Disproportionate water quality impacts from the century-old Nautanen copper mines, northern Sweden

Supplementary Material

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S1. Temperature and precipitation data:

Temperature and precipitation data were taken from the CRU TS 4.02 grid-box data at 0.5° resolution produced by the Climatic Research Unit (CRU) at the University of East Anglia (available at https://crudata.uea.ac.uk/cru/data/hrg/ and described by Harris et al. [27]. The cell 67.25 N, 20.75 E had monthly data from 1901 to 2017 and was used for water balance calculations and linear regression analysis in R to determine long-term trends.

S2. Water sampling procedure and laboratory analyses:

During the measurement field campaign at Nautanen 2017, Table S1 describes the water sampling procedure. Water samples were collected as grab sampling in plastic polypropylene 1L bottles (rinsed before the sample collection) just below the water surface. After filtering and acidification (Table 1) samples were transferred into 10 ml (metals, cations and anions) and 50 ml (organic carbon) high density polypropylene test tubes in three replicates. In addition to the water sampling, the following instruments were used directly in the field: Hanna Instrument pen (HI 98129; for water temperature, pH and electric conductivity), Hanna Checker®HC Handheld Colorimeter (for alkalinity), and a Hach 2100Q Portable Turbidimeter (for turbidity).

Table S1. Water sampling protocol for the Nautanen field campaign 2017.

Water analysis	Filtering	Preservation in the field	Until laboratory	Analysis instrument
Metals and cations	Dissolved phase: Filtropur S 0.22 µm syringe filters	Acidified* with HNO_3 (69%)	Cool and dark	ICP-OES** and CETAC Ultrasonic Nebulizer***
	Total phase: no filtering	Acidified* with HNO_3 (69%)	Cool and dark	ICP-OES** and CETAC Ultrasonic Nebulizer ***
Organic carbon	Dissolved organic carbon (DOC): Filtropur S 0.22 µm syringe filters	Acidified* with HNO_3 (69%)	Cool and dark	Shimadzu TOC-V CPH Instrumental accuracy: ±0.2 mg C l^{-1}
	Total organic carbon (TOC): no filtering	Acidified* with HNO_3 (69%)	Cool and dark	Shimadzu TOC-V CPH. Instrumental accuracy: ±0.2 mg C l^{-1}
Anions	Total phase: no filtering	-	Cool and dark	Thermo Scientific™ Dionex™ Ion chromatography. Instrumental accuracy: 10%

* Corresponding to 1% of the sample volume.
** Inductive coupled plasma optical emission spectrometry. Instrumental accuracy: 10% (±5%).
*** For trace element concentrations.

All the water samples collected in the field 2017 were analyzed at Stockholm University, Sweden. Specifically, the metals and cations were analyzed at the Department of Geological Sciences, and the organic carbon and anions were analyzed at the Department of Environmental Science and Analytical Chemistry. Analysis of metal and cation concentrations was tested for about 50 different elements at the laboratory. From the analysis results, the following selection processes included removing elements if they:

(1.) had more than 85% of its values below the instrumental detection limit, or

(2.) had a difference larger than 10% between the calculated mean values (i) and (ii), obtained by assuming that (i) all values below the detection limit were equal to zero, and (ii) all values below the detection limit were equal to the detection limit, or

(3.) had an average triplicate coefficient of variation (CV) of more than 0.15 [34].

This resulted in 37 remaining elements: Al, Ba, Be, Ca, Cd, Ce, Cl, Co, Cu, F, Fe, K, La, Li, Mg, Mn, Mo, Na, Ni, P, S, Si, Sr, Ti, V, Y, Yb as well as SO_4 and DOC. From this list, the 11 elements; Al, Ba, Cd, Co, Cu, Fe, Mn, Mo, Ni, DOC and SO_4, were chosen for more detailed analysis due to their common association with mining activities and related geochemical processes [32]. An exception to the above selection process was Zn, that had all its values above the detection limit but the triplicate CV was 0.20 (compared to the threshold of 0.15). The higher CV came mostly from triplicates of samples with lower Zn concentrations (<10 µg/L) while the majority of the samples had their triplicate CV below 0.15. Since a high content of Zn in tailings could increase formation of acid mine drainage [33] we included Zn to the list of elements for further analysis. As, Pb and Cr had all values close to or below the detection limit and were not included in further analysis. The difference between dissolved and total concentrations, as well as the difference between samples collected in May and August, were analyzed through paired (dependent) t-test in R.

The historical field data were reported to have been analyzed with inductive coupled plasma mass spectrometry (ICP-MS), or sector field mass spectrometry (-SFMS) or atomic emission spectroscopy (-AES) at SWEDAC accredited laboratories SGAB (Svensk Grundämnesanalys AB) and ALS Scandinavia between 1993 and 2014. Most of the sampling locations of these previous campaigns were similar to our sampling locations in 2017, however they used other reference streams and some additional downstream locations below our most downstream location (D2 at 4 km downstream of the main mining zone).

S3. Water balance calculations:

The water balance calculations were based on temperature and precipitation data from CRU (described in S1). The monthly temperature data was further averaged into an average temperature for each year (*T*), and the monthly precipitation data was summed to an annual total precipitation (*P*). Thus, for each year, the water balance was calculated through:

$$P = ET_a + R + \Delta S \tag{S1}$$

where ET_a is annual actual evapotranspiration, *R* is annual runoff and ΔS is the change in storage. If assuming ΔS is zero over a hydrological year, then solving for *R* reduced the equation to:

$$R = P - ET_a \tag{S2}$$

Actual evapotranspiration, ET_a, was calculated through the equation by Turc [36]:

$$ET_a = \frac{P}{\sqrt{0.9 + \frac{P^2}{ET_p^2}}} \tag{S3}$$

where the potential evapotranspiration, ET_p, was derived by Langbein [37] as:

$$ET_p = 325 + 21T + 0.9T^2 \tag{S4}$$

The discharge at the D2 location, Q_{D2}, was calculated by:

$$Q_{D2} = R * A \tag{S5}$$

where *A* is the catchment area (6.6 km^2) at the D2 location 4 km downstream of the main mining zone. Finally, the discharges were averaged over the considered time period (e.g. the 25-year period of 1993 to 2017, or the 110-year period of 1908-2017) to yield an average discharge ($\bar{Q}_{L,D2}$ and $\bar{Q}_{100,D2}$, respectively).

Table S2. Results in base chemistry of surface water samples from the 2017 measurement campaign at Nautanen. Coordinates are in WGS 1984.

Sampling zone		Sampling point description	N-coordinate	E-coordinate	Month	Q (l s^{-1})	pH (-)	Temp. (°C)	EC (µS cm^{-1})	Alkalinity (ppm $CaCO_3$)	Turbidity (NTU)
Local background	Upstream	Upstream headwater lake	67.20631	20.86605	Aug	5.18	3.78	13	1	3	0.63
Local background	Upstream	Upstream the Dagny mine	67.20137	20.86803	Aug	16.8	5.9	6.1	8	11	0.95
Local background	Ref. River	Nietsajoki stream, before junction with Imetjoki	67.17471	20.94924	May	1180	6.91	2.92	5	6	-
					Aug	1100	6.78	9.42	11	5	1.06
Local background	Ref. River	Lina River, close to Koskullskulle village	67.19270	20.75793	May	-	6.86	3.71	22	13	-
					Aug	-	6	10.5	49	12	1.29
Mining zone		Northern Lake outlet	67.19771	20.87255	May	8.5	6.02	2.21	7	11	-
					Aug	4.97	6.1	13.5	21	14	0.7
Mining zone		Imetjärvi Lake inlet	67.19686	20.87686	May	15.4	6.46	3.11	5	8	-
					Aug	21.6	6.12	10.5	11	12	0.61
Mining zone		Inside Maria mine	67.19313	20.87471	Aug	-	6.32	2.52	21	13	1.76
Mining zone		Maria Lake outlet	67.19465	20.87921	May	-	5.7	6.89	7	10	-
					Aug	-	5.65	13.9	11	4	1.32
Mining zone		Small stream at industrial area, upper part	67.19508	20.88327	May	-	3.26	6.77	594	0	-
					Aug	-	4.79	11.3	132	8	63.7
Mining zone		Smaller stream at industrial area, lower part	67.19455	20.88484	May	2.85	6.23	4.68	181	9	-
					Aug	17.9	6.11	11.5	171	12	1.29
Mining zone		Imetjärvi Lake outlet	67.19550	20.87952	May	48.6	6.05	2.12	8	14	-
					Aug	24.2	5.85	13.5	11	11	1.01
Mining zone		Max mine outflow	67.18951	20.88706	Aug	-	6.82	3.5	60	23	0.84
Downstream 1		Directly below industrial area	67.19420	20.88862	May	110	7.1	2.13	8	12	-
					Aug	55.6	6.84	11.3	19	7	0.89
Downstream 1		Further below industrial area, after wetland	67.19415	20.88998	Aug	-	6.72	11.4	17	10	0.9
Downstream 1		Small brook in the forest draining the area 250m below Fredrik mine	67.19120	20.88791	May	-	6.54	1.16	29	17	-
Down-stream 2		Downstream Imetjoki before junction with Nietsajoki River	67.17489	20.94776	May	82	6.81	3.88	13	4	-
					Aug	158	6.98	9.81	17	15	0.91

Table S3. Results of total element concentrations in surface water samples from the 2017 measurement campaign at Nautanen. All concentrations are in µg/L and are the triplicate median. Numbers in red had values below detection limit and was therefore replaced by the detection limit value (see text S2).

Sampling zone		Sampling point description	Month	Cu	Zn	Co	Cd	Ni	Mo	Ba	Mn	Al	Fe	DOC	SO_4
		Detection limit value:		0.0278	0.0604	0.032	0.00904	0.07	0.0137	0.0174	0.00485	0.0294	0.0324	200	200
		% below detection limit:		0	0	14	1	56	4	0	0	0	0	0	4
Local background	Upstream	Upstream headwater lake	Aug	0.953	4.14	0.1	0.0135	0.07	0.0137	4.5	7.69	104	187	11600	200
Local background	Upstream	Upstream the Dagny mine	Aug	9.17	3.28	0.032	0.0145	0.07	0.325	3.47	1.23	31.1	14.2	2540	1290
Local background	Ref. River	Nietsajoki stream, before junction with Imetjoki	May	0.574	1.36	0.032	0.0192	0.07	0.154	5.81	12	31.2	556	5400	909
			Aug	0.603	2.42	0.032	0.0217	0.07	0.214	7.56	18	34	451	7400	945
Local background	Ref. River	Lina River, close to Koskullskulle village	May	0.755	1.38	0.0545	0.0254	0.07	0.251	6.08	9.11	45.2	609	6460	5890
			Aug	1.83	2.29	0.224	0.0181	0.0982	0.784	8.08	11.4	45.4	363	6820	11600
Mining zone		Northern Lake outlet	May	53.6	5.31	0.678	0.0124	0.07	0.517	8.54	15.8	79.2	155	4480	3180
			Aug	28.3	3.98	0.122	0.0131	0.07	1.17	10	5.57	38.6	97	4800	5350
Mining zone		Imetjärvi Lake inlet	May	11.4	2.92	0.235	0.0177	0.07	0.331	6.11	26.8	56.8	274	5330	1420
			Aug	13.2	3.73	0.325	0.0288	0.07	0.422	7.9	25.4	82.5	462	8960	1170
Mining zone		Inside Maria mine	Aug	344	16.6	2.73	0.0255	0.57	0.508	24	34.3	110	157	3160	7620
Mining zone		Maria Lake outlet	May	245	9.88	1.98	0.0338	0.198	0.132	22.3	41.5	175	458	6800	3110
			Aug	269	11.6	2.33	0.031	0.248	0.285	23.4	48.3	157	457	8350	5130
Mining zone		Small stream at industrial area, upper part	May	5060	4380	40.6	14.8	0.07	0.526	38.7	707	3910	15800	1540	153000
			Aug	1250	843	7.03	2.8	1.81	0.807	25.5	248	848	1120	2050	56100
Mining zone		Smaller stream at industrial area, lower part	May	2920	776	12	2.69	5.57	0.76	36.8	389	274	26.8	1310	65800
			Aug	2530	721	7.9	2.65	4.58	0.823	29.9	295	248	30.3	1810	72900
Mining zone		Imetjärvi Lake outlet	May	66	4.93	0.682	0.0262	0.07	0.318	11.5	48	80.1	308	5490	1890
			Aug	57.9	6.19	0.267	0.0203	0.07	0.499	9.74	31.8	60.4	248	6050	2180
Mining zone		Max mine outflow	Aug	582	20	5.31	0.0425	0.806	3.08	11.2	41.6	34.4	27	2000	12900

Downstream 1	Directly below industrial area	May	90.7	22	0.525	0.0828	0.07	0.366	9.4	38.9	64	340	5200	3070
		Aug	148	46.1	0.428	0.163	0.228	0.453	11.7	28.6	61.6	309	6730	5400
	Further below industrial area, after wetland	Aug	138	44.1	0.47	0.155	0.182	0.474	11.2	36.2	61.5	358	6600	4930
	Small brook in the forest draining the area 250m below Fredrik mine	May	19.9	3.53	0.032	0.00922	0.0791	0.875	8.65	0.386	60.2	24.8	5270	7620
Downstream 2	Downstream Imetjoki before junction with Nietsajoki River	May	39.6	9.47	0.141	0.0416	0.07	0.245	10.6	42.7	42.4	495	5300	1860
		Aug	37.2	11.3	0.105	0.0403	0.07	0.334	12.7	47.8	35.3	382	6560	1610

Table S4. Synthesis of historical field measurement campaigns at Nautanen.

Year	Source	Total Cu concentration (μg/L)	Original sampling ID	Sampling zone	Description
1993	Larborn, 1993 [19]	230	-	Main mining	Stream at the industrial area
		240	-	Main mining	Stream at the industrial area
		4.6	-	Far downstream*	Downstream of the Imetjoki-Nietsajoki junction
1994	Eriksson, 1994 [31]	0.79	Ref 2	Local background	Up on the hill next to Dagny mine
		3.2	Ref 3	Local background	In the forest NE of main mining zone
		190	Naut 1	Downstream 1	Downstream industrial area, below wetland
		51	Naut 4	Downstream 2	Downstream Imetjoki, before Nietsajoki junction
		7.9	Naut 5	Far downstream*	Downstream of the Imetjoki-Nietsajoki junction
2001	Bergman 2002 [18]	1.7	Naut bäcken	Local background	Nautanen stream (south of the Nautanen hill)
		<1	Nietsajoki	Local background	Nietsajoki stream
		19	Dagny 5	Main mining	Stream from Dagny mining site
		11	Mellansjö 3	Main mining	Stream to Imetjärvi
		660	16	Main mining	Surface water, Maria mine
		860	-	Main mining	Stream between Maria Lake and Imetjärvi
		860	8	Main mining	Stream between Maria Lake and Imetjärvi
		58	5	Main mining	Stream from Imetjärvi

		58	4	Main mining	Small stream towards industrial area
		103	4	Main mining	Small stream towards industrial area
		260	4	Main mining	Imetjoki, upper part of industrial area
		440	3	Main mining	Stream through industrial area
		120	3	Main mining	Imetjoki after junction at industrial area
		79	3	Main mining	Stream through industrial area after junction
		704	9	Main mining	Surface water Max mine
		120	-	Downstream 1	Downstream industrial area
		35	-	Downstream 2	Downstream Imetjoki, before Nietsajoki junction
2005-2009	Jonasson and Grahn 2015 [23]	27-81	7 OF	Main mining	At Dagny mine
		16-30	6 OF	Main mining	Into Imetjärvi
		1010-1700	5 OF	Main mining	Maria mine
		380-760	4 OF	Main mining	Stream between Maria Lake and Imetjärvi
		57-91	8 OF	Main mining	Outflow Imetjärvi
		43-97	2 OF	Main mining	Upper industrial area
		590-1060	1 OF	Main mining	Max mine
		107-170	3 OF	Downstream 1	Downstream industrial area
2014		0.16-2.4	C16 OF	Local background	Nietsajoki stream, further upstream of junction with Imetjoki
		5.8-8.6	A11 OF	Main mining	Outflow from Northern Lake
		9.2-18	7 OF	Main mining	At Dagny mine
		7.0-12	6 OF	Main mining	Into Imetjärvi
		330	5 OF	Main mining	Maria mine
		330-340	4 OF	Main mining	Stream between Maria Lake and Imetjärvi
		68-86	8 OF	Main mining	Outflow Imetjärvi
		28-50	2 OF	Main mining	Upper industrial area
		780	1 OF	Main mining	Max mine
		120-160	3 OF	Downstream 1	Downstream industrial area
		120-140	9 OF	Downstream 1	Downstream industrial area
		120-130	B12 OF	Downstream 1	Downstream industrial area, about 670m downstream Imetjärvi at the second wetland
		3.9-6.6	D OF	Far downstream*	Downstream, 7 km below main mining zone

** Further downstream than our sampling zone D2.*