

COMPARISON OF DISSOLVED COPPER CONCENTRATION TRENDS IN TWO RIVERS RECEIVING ARD FROM AN INACTIVE COPPER MINE (MARINDUQUE ISLAND, PHILIPPINES)¹

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Abstract. The Boac and Mogpog Rivers in Marinduque Island (Philippines) receive acid rock drainage from the inactive open-pit Marcopper Mine. Fairly similar dissolved Cu concentrations (20-25 mg/L) enter both rivers from the mine site. However, due to differences in size, hydrology and the acid neutralization ability of rocks between each watershed, the downstream geochemical impacts of the acid-rock drainage become markedly divergent. Dilution, interaction with waters and minerals having high acid-neutralizing capacity, precipitation, and particulate settling are the prevalent processes in the attenuation of dissolved Cu loads. Understanding the importance of each of these mechanisms will help in the selection and optimization of remediation efforts in the mine site to be able to achieve a minimum acceptable river water quality downstream.

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Introduction

The Marcopper Mine on Marinduque Island used to be one of the largest open pit-Cu mines in the Philippines. Developed on two adjacent porphyry Cu-type deposits (Loudon, 1976), the Tapan open pit was mined from the late 1960's through the late 1980's, and the San Antonio open pit to the north was mined from 1990 to 1996 (Fig. 1). In 1993, Marcopper received considerable public attention when mine wastes were released into the Mogpog River as a result of the collapse of the Maguilaguila siltation dam on the northern side of the mine site. The mine was closed in 1996 after a tunnel bulkhead failure led to the release of mill tailings from the Tapan open pit impoundment south into the Makulapnit and Boac rivers (Fig. 1). At present, mine wastes continue to erode into the Mogpog River system and the rebuilt Maguilaguila siltation dam and two other siltation dams holding back eroded mine wastes on the mine site are in danger of collapse (Futures, 2004). Also, acid-rock drainage (ARD) continues to flow from the mine site and has become a major cause of water quality degradation in both river systems (David, 2003; Futures, 2004).

Both the Mogpog and Boac river systems receive ARD that is geochemically similar. However, differences in size and bedrock geology between the two river systems affect the resulting changes in pH and downstream metal concentrations. These conditions allow us to compare natural processes controlling acid neutralization and dissolved metal concentration variations as a function of watershed size and geology.

ARD neutralization can come from several processes. Dilution by uncontaminated waters, especially those of higher pH and alkalinity, provides an effective means for raising the pH; the contribution of an uncontaminated source is readily predictable given its discharge rate relative to that of the ARD input (Laudon and Bishop, 1999). Also, waters draining carbonate rocks have higher alkalinity and acid-neutralizing capacity than waters draining volcanic rocks or silicic intrusive rocks (Plumlee, 1999). Carbonates and to a lesser extent aluminosilicates such as chlorites in bed sediments provide some potential for ARD neutralization (Paktunc, 1999), although flow into and chemical interactions between stream waters and bed sediments can be limited. As a consequence of decreased acidity, dissolved metal concentrations decrease with direct precipitation and with adsorption onto inorganic and organic particulates (Chapman et al., 1983).

The processes responsible for metal attenuation in the Mogpog and Boac river systems are investigated by comparing dissolved and total metal concentrations downstream from the rivers' confluences with ARD input from Marcopper. The partitioning of Cu, Al, and Fe between dissolved and particulate phases is also explored.

Methods

Sampling of surface water was done at the same stations along the Makulapnit-Boac and Mogpog Rivers in 2002-2004. The data set summarized in this paper is primarily from September 2003, which was the most extensive sampling carried out. This represents the hydrology for moderate rainfall, as the sampling occurred during the end of the area's rainy season (June-October). Two types of water grab samples were collected in each site: filtered (for analysis of dissolved metals) and unfiltered (for analysis of dissolved plus suspended particulate metals) samples. Filtering was done on site and accomplished by using a 0.45- μm nitrocellulose filter (Millipore, Inc.). All samples were acidified with concentrated HNO_3 , and stored in pre-

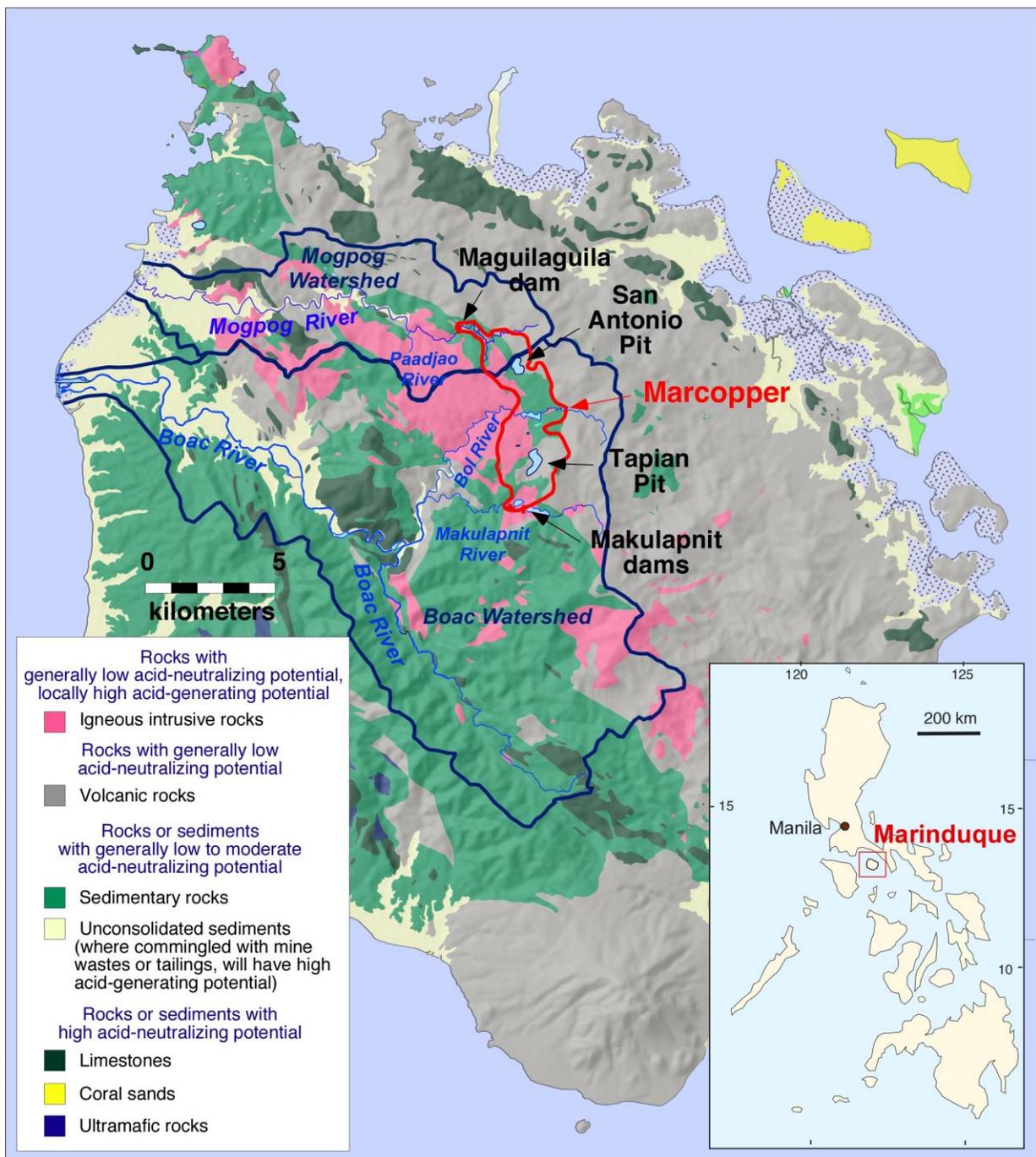


Figure 1. Environmental geology map of Marinduque showing the position of the Marcopper mine site within the Boac and Mogpog River basins, and showing the distribution of rock types with different acid generating or acid neutralizing capacities. The map was modified (Futures, 2004) from 1:50,000 scale geologic map sheets originally prepared by the Philippine Bureau of Mines (1970). The environmental geology characteristics for the different rock units were inferred based on geologic descriptions provided on the original geologic maps.

cleaned polyethylene bottles at 4°C prior to analysis. Trace metal analyses were done using inductively coupled plasma atomic emission spectrometry (ICP-AES) at the US Geological Survey in Menlo Park, CA. Water temperature and pH were measured on site; discharge estimates were also made on-site using a digital flowmeter (Globalwater, Inc.).

Results and Discussion

Evident in Fig. 1 is the relative difference in watershed size between the Makulapnit-Boac River watershed (~214 km²) and the Mogpog River watershed (~58 km²) (Futures, 2004). Moreover, the former has two large uncontaminated water sources (Upstream Makulapnit River and Upstream Boac River). It is also important to note that the Makulapnit-Boac River has two sources of ARD from Marcopper: waters draining mine waste piles on the southern side of the mine site into the Makulapnit River (subsequently referred to as the south Tapanian outflow), and overflow from the Tapanian open pit lake into the Bol River. In contrast, the Mogpog River flow is dominated by waters draining mine waste piles on the northern portion of the mine site, and its sources of uncontaminated water are limited, such as the perennial but minor inflow from the Paadjaio River.

In addition to the differences in size of the two watersheds and amounts of dilution by uncontaminated streams, the watersheds' environmental geology characteristics also play a role in acid neutralization and heavy metal attenuation. The Makulapnit-Boac River system drains mostly sedimentary formations such as sandstones and conglomerates as well as carbonate rocks along the mid- to upper reaches of the watershed. These formations may have moderate to high acid neutralizing capacity. Pyritic mill tailings deposits from the 1996 spill have largely been washed out to the western coast or buried, and there are relatively few sites where these tailings remain in contact with surface water (Futures, 2004). Therefore, only very localized additional ARD generation is expected in the Makulpanit and Boac Rivers. The situation in the Mogpog River is substantially different. A significant portion of the Mogpog watershed is underlain by andesite volcanics and diorite intrusive rocks, which have low acid neutralizing potential. There are some limestone lenses found in the lower parts of the watershed, which may contribute some alkalinity in these reaches of the river. Much of the Mogpog River substrate is dominated by pyritic, acid-generating mine wastes eroded from mine-waste piles north and west of the San Antonio open pit. These mine wastes were initially released into the Mogpog as a result of the 1993 Maguilaguila siltation dam failure, but have continued to be released after the siltation dam was rebuilt in the mid-1990's, due to the refilling of the siltation impoundment behind the dam and transport of eroded mine wastes over the dam spillway (Fig. 1; Futures, 2004).

A comparison of pH and dissolved Cu between the Boac and Mogpog Rivers shows that the starting ARD composition is relatively similar (20-25.5 mg/L Cu, pH<4) (Figs. 2 and 3). Both parameters rapidly approach baseline conditions (0.01 mg/L Cu and pH~7) downstream on the Boac River within 6 km of the south Tapanian outflow, despite of the addition of ARD from the Bol River within 4 km from the Tapanian outflow. In fact, a significant decrease in dissolved Cu occurs downstream from the confluences with both uncontaminated tributaries (Upstream Makulapnit River, Upstream Boac River, etc.). Dissolved Cu is further reduced downstream along stretches of the river where there are no obvious surface inputs of uncontaminated waters, indicating that processes other than dilution are in operation. In contrast, the Mogpog River shows a smaller downstream increase in pH and decrease in dissolved Cu concentration; for example, in the first 7 km of the Mogpog River, dissolved Cu only decreases from 25.5 to

20.0 mg/L Cu and pH only increases from 3.3 to 3.6.

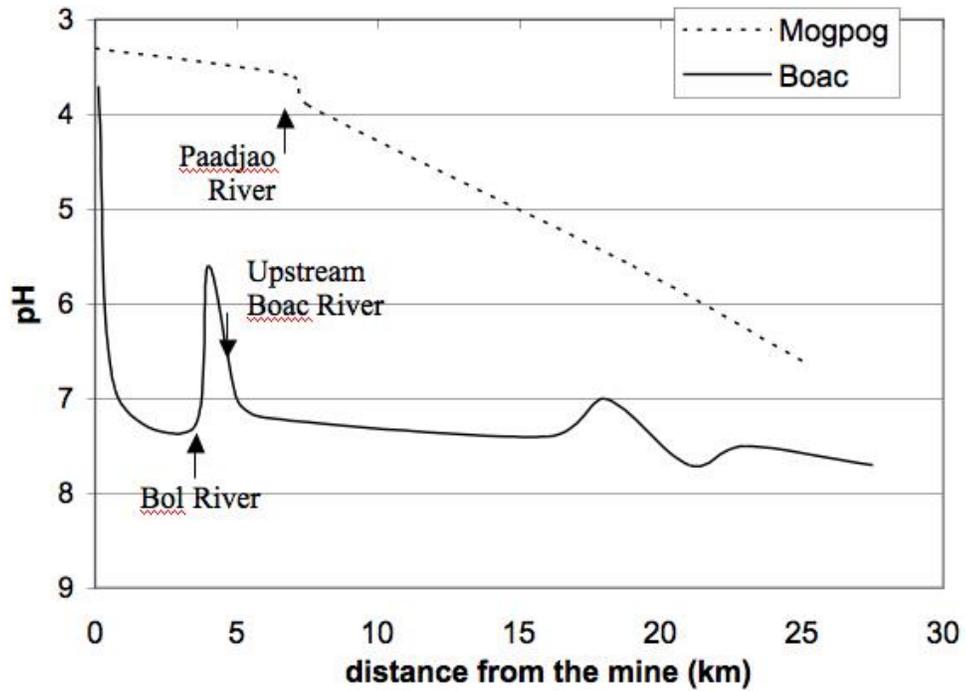


Figure 2. Trends in pH for the Mogpog and Boac Rivers.

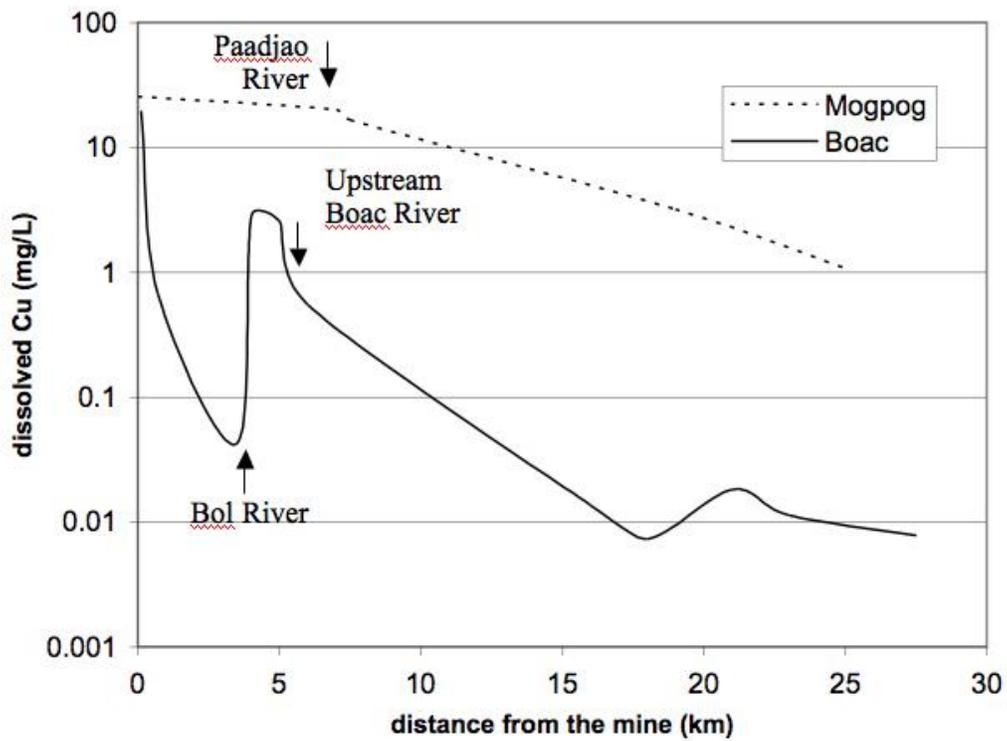


Figure 3. Trends in dissolved Cu concentration for the Mogpog and Boac Rivers.

Comparison of Cu loads (total, dissolved and particulate) measured in three stream confluences along the Makulapnit-Boac River and one along the Mogpog River (Fig. 4 and Table 1) provide further constraints on in-stream processes leading to Cu attenuation. As seen in Table 1, the ARD-contaminated sources have high, predominantly dissolved, Cu loads. However, where ARD-contaminated streams mix with uncontaminated or less contaminated streams, the total Cu load decreases in the combined stream. With dilution alone, there should be no change in the total Cu loads from above to below the confluence, and so differences in total Cu loads may be attributed to other processes such as precipitation, sorption, and particulate settling. Below the south Tapian-Upstream Makulapnit confluence, as much as 71% of the total Cu load was lost. In contrast, only 17% of the Cu load was lost below the Mogpog-Paadjao River confluence.

The suspended particulate loads also increase in proportion relative to the dissolved loads in the combined streams below the confluences, and the ratio of the two compartments varies with the resultant pH. In situations where suspended particulates dominate, it is interpreted that the settling of Cu-rich particulates (either Cu phases or Cu sorbed onto particulates of iron and/or aluminum) into the bed sediments is the dominant process that explains the observed decrease in total Cu load.

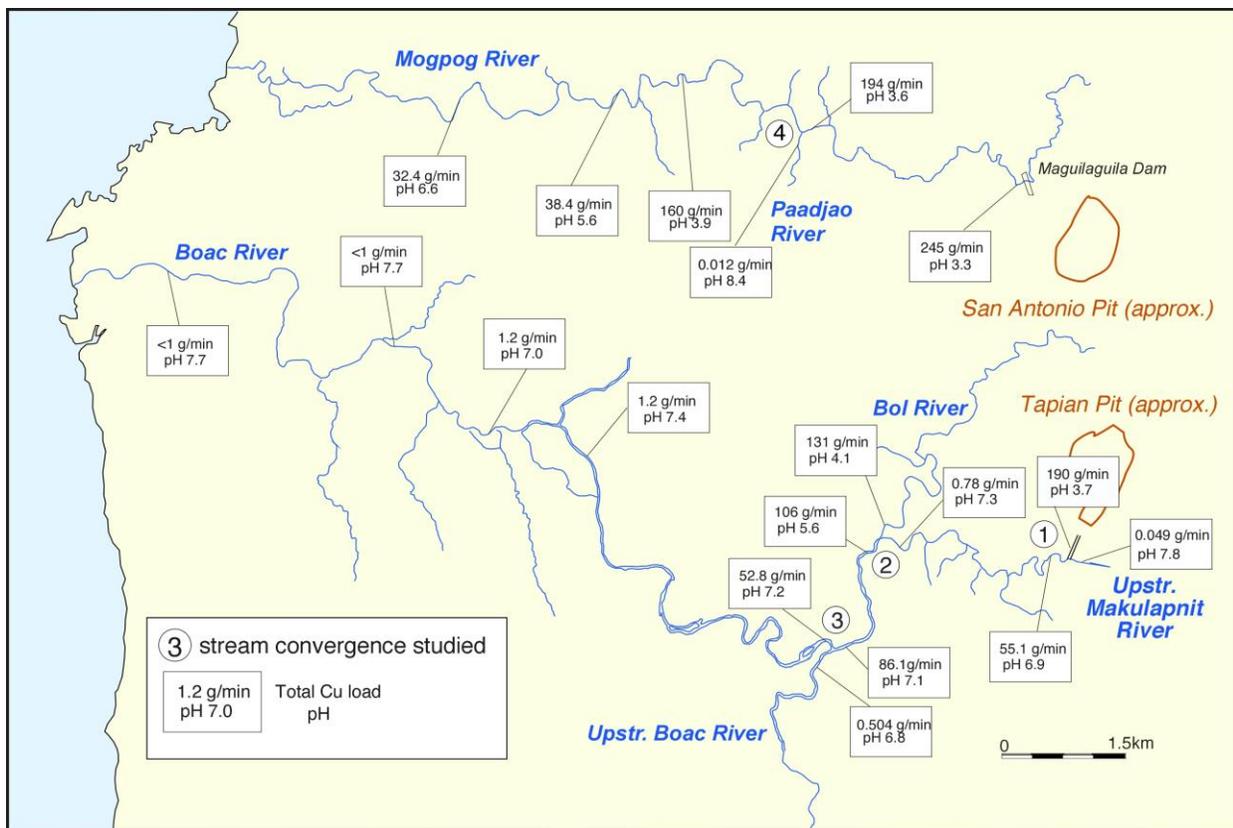


Figure 4. Total Cu load (g/min) in the Boac and Mogpog Rivers.

Table 1. Comparison of Cu loads in four stream confluences studied in 2003. ¹Data from 2004.

	Confluence	Discharge (m³/min)	pH	Total Cu Load (g/min)	Dissolved Cu Load (g/min)	Suspended particulate Cu Load (g/min)
1	South Tapian Outflow	9.6	3.7	190	189	0.96
	Upstr. Makulapnit River	16	7.8	0.049	0.049	<0.02
	Combined (observed)	40	6.9	55.1	26.9	28.2
2	Bol River	18	4.1	131	125	5.76
	Makulapnit River	16	7.3	0.778	0.697	0.081
	Combined (observed)	34	5.6	106	93.7	12.8
3	Makulapnit River	34	7.1	86.1	7.96	78.1
	Upstr. Boac River	72	6.8	0.504	0.432	0.072
	Combined (observed)	96	7.2	52.8	8.64	44.2
4	Mogpog River	9.6	3.6	194	192	1.92
	Paadjao River	<6.0 ¹	8.4 ¹	0.012	0.012	<0.006
	Combined (observed)	9.6	3.9	160	157	2.88

Similar trends are observed for other metals such as Fe and Al (Table 2). All Al and most of the Fe partition to the particulate phase or precipitate out at river confluences. Most of the Al and Fe come from the Marcopper ARD. However, at the confluence of the Makulapnit River with the Upstream Boac River, more Al and Fe were observed below the confluence than above, suggesting that these metals are coming from another source, most likely resuspended bed sediments. The Mogpog-Paadjaio River confluence shows minimal changes in Al and Fe loads, similar to the trend observed for Cu.

Copper precipitation occurs in all three Makulapnit-Boac River confluences studied (Figs. 5a-c) although it is in the south Tapian-Makulapnit convergence where precipitates are most extensive (100m extent from the confluence). A bright green precipitate (Fig. 5a) is noticed as soon as the pH passes above the dissolved Cu pH threshold of 5-6 (Forstner and Whitmann, 1979).

Table 2. Comparison of Al and Fe loads in four stream confluences studied in 2003. ¹Data from 2004.

	Confluence	Discharge (m ³ /min)	Dissolved Al Load (g/min)	Suspended particulate Al Load (g/min)	Dissolved Fe Load (g/min)	Suspended particulate Fe Load (g/min)
1.	South Tapan Outflow	9.6	115	1.25	7.51	3.35
	Upstr. Makulapnit River	16	<8.0	<8.0	<0.3	0.567
	Combined (observed)	40	<20	29.1	<0.02	0.134
2.	Bol River	18	152	41.9	7.94	23.9
	Makulapnit River	16	<0.8	<0.8	<0.3	<0.3
	Combined (observed)	34	<17	24.8	0.773	1.80
3.	Makulapnit River	34	<17	<17	33.3	<0.7
	Upstr. Boac River	72	<36	<36	<1.4	<1.4
	Combined (observed)	96	<48	81.3	2.51	68.4
4.	Mogpog River	9.6	239	1.63	84.1	41.2
	Paadjao River	<6.0 ¹	<3	<3	<0.1	<0.1
	Combined (observed)	9.6	174	9.02	35.6	47.3



Figure 5a. Blue Cu-rich precipitates coat the streambed as ARD from mine waste piles south of the Tapan Pit is diluted by fresh waters from the Upstream Makulapnit River watershed. X-ray diffraction analysis of these precipitates shows that they are a complex mixture of Cu-silicates and Cu- (\pm K- \pm Al) sulfates. Photo by Terry Boyle, reproduced from Futures (2004).



Figure 5b. Confluence of the Makulapnit River (left) with the Bol River (right), looking downstream. Note that the Makulapnit River waters appear relatively clear, indicating substantial dilution and settling of particulates has occurred in the Makulapnit downstream of ARD input shown in Fig. 5a. Photo by Geoff Plumlee, reproduced from Futures (2004).

Table 3 gives a sample composition of a silicate-rich precipitate from Tapan compared with an Al-rich precipitate that occurs at a slightly lower pH. It should be noted that the composition of the precipitates slightly varies between each confluence although Cu typically only ranges from 30-33%. Some of the Cu may also be sorbing onto mineral surfaces; however, it is still poorly understood in terms of how much sorption versus direct precipitation contributes to decreasing dissolved metal levels in these streams (Kalin and Harris, 2005). In the Mogpog River, however, there are no voluminous Cu precipitates observed in the stream bed where pH rises above 6. Instead, small amounts of a greenish, lacy precipitate and abundant orange, Fe-rich particulates are commonly observed along the downstream Mogpog River (Fig. 6) after every storm event. This suggests that there are factors other than pH that control where Cu-rich precipitates will occur.



Figure 5c. Confluence of the Paadjao River (left) with the Mogpog River (right), looking downstream. Photo by Mark Logsdon, reproduced from Futures (2004).

Summary

The natural recovery of a river system from acid rock drainage is influenced by several processes, including dilution, interaction with sources of alkalinity, precipitation/sorption of metals, and settling of particulates. The relative magnitude of metal attenuation due to each of these processes is still relatively poorly quantified for the rivers affected by ARD from Marcopper. However, transfer of Cu from dissolved to particulate phase (suspended then incorporated in bed load) is seen as the primary route for Cu removal from surface waters. Such is the case with the south Tapan outflow, whose impacts on water quality are rapidly mitigated downstream via dilution by fresh waters having high alkalinity, and the resulting precipitation of Cu silicates and sulfates. The chemical and physical stability of these precipitates, as well as their impacts on aquatic life, are in need of further study. Nonetheless, the rapid downstream attenuation of acid, Cu and other metals in the Makulapnit/Boac river system is in stark contrast to the Mogpog River, where the acidity and dissolved Cu levels remain high even in stations more than 15-20 km downstream from Marcopper. The contrast between the Makulapnit/Boac and Mogpog watersheds in their ability to self-mitigate acid-rock drainage is directly tied to their size and geology, with the most extensive downstream self-mitigation occurring in the larger watershed with a greater component of carbonate-rich bedrock. Further studies of the flow and alkalinity of diluting tributaries in the two watersheds over the rainy and dry seasons will help elucidate the relative importance of watershed size versus bedrock type in this self-mitigation. Further studies will also involve more detailed characterization of the Cu precipitates, chemical modeling of dilution/precipitation processes, and examination of how suspended particulates are incorporated into bed sediments.

Table 3. Composition of Al and Cu precipitates observed in the South Tapian and Makulapnit River confluence. The overlying water where the precipitate samples were collected were also analyzed. ND (not detected). Data from 2002.

Element	White Al-rich precipitate		Green Cu-rich precipitate	
	Precipitate	Overlying water ($\mu\text{g/ml}$)	Precipitate	Overlying water ($\mu\text{g/ml}$)
pH	--	5.0	--	5.7-6.62
Aluminum	18.8%	8.05	7.24%	0.024-0.060
Iron	4.38%	0.612	1.70%	ND-0.003
Silicon	3.09%	ND	2.90%	ND
Copper	0.33%	23.3	30.4%	2.52-3.87
Cadmium	2.54ppm	0.005	15.6ppm	0.002
Calcium	1,240ppm	277	5010ppm	262-310
Cobalt	2.35ppm	0.316	127ppm	0.077-0.091
Lead	3.55ppm	ND	ND	ND
Magnesium	974ppm	51.5	3240ppm	50.0
Manganese	73ppm	11.0	1940ppm	8.61-9.87
Potassium	170ppm	6.16	21.7ppm	3.47-4.41
Nickel	1.67ppm	0.102	69.7ppm	0.025-0.027
Sodium	440ppm	32.7	580ppm	21.8-25.9
Silver	1.06ppm	ND	ND	ND
Titanium	1.91ppm	ND	ND	ND
Vanadium	155ppm	0.01	53.9ppm	0.005
Zinc	2.17ppm	2.09	4100ppm	0.541-0.694
Sulfur	6.27% (as S)	281 (as SO_4)	2.84% (as S)	210 (as SO_4)
Cl	ND	0.43	ND	0.36
Phosphate	ND	1.70	ND	ND
Total Carbon	0.50%	--	0.75%	--



Figure 6. Photograph of the Mogpog River, looking downstream, approximately 7 km downstream from the confluence with the Paadjao River. Photo by Geoff Plumlee reproduced from Futures (2004).

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