Chemical composition of the attributors to Storån, Uppsala, and the potential link to acid sulfate soil leaching.

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Abstract

Acid sulfate soils (ASS), are an important environmental problem for the Swedish coast. Oxidation of the sulfide-bearing soils can release sulfate, acid, and several metals to the surrounding waters. This project investigates whether tributaries in the Storån, outside Uppsala, show any evidence of elevated sulfate concentrations related to acid sulfate soils. It also investigates if the sulfate and selected elements occur in their dissolved or colloidal phase, and the stable isotope data on water and carbon point to a specific source. Water samples were collected from two tributaries and analysed for pH, conductivity, alkalinity, major ions, trace elements, stable water isotopes ($\delta^{18}O$, $\delta^{2}H$), and dissolved inorganic carbon isotopes ($\delta^{13}C$-DIC). 0.2µm filtration and tangential flow filtration were used to investigate the composition of the different fractions. The results suggested that Fe and Al were more strongly associated with colloidal material, whereas sulfate appeared to be mainly in the truly dissolved phase. The result showed a clear hydrochemical difference between the two tributaries. Tributary 1 showed higher sulfate concentrations, lower pH, lower alkalinity, and higher concentrations of Al, Mn, and Fe, indicating potential acid sulfate soil influence. Tributary 2 showed higher pH, higher alkalinity, and higher chloride and sodium concentrations. Stable water isotopes indicate a similar meteoric water source for both tributaries, while the $\delta^{13}C$-DIC suggests a mixed carbon source influence in the tributaries. Overall, at least one of the studied tributaries was potentially affected by the acid sulfate soil that warrant further analyses.

Keywords: Acid sulfate soils, sulfate, Storån, hydrochemistry, tangential flow filtration, dissolved inorganic carbon, $\delta^{13}C$, DIC, stable water isotopes, $\delta^{18}O$, $\delta^{2}H$, trace elements

Innehåll

Introduction

1.1 Background

The geochemical impact of the acid sulfate soils (ASS) (Asif et.al., 2025) oxidation is closely linked to the elements sulfur (S) and iron (Fe). Iron sulfides like pyrite (FeS_2) and other sulfide minerals oxidize, producing sulfuric acid and releasing sulfate ions (SO_4^{2-}) that strongly affect the water chemistry and the surrounding soils (Nyman, 2025). It also enhances the release of metals such as Cd, Co, Mn, Ni, and Zn, and increases their mobility, which makes these acid sulfate soils an important source of acidification and contamination in aquatic systems (Johnson, 2024). Rivers affected by acid sulfate soils are therefore characterized by elevated sulfate concentration, low pH, and an increased concentration of dissolved or mobilized metals (Nyman et al., 2023; Nystrand et al., 2013).

One of the main environmental problems we face today along the Swedish coast is the high content of sulfide phases (usually Pyrite) in soils and sediments, or acid sulfate soils (ASS) (Asif et.al., 2025). When these types of soils are waterlogged, they are usually relatively stable, but when they are exposed to oxygen, the minerals begin to oxidize and generate acidity, lowering the pH and releasing sulfate to the surrounding waters as sulfuric acid (Nyman, 2025; Johnson, 2024). This can occur when the groundwater table is lowered naturally or via construction and mine related drainage (Lundgren et al., 2022).

In the Baltic region, accumulation of organic matter has been deposited under low oxygen conditions, creating sediments bearing sulfides and eventually acid sulfate soils. The deposition of these sediments mainly occurred in a postglacial marine environment that was later uplifted through isostatic rebound (Nyman, 2025). Sweden and Finland, therefore, host most of the boreal acid sulfate soil environments in Europe. There are several recent research projects pointing to the extension of sulfate soils and their widespread occurrence in Sweden (Åström, 2022). It has been known in northern Sweden, but only recently has it also been recognized in the southern parts of Sweden. The Swedish Environmental Protection Agency concludes in their report that these soils can contaminate the nearby watersheds by releasing high amounts of acid and metals to the groundwater and surface runoff, which is an important environmental issue, especially for areas that used to be below the sea level (Åström et al., 2024). Some studies in Finland and Sweden have pointed out that sulfate and metal leaching from acid sulfate soils can increase after drought. When dry conditions lower the water table, the soils bearing sulfide could be exposed to oxygen. Subsequent oxidation of sulfide-bearing soils releases sulfate and metals into rivers. In several examined places, the sulfate concentration increased after the drought and remained elevated for several years afterwards (Åström, 2022).

1.2 Sulfate transport, water source, and carbon source

Sulfate is one of the most important indicators of sulfide oxidation. However, sulfate concentrations alone are not enough to prove that acid sulfate soils are the source, since the river sulfate can also come from other sources like atmospheric deposition, weathering, or local inputs (Wang et al., 2025). For that reason, sulfate must be interpreted together with other hydrochemical variables, such as pH, alkalinity, major ions, trace elements, and isotope data (Wang et al., 2025).

It is also important to understand whether S and the associated elements are associated with the particles and colloidal in the river. Substances in their truly dissolved phase are generally more mobile

than substances connected with colloids or larger particles. To this aim, we apply tangential flow filtration to separate and analyse the individual fractions (Dabrin, Roulier and Coquery, 2013).

Stable isotopes of water are included in this project to help identify the source of water in the tributaries. The isotopic composition of water, expressed as $\delta^{18}O$ and $\delta^{2}H$, can be used to understand recharge, mixing, and evaporation. Comparing these values with meteoric water lines is a method often used in hydrology and can tell us about the water origin (IAEA, 2013). In the same way, stable carbon isotopes of dissolved inorganic carbon ($\delta^{13}C$-DIC), together with alkalinity and pH, can be used to understand carbon sources and processes (IAEA, 2013).

Although acid sulfate soils in Sweden are now better recognized than before, there are still some important knowledge gaps at the catchment scale. National studies have shown that these soils are widespread and environmentally significant, but the hydrochemical responses of many local river systems remain poorly constrained. This means that these types of field studies are needed, especially in areas where soil samples already collected show proof of acid sulfate soil (Nyman et.al., 2023). The Storån area is therefore a good starting point for investigating if local tributaries show any evidence of sulfate and metal release related to acid sulfate soil processes.

1.3 Aim of the project

This project investigates the chemical composition of two tributaries in Storån, Uppsala, and evaluates whether the sulfate concentration in these waters could be linked to acid sulfate soils from the surrounding catchment (Nyman et.al., 2023). In addition to this, the project also aims to examine whether the sulfate is mainly present in the truly dissolved phase or associated with the colloidal phase, which is investigated through tangential flow filtration. By using stable isotope analyses of water and dissolved inorganic carbon (DIC), we analyse the origin of the water source and possible contamination and pollution in the water. The approach to this project combines field measurements, trace element analyses, alkalinity and pH measurements, isotopes analyses, and other analyses that give us a comprehensive chemical profile of the sampled water from the tributaries in the study area.

This project will address the following questions:

-Do the rivers from the Storån area contain a high concentration of sulfate that can potentially be attributed to acid sulfate soils in the area?

-Is the sulfate present in the truly dissolved phase or associated with the colloidal phase?

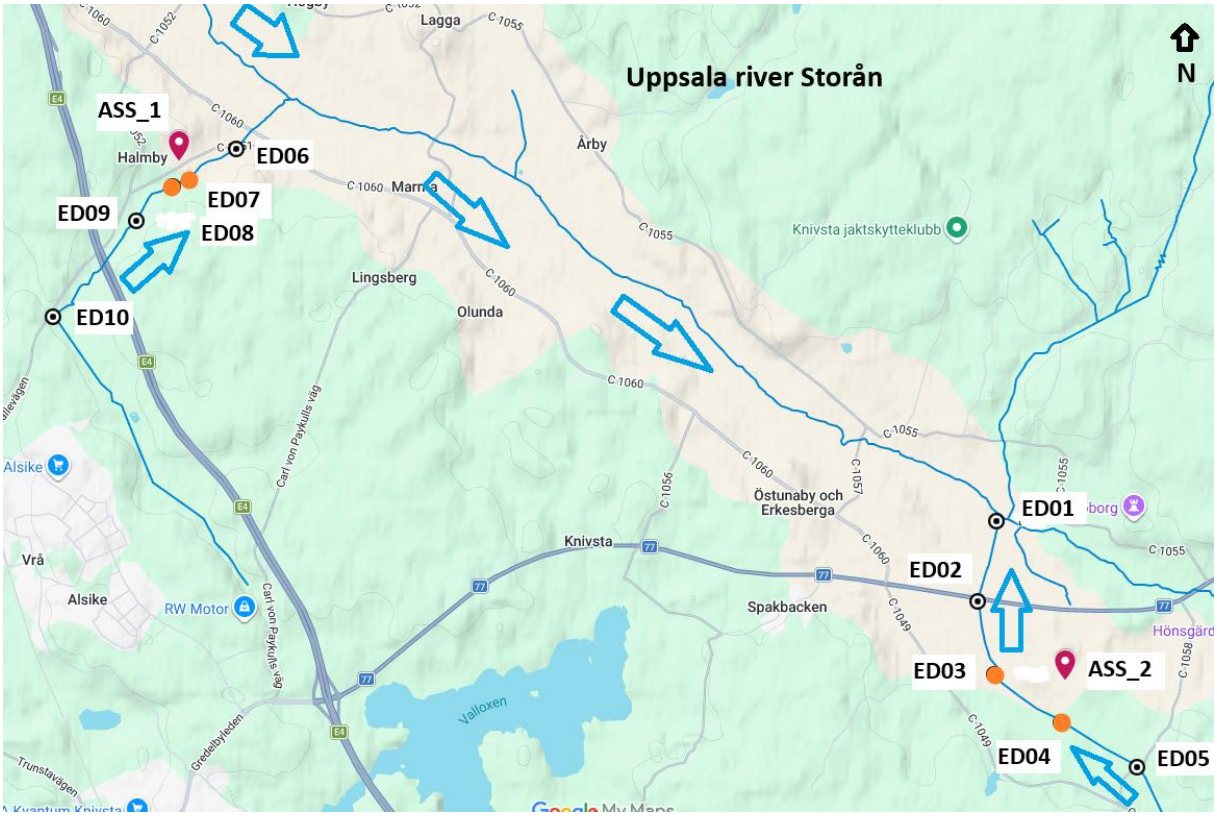
-What is the source of water, based on the stable water isotope analyses?

-What is the source of carbon based on carbon isotope analyses of dissolved inorganic carbon?

Materials and methods

2.1 Study area and field sampling

Water samples were collected from two tributaries connected to the Storån river system in the Uppsala area (Map 1). The sampling sites were selected to represent tributaries located close to areas where acid sulfate soils have already been reported (Nyman et.al., 2023).



Map 1. Map of the sampling site at Storån River. Blue arrows indicate the direction of water flow. Samples are marked with ED01-ED10, whereas ED01-ED05 belong to Tributary 1 and ED06-ED10 belong to Tributary 2. ASS_1 and ASS_2 mark the ASS previously identified by Nyman et.al. (2023). At the two range markings, a larger container of water was collected. Sampling occurred in order from ED01 to ED10.

The purpose of this project was also to compare the two sites with each other and their hydrochemistry to assess if any evidence of acid sulfate soil leaching can be found from the tributary. The sampling was carried out on the 8th of April 2026 (Map 1). At each site, surface water samples were collected in acid-washed 10 mL sampling tubes. pH and temperature measurements were performed on site using a WTW Multi 3510 IDS meter with a WTW FDO© 925 probe. The electric conductivity measurements were not performed in the field but later that day in the lab due to malfunctioning equipment (using a HANNA HI 991300 ph/EC/TDS meter). For 4 of the sites, two from each tributary, a larger 5 L container of water was also collected in addition to the smaller 10 mL sampling tube (see map 1). All water samples were stored in closed, chilled boxes during transport to maintain the in-situ temperature of the river samples.

2.2 Laboratory analyses

Membrane filter (0.2 µm) filtration

After the fieldwork, the samples were prepared for a series of laboratory analyses. The 10mL samples collected from each location were filtered with 0.2 µm syringe filters later in the lab. To investigate the phase distribution of sulfate and associated elements, 4 different samples were chosen to be first filtered through 0.2µm polycarbonate filters, PC (Sartorius polycarbonate track-etched filters type 23007 with Dim: 47mm). The samples chosen to be filtered were 2 from each tributary and closest to the 2 sampling points of the acid sulfate soil already found in the area (Map 1). The PC filters were stored in petri dishes and weighed before starting the filtration. The set-up of the 0.2 µm filtration contained the weighed filters, 4 different water samples collected, a vacuum pump, beakers for the samples with filter holders in the bottom, and collection flasks with water guards (Figure 1). At the start of the filtration, before introducing the water samples, the PC filters were acid washed with 50 mL 12% triple-distilled high grade HCl and then rinsed with distilled water (MQ) to prevent any contamination. In total, 32 filters were used for 4 samples. After the acid wash, the water samples were added to the filtration, and 3 L in total were filtered for each sampling station. The filters were then freeze dried and weighed again. These filters were then examined using a scanning electron microscope (SEM). The SEM observations were primarily used as a complementary approach to provide some insight into particle morphology, the presence of organic material, and possible mineral phases that could be relevant to sulfur and metal transport.

Figure 1. 0.2µm filtration complete setup with PC filters, water samples, vacuum pump, beakers with filter holders, and collection flasks with water guards.

Tangential flow filtration

After the 0.2µm filtration, two of the collected filtrates of 2L per sample were then used further in the tangential flow filtration method (TFF). The TFF (Easy-load Masterflex 1/P Millipore) used a microfiltration filter (Pellicon 3 0.57m^2 cassette from Millipore) and was then set up using the pump, speed 8 with tightening 3, together with the Pellicon filter that had been stored in 0.16 M Acetic Acid with pH between 2-3 before use. The filter was then rinsed with pH=2 HCl (500µl 30% triple-distilled high grade HCl in 1 L MQ water) for 10 minutes, rinsed with 1 L of MQ for 10 minutes times 2, and then with 0.5L of the sample. This was to prevent any contamination (Figure 2). The TFF took around 2 hours,

and 0.8 L Permeate and 1.2 L Retentate were then collected from both samples (Figure 2). TFF can be used to distinguish between the truly dissolved fraction and the colloidal fractions (Dabrin, Roulier, and Coquery, 2013).

Figure 2. Tangential flow filtration setup and collected retentate and permeate to illustrate the clear difference after filtration.

Ion chromatography

The major dissolved ions were analysed by using ion chromatography (IC). Prior to the analyses, all 10 samples in their original state were diluted 10x and 100x in acid washed vials. (Shimadzu Ion Chromatograph Dual Channel System and 15 standards. 4 MU4 1000 ppm standards, 5 IV-59 1000 ppm standards, one A4 1 ppm and one A5 2 ppm standard, also, an MQ blank (distilled water) and an IAPSO 1000 standard).

Inductively coupled plasma-Mass spectrometry (ICP-MS)

For analysing the trace elements and metals, we used the ICP-MS (Inductively Coupled Plasma Mass Spectrometry) (Thermo Scientific iCAP TQ ICP-MS) This was to evaluate whether sulfate enrichment, together with metal concentrations, could point to ASS influence. The analysis in ICP-MS used certified standard SLRS-6 for the metals and in-house standard (Si_H) for silicate, these were added twice in the measurement. Dilution correction was performed, and the limit of quantification (LOQ) for the replicates was also calculated (Table 2). These results were later compared between tributaries and between filtered fractions. This dataset was used mainly to assess whether sites with lower pH or higher sulfate also showed elevated concentrations of metals.

Total Alkalinity analysis

For the measurement of total alkalinity (TA), we used acid titration (Metrohm auto alkalinity titration). 9 out of 10 samples were measured (Table 1). The samples were diluted 50x in non-acid-washed Falcon tubes to a total volume of 30ml. In this thesis, alkalinity was interpreted together with pH, conductivity,

major ions, and δ^{13}C-DIC to evaluate whether differences between tributaries were related to variations in buffering capacity and possible carbonate dissolution (Rounds and Wilde, 2012).

Water isotope analysis

For the water isotope, we used a Water Isotope Analyzer (Cavity Ring-Down Spectroscopy from Picarro located in the stable isotope lab at SU). The certified QC standard MIX4 was analysed 3 times in the analysis. The water isotope data were used to compare the tributaries and to assess whether they reflected similar or different source water signatures compared to the global meteoric water line (Figure 12).

Carbon isotope analysis

Lastly, we analysed the stable carbon isotopic ratio of dissolved inorganic carbon with isotopic ratio mass spectroscopy (Isolink Elemental Analyzer coupled with DeltV Advantage IR-MS from Thermofischer Scientific). First, 10 exetainers were prepared by adding phosphoric acid and then flushed with helium. The sampled water was then injected into the vials, and then analysed in the stable isotope lab at Stockholm University. 4 different standards were used, in-house standard Merck (Ca_2CO_3), and Carm2 (Ca_2CO_3), and certified standards NBS18 and IAEA603, which were also used for calibration. The δ13C-DIC data were then evaluated together with TA and pH to interpret possible carbon sources and geochemical controls in the river water (Singleton, Kinga, and Coplen, 2012).

2.3 Data treatment

The data was compiled and processed in Excel and in the free software Matplotlib using the Python programming language. The concentrations were corrected for dilution where it was relevant, and the results were then grouped by tributary and sampled order to compare them to each other. Standard deviation, minimum, maximum, median, and mean were calculated when appropriate, and the data were visualized using different types of plots presented in the results section. Analytical quality was assessed using standards, replicate measurements, dilution correction, and limit of quantification (LOQ) checks where it was relevant. These steps were included to improve the credibility of the concentration data used in the interpretation. The visualization of the data aims to highlight differences among the tributaries and relationships among sulfate, alkalinity, pH, conductivity, isotopes, and trace elements. Ion ratios were also evaluated as a part of the chemical interpretation.

Results

3.1 Overview of tributaries' hydrochemistry.

Figure 3 and Table 1 show an overview of the main hydrochemical variables measured in the two tributaries. The pH values were generally lower in Tributary 1 than in Tributary 2. Tributary 1 ranged from 6.23 to 6.80, with a mean of 6.52, while Tributary 2 ranged from 6.96 to 7.56, with a mean of 7.20. A similar pattern was observed for alkalinity. Tributary 1 had lower alkalinity values, ranging from 2.49 to 3.25 µeq/L, and Tributary 2 ranged from 3.16 to 3.60 µeq/L. The alkalinity statistics for Tributary 1 are based on four samples, since ED02 had no alkalinity measurement due to a spilled water sample.

Regarding conductivity, Tributary 1 contained both the highest and the lowest values in the dataset, otherwise it overlaps with Tributary 2 (Figure 4). The stable isotope values are similar in both tributaries, but Tributary 1 shows a little more spread in the values, and Tributary 2 has a narrower range. The δ^{13}C-DIC values differ more clearly between the Tributaries. Tributary 2 showed lower and less variation in the δ^{13}C-DIC values than Tributary 1 (Figure 3). Additional plots of pH vs alkalinity, pH vs conductivity, and conductivity vs alkalinity are used to compare the hydrochemical relationship between the tributaries (Figure 4). These plots show that Tributary 2 has higher alkalinity and higher pH, while conductivity overlaps across the tributaries.

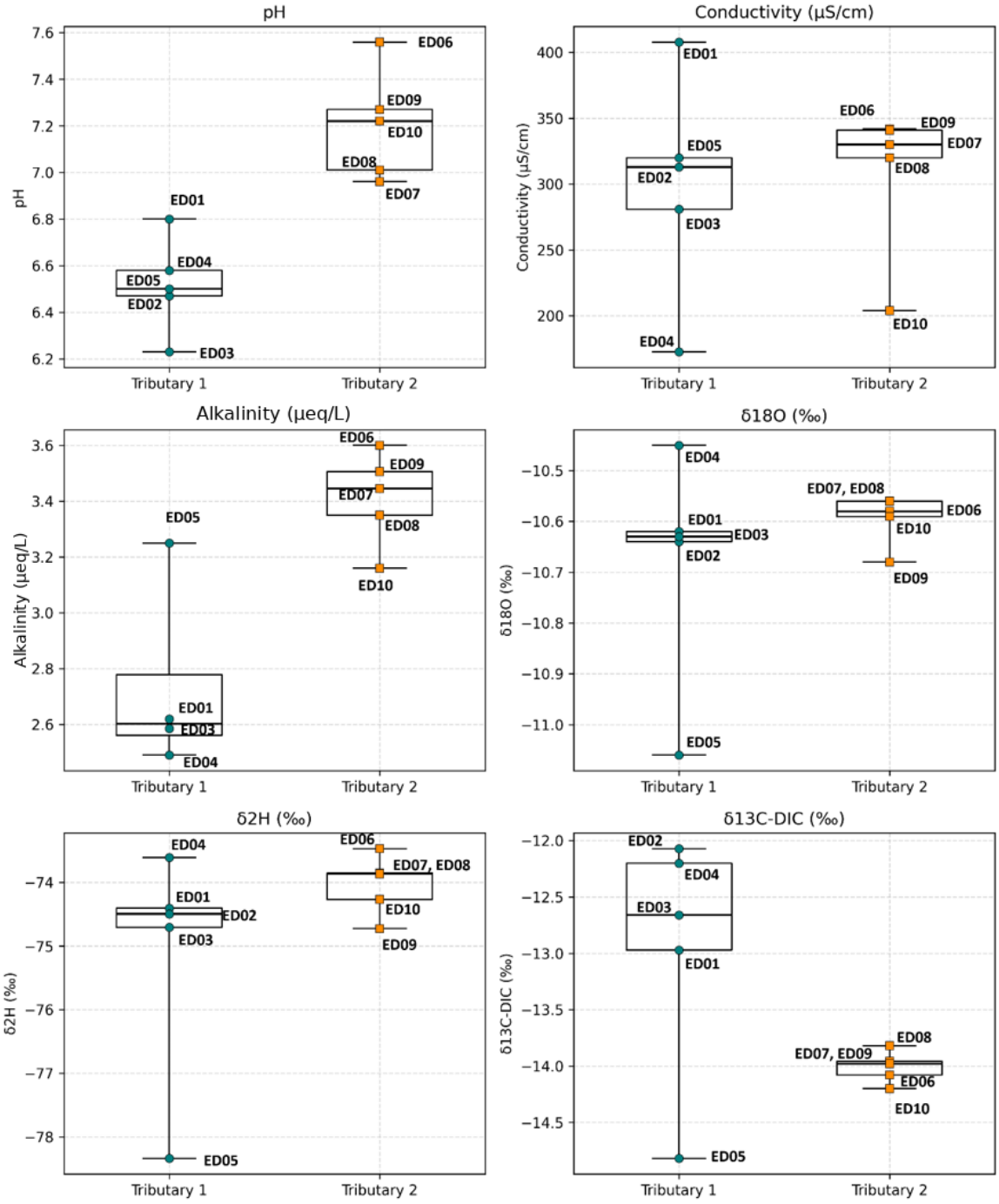


Figure 3. Overview of tributary hydrochemistry in the Storån study area. Boxplots showing pH, conductivity, alkalinity, δ^{18}O, δ^{2}H, and δ^{13}C-DIC for the two sampled tributaries. Tributary 1 includes samples ED01–ED05 (except the ED02 sample, which is missing in alkalinity measurement), and Tributary 2 includes samples ED06–ED10. The central line in each box represents the median, and the error bars show the mean ± standard deviation.

Table 1. Statistics for the measured hydrochemical variables in Tributary 1 and Tributary 2

Variable	Tributary	n	Mean	Median	Minimum	Maximum
pH	1	5	6.516	6.5	6.23	6.8
pH	2	5	7.204	7.22	6.96	7.56
TA (µeq/L)	1	4	273.625	26.025	2.49	3.25
TA (µeq/L)	2	5	3.412	3.445	3.16	3.6
Conductivity (µS/cm)	1	5	298.92	313	172.6	408
Conductivity (µS/cm)	2	5	307.4	330	204	342
δ^{13}C-DIC	1	5	-12.944	-12.66	-14.82	-12.07
δ^{13}C-DIC	2	5	-14.008	-13.98	-14.2	-13.82
δ^{18}O	1	5	-10.68	-10.63	-11.06	-10.45
δ^{18}O	2	5	-10.594	-10.58	-10.68	-10.56
δ^{2}H	1	5	-75.114	-74.5	-78.34	-73.61
δ^{2}H	2	5	-74.04	-73.87	-74.73	-73.47

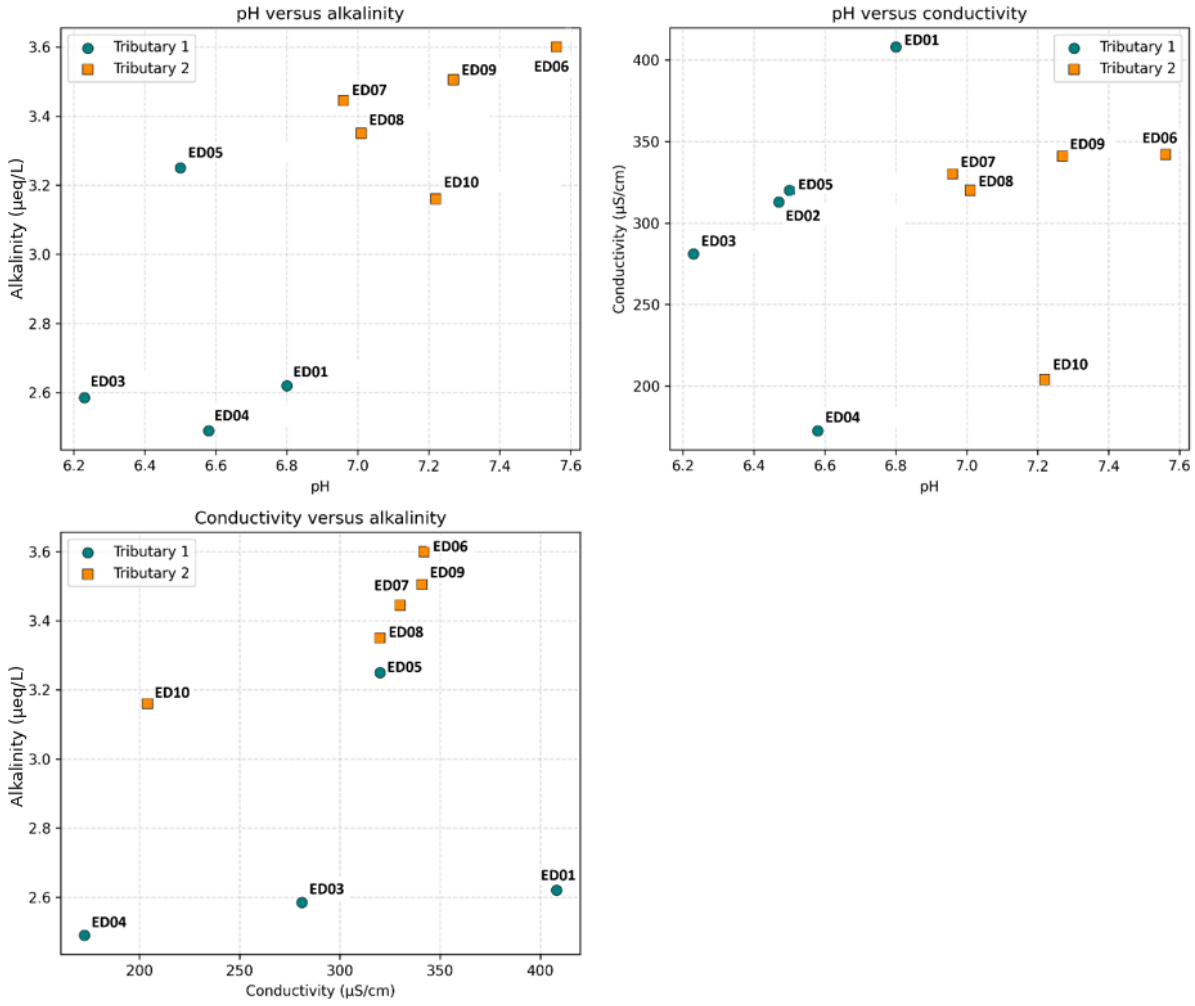


Figure 4. pH vs alkalinity, pH vs conductivity and alkalinity vs conductivity plots for samples from Tributary 1 and Tributary 2.

3.2 Major ions and sulfate concentrations

There are differences between the two Tributaries regarding the measured major ions. Sulfate is higher in Tributary 1, where Tributary 2 showed a higher concentration of chloride and sodium. Calcium was high in both tributaries, while magnesium was higher in Tributary 1 (Figure 5).

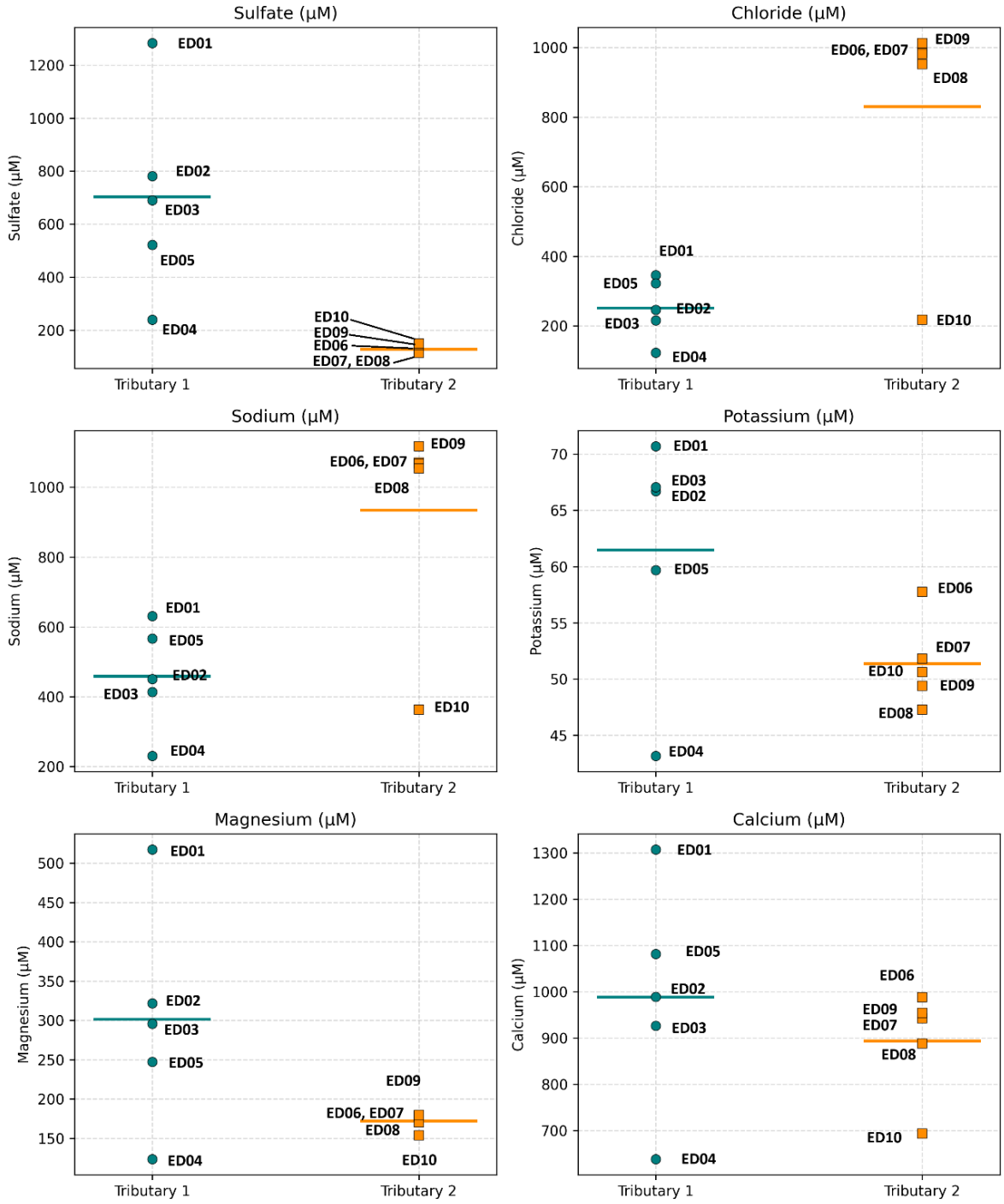


Figure 5. Concentrations of the main dissolved ions in Tributary 1 and Tributary 2. It includes sulfate, chloride, sodium, potassium, magnesium, and calcium. The horizontal lines are the mean concentration for the tributary.

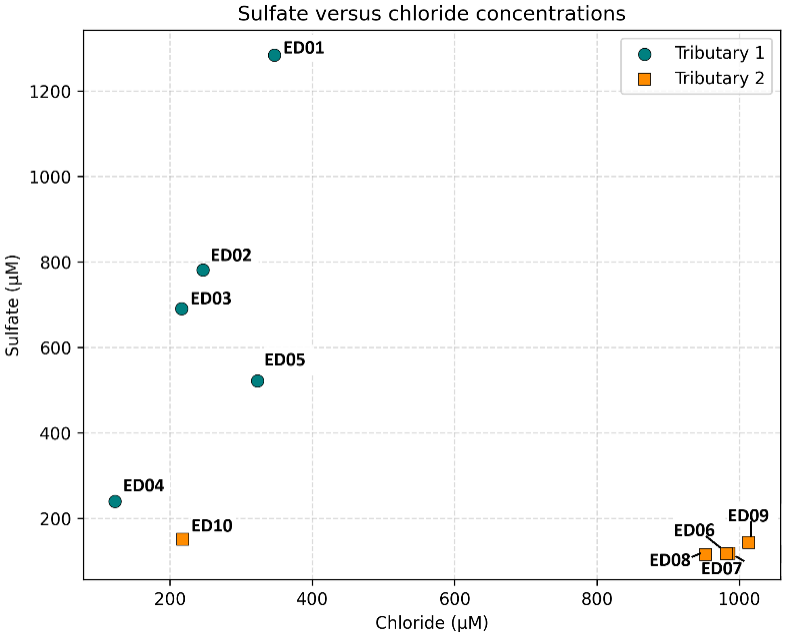


Figure 6. Sulfate concentration plotted against chloride concentration for samples from Tributary 1 and Tributary 2.

Figure 6 illustrates sulfate vs chloride for the two tributaries. The samples clearly differentiate from each other. Tributary 1 has higher sulfate and lower chloride concentrations, and Tributary 2 has higher chloride and lower sulfate concentrations. Figure 7 below shows the relationship between calcium and chloride in the two tributaries.

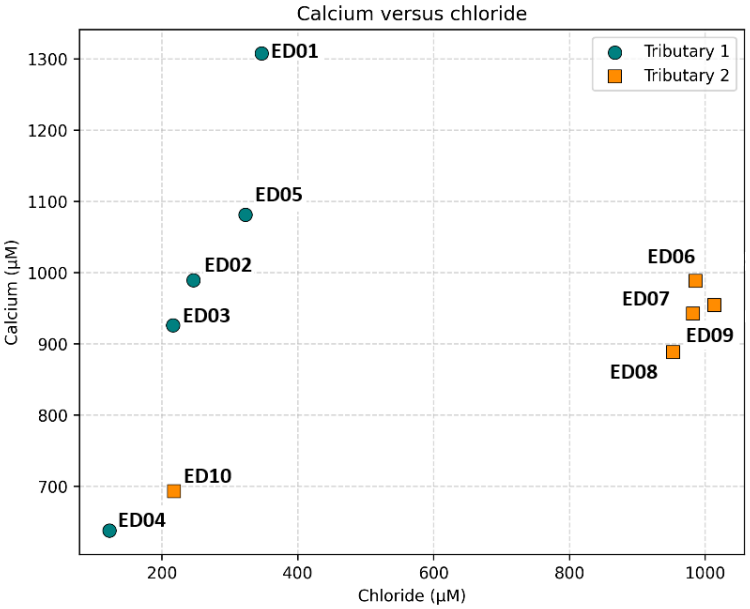


Figure 7. Calcium concentration plotted against chloride concentration for samples from Tributary 1 and Tributary 2.

Table 2. Major ion concentrations in both tributaries were corrected for dilution. Values are reported in µM. The x10 results were used as the main dataset, but for the ED02 sample, the x100 dilution values were used instead. Replicate measurements for ED05 and ED10 were averaged.

Sample ID	Tributary	DF	Cl^- (µM)	SO_4^{2-} (µM)	NO_3^- (µM)	Na^+ (µM)	K^+ (µM)	Mg^{2+} (µM)	Ca^{2+} (µM)
ED01	1	x10	346	1284	189	631	71	518	1307
ED02	1	x100	247	781	n/a	450	67	322	989
ED03	1	x10	216	690	121	413	67	296	926
ED04	1	x10	123	240	64	230	43	123	638
ED05 (averaged replicate)	1	x10	323	522	141	567	60	247	1081
ED06	2	x10	986	118	51	1070	58	178	988
ED07	2	x10	982	117	45	1067	52	178	942
ED08	2	x10	953	115	38	1054	47	170	888
ED09	2	x10	1013	143	44	1118	49	180	954
ED10 (averaged replicate)	2	x10	218	151	32	363	51	154	693

3.3 Trace elements and associated geochemical variables

The result from the ICP-MS concentration of selected trace elements, where only the unfiltered water samples were used, is presented below (Table 3). A comparison between Tributary 1 and Tributary 2 was made to indicate the trace element distribution of the waters before the filtration. Figure 8 shows that Tributary 1 has a higher concentration of Al, Si, Mn, and Fe, and that Zn varied between the tributaries, with the highest value in Tributary 1. Figure 9 presents the relation between sulfate and selected trace elements in the unfiltered samples. Tributary 1 has higher sulfate concentration and also higher Al, Mn, and Fe concentrations, while Tributary 2 has lower sulfate concentration and lower values for most variables. Zinc seems to be mostly scattered in both tributaries (Figure 8).

Table 3 shows the different trace element concentrations in the unfiltered ICP-MS samples from the two tributaries, and the values are reported in µg/L. Only the unfiltered samples are included in this table (ED01, ED02, ED05, ED06, ED09, ED10). The rest of the samples were also tested, but not as unfiltered, since we did not have enough water. Instead, we tested filtered and permeate samples (ED03, ED04, ED07, ED08). These are treated separately in Section 3.4.

Table 3. Trace element concentrations in the 0.2 µm filtered dilution corrected ICP-MS samples.

Sample ID	Type	Al (µg/l)	Si (µg/l)	Mn (µg/l)	Fe (µg/l)	Cu (µg/l)	Zn (µg/l)
ED01	unfiltered	176	9710	201	313	4	24
ED02	unfiltered	353	9357	188	744	5	23
ED05	unfiltered	198	8652	158	447	5	41
ED06	unfiltered	99	5491	19	154	4	37
ED09	unfiltered	97	5982	30	154	4	13
ED10	unfiltered	152	6940	32	428	4	10

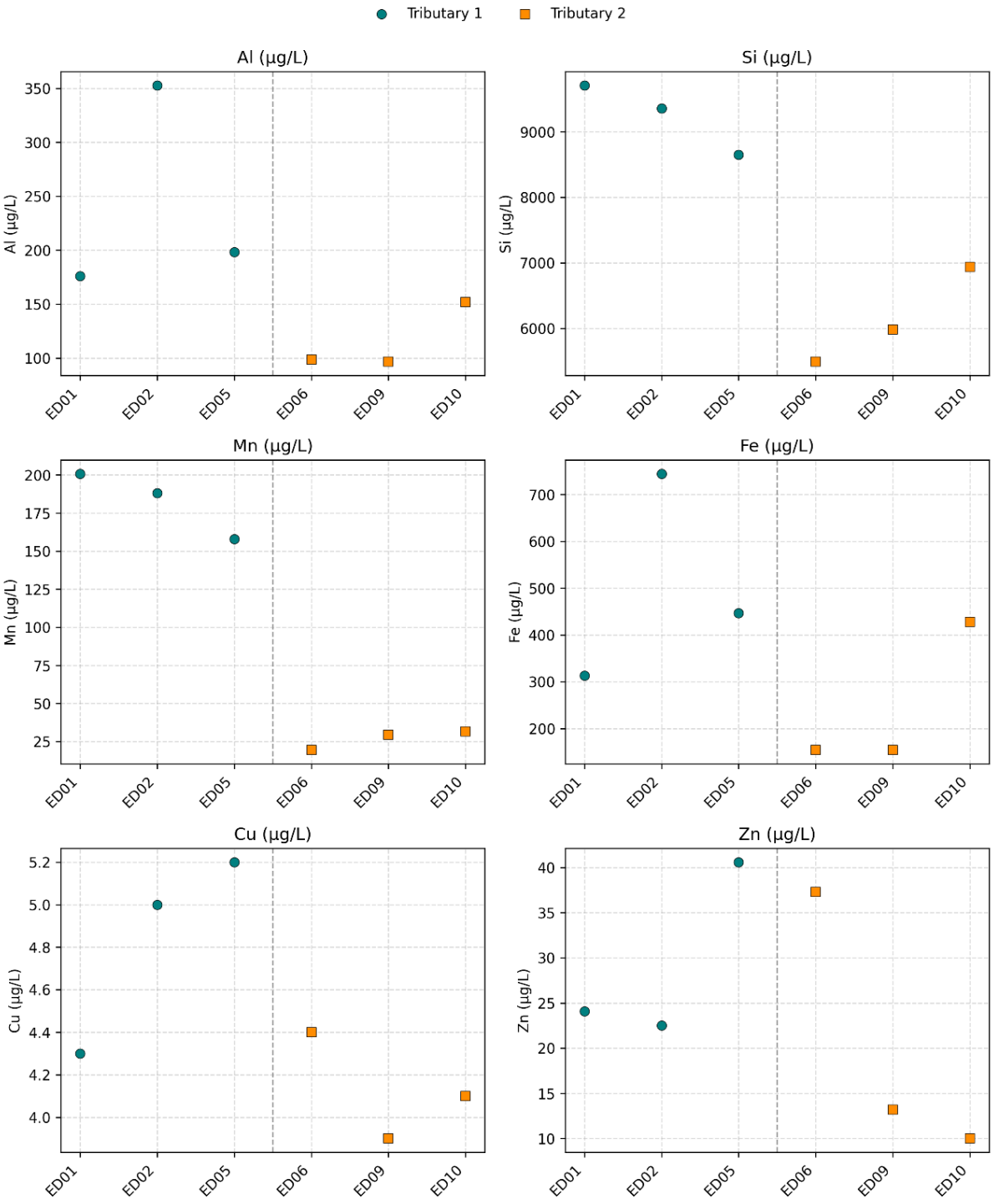


Figure 8. Concentrations of selected trace elements in the 0.2 µm filtered ICP-MS samples. The plots include Al, Si, Mn, Fe, Cu, and Zn. Samples from Tributary 1 and Tributary 2 are shown, and the dashed vertical line marks the division between the two tributaries.

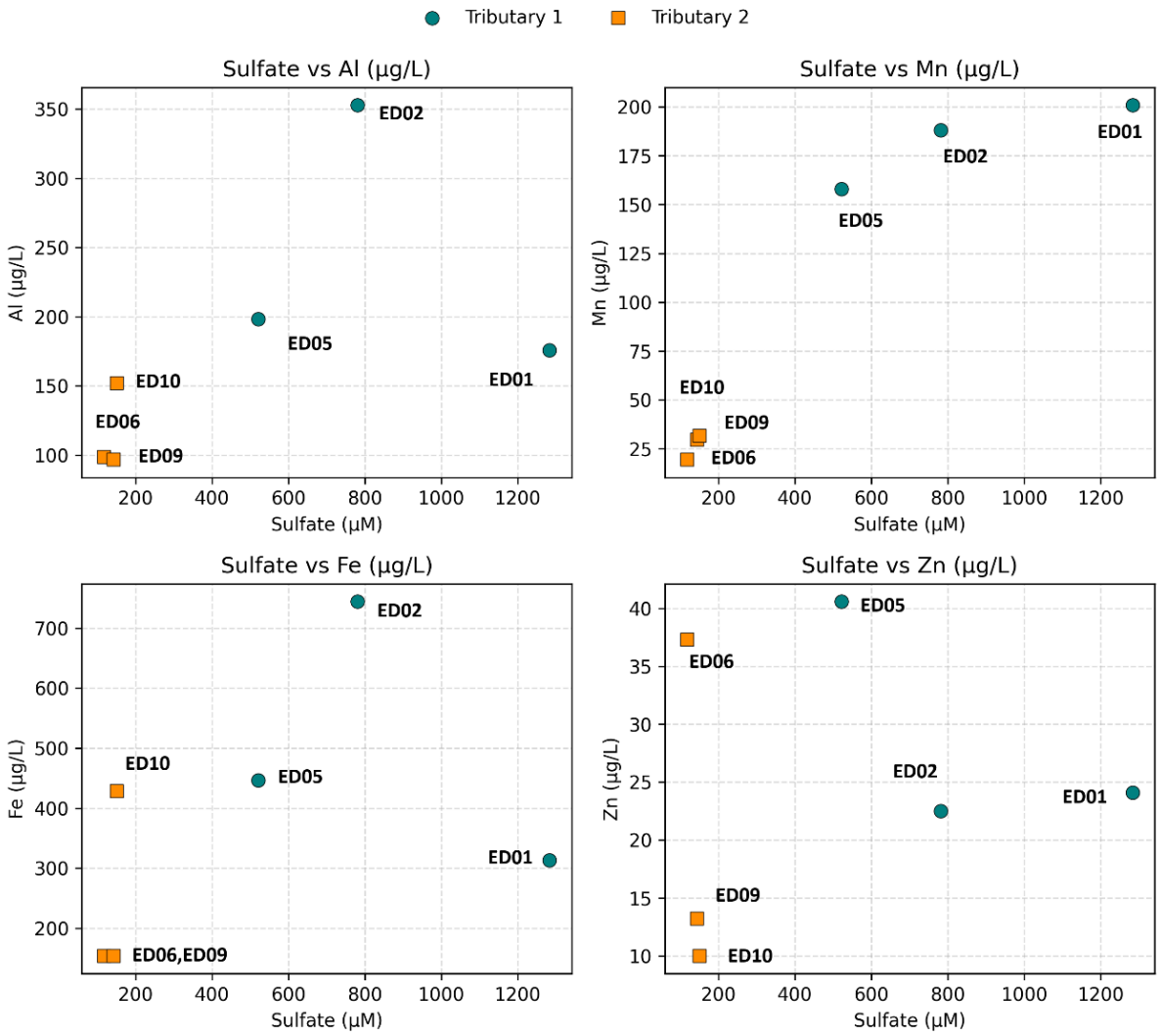


Figure 9. Sulfate concentration vs selected trace elements in the 0.2 µm filtered samples. The plots include Al, Mn, Fe, and Zn. Samples from Tributary 1 and Tributary 2 are shown separately.

3.4 Dissolved versus colloidal partitioning

The results for the dissolved vs colloidal partitioning are presented by comparing the 0.2 µm filtered and permeate fractions for the selected elements to be able to interpret if they are in dissolved form or associated with colloidal material. Table 4 shows that concentrations of Al, Fe, Mn, and Zn were lower overall in the permeate fraction than in the 0.2 µm filtered fraction. Figure 10 shows the difference between filtered and permeate fractions and shows a clear decrease in Fe and Al, while Mn has a smaller decrease for both fractions, and Zn stayed more consistent with only a minimal change for sample ED07. A complement to the fractionation result and filtration, a SEM photo is also added as a representative of the characteristics of the solid material picked up by the 0.2µm filtration (Figure 11).

Table 4. Concentrations of selected trace elements in the 0.2 µm filtered and permeate fractions based on the ICP-MS data. Values are reported in µg/L. Only values from sample ED03, ED04, ED07, and ED08 are available and presented.

Sample ID	Type	Al (µg/l)	Si (µg/l)	Mn (µg/l)	Fe (µg/l)	Cu (µg/l)	Zn (µg/l)
ED04P	Permeate	22	7103	22	16	1	2
ED07P	Permeate	31	5905	19	14	1	1
ED03	0.2µm filtrate	191	9366	177	348	3	9
ED04	0.2µm filtrate	133	6795	26	380	3	2
ED07	0.2µm filtrate	93	6298	23	159	3	1
ED08	0.2µm filtrate	91	6339	27	178	3	1

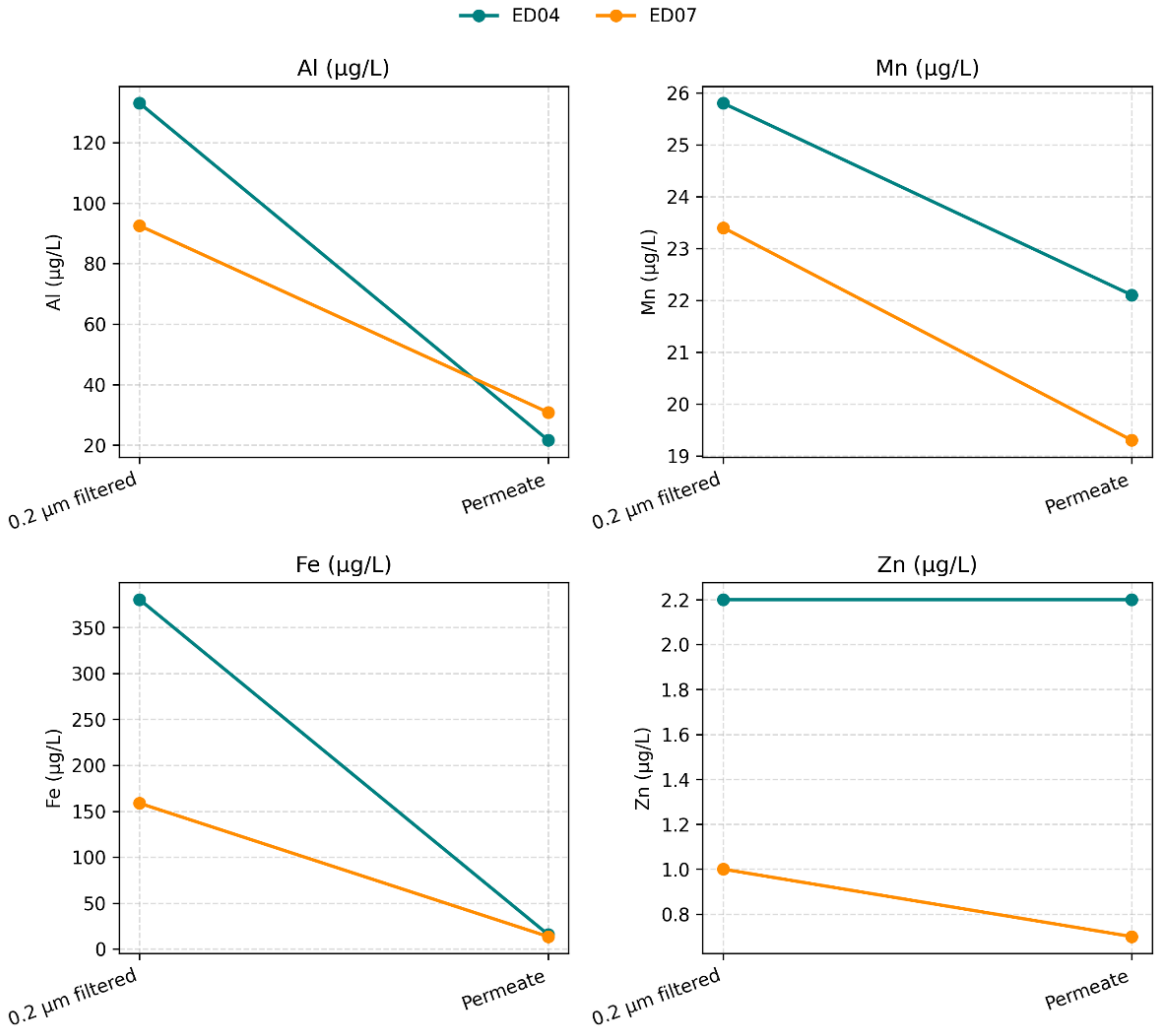


Figure 10. Selected trace element concentrations between the 0.2 µm filtered and permeate fractions for the samples ED04 (Tributary 1) and ED07 (Tributary 2). The plots include Al, Mn, Fe, and Zn. The changes between the fractions show whether the elements stayed in a smaller dissolved fraction or decreased between the filtered and permeate fractions.

Figure 11. One example of an SEM photo from 0.2µm PC filter showing organic material with high concentrations of Si, O, C, and some trace elements.

3.5 Stable isotopes of water and carbon isotopes of dissolved inorganic carbon

Results for the stable isotope composition of water and dissolved inorganic carbon are presented below. Table 5 summarizes $\delta^{18}O$, $\delta^{2}H$, $\delta^{13}C$-DIC, alkalinity, and pH, and Figure 12 points out the relation between the $\delta^{18}O$ and $\delta^{2}H$. The water isotope data show a cluster of samples with a narrow range for the samples. Figure 13 presents the distribution of $\delta^{13}C$-DIC values, and it points to a difference between the two tributaries. Tributary 2 shows lower and less varied data than Tributary 1.

Table 5. Stable isotope and DIC variables in the sampled tributaries. The table includes $\delta^{18}O$, $\delta^{2}H$, $\delta^{13}C$-DIC, alkalinity, and pH for the field samples.

Sample ID	Tributary	δ18O (‰)	δ2H (‰)	δ13C-DIC (‰)	Alkalinity (µeq/L)	pH
ED01	1	-10.64	-74.41	-12.97	2.62	6.8
ED02	1	-10.62	-74.5	-12.07	n/a	6.47
ED03	1	-10.63	-74.71	-12.66	2.585	6.23
ED04	1	-10.45	-73.61	-12.2	2.49	6.58
ED05	1	-11.06	-78.34	-14.82	3.25	6.5
ED06	2	-10.58	-73.47	-14.08	3.6	7.56
ED07	2	-10.56	-73.86	-13.96	3.445	6.96
ED08	2	-10.56	-73.87	-13.82	3.35	7.01
ED09	2	-10.68	-74.73	-13.98	3.505	7.27
ED10	2	-10.59	-74.27	-14.2	3.16	7.22

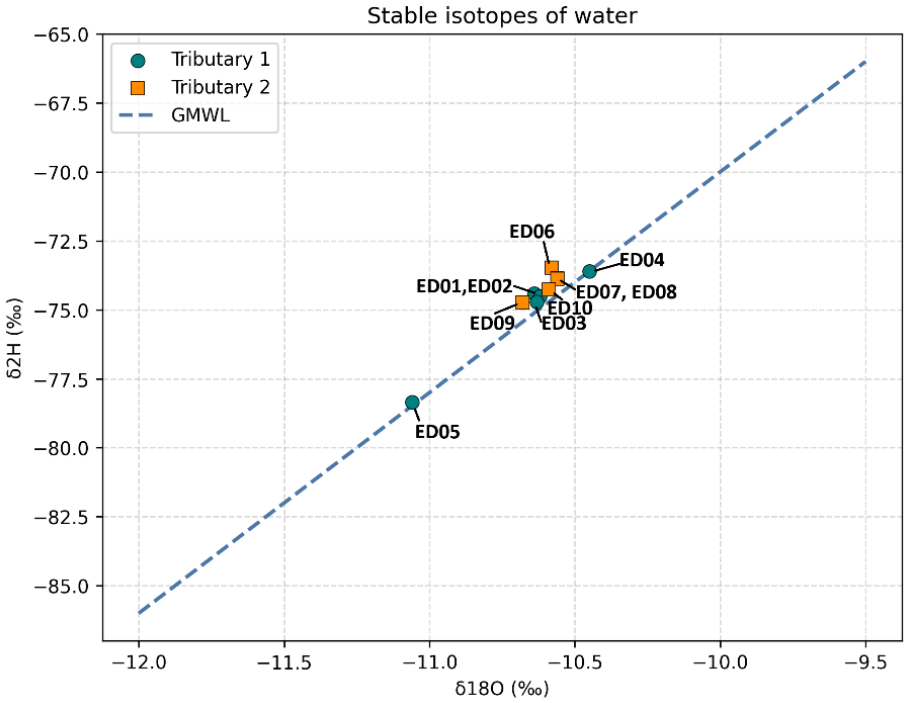


Figure 12. Stable isotope composition of water in the tributaries, presented as $\delta^{18}O$ and $\delta^{2}H$. Samples from Tributary 1 and Tributary 2 are shown separately, and the dashed line is the Global Meteoric Water Line (GMWL), defined as $\delta^{2}H = 8 \cdot \delta^{18}O + 10$. (Craig, 1961)

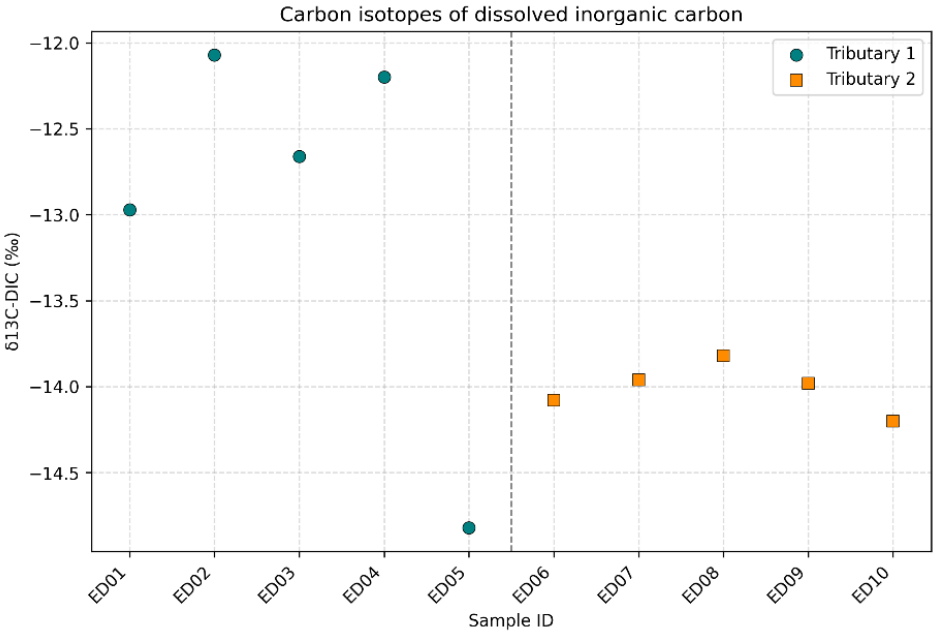


Figure 13. Carbon isotope composition of dissolved inorganic carbon $\delta^{13}C$-DIC, in the tributaries. Samples from Tributary 1 and Tributary 2 are shown separately, and the dashed vertical line shows the division between the two tributaries.

3.6 Summary of the results

By looking at the full result data, we can see that the tributaries differ in their hydrochemistry, major ion composition, trace element concentration, and carbon isotope composition. The stable water isotope data were more similar between the two tributaries.

Tributary 1 had a lower pH and lower alkalinity, while Tributary 2 had a higher pH and higher alkalinity. Conductivity was overlapping between the two tributaries, but Tributary 1 showed a wide range with both the lowest and the highest value.

In the major ion composition data, we can see a difference between the tributaries. Tributary 1 had a higher sulfate concentration, while Tributary had a higher chloride and sodium concentrations. Calcium was relatively high in both tributaries, and magnesium was higher in Tributary 1, so the tributaries differ in their concentration levels and in their ion composition. For the tested unfiltered samples in the trace element analysis, Tributary 1 had a higher concentration of Al, Mn, Fe, and Si than that of Tributary 2. Cu varied less between the two tributaries, and Zn showed no clear pattern of difference between them. In the comparison between the selected trace elements and sulfate, we can see that Tributary 1 clustered at a higher sulfate concentration and had a higher concentration of several trace elements.

From the fractionation results, we can see a difference in the data. Fe and Al decreased more strongly from the 0.2µm filtered fraction to the permeate fraction than Mn and Zn. This indicates a difference in the distribution of the elements between these fractions. The stable water isotope data showed a similar result for Tributary 1 and Tributary 2 in their values, while the δ^{13}C-DIC showed a clearer difference. Tributary 2 had a generally lower and less variation in the δ^{13}C-DIC values compared to Tributary 1.

Discussion

4. 1 Discussion based on the 4 main questions

This project aimed to investigate whether tributaries in the Storån river area showed any evidence of sulfate concentrations related to acid sulfate soils, and to evaluate how the sulfate and selected elements were distributed in the different tributaries and if they were mainly in dissolved or colloidal fractions. The result pointed out a clear hydrochemical difference between the two tributaries. Tributary 1 showed low pH, a higher sulfate concentration, and several trace element concentrations, whereas Tributary 2 showed higher pH, higher alkalinity, and higher chloride and sodium concentrations. With the 4 main questions as a starting point, I will go through the patterns visible in the results and evaluate the relation to acid sulfate soil processes.

The first and most important question in this project was whether the tributaries showed any evidence of sulfate derived from acid sulfate soils. In Tributary 1, there are several lines of evidence suggesting the potential influence of ASS. Tributary 1 had higher sulfate concentrations, lower alkalinity and pH, and higher concentrations of several trace elements, including Al, Mn and Fe than that of Tributary 2. This specific pattern agrees with a former study pointing out that oxidation of sulfate soil can acidify waters, increase the sulfate concentration, and mobilize metals to nearby streams or rivers (Lindgren

et.al., 2022). Together with a more recent study on acid sulfate soils in Sweden, mentioning that oxidation is associated with sulfur release and mobilization of metals when in low pH conditions (Nyman et.al., 2023). Another study also pointed out that waters or river systems affected by acid sulfate soil can contain elevated metal concentrations in different size fractions (Nystrand and Österholm, 2013).

But something to consider here, sulfate alone is not sufficient to prove the source, because river sulfate may also come from atmospheric deposition, weathering, or even local inputs. For this specific reason, the interpretation must be based on the full extent of the combined results and analysis performed. In this dataset, as already mentioned, the Tributary 1 results point towards being affected by acid sulfate soils or processes much more than Tributary 2.

The second question we wanted to address in this project was whether the sulfate was present in its dissolved phase or in the colloidal phase after the TFF was performed. The fractionation results provided us with some information on how the elements are transported. When we compare the 0.2 µm filtered results and the permeate fractions results, it showed that Fe and Al decreased more strongly than Mn and Zn. This would indicate that these elements were associated with larger colloidal material. This is in line with previous studies using TFF showing that metals and metalloids may partition differently between dissolved, colloidal, and particulate fractions (Nystrand and Österholm, 2013). In contrast, sulfate is often expected to occur in dissolved form in affected waters, even when metals show a colloidal association, which makes the interpretation a bit harder.

For the third question, we wanted to address the source of the sampled water. The stable water isotope data showed only a small difference between the two tributaries, the $\delta^{18}O$ and $\delta^{2}H$ values cluster within a narrow range, and this would suggest a similar water source or recharge history. When comparing with the GMWL data, we wanted to assess if it went through a mixing process, evaporation process, or had some recharge history. Since the hydrochemical variables differed between the tributaries but showed a similar isotope hydrology, the conclusion would be that they share a similar water source, possibly local meteoric water, but one tributary might have undergone different geochemical interactions along its flow path, like soil and sediment interactions related to acid sulfate soil processes (IAEA, 2013).

The last question we wanted to address was the source of carbon based on the carbon isotope analyses of DIC. The $\delta^{13}C$-DIC result showed a difference between the tributaries compared to the water isotope data. Tributary 2 had a lower and less variation in the $\delta^{13}C$-DIC values, together with a higher alkalinity and pH values. Usually, the $\delta^{13}C$-DIC values are interpreted with the alkalinity and pH because dissolved inorganic carbon is a pH dependent mixture of carbonate species, and its isotopic composition could reflect both source inputs and a fractionation between species (Liu and Han, 2020). Tributary 2, with a higher alkalinity and less variation in the $\delta^{13}C$-DIC values, may reflect a stronger buffering or weathering influence than that of Tributary 1. This suggests that the DIC values in our tributaries differed not only by sulfur and metal chemistry but also in the DIC processes that had occurred. Which processes these are would have to be investigated further in future projects.

4.2 Uncertainties and limitations

This project had several limitations that should be considered when interpreting the results. First, is that the number of samples was limited, especially for the fractionation analysis, we only had a subset of samples to use when comparing the size fractions. This means that the interpretation of dissolved versus colloidal partitioning is based on a relatively small number of observations and is not statistically founded. In addition to this, the sulfate source cannot be proven from concentration data alone, because sulfate in the river may reflect several different possible inputs. This is why the interpretation in this project is based on the combined hydrochemical pattern rather than just one variable like sulfate. Second thing to consider is that this project did not include any direct sulfur isotope measurement, which could more specifically tell us the closer sulfate source. A third limitation to our analysis is that the isotope data is not representative of the full year, since the isotopes may vary seasonally with recharge conditions, flow paths, and temperature (Liu et.al., 2021).

In this dataset, it is also important to distinguish between accuracy and precision. Accuracy refers to how close the measured value is to the true value, while precision refers to how closely repeated measurements agree with each other. This tells us how confident we can interpret our data. In this project, we had several cases where the samples showed similar or very close values to each other, and in those cases, we cannot with certainty state that these samples were chemically different, rather than being similar with some uncertainty. This was especially important when the differences are small between the samples relative to the precision of the method used or when the concentrations are low. For this reason, this project's conclusion is based on the overall patterns between the tributaries and not on small differences between individual samples.

4.3 Future work

A knowledge gap in this study is that the sulfate source was inferred indirectly from hydrochemical patterns rather than traced directly. So future work should include sulfur isotope analyses of dissolved sulfate combined with sulfur isotope measurements of sediments containing sulfur and local acid sulfate soils. Since stable sulfur isotopes are used to trace the source of sulfur and its transformations, they would give us a clear and direct comparison between the dissolved sulfate in the water and potential sulfur sources in the sediments (Zhao et.al., 2025). Future work should also include an increase in the number of samples and sampling occasions, taking into account the season variability. Repeated sampling during different conditions, especially after dry periods and strong water flow events, would make it easier to determine whether sulfate and metal release vary through time, which is typical of acid sulfate soil systems (Saarinen and Kløve, 2012). In addition to this, a larger dataset of samples going through filtration could also improve our interpretation of dissolved versus colloidal partitioning and reduce the uncertainty.

Conclusion

In summary, the results show that the two tributaries in the Storån river area differ clearly in the hydrochemistry. Tributary 1 had higher sulfate, lower pH, lower alkalinity, and higher concentrations of Al, Mn, and Fe, while Tributary 2 had higher pH, higher alkalinity, and higher concentrations of chloride and sodium. This pattern suggests that acid sulfate soil is influencing the Tributary 1.

The fractionation results suggest that sulfate is mainly present in the truly dissolved phase, where Al and Fe are associated with colloidal material. The stable water isotope data indicate a similar meteoric water source for both tributaries, and the δ^{13}C-DIC data suggest a mixed carbon source involving some weathering processes and carbon originating from the soil.

Overall, the project suggests that acid sulfate soil influences at least one of the tributaries, and combining hydrochemistry, filtration, and isotope analyses is a useful way to investigate this.

Further work is important and could provide us with a stronger understanding of how the acid sulfate soil processes are affecting the chemistry in the Storån river area.

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