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TECHNICAL ARTICLE

Effects of Manganese Mining on Water Quality in the Caucasus Mountains, Republic of Georgia

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Abstract One of the world's richest manganese (Mn) deposits and largest Mn mining areas lies in the foothills of the Caucasus Mountains, near the city of Chiatura in the Republic of Georgia. This study was an initial evaluation of the effects of Mn mining on water quality in the Chiatura region. Seven river and stream locations (three on the Kvirila River and four on tributaries), five untreated drinking water supplies (four springs and one groundwater well), and one untreated industrial wastewater discharge (Mn processing) were sampled and analyzed for field indicator parameters, anions, cations, and metals. Five river bed sediment sites (co-located with river water sites) were also sampled and analyzed for metals. Three of the public water supplies were contaminated by coliform bacteria, and concentrations of dissolved Mn, Fe, and Ni exceeded Georgian drinking water criteria in the groundwater supply well. The Kvirila River had very high concentrations of total Mn and Fe relative to an upstream location, especially downstream of the industrial discharges. Several tributaries also had elevated concentrations due to nonpoint source pollution from mine waste near the streams. Mn and Fe loads in the Kvirila River and tributaries were primarily in the particulate form. The river bed sediments at all five sampled river sites contained elevated metal concentrations. Mn and Ni, in particular, were very high in the Kvirila River near the discharges compared to background soil levels. Although Mn and Fe oxide solids in sediment can increase adsorption and attenuation of other metals from the water column, the contaminated sediments can also serve as a long-term residual source of metal contamination of river water, with potentially significant adverse ecological and human health effects.

Keywords Georgia · Manganese · Metals · Mining · Water quality

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Introduction

Numerous former Soviet Union (FSU) nations have diverse mining industries that account for a relatively large percentage of their economic output. The Republic of Georgia's output of ferrous and nonferrous metals, ferroalloys, industrial minerals, and fuels is second only to agriculture in terms of gross national product (Levine and Wallace 2004). The country has more than 300 explored mineral deposits, only about half of which (copper, iron ore, barite, lead, zinc, arsenic, clay, sand, gravel, and a range of secondary metals, including gold and silver) have been brought into production. Georgia has been a major producer of high-grade manganese (Mn) for about a century. It has one of the world's richest Mn deposits and largest Mn mining areas in the foothills of the Caucasus Mountains, centered around the city of Chiatura, in the Imereti region of western Georgia.

The Mn ore deposits near Chiatura, first discovered in 1849, have been exploited since 1879. The ores include pyrolusite and psilomelane (oxide ores) and rhodochroisite (carbonate ore). The country's largest producer, Chiaturmarganets, mines Mn ores from open cast and underground operations in Chiatura, which are supplied to the nearby Zestafoni ferroalloys plant. The Chiatura deposit was estimated to be 215 metric tons of Mn ore, of which about half has been depleted since mining began (Table 1 shows carbonate ore reserves). Following the dissolution of the Soviet Union, mineral production in Georgia declined sharply. However, Mn has become a critical component in metallurgy, where it has a twofold application: it scavenges impurities such as oxygen, sulfur, and other elements during the steel-making process, and imparts toughness, hardness and abrasion resistance as an additive to steel. Approximately 90% of the Mn consumed in the world is used in Mn ferroalloys. The rest is used to produce nonferrous products, such as aluminum alloys, fertilizers, bricks, and paint, and for water purification.

Although the mining and processing industries in FSU nations have provided many economic and societal benefits, they also have caused significant environmental impacts, including acid mine drainage (AMD) in some areas and contamination of groundwater, surface water, and soils. The degree and significance of AMD and metal contamination of water and soils are affected by complex biochemical reactions in the disturbed ore bodies and associated mine waste materials (tailings and waste rock; Caruso and Bishop 2009; Church et al. 2007; Nimick et al. 2004). Microbes in soils and water help to oxidize the sulfide minerals and catalyze acid- and dissolved metal-generating reactions. However, in Mn deposits, AMD generation is often not the major problem.

Mn is a redox sensitive metal that can exist in water as the manganous ion (Mn^{2+}), or in the oxidized state (Mn^{4+}). Most Mn salts are very soluble in water, but Mn oxides are not and can easily form solid oxy-hydroxide precipitates that can coat streambeds where concentrations are high. Mn speciation is governed by pH and redox conditions, with Mn^{2+} dominating at lower pH and redox potential, and an increasing proportion of colloidal Mn oxy-hydroxides above pH 5.5 (Scott et al. 2002). Dissolved concentrations undergo diel variations in streams (Brick and Moore 1996; Filipek et al. 1987). Toxic metals and nutrients can co-precipitate with or sorb to Mn oxides (MnOx) on the streambed. Surface catalyzed oxidation and photoreduction can be important processes with regard to fate and transport, particularly in mountain streams (Scott et al. 2002). Light promotes oxidation, precipitation of MnOx, and removal from streams through photosynthetically enhanced oxidation processes (Scott et al. 2002).

Mn in water can be significantly bioconcentrated by aquatic biota at lower trophic levels. Uptake by aquatic invertebrates and fish greatly increases with temperature and decreases with pH, but is not significantly affected by dissolved oxygen (DO). Dissolved Mn concentrations of about 1 mg/L can cause toxic effects in aquatic organisms, and many countries have adopted 0.2 mg/L for protection of 95% of species with 50% confidence (Howe et al. 2004). Mn can be toxic to humans through exposure routes that include ingestion, dermal exposure, and inhalation of particulate forms in air. Inhalation of particulates, especially by workers at Mn mines and processing plants as well as nearby residents, is one of the primary exposure mechanisms and human health risks in the Chiatura mining region. Ingestion of contaminated water or soils/waste material and dermal exposure of residents are also major risks. These risks can be particularly high given the lack of regulations and pollution control, and the high density of poor communities interspersed with the mines, processing facilities, and waste piles, as well as downstream. Mn compounds are well known neurotoxic substances that may cause manganism in humans, a severe neurological disorder characterized by disturbances of movement, as well as Parkinson's disease (Howe et al. 2004; Olanow 2004).

The primary objective of this study was to evaluate the extent and significance of metal contamination, in particular Mn, in waters in the Chiatura region and potential risks to human health from operational and abandoned mines and mine facilities. The study was conducted in collaboration with the Science and Technology Center of the Ukraine, Georgia National Center for Disease Control and Public Health, and the Technical University of Ukraine through the US State Department and US Environmental Protection Agency's Biochemical Weapons Redirect Program. The goal of this program is to aid FSU states in redirecting their biochemical research institutes and scientists to peaceful objectives.

Table 1 Reserves of carbonate Mn ore within the Chiatura Manganese Company, as of Jan. 2006

Type of ore	Reserves (kg)	Mn content in ores (%)
Acid	47,211	26.5
Including dioxide	4,977	38.3
Carbonate	68,918	21.6
Acid	20,196	21.7
Mixed	23,097	21.6
Other	594	24.2
Mn small particles	60	10.2
Total	160,076	

Fig. 1 Location map of the Republic of Georgia, Greater Caucasus Mountains, and Chiatura

Study Area

Chiatura is located in the Imereti region of western Georgia in a canyon of the Racha Mountains, in the southern foothills of the Greater Caucasus Mountains, 180 km west of Tbilisi, the capital and largest city (Fig. 1). The mines, main factory, and other industrial facilities are situated over an area of 50 km^2. The city lies in a mountain valley along the Kvirila River (named because of its yellow color); the main Chiatura Mine is also located in the valley adjacent to the city (Fig. 2). The city and its ore-enriching plants cluster in the narrow valley, with mines in the surrounding hills linked by cable railways and aerial carriers. The smelter receiving Mn concentrate from mines in Chiatura is located in the city of Zestafoni, 30 km to the southwest. The primary Mn factory (owned and operated by the Chiatura Manganese Company) is located adjacent to the left bank of the river in the village of Perofi in the Darkveti area. There is a railway connection between Chiatura and Zestafoni.

The Chiatura Mn deposits are situated in the north periphery of the Dzirula crystalline massif, in the middle reach of the Kvirila River. The area represents an almost horizontal plateau, divided by the Kvirila River and its tributaries. The ancient rocks are Palaeogene formations overlain by Jurassic rocks. These are overlain by Cretaceous sediments. Oligocene rocks are in upper layers with Mn beds, topped with middle-upper Miocene and ancient–modern Quaternary alluvial formations. The deposits are confined by major faults to the southwest. Within the boundaries of the deposit, Quaternary, Tertiary, Upper Cretaceous, Jurassic, and Palaeozoic hydrogeological complexes can be delineated. Alluvial water-bearing horizons generally have high concentrations of Mn. Waters of the Sarmatian water-bearing horizons are used for water supply by the settlements on the left bank of the Kvirila River. The average hydraulic conductivity of these formations is approximately 0.8–0.9 m/day; the depth to water is 6–8 m and the water is dominantly calcium bicarbonate, with 0.6–0.8 g/L of total dissolved solids and 9.8 mg-eq of hardness.

The climate in Chiatura is humid; the winters are moderately cold and the summers are hot and dry. Due to its location in the foothills of the Greater Caucasus Mountains, the Chiatura region receives a significant amount of precipitation, including a high snowpack with peak seasonal snowmelt in spring. The average annual precipitation is 1,100–1,200 mm, with greater depths at higher elevations and a maximum in autumn and winter. This water can drive the mobilization and transport of pollutants, including metals, from source areas such as tailings and waste rock piles to ground and surface waters in the form of nonpoint source pollution. Drinking water in the area is supplied primarily by four springs with headworks and one communal groundwater well; no water treatment or chlorination occurs.

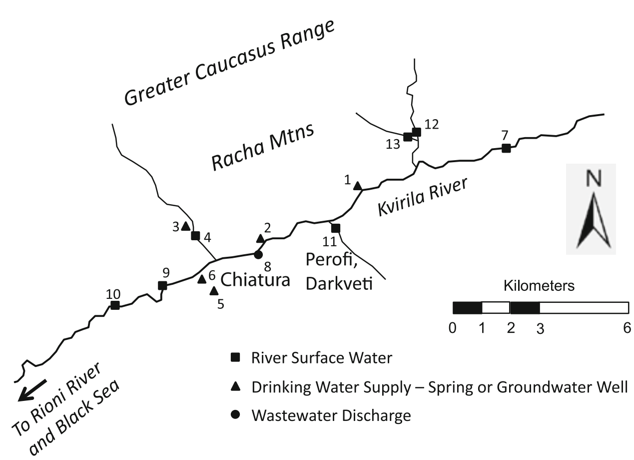

Fig. 2 Sampling location map for Chiatura. Sites numbers refer to locations in Table 2

There are approximately 20 Mn mines in the Imereti District and Chiatura region. Eleven mines are open pit and nine are underground mines. Sixteen of the 20 mines are located in tributary watersheds north of the Kvirila River and four are located south of the river. It is not known how many of these mines are currently operating because this type of information is not readily available from Georgian authorities or from the mining company. The Kvirila River flows through the center of the main Chiatura Mn deposit and is a tributary of the Rioni River, which flows west to the Black Sea. Numerous small mountain rivers and streams discharge to the Kvirila River, and several villages are located in the canyons of these tributaries. Mn mines are also located near some of these villages. Tailings and slag waste is present in large quantities above ground throughout the area. The waste contains primarily Zn, Pb, Ni, Co, Mn, and other potentially toxic substances based on preliminary information from the mining company. Industrial wastewater is also directly discharged untreated from the Chiatura Mn factories (including the peroxide enrichment factory (PEROF) and the "central keeping facility" (CKF), which is the main ore processing facility) to the Kvirila River. The environmental conditions, the proximity of the mines, tailings, and discharges to the river and human settlements, and the lack of adequate management or regulation of operations cause significant environmental and human health risks not only to the Chiatura region, but to all territories that the river flows through on its way to the Black Sea.

Methods

Sampling and Analysis

Water quality samples were collected at seven river and stream locations and five drinking water supply locations (four springs and one groundwater well) throughout the Chiatura study area (Fig. 2; Table 2). One sample was also collected directly from the industrial wastewater discharge from the main Mn factory (Perophi peroxide enrichment factory). Samples were collected as part of three synoptic sampling events during spring (April high flow) and late summer/autumn (September low flow) 2009, and early summer (June high flow) 2010.

Field indicator parameters included temperature, pH, DO, and specific conductivity (SC). Laboratory analytes included alkalinity, chloride (Cl), sulfate (SO_4), nitrate (NO_3), 5-day biochemical oxygen demand (BOD_5), chemical oxygen demand (COD), *E. coli*, metals (Na, K, Ca, Mg, Al, Cd, Co, Cu, Fe, Mn, Ni, Pb, and Zn), and As. All water quality-sampling tasks followed USEPA Region 8 standard operating procedures (SOP) for field sampling protocols (USEPA 2002). Field meters were calibrated according to the USEPA Region 8 SOP for the HydroLab multiprobe (USEPA 2003). Precision and accuracy for field indicator parameters were based on the USEPA field sampling protocols (USEPA 2002), or the manufacturer's specifications. Total carbonate hardness was estimated from Inductively Coupled Plasma Mass Spectrometry measurements of dissolved calcium and magnesium as $CaCO_3$. Samples for hardness, alkalinity, SO_4, NO_3, and Cl were collected in 250 mL HDPE containers and chilled to 4°C for preservation. A minimum of 125 mL of sample was collected for both dissolved and total metals analysis. Dissolved metals samples were filtered within 15 min of collection using a 0.45 μm filter (USEPA 2002). Total and dissolved metals were only sampled and analyzed during the first sampling round in April 2009. Only dissolved metals were sampled and analyzed during the other two sampling events. All metals samples were collected into HDPE or LDPE containers and preserved with 0.5 mL

Table 2 Summary of Chiatura area water quality sampling locations

Site	Location	Description	Type
1	Grudo water supply	Near village of Grudo	Drinking water supply/spring
2	Monasteri water supply	Water collecting reservoir near Fasknara	Drinking water supply/spring
3	LeJubani water supply	Near village of LeJubani	Drinking water supply/spring
4	Rgani Stream	Right bank tributary	Tributary
5	Gagarin well	On Gagarin Street	Drinking water supply/well
6	Sakurdglia water supply	Near village of Sakurdglia	Drinking water supply/spring
7	Kvirila River upstream	Near village of Sareki upstream of most mines	Main stem river
8	PEROF	Peroxide enrichment factory	Industrial wastewater discharge
9	Kvirila River upstream of CKF	Near admin building and village of Tiri	Main stem river
10	Kvirila River downstream of CKF	Downstream of most mines	Main stem river
11	Shuqruti Stream	Left bank tributary	Tributary
12	Jruchula Stream	Right bank tributary	Tributary
13	Darkveti Stream	Right bank tributary	Tributary

nitric acid in the field. Samples were analyzed by either a privately contracted laboratory (GAMMA), the Georgia Ministry of Environment Protection and Natural Resources, or the Technical University of Ukraine. Chain-of-custody procedures followed the USEPA field sampling protocols (USEPA 2002).

Dissolved As, Pb, and Zn were not sampled or analyzed after the first sample round in April 2009 because neither the total or dissolved forms of these metals were detected at any locations during that round. This was also partly the result of our limited budget for analysis, a typical issue in FSU countries. It is believed that these metals are only present at very low concentrations in the ore and the Chiatura environment, but the reason for their low levels is not known. Ca and Mg, alkalinity, sulfate, Cl, NO_3, BOD_5, and COD were also not sampled or analyzed during the last sampling round (June 2010) due to funding limitations. *E. coli* was only sampled and analyzed once during the first sampling round at the drinking water supply locations.

River bed sediment samples were collected at five locations during the three water quality sampling events. These were co-located with five of the surface water sampling sites: the Kvirila River upstream of Chiatura, the Kvirila River upstream and downstream of the CKF, Shuqruti stream, and the Jruchula River.

Field and analytical results were evaluated over time/between high and low flow sampling events and across locations and water types (river surface waters, spring or groundwater drinking water supply, and wastewater discharge). Results were also compared to applicable water quality standards and criteria (Table 3). Georgian Ministry of Labour, Health and Social Affairs (2007) maximum allowable concentrations (MACs) for drinking water were used for most analytes. Georgian regulations do not include MACs for toxic substances (including metals) in river bed sediments. Therefore, representative reference or 'background' values for Georgian soils (Ministry of Justice of Georgia 2003a, b) were used for comparison (Table 3).

Results

Field Indicator Parameters

Across the 13 sampling locations and three sampling events, the surface water temperature range was 8–18.5°C. Such temperatures are generally not a concern for any fish or aquatic life in rivers in the region. DO varied from 5.7 to 11.4 mg/L for all river, stream, and spring water supply sites, so these waters were essentially saturated with DO (Fig. 3a). However, DO was very low (0.6–2.9 mg/L) in the one groundwater sample location (the Gagarin well). This well was not purged before sampling and low DO levels were expected. Values for pH across the sites ranged from 6.5 to 8.8, reflecting circumneutral or slightly alkaline conditions (Fig. 3b). SC values were greatest in the Darkveti (up to 1,869 µS/cm) and Shuqruti stream samples (up to 1,208 µS/cm), but were also elevated above 900 µS/cm in the PEROF discharge (Fig. 3c). These elevated values likely reflect nearby pollution sources discharging to the two tributaries, as well as untreated industrial wastewater discharge from PEROF. SC in the Monasteri water supply exceeded 700 µs/cm for all three sampling events.

Additional Analytes

Across all sites and sampling events, hardness (Ca + Mg) was greatest in the Darkveti (16.8–22 me/L) and Shuqruti stream samples (12.3–13.6 me/L), and <10 me/L at all other locations (hardness was not sampled or analyzed in the PEROF discharge; Fig. 3d); the Georgian criterion is 10 me/L. These values generally represent moderate hardness. Alkalinity was low and within the guidelines, with a range of 1.9–5.4 mg/L (alkalinity was also not sampled or analyzed in the PEROF discharge; Fig. 3e). Sulfate was above 100 mg/L in Shuqruti and Darkveti stream samples and the Jruchula stream samples, although all values were below the criterion of 250 mg/L, and

Table 3 Analyte maximum allowable concentration (MAC) for water under the Georgian National Water Regulations, and background values for river bed sediment. Sediment values are based on representative reference or 'background' values for Georgian soils (Ministry of Justice of Georgia 2003a, b) for comparison to river bed sediment sampling results

Analyte	Drinking water	Surface water	Sediment
Na	200 mg/L		
K	20 mg/L		
Ca	140 mg/L		
Mg	85 mg/L		
Fe	0.3 mg/L	0.3 mg/L	
Pb	0.01 mg/L	0.03 mg/L	32 mg/kg
Zn	3.0 mg/L	1.0 mg/L	23 mg/kg
Cu	2.0 mg/L	1.0 mg/L	3 mg/kg
As	0.01 mg/L	0.05 mg/L	2 mg/kg
Al	0.1 mg/L	0.5 mg/L	
Co	0.1 mg/L	0.1 mg/L	5 mg/kg
Ni	0.07 mg/L	0.1 mg/L	4 mg/kg
Mn	0.4 mg/L	0.1 mg/L	1,500 mg/kg
Cd	0.003 mg/L	0.001 mg/L	0.5 mg/kg
NO_3	50 mg/L	45 mg/L	
Alkalinity	0.5–6.5 meq/L		
Hardness	7–10 meq/L		
BOD_5		6.0 mg/L	
COD		30 mg/L	

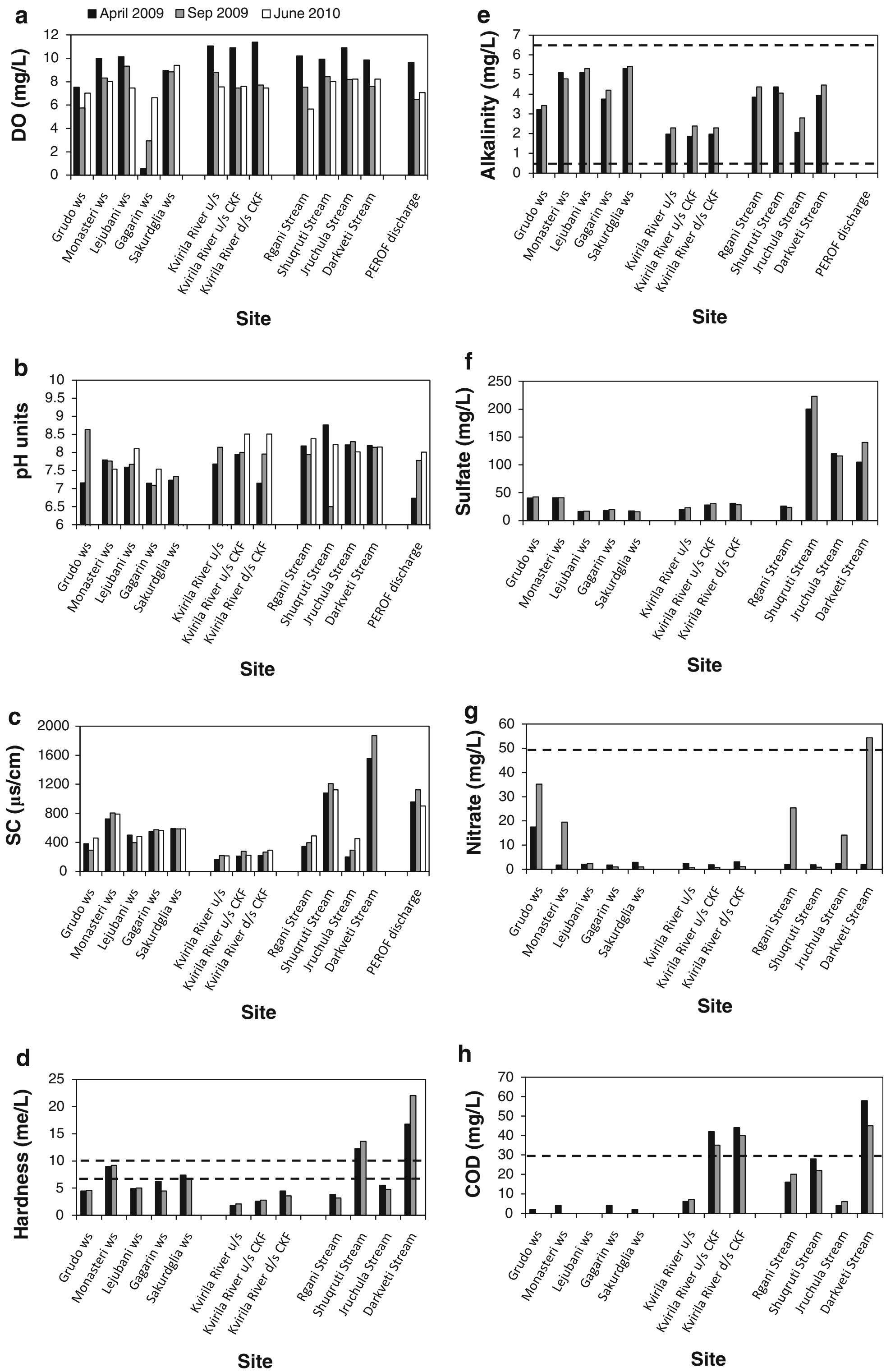

Fig. 3 Chiatura field indicator parameter and additional analyte results in water for **a** DO, **b** pH, **c** specific conductance (SC), **d** hardness, **e** alkalinity, **f** sulfate, **g** nitrate, and **h** COD. *Dashed line* is Georgian maximum allowable concentration (MAC). MAC for hardness, alkalinity, and nitrate is for drinking water; MAC for COD is for surface water; *ws* water supply; *u/s* upstream; *d/s* downstream

concentrations at other sites were low (Fig. 3f). The specific source of this sulfate is currently not known. Cl concentrations ranged from 12.5 to 33 mg/L, well below the 250 mg/L criterion. Nitrate was relatively high (17.5 mg/L) at the Grudo water supply during the first sampling round in April 2009, but was <3.5 mg/L at all other locations (Fig. 3g). During the second sampling event in September 2009, NO_3 was elevated at the Grudo water supply (35.2 mg/L) as well as at four other locations, ranging from 14.1 to 54.4 mg/L (in Darkveti Stream), including the Monasteri water supply (19.5 mg/L). All other values were low and only the highest value, in Darkveti Stream, exceeded the criterion of 50 mg/L (as NO_3).

BOD_5 concentrations ranged from 0.2 to 3.3 mg/L, below the criterion of 6 mg/L. COD values were 0–58 mg/L, with the highest concentrations in the Darkveti stream samples; the criterion of 30 mg/L was also exceeded (35–44 mg/L) in the Kvirila River (upstream and downstream of the CKF), and almost exceeded in a Shuqruti stream sample (Fig. 3h). In April 2009, *E. coli* values were less than the criterion (<1 cfu/100 mL) at the Gagarin water supply well and Sakurdglia, but exceeded it at the other three locations (up to at 12 cfu/100 mL at the Grudo water supply).

Metals

For total metals sampled and analyzed in April 2009, Mn and Fe concentrations exceeded the MACs in most surface water samples. Values in the Kvirila River downstream of the CKF exceeded the criteria by factors of 14.7 and 45.3, respectively. Total Mn concentrations were also very high upstream of the CKF, and in the Darkveti and Shuqruti stream samples. The total Fe concentration in the Rgani stream September 2009 sample (21.1 mg/L) exceeded the Fe MAC by 70.3 times. In the PEROF discharge (peroxide enrichment factory), total Mn concentrations ranged from 0.85 to 7.62 mg/L. Total Fe concentrations increased to 18.4 and 22 mg/L in September 2009 and June 2010 (Table 4). These increases were likely due to increased mining and processing operations during this time period.

Ca was elevated above the MAC in September 2009 in the Monasteri water supply (154 mg/L), but values were greatest in the Darkveti (203–257 mg/L) and Shuqruti (184–198 mg/L) stream samples during April and September 2009, contributing to the higher hardness and alkalinity at these locations. Mg was below the criterion at all locations for all sampling events. Na and K varied from very low values in the water supplies to much higher values in the Darkveti stream samples.

With regard to dissolved metals, Mn concentrations were very high in the Darkveti September 2009 (2.4 mg/L) and June 2010 (6.65 mg/L) stream samples relative to the MAC of 0.4 mg/L (Fig. 4a). Only two other locations exceeded the MAC: the Shuqruti April 2009 stream sample (0.91 mg/L) and the Gagarin water supply well in both April and September 2009 (0.52–0.89 mg/L). Dissolved Mn concentrations in the PEROF discharge ranged from <0.2 to 0.34 mg/L. Mn loads in most surface waters are dominated by suspended Mn, as shown by comparison of dissolved and total Mn for six of the seven surface water locations in April 2009 (Fig. 5). The exception was the Shuqruti stream sample, where dissolved Mn was the dominant form due to the lower pH at this location during this sampling event.

Dissolved Fe was only detected above the MAC in the PEROF discharge (0.68 mg/L) during the second sampling round in September 2009, and in the Rgani stream (0.8 mg/L) and Gagarin water supply samples in June 2010 (Fig. 4b). Similar to Mn, dissolved and total Fe data also indicate that Fe loads in the Kvirila River are dominated by particulate Fe.

One dissolved Ni concentration (0.1 mg/L) in the Gagarin water supply well exceeded the criterion in September 2009 (Fig. 4c). Dissolved Co and Cu were only occasionally detected below the MACs. Si concentrations varied across all sites and sampling events from 2.5 to 6.4 mg/L. Dissolved Al, As, Cd, Pb, and Zn were not detected.

River Bed Sediment

At all five surface water sites, the analyzed metals were elevated in the river bed sediment (Table 5). Background concentrations from Georgian estimates for soils were not available for Al and Fe, but Al values ranged from 3.9% in the Kvirila River upstream of the CKF to 6.7% in the Jruchula stream sediment sample (Fig. 6a). Cd concentrations exceeded the background value of 0.5 mg/kg at all five locations, and were highest in the Kvirila River upstream and downstream of the CKF (3.2–4.5 mg/kg;

Table 4 Total metal concentrations (mg/L) in water samples collected from the PEROF discharge 2009–2010 (Perophi peroxide enrichment factory)

Analyte	April 2009	September 2009	June 2010
Al	<0.02	<0.02	<0.02
Cd	<0.001	<0.001	<0.001
Co	<0.003	<0.003	<0.003
Cu	<0.003	0.014	<0.003
Fe	0.11	18.4	22.0
Mn	0.38	0.85	34.0
Ni	<0.005	0.03	<0.005

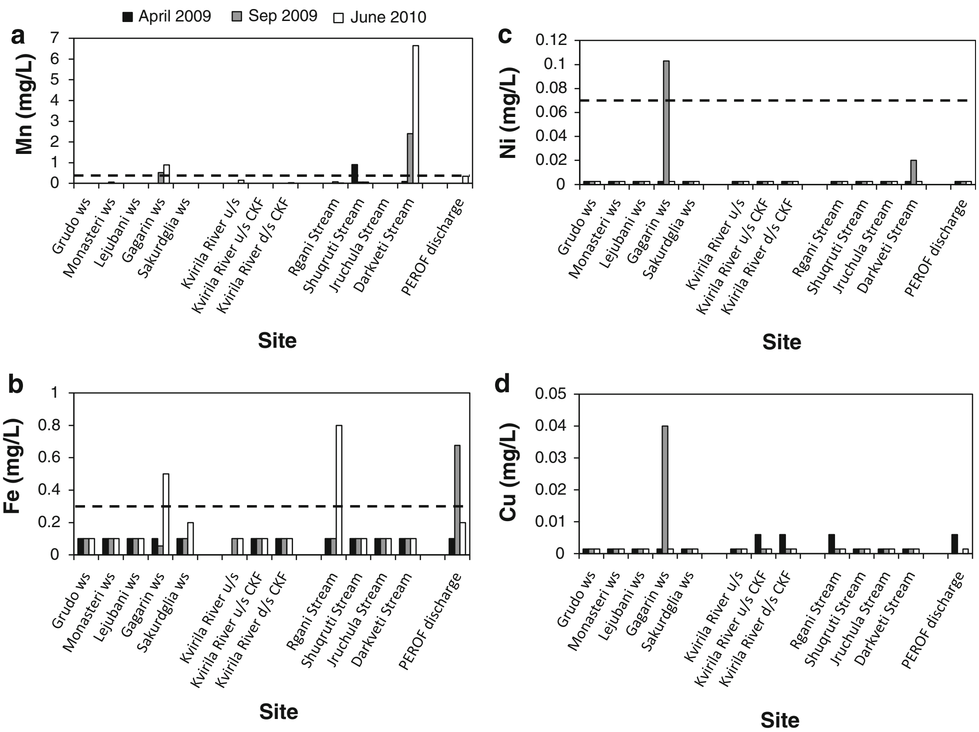

Fig. 4 Chiatura dissolved metals results in water for **a** Mn, **b** Fe, **c** Ni, and **d** Cu. *Dashed line* is Georgian maximum allowable concentration (MAC). All MACs are for drinking water; MAC for Cu is 2.0 mg/L (not shown); *ws* water supply; *u/s* upstream; *d/s* downstream

Fig. 6b). Cu values followed a similar pattern, exceeding the background concentration of 3 mg/kg and having the greatest values at those two locations (44–70 mg/kg; Fig. 6c). Mn concentrations in the Kvirila River upstream and downstream of the CKF were very high and exceeded the background value for soils of 1,500 mg/kg (in the range of 80,000–95,000 mg/kg or 8–9.5%; Fig. 6d). Mn values exceeded the background value at the other sites as well. Fe concentrations ranged from 1.5% in the Kvirila River upstream of the CKF to 3.9% for the furthest upstream Kvirila River sample (Fig. 6e). Fe concentrations were also elevated in the Kvirila River upstream and downstream of the CKF during some sampling rounds (2.4–3.6%). Ni concentrations at all five locations exceeded the background value (4 mg/kg), and values in the Kvirila River upstream and downstream of the CKF were very high (185–290 mg/kg; Fig. 6f).

Correlation analysis indicated a positive correlation between Mn and Cd, Co, Cu, and Ni, which indicates a common source for those metals. However, Fe and Al were negatively correlated with those elements.

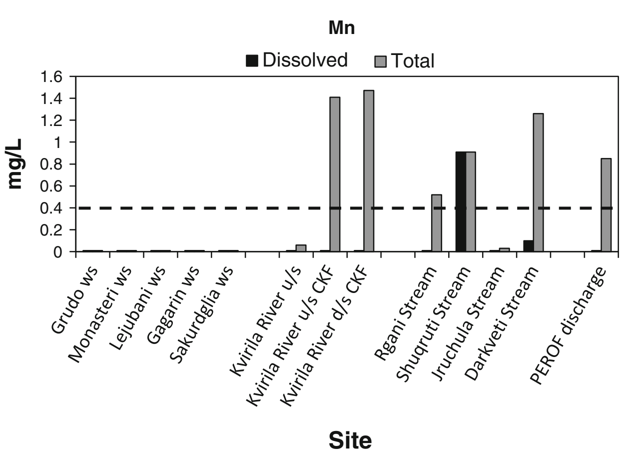

Fig. 5 Dissolved versus total Mn concentrations in water samples collected April 2009. *Dashed line* is Georgian maximum allowable concentration (MAC) for drinking water; *ws* water supply; *u/s* upstream; *d/s* downstream

Discussion

Surface water DO concentrations reflecting saturation were expected in these high gradient mountain rivers and streams with relatively high velocities and turbulent mixing. Low DO in the Gagarin water supply well, which was not purged before sampling, was also expected due to the lack of contact with air. SC was highest in the tributaries (but also most variable among these sites) and in PEROF. Values were more consistent between locations in springs and groundwater and the Kvirila River, and also lowest in this river. Elevated SC in the two tributaries (the Darkveti

Table 5 Metal concentrations in river bed sediments

Analyte	Date	Site 7 Upstream in Kvirila River	Site 9 Kvirila River upstream of CKF	Site 10 Kvirila River downstream of CKF	Site 11 Shukruti Stream	Site 12 Jruchula River
Al (%)	04/2009	6.63	3.87	4.05	4.79	6.72
	10/2009	5.25	–	–	4.42	4.97
	07/2010	6.4	–	–	5.81	6.73
Cd (mg/kg)	04/2009	2.5	4.5	4.5	2.9	2.9
	10/2009	<2.5	<2.5	<2.5	<2.5	<2.5
	07/2010	3.7	3.2	3.2	2.7	2.7
Co (mg/kg)	04/2009	20	25	25	10	20
	10/2009	15	33	31	15	16
	07/2010	18	20	25	14.5	15
Cu (mg/kg)	04/2009	30	70	60	25	35
	10/2009	20	50	50	20	40
	07/2010	30	50	44	27	36
Fe (%)	04/2009	3.5	2.4	2.2	2	3.55
	10/2009	3.15	1.5	1.5	2.1	3.05
	07/2010	3.85	2.1	1.75	2.6	3.4
K (%)	04/2009	1.48	1.46	2.06	1.92	1.67
	10/2009	1.86	1.89	1.41	2.55	1.62
	07/2010	1.43	1.6	1.22	1.92	1.53
Mn (%)	04/2009	0.08	9.5	8.5	0.12	0.5
	10/2009	0.08	8	8	0.13	1.45
	07/2010	0.10	5.35	4.8	0.25	0.15
Na (%)	04/2009	2.17	1.73	2.26	1.36	2.24
	10/2009	2.42	1.42	0.99	1.03	1.07
	07/2010	2.79	1.89	0.88	1.76	2
Ni (mg/kg)	04/2009	35	290	250	35	40
	10/2009	15	255	240	30	50
	07/2010	35	235	185	68	47.5

and Shuqruti stream samples) likely results from their high sulfate concentrations, and may indicate nearby mines, ancillary processing sites, mine waste sources, or contaminated surface or groundwater discharging to the streams via point and diffuse sources of pollution. High SC in the PEROF discharge was expected from the untreated industrial discharge. However, the reason that the two stream locations actually had higher values than the discharge is not clear and needs further evaluation. It is possible that the high SC in Shuqruti Stream may have been due to the greater dissolved Mn fraction at this location. Although SC increased somewhat from an already high value in Darkveti Stream in September 2009, it generally did not exhibit much variation between sampling events/flow regimes at other locations.

Hardness followed a very similar pattern to SC among locations, with tributaries (Darkveti and Shuqruti streams) having the greatest and most variable (among locations) values, and springs/groundwater and the Kvirila River having lower and generally more consistent values across locations. The fact that the Kvirila River had the lowest hardness values was expected, but springs and groundwater might be expected to have higher hardness than the tributaries. This potentially indicates pollution in these tributaries from nearby sources. Alkalinity was low and within the guidelines, but was generally highest in springs and groundwater and lowest in the Kvirila River, which was expected. No significant patterns in hardness or alkalinity were observed from the two sampling events when these were analyzed.

Sulfate was elevated in several of the tributaries but low at all other locations, and consistently below the MAC criterion. The circumneutral or slightly alkaline conditions and relatively low SO_4 concentrations indicates that AMD is not a problem in this area. No temporal trends in SO_4 were observed. Only the highest NO_3 value in Darkveti Stream exceeded the criterion, so this doesn't appear to be a significant issue in this mining area compared to potential

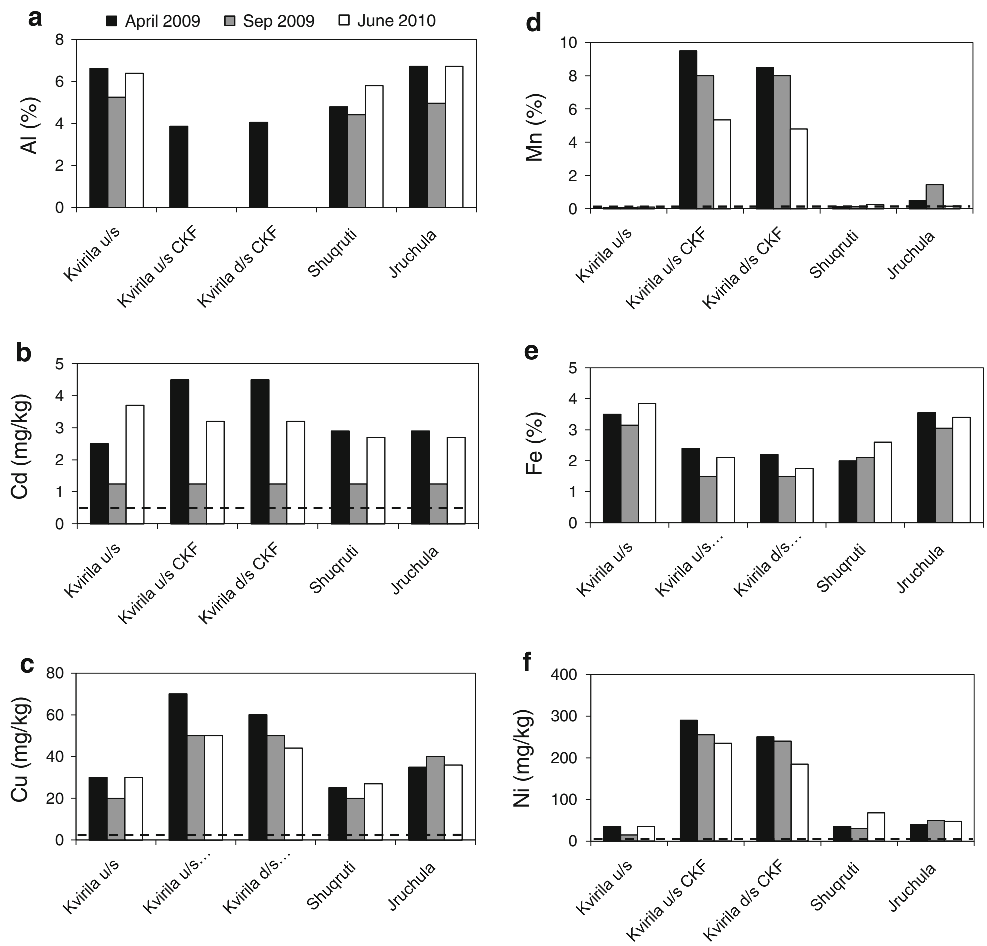

Fig. 6 Chiatura metals results in river bed sediment for **a** Al, **b** Cd, **c** Cu, **d** Mn, **e** Fe, and **f** Ni. *Dashed line* is value based on representative reference or 'background' values for Georgian soils (Ministry of Justice of Georgia 2003a, b) for comparison to river bed sediment sampling results

high concentrations in agricultural areas (Driscoll et al. 2003).

COD values exceeded the criterion in Darkveti Stream and the Kvirila River upstream and downstream of the CKF, with values approaching the criterion in Shuqruti Stream. High COD indicates some type of biodegradable organic pollution (Huch 1990). In this case, the specific organic pollutants and sources are unknown, and may or may not be associated with mining. *E. coli* values exceeded the criterion at three drinking water supply locations, and were greatest at the Grudo water supply. *E. coli* is the standard indicator of fecal contamination of water (Edberg et al. 2000). The observed bacterial contamination could be due to inadequate treatment of wastewater from nearby small communities, or from livestock or wild animals within the catchments. None of the five water supply locations are currently chlorinated or treated in any other way due to inadequate regulations and financial resources. This could result in elevated risks to human health with regard to infectious diseases compared to potential exposure to and effects from metal contamination.

With the exception of Mn and Fe, few samples had dissolved or total metal/semi-metal concentrations that exceeded drinking water MACs, and even the frequency of detection was rather low. Concentrations of dissolved and total Al, As, Cd, Pb, and Zn were all below detection limits. All drinking water supply samples met the criteria for metals, except for the Gagarin groundwater supply well, where dissolved Mn, Fe, and Ni exceeded the MACs on at least one occasion. Dissolved Cu was also very high in September 2009. The June 2010 Mn and Fe concentrations were higher than in the previous sampling events in the Gagarin groundwater supply. Total and dissolved metal concentrations were very similar between the other four public drinking water supplies.

In surface waters, the only dissolved or total metals that exceeded drinking water MACs were Mn and Fe at numerous locations and Ni in Darkveti Stream. Darkveti Stream generally had the highest concentrations of most metals, but values in the Kvirila River upstream and downstream from the CKF, and in Jruchula, Shuqruti, and Rgani streams, also sometimes exceeded criteria. As expected, the PEROF industrial discharge from the enrichment factory, which is untreated, had the highest levels of total Mn and Fe, but relatively low levels of dissolved Mn and Fe.

Concentrations of dissolved Mn increased in Darkveti Stream from April 2009 to June 2010. Increases of Na, K, Ni, and Co were also observed in 2010. These increases are generally attributed to greater inputs from metal sources and concentrations over time, rather than correlation with season or river flows; this type of time trend and correlation with flows should be evaluated further with greater temporal sampling and analysis. Both Mn and Fe concentrations were greater in the PEROF discharge in 2010 compared to previous years (Table 4). Total Mn increased to 34 mg/L in the PEROF discharge in 2010, which was much higher than previous values.

Mn oxides do not readily dissolve and can easily form solid oxy-hydroxide precipitates that can coat streambeds where high concentrations occur, or can be transported as suspended particles under adequate hydraulic conditions (Scott et al. 2002). Other metals and nutrients can co-precipitate with or sorb to Mn oxides (MnOx) on the streambed (Butler and Caruso 2009; Gadde and Laitinen 1974). This adsorption can increase significantly with an increase in pH (Gadde and Laitinen 1974). Therefore, hydrous Mn oxides can play an important role in the fate and transport of other metals in rivers, such as Cd, Cu, and Zn, and should be considered in modeling and remediation (Butler and Caruso 2009). Adsorption of metals to bed sediment is also a function of the percent of fine particles and clay, as well as organic matter/carbon (Caruso and Bishop 2009). The physical and chemical characteristics of the bed sediment and form of solid Mn and Fe on the river bed in the study area should be analyzed further.

The oxides and hydrous oxides of both Mn and Fe dissolve under reducing conditions that can occur with burial or mixing below surface layers of sediments beneath oxygenated waters (Van Cappellen and Wang 1996). Fe^{2+} and Mn^{2+} in pore water generated in the anaerobic zone can adsorb onto sediment, co-precipitate as a number of mineral phases, or move (by pore water diffusion and dispersion) back to the sediment-water interface. Redox of Fe and Mn is complex and can occur through a number of pathways, including benthic microbial and macroinvertebrate activity (Van Cappellen and Wang 1996). Biotic oxidation is an important process for removal of Mn^{2+} onto Mn oxides in the hyporheic zone and is directly proportional to Mn^{2+} concentration and pH (Fuller and Harvey 2000; Harvey and Fuller 1998; Marble 1998). Surface catalyzed oxidation and photoreduction can also be important with regard to fate and transport, especially in mountain streams (Scott et al. 2002).

The Kvirila River bed sediment metal concentrations generally were higher in 2010 than in 2009 with the exception of two locations (upstream and downstream of the CKF) where Mn concentrations in 2010 decreased (5.35 and 4.8%) compared to 2009 (9.5–8.0 and 8.5–8.0%, respectively). Cu and Ni values also decreased somewhat at these two locations. The reason for these decreases is not known, but transport and flushing of sediment from high flows could be a factor, as could dissolution of metal oxides or adsorbed metals to the water column. No other temporal trends were apparent in sediment concentrations at other locations. Although MACs for metals in river bed sediments have not been established by the Georgian government, comparison of Mn and Fe concentrations in sediment samples from the Kvirila River upstream and downstream of the CKF with Georgian background values for soils indicates that the sediments meet the criteria for “highly-polluted soils”; sediment samples from the Jruchula and Shuqruti streams meet the criteria for “low-polluted soils” (Georgia Ministry of Labour, Health and Social Affairs 2007b).

With regard to human health risks from Mn and other metals in waters in the Chiatura area, contaminant levels are not as great as might be expected and may not currently pose a significant risk, based on Georgian drinking water regulations, at most locations, with the exception of Darkveti Stream and immediately downstream from the PEROF discharge and the CKF. This water is generally not used for drinking water, but some residents may drink the water or could ingest it incidentally through swimming or other recreational activities. In the US, Mn has a USEPA standard of 0.05 mg/L, although it is considered a ‘non-priority pollutant’ and the standard is intended to minimize objectionable qualities such as laundry stains and objectionable tastes in beverages (USEPA 2009). This standard is quite a bit lower than the value of 0.4 mg/L in the Georgian regulations. Chronic or acute inhalation of Mn-contaminated dust particles from mines, processing facilities, and solid waste materials by occupational workers and nearby residents likely poses a greater human health risk than Mn and other metals in water. It appears that the more immediate health risks from water may be from fecal bacteria contamination of drinking water supplies. However, contaminated river bed sediment can serve as a chronic secondary, residual source of water pollution due to metal migration from the bed, and could pose considerable longer-term risks to human health if this water is used for drinking, economic, or recreational purposes. This can be influenced by the sediment characteristics (grain size distribution, organic matter content, etc.), sediment transport, and potential flushing during high flows (Caruso and Bishop 2009). These factors have not been studied and may require further analysis in the future.

The ecological and toxic effects of Mn and other metals to aquatic macroinvertebrates and fish have not been directly considered in this study, and these populations have not been studied in detail in Georgia or the Chiatura area. However, these biota are generally more sensitive to metals than humans and standards are typically more stringent for fish. Acute and chronic effects of the bioavailable form of many dissolved metals, such as Cd and Zn, are dependent on hardness (and alkalinity; USEPA 2009) and may be reduced if other ligands are present. International water quality standards, such as those developed by USEPA, are therefore based on this hardness dependence (USEPA 2009). Although the USEPA does not have a hardness-dependent standard for Mn, toxicity studies reporting low concentrations being toxic were done in soft water, indicating such dependence (Kleinmann and Watzlaf 1986). Mn in water can be significantly bioconcentrated by aquatic biota at lower trophic levels. Uptake by aquatic invertebrates and fish greatly increases with temperature and decreases with pH, but DO has no significant effect. Dissolved Mn concentrations of about 1 mg/L can cause toxic effects in aquatic organisms and many countries have adopted 0.2 mg/L for protection of 95% of species with 50% confidence (Howe et al. 2004).

Conclusions and Recommendations

Drinking water samples taken from three of the public water supplies (Grudo, Monasteri, and LeJubani) in the Chiatura mining area were contaminated by coliform bacteria. *E. coli* concentrations exceeded the criterion of 4 cfu/100 mL in samples from the Grudo and Monasteri supplies. Concentrations of dissolved Mn, Fe, and Ni exceeded the drinking water MAC in the Gagarin groundwater supply well.

Simple water treatment systems should be installed for the Grudo, Monasteri and LeJubani water supplies. The water should not be used for drinking without disinfection due to the risk of water-borne infectious and viral diseases. Drinking water in the catchment reservoirs of the Grudo, Monasteri, and LeJubani water supply systems should also be routinely disinfected. Drinking water quality in Chiatura's central water supply lines should be monitored based on Georgian government requirements and standard international practice to protect public health.

The communal Gagarin Street groundwater supply well should be cleaned and disinfected in accordance with Georgian government regulations and standard practices. Long-term consumption of this water may damage the digestive tract. The well should be re-sampled and analyzed for Mn, Fe, and Ni on a routine basis. If these metals continue to occur at levels above the MACs, the use of well water for drinking should be discontinued.

The Kvirila River is contaminated with Mn and Fe relative to the upstream location. Total Mn levels were almost 15 times the MAC downstream of the discharge from the CKF. Concentrations of total Mn were 2–12 times the MAC in Darkveti, Shuqruti, and Rgani streams, and total Fe values were 8–55 times the MAC in these tributaries. Mn and Fe loads in the Kvirila River and most tributaries are primarily in the particulate form. Concentrations of dissolved metals in samples from the seven surface water locations were below the MAC except for dissolved Mn in Darkveti Stream and the Kvirila River upstream and downstream of the CKF. The primary sources of Mn and Fe in the Kvirila River are the untreated industrial wastewater discharged from the CKF, tailings and waste rock associated with the Mn ore disposed of on the Kvirila River floodplain, and the main tributaries (primarily Darkveti and Shuqruti streams).

Concentrations of all metals, including Mn and Fe, in river bed sediments were elevated at all seven river sites. Mn and Ni, in particular, were very high compared to background soil levels in the Kvirila River upstream and downstream of the CKF. Although Mn and Fe oxide solids in sediment can increase adsorption and attenuation of other metals from the water column, contaminated sediments can also serve as a long-term residual source of metal contamination of river water with significant adverse ecological and potential human health effects.

Use of the Kvirila River before and after the CKF, as well as Darkveti Stream, for drinking, economic, cultural, and household purposes should be prohibited. Based on Mn concentrations, these areas are extremely highly polluted water, according to Georgian regulations. Use of these rivers may result in increased exposure to Mn and associated diseases and symptoms. Water in Shuqruti and Rgani streams meets the criterion for moderately polluted water. Water from these rivers may be used as a drinking and economic water supply source only if the pollution level is reduced through end-of-the-pipe treatment.

Solid mine waste (tailings and waste rock) have been disposed of on the floodplain surface along the Kvirila River and some tributaries. This waste material is a significant source of metals that will continue to impact the water quality and ecological health of the Kvirila River and some tributaries. Industrial mine waste from the enrichment and processing plants should be managed in a way that isolates the material from the rivers and groundwater. The specific pollution sources in the Kvirila River should be identified and evaluated, and routine sampling of the river should be conducted at key locations. Discharge of untreated wastewater from the peroxide enrichment factory into surface waters should be discontinued as soon as possible and treatment facilities should be installed at the plant.

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