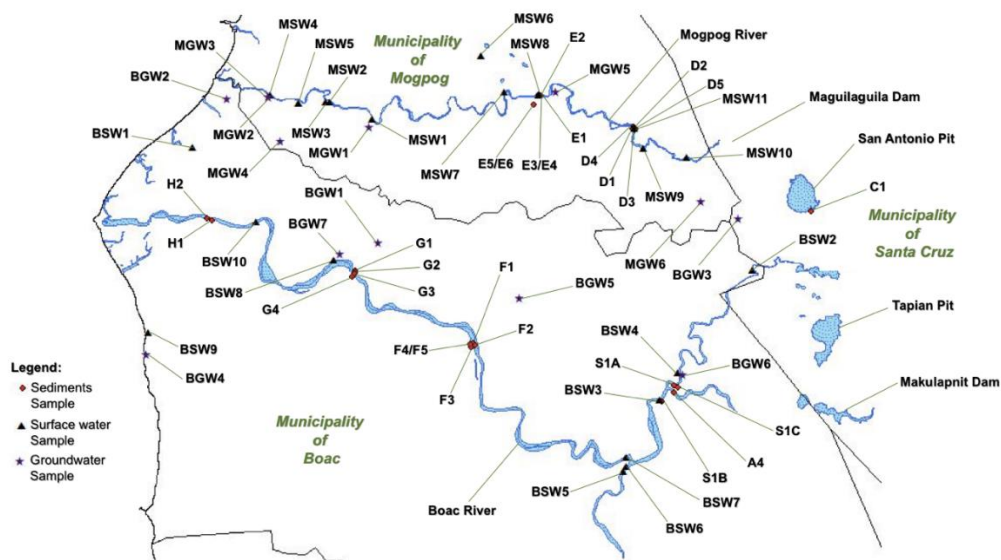


Figure 2. Sampling locations of the sediments, surface water and groundwater in the Mogpog and Boac River.

2.2 Data assessment: areal-aerial technique and in-situ detection

Determination of sampling locations was aided by Unmanned Air Vehicle (UAV) Model DJI Mavic Air. Historical images were extracted using Google Earth. The 32 sediment samples were analysed in-situ for heavy metal concentration using the SciAps X-300 Handheld X-ray Fluorescence (XRF). Numerical Sediment Quality Guidelines (SQG) were used to evaluate the metal concentrations of the sediment samples. The metal concentrations were checked with TEC/PEC (Threshold Effect Concentration/Probable Effect Concentration) standards [5,6]. Lower metals concentration in sediments compared with TEC, will mean detrimental effects are unlikely to occur. On the contrary, if the metals exceeded the PEC, adverse effects are expected to be observed [7]. The 34 surface and groundwater samples were analysed by its physical and chemical parameters such as temperature ($T=^{\circ}\text{C}$), pH, total dissolved solids ($\text{TDS}=\text{mg L}^{-1}$), and electrical conductivity ($\text{EC} = \mu\text{S/cm}$) using Hannah Multi – parameter HI 9811-5 portable meter with HI 1285-5 probe and HI 70007, 70031, 70032 and 700661 solutions.

2.3 Data mapping and analysis

The ArcGIS Spatial Analyst extension, included in ArcMap 10.0, was used in mapping the concentration of metals in the sediments and the physic-chemical parameters of the surface water. It offers a toolset for assessing and exhibiting spatial data. In order to create a surface grid in ArcGIS, the spatial analyst extension employs several interpolation techniques centered on the principle of spatial autocorrelation. It identifies the degree of relationship concerning near and distant objects. Under the ArcGIS Spatial Analyst extension tool are the distinct interpolation techniques that employed to implement spatial analysis.

2.4 Spatial distribution of physico-chemical parameters of water

The Inverse Distance Weighting (IDW) method, a deterministic spatial interpolation model, has been employed considering the utilization of geoscientists and geographers [8]. The IDW Method, employed in this study included the method of giving values to unidentified points by utilizing values from a dispersed set of identified points. The value at the unknown point is a weighted sum of the values of “N” known points as shown in Eq. (1) [9].

$$C_p = \sum_{i=1}^N w_i C_i \quad (1)$$

$$w_i = \frac{\frac{1}{d_i}}{\sum_{i=1}^N \frac{1}{d_i}} \quad (2)$$

where C_p denotes the unknown concentration data; C_i signifies the known rainfall data; N is the quantity of sampling stations; w_i is the weighting of individual stations, d_i is the distance from every stations to the unknown point.

3. Results and discussion

3.1 Physical environment analysis

Below images demonstrates the historical areal-aerial images of Mogpog (figure 3) and Boac River (figure 4), the San Antonio photographs (figure 5) and current state of Mogpog and Boac River (figure 6). Figures 3 and 4 were captured by Google Earth 2019, while figure 5 was captured by the UAV Mavic Air. The historical images helped in the comparative analysis of the areal conditions of the Mogpog-Boac River Basin right after the disaster until the present condition. The UAV aided the team to determine potential sampling locations and choose appropriate routes. Further, it provides

researchers the scenario necessary to figure out and promptly assess the environmental condition. It helped the researchers in making prompt decision on which direction to proceed.

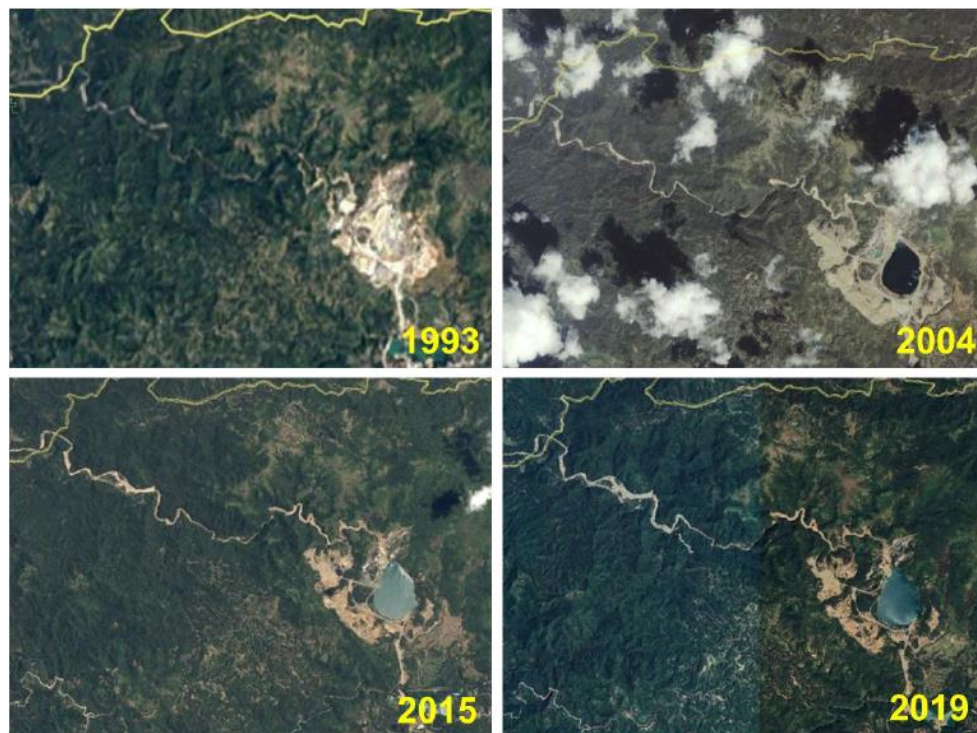


Figure 3. Historical aerial photos of Mogpog River Basin [10].



Figure 4. Historical aerial photos of Boac River Basin [10].



Figure 5. Aerial photograph captured by the UAV in Brgy. San Antonio.



Figure 6. Aerial photograph taken by the UAV – Mogpog and Boac River.

3.2 Ground sampling, detection and analysis of metals

Results of the sediments collection, metal concentration detection and analysis using handheld XRF in Boac and Mogpog River are summarized in table 1. The recorded metals of concern were chromium (Cr), manganese (Mn), iron (Fe), lead (Pb), cadmium (Cd), zinc (Zn), nickel (Ni) and copper (Cu). All metals shown a significant positive skew distribution and skew up to 5.25. The highest average concentrations were Fe, Mn and Cu with 65,652.41, 1,381.16 and 1,020.48 ppm, respectively.

Table 1. Heavy metal concentration (in ppm) in sediments of Boac and Mogpog River.

Parameter	Cr	Mn	Fe	Pb	Cd	Zn	Ni	Cu
Minimum	0.00	18.80	11.00	1.00	3.70	2.00	13.10	4.70
Maximum	323.00	10,006.20	192,443.20	53.60	7.50	995.00	42.30	15,396.5

Mean	99.48	1,381.16	65,652.41	8.81	4.47	126.42	18.83	1,020.48
Median	73.55	851.00	54,453.55	6.20	4.35	72.65	16.45	413.20
SD	89.76	1,889.75	35,176.64	9.10	0.64	185.61	5.95	2,689.73
Kurtosis	0.87	14.31	4.71	19.83	16.88	16.41	7.19	28.65
Skewness	1.30	3.47	1.71	4.11	3.62	3.85	2.41	5.25

Note: SD – Standard Deviation.

The recorded concentrations of the metals in sediments were compared with past recorded concentrations (table 2). It has been observed that the concentration of Cu and Mn in the sediments was 5 and 158 times higher, respectively, than the concentrations [4] detected in 1998. Dry season in a tropical country may have contributed to the increased concentration Mn and Cu. This is a similar result obtained by the work of Montalvo [11].

Table 2. Concentration comparison of some metals detected in 1998 and 2019 with limit reference guidelines.

Name of metal	Range of concentration, ppm		
	Limit reference guidelines [12]	Downstream in 1998 [4]	River stretch in 2019
Manganese (Mn)	300 – 600 (normal)	445 - 1060	18 – 68,169
Lead (Pb)	30 - 85	43 - 56	1 - 54
Zinc (Zn)	120 - 200	131 - 276	2 -260
Copper (Cu)	16 - 65	706 - 3080	4 – 15,400

Concentration of Fe was highest in the Mogpog and Boac River followed by Mn, Cu, Zn, Cr, Ni, Pb and Cd (Fe>Mn>Cu>Zn>Cr>Ni>Pb>Cd). Cadmium recorded the lowest concentration among heavy metals in all sampling stations. The mean of all heavy metals identified, excluding lead and nickel, surpassed the TEC limits. The Fe, Mn, and Cu exceeded the PEC limit, therefore, adverse effects are likely to occur. Table 3 shows the comparison of heavy metals concentration with the TEC and PEC.

Table 3. Comparison of heavy metals (ppm) in sediments of Mogpog and Boac River to TEC and PEC.

Parameter	Cr	Mn	Fe	Pb	Cd	Zn	Ni	Cu
Minimum	0.00	18.80	11.00	1.00	3.70	2.00	13.10	4.70
Maximum	323.00	10,006.20	192,443.20	53.60	7.50	995.00	42.30	15,396.5
Mean	99.48	1,381.16	65,652.41	8.81	4.47	126.42	18.83	1,020.48
TEC [5,6]	43.3	460	20,000	35.8	0.99	121	22.70	31.6
PEC [5,6]	111	1,100	40,000	128	4.98	459	48.60	149

3.3 Analysis of spatial distribution of heavy metal in sediment

The spatial distribution pattern of heavy metals and the physicochemical parameters in the sediments samples of Boac and Mogpog River been reflected on the contour map based on the concentration of each sampling location. Commonly, the metal concentrations display oscillations between different stations. The Brgy. San Antonio recorded (figure 7a) with the highest Fe concentration. Brgy. Hinapulan recorded high concentration on not only Fe but also Mn (figure 7b) and Cu (figure 7c). Brgy. Butansapa is also high in Mn, and Brgys

Mahinhin, Labo, Putting Buhangin, part of Bantay and Ogbac were likewise high in Cu concentration.

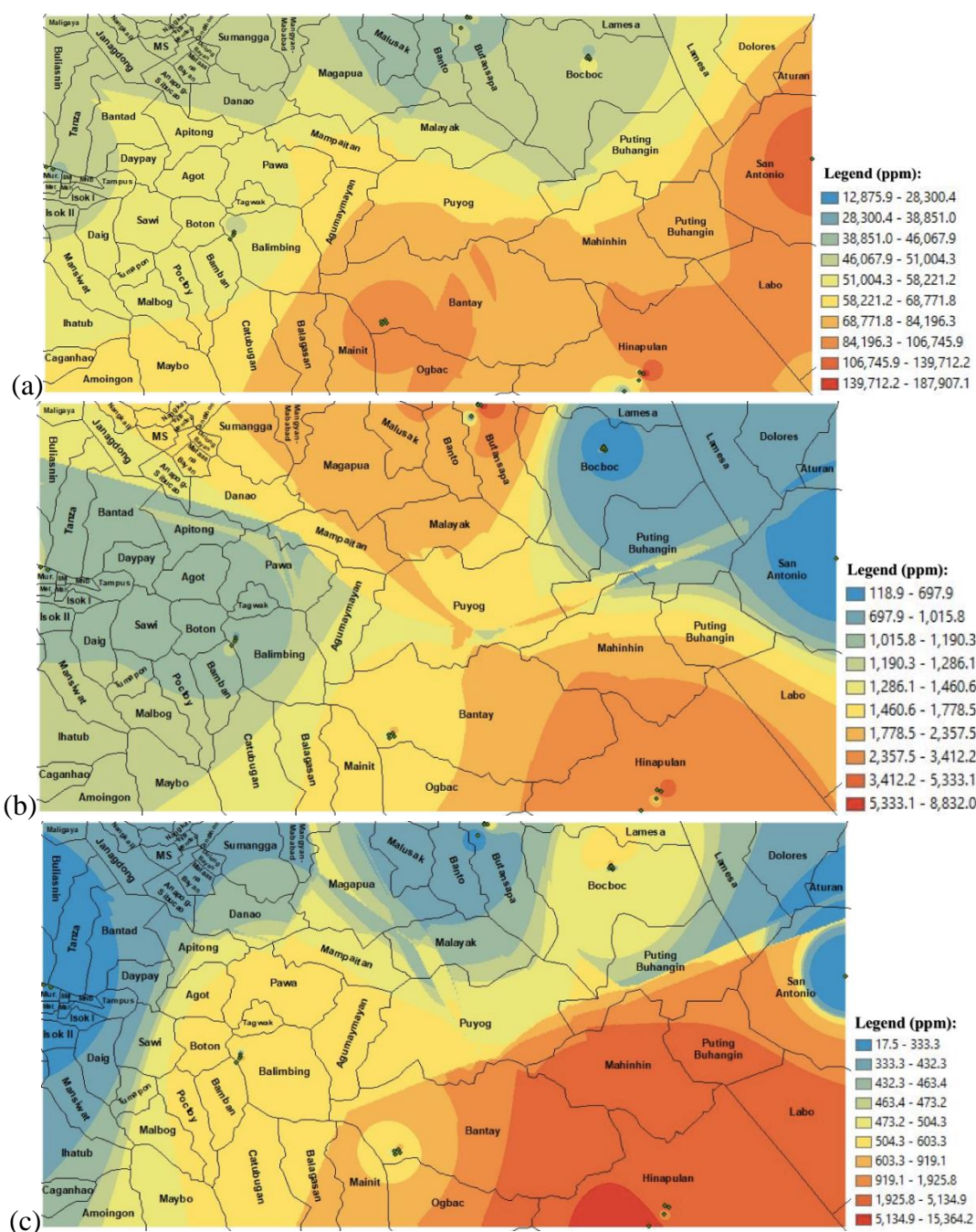


Figure 7. (a) Spatial distribution map of Fe concentration; (b) Spatial distribution map of Mn concentration; (c) Spatial distribution map of Cu concentration.

3.4 Surface and groundwater analysis

The physicochemical parameters recorded using Hanna Multi-parameter HI 9811-5 with HI 1285-5 probe and and HI 70007, 70031, 70032 and 700661 solutions were temperature (T), pH, electrical conductivity (EC), and total dissolved solids (TDS). The results for surface water quality is shown in table 4 as follows: the pH, TDS and EC show significant positive

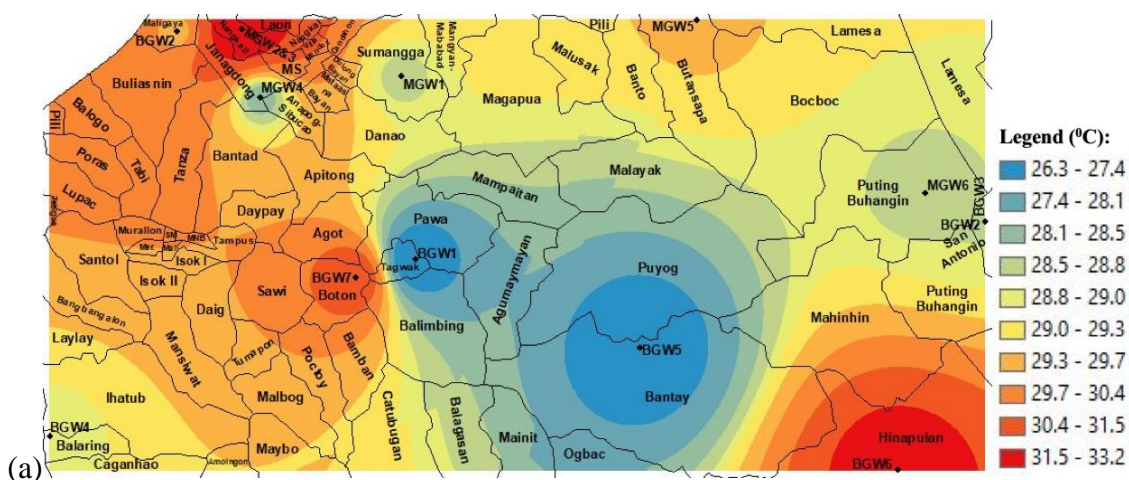
skew distribution and skew up to 7.36, 7.85 and 7.90, respectively. The average values of T, pH, EC and TDS were 31.21 °C, 7.14, 761.43 µS/cm and 371.52 mg/L, respectively. Among the physicochemical parameters considered, the EC and TDS have the widest distribution range. These values were 2,430 µS/cm for EC and 1,210 mg/L for the TDS and these values were associated with the concentrations of metals detected in the sediments.

Table 4. Physicochemical parameters of surface and groundwater in Boac and Mogpog, Marinduque.

Parameter	T (°C)	pH	EC (µS/cm)	TDS (mg/L)
Minimum	27.10	4.10	310.00	150.00
Maximum	34.60	8.30	2,740.00	1,360.00
Mean	31.21	7.14	761.43	371.52
Median	31.20	7.30	560.00	270.00
SD	1.77	0.86	555.51	277.86
Kurtosis	0.74	7.36	7.90	7.85
Skewness	-0.16	-2.20	2.62	2.61

The data collected in March 2019 were compared with the data collected by USGS (United States Geological Survey) in May 2000. It was observed that based on the work in the year 2000 [13], the results were as follows: pH range equals 3.08 – 8.3 and EC range was 800 – 1,610. The current pH range of the water did not have significant deviation. The pH of San Antonio pit water was 2.9. The water from this pit flow through Mogpog River. However, the EC range became wider; i.e., from 800 – 1610 to 310 - 2740.

The spatial distribution of the physicochemical parameters of groundwater (GW) is shown in figure 8a-d. The highest recorded groundwater temperature was at Hinapulan, Laon and Nangka II. While the highest pH was recorded in Bantay and Boac, Marinduque. The highest EC recorded was located at Maligaya. The highest TDS concentration was in Maligaya and Tagwak. As a summary for the physicochemical GW properties, the T, pH, EC and TDS values ranged were 26.3 to 35 degrees Celsius, 6.2 to 7.7, 230 to 2350 $\mu\text{S}/\text{cm}$ and 100 to 1150 mg/L , respectively. Both surface and groundwater of some areas contain increased EC and TDS. Some areas have low pH surface water and ambient water with increased EC and TDS (both surface and groundwater) is a contaminated environment.



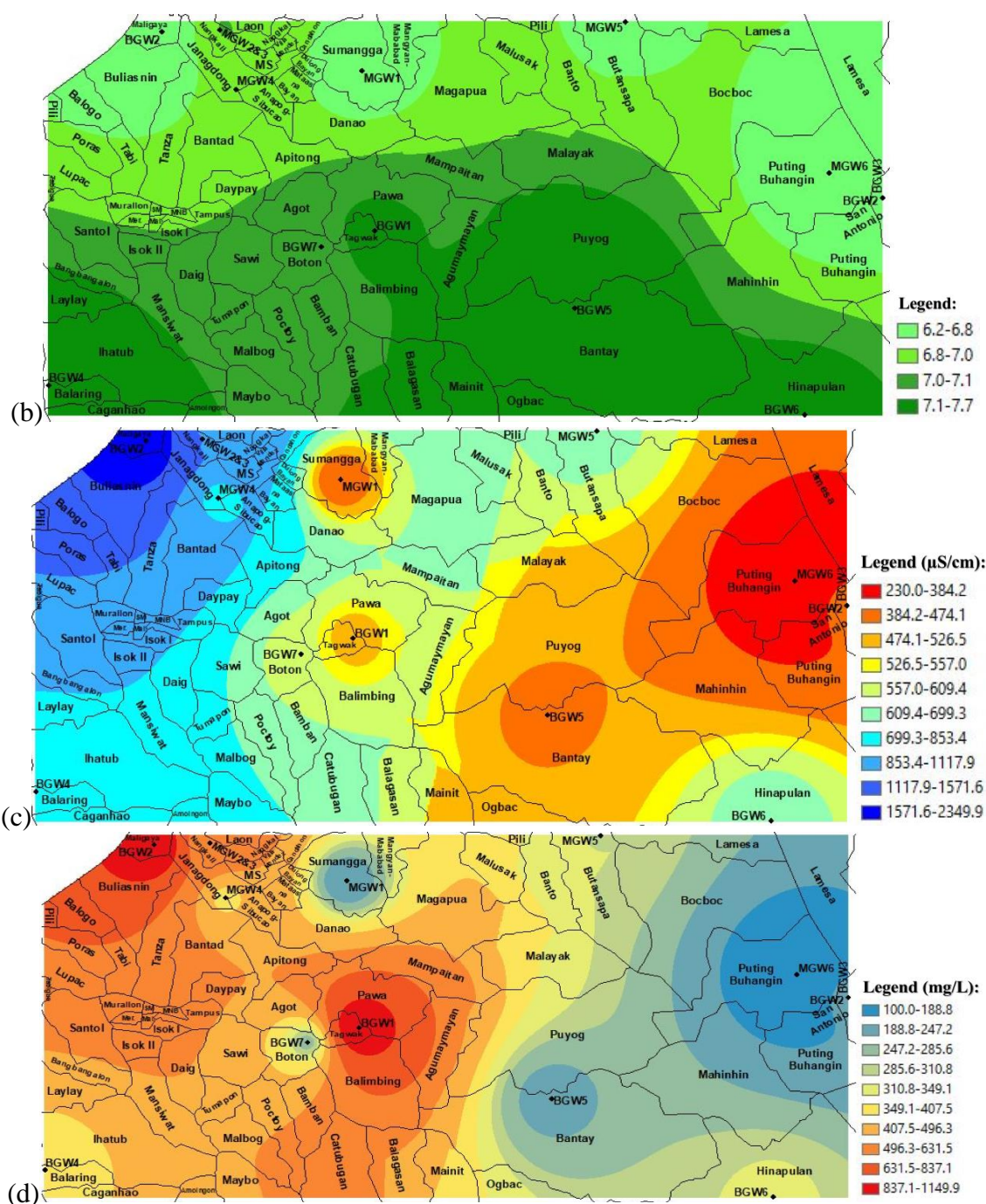
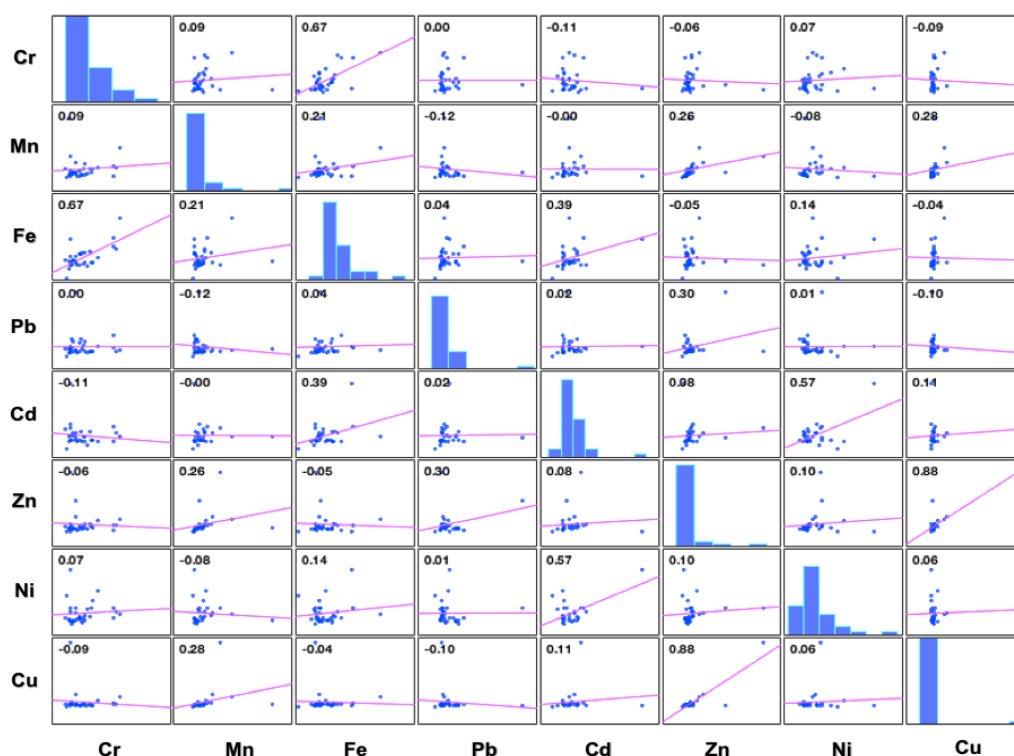


Figure 8. (a) Spatial distribution map of groundwater temperature; (b) Spatial distribution map of groundwater pH; (c) Spatial distribution map of groundwater electrical conductivity; (d) Spatial distribution map of groundwater total dissolved solids.

A correlation analysis was conducted using MATLAB R2018a. The results of the analysis are tabulated in table 5 and illustrated in figure 9 as correlation plot. Only the relationship of Cu to Zn, Ni to Cd and Fe to Cr shown significant positive correlation results. The Pearson correlation “R” of Cu to Zn was 0.88, Ni to Cd was 0.57, and Fe to Cr was 0.67. Positive correlation results may indicate that the abovementioned metals had common source as signified by the positive trend in the correlation plots.

Table 5. Correlation analysis between elements considered in the study.

Element	Cr	Mn	Fe	Pb	Cd	Zn	Ni	Cu
Cr	1.00000	-	-	-	-	-	-	-
Mn	0.09161	1.00000	-	-	-	-	-	-
Fe	0.66823	0.20914	1.00000	-	-	-	-	-
Pb	0.00083	-0.12431	0.03719	1.00000	-	-	-	-
Cd	-0.11066	-0.00448	0.38943	0.01733	1.00000	-	-	-
Zn	-0.05998	0.26188	-0.04554	0.29821	0.08343	1.00000	-	-
Ni	0.07350	-0.08105	0.14318	0.00524	0.56983	0.10319	1.00000	-
Cu	-0.08504	0.27976	-0.04082	-0.09671	0.10707	0.88030	0.05620	1.00000

**Figure 9.** Correlation plots of each heavy metals.

4. Conclusion

The Boac and Mogpog River basin quality was assessed, analysed and evaluated using an Unmanned Air Vehicle (UAV) DJI Mavic Air, google earth, SciAps X-300 handheld XRF and water quality multiparameter. Based on the results, the following conclusions were obtained: (1) the mean concentration of Cr, Mn, Fe, Cd, Zn and Cu was higher than the threshold effect concentration (TEC); (2) the concentration of Cu and Mn in the sediments in 2019 was 5 and 158 times higher, respectively, than the concentrations detected in 1998; (3) the positive correlation of Cu to Zn, Ni to Cd and Fe to Cr indicated a possible common source. The increased concentration of Cu and Mn in the river sediment implied continuous flow of tailings in the river. The spatial distribution map showed that the current pollution hot spot for contaminated sediments is located at Brgy. Hinapulan in the Municipality of Boac. The metals concentration trend was Fe>Mn>Cu>Zn>Cr>Ni>Pb>Cd.

Acknowledgments

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