

## Article

# Biogeochemical Controls on $^{13}\text{C}_{\text{DIC}}$ Signatures from Circum-Neutral pH Groundwater in Cu–W–F Skarn Tailings to Acidic Downstream Surface Waters

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**Abstract:** Regular features of ground and surface waters affected by drainage from mine waste include their acidity and elevated concentrations of dissolved metals, with their attendant negative effects on drinking water quality and aquatic life. One parameter that aids in buffering these waters against acidity and sustains aquatic life is dissolved inorganic carbon (DIC). In this study, the chemical and isotopic ( $\delta^{13}\text{C}$ ) composition of primary calcite and DIC ( $\delta^{13}\text{C}_{\text{DIC}}$ ) in groundwater and surface waters within and downstream, respectively, of abandoned Cu–W–F skarn tailings at Yxsjöberg, Sweden, were used to trace the biogeochemical processes controlling their respective  $\delta^{13}\text{C}_{\text{DIC}}$  signatures. In addition, the  $\delta^{13}\text{C}$  signatures of the inorganic (carbonate) fractions of the tailings were used to verify the formation of secondary carbonates within the tailings. Lower average  $\delta^{13}\text{C}$  values of the carbonate fractions ( $\delta^{13}\text{C}_{\text{carb}} = -2.7\text{‰}$ ) relative to those of the primary calcite ( $\delta^{13}\text{C} = +0.1\text{‰}$ ) from the orebodies from which the tailings originated pointed to the precipitation of secondary carbonates. These lower  $\delta^{13}\text{C}_{\text{carb}}$  signatures were assumed to represent mixed-source C signals involving isotopically light  $\text{CO}_2$  from the atmosphere, the degradation of organic matter in the upper part of the tailings and  $\text{HCO}_3^-$  from calcite dissolution. The groundwater  $\delta^{13}\text{C}_{\text{DIC}}$  values ( $-12.6\text{‰}$  to  $-4.4\text{‰}$ ) were far lower than the hypothetical range of values ( $-4.6\text{‰}$  to  $+0.7\text{‰}$ ) for primary calcite and secondary carbonate dissolution. These signatures were attributed to carbonate (calcite and secondary carbonate) dissolution and the degradation of dissolved organic carbon (DOC) from various organic sources such as peat underneath the tailings and the surrounding forests. Downstream surface water samples collected in May had low  $\delta^{13}\text{C}_{\text{DIC}}$  values ( $-16\text{‰}$ ) and high DOC (14 mg C/L) compared to the groundwater samples. These signatures represented the oxidation of the DOC from the wash out of the mires and forests during the snowmelt and spring flood. The DOC and  $\delta^{13}\text{C}_{\text{DIC}}$  values of the surface waters from June to September ranged from 6–15 mg·C/L and  $-25\text{‰}$  to  $-8.6\text{‰}$ , respectively. These signatures were interpreted to reflect mixed C sources, including carbonate dehydration by acidity from  $\text{Fe}^{3+}$  hydrolysis due to the mixing of groundwater with surface waters and the subsequent diffusive loss of  $\text{CO}_2(\text{g})$ , aquatic photosynthesis, photooxidation, DOC degradation, as well as microbial respiration. Although the  $^{13}\text{C}_{\text{DIC}}$  signatures of the downstream surface waters seemed to be seasonally controlled and influenced by variable groundwater contributions, the lack of data with respect to DIC concentrations, coupled with multiple potential biogeochemical processes that could influence the DIC pool and  $^{13}\text{C}_{\text{DIC}}$  values, made it difficult to identify the major regulating process of the  $^{13}\text{C}_{\text{DIC}}$  signatures. Therefore, other complimentary isotopes and elemental concentrations are recommended in order to decipher the dominant biogeochemical process.

**Keywords:** dissolved inorganic carbon; secondary carbonates; skarn tailings; ground and surface waters; carbonate dissolution; stable carbon isotopes

## 1. Introduction

The complex biological, chemical and thermal processes of sulphide mineral oxidation, mainly due to their exposure to water and oxygen and the subsequent dissolution of acid-neutralising minerals in mine waste, result in the production of sulphate ( $\text{SO}_4^{2-}$ ), dissolved metal-(loids) and variable pH drainage, commonly referred to as acid mine drainage (AMD) or neutral mine drainage (NMD) [1]. These drainages usually contain toxic and potentially hazardous metal-(loids) such as Co, Cu, Ni, Zn, As, Mo, Sb, Tl and W [2,3]. At historical or abandoned mining sites, for example, where there is usually no legally binding responsible person(s), these drainages, with their attendant chemical constituents, are released into the surrounding soils, groundwater and downstream surface water bodies [4], causing significant ecological and health risks.

Dissolved inorganic carbon (DIC), which consists of carbon dioxide ( $\text{CO}_{2(\text{aq})}$ ), carbonic acid ( $\text{H}_2\text{CO}_3$ ), bicarbonate ( $\text{HCO}_3^-$ ) and carbonate ( $\text{CO}_3^{2-}$ ), plays a very critical biogeochemical role in such mine-impacted surface waters due to its capacity to buffer the pH in these waters. In addition, it provides ecological importance by sustaining organic productivity such as photosynthesis [5] in such waters. The redistribution of the various DIC species is pH dependent [6]. Several biogeochemical processes including mineral (e.g., carbonate and silicate) weathering, organic matter (DOC) oxidation, microbial respiration and photosynthesis, and exchanges between the DIC of surface water and atmospheric  $\text{CO}_2$  have been reported, among others, as the major processes that impact significantly on the DIC pool in ground and surface waters [7–9]. However, the stable carbon isotope composition of DIC ( $\delta^{13}\text{C}_{\text{DIC}}$ ) is non-conservative and hence the pH-dependent transformation of the various DIC species causes shifts in the DIC pool and the  $\delta^{13}\text{C}_{\text{DIC}}$ .

This study focus on the historical copper–tungsten–fluorite (Cu–W–F) mine tailings deposit at Yxsjöberg in south–central Sweden, which is related to the mining of a limestone skarn ore body during three different periods of mining from 1887 to 1989 [10–12]. The tailings have a heterogeneous and complex mineralogy, including silicates (e.g., the helvine group of minerals:  $[(\text{Fe}, \text{Mn}, \text{Zn})_4\text{Be}_3(\text{SiO}_4)_3\text{S}]$ ), oxides (e.g., scheelite:  $\text{CaWO}_4$ ), halides (such as fluorite) and sulphides (mainly pyrrhotite, chalcopyrite, pyrite and sphalerite). The sulphide and silicate minerals in the upper section of the tailings are weathered, whereas calcite has been consumed in this section by the acidity from sulphide oxidation [13]. The tailings were discharged into an area consisting of bogs (mainly peat) and swamps [14]. Moreover, a thin layer of sewage sludge was applied on the surface of the tailings in 1994 with the primary aim of establishing vegetation cover to suppress dust. Currently, the tailings are covered by vegetation (trees and grasses) and surrounded by vast forests. Recent studies by [15] indicated that the surface waters downstream of the tailings represent a mix of groundwater from the tailings and surrounding surface waters, resulting in mixed surface waters exhibiting a low pH and dissolved ion concentrations relative to that of the groundwater. This was partly attributed to  $\text{Fe}^{2+}$  oxidation to  $\text{Fe}^{3+}$ , hydrolysis and the formation of Fe(III)-oxyhydroxides [16] at the outlet of the tailings' impoundments due to a change in redox (from reduced to oxidised) conditions. In such surface waters, the loss of  $\text{CO}_{2(\text{g})}$  as a result of the dehydration of  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$  by the acidity from the hydrolysis of  $\text{Fe}^{3+}$  [16,17] will cause changes in the DIC concentration and  $\delta^{13}\text{C}_{\text{DIC}}$  values [18]. Additionally, the vegetation and organics (peat) on and beneath the tailings, respectively, as well as the surrounding forests may produce DOC, which may be oxidised to  $\text{CO}_{2(\text{aq})}$ , ultimately contributing to the DIC pool of the ground and surface waters, with their attendant  $\delta^{13}\text{C}_{\text{DIC}}$  signatures. Other potential in-stream processes may also serve as either input or output sources of DIC and subsequently cause shifts in the  $\delta^{13}\text{C}_{\text{DIC}}$ . Therefore, identifying the potential sources and cycles of DIC is critical for the understanding of water quality and aquatic biogeochemistry, especially in downstream mixed surface waters.

Furthermore, a study by [13] observed two different calcite morphologies or shapes in the tailings: rhombohedral and orthogonal. The former was consistent with a form of primary calcites, whereas the latter was considered to represent the formation of secondary calcite but this was not conclusive due to the complexities associated with the formation of secondary carbonates, especially in complex mineralogical settings such as skarn tailings. The formation of secondary carbonates is considered

very important in CO<sub>2</sub> sequestration [19]. Therefore, the objectives of this study are (i) to verify the potential formation of secondary carbonates within the tailings; (ii) to elucidate the spatial and temporal biogeochemical processes controlling  $\delta^{13}\text{C}_{\text{DIC}}$  signatures from the groundwater in the tailings to downstream mixed surface waters.

## 2. Materials and Methods

### 2.1. Study Area

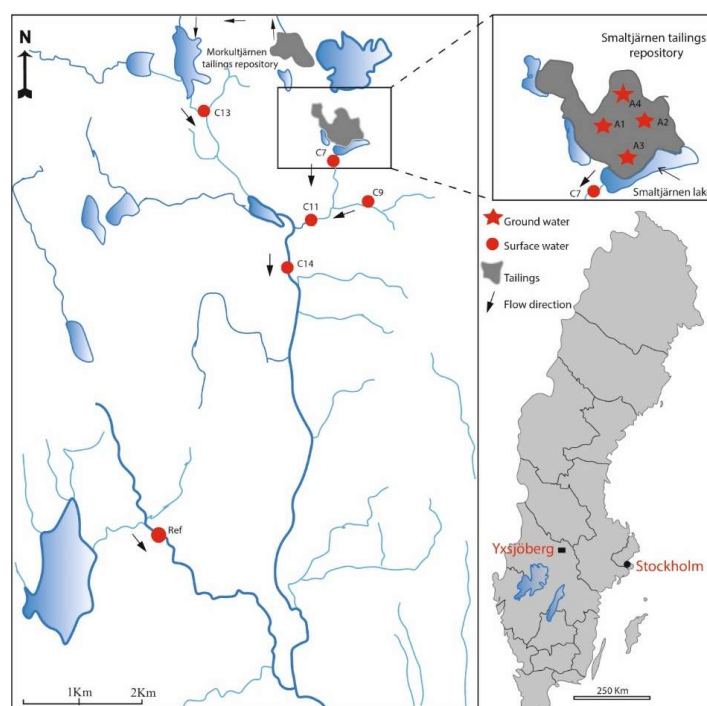
The site for this study is the abandoned Yxsjöberg Cu–W–F skarn mine tailings deposit in Ljusnarsberg Municipality in Västmanland, south-central Sweden, which was generated from the mining of Cu, W and F from the Yxsjöberg skarn ore deposit during 3 different mining periods [11,12]. Three different mineralisations have been reported to constitute the skarn deposit and these include Kvarnåsen, Nävergruvan and Finngruvan [11,12]. Uranium–lead (U–Pb) isotope dating by [20] estimated the age of the skarn deposit to be approximately 1800 Ma. Further and more detailed information regarding the geological setting of the skarn tailings are provided in [12,20–22]. The abandoned Cu–W–F skarn tailings at Yxsjöberg are of two categories and these include the Smaltjärnen and Morkulltjärnen repositories (Figure 1), of which the former is the oldest, with an estimated 2.8 million tons of tailings.

The tailings of the Smaltjärnen repository arose from the mining of Cu, F and W between 1887 and 1963 [10]. Primary sulphide minerals, including pyrrhotite (~2.4 wt %), chalcopyrite (~0.2 wt %), pyrite (~0.1 wt %) and sphalerite (traces), were observed in the tailings. The major primary carbonate mineral identified in the tailings was calcite, which accounted for approximately ~5.7 wt %. The most abundant minerals were the silicates (~87 wt %) and these included biotite, plagioclase, pyroxene, garnet, amphibole, K-feldspar, muscovite and the helvine group of minerals, predominantly danalite ( $\text{Fe}_4\text{Be}_3(\text{SiO}_4)_3\text{S}$ ). Oxide (scheelite and magnetite) and halide (fluorite) minerals were also identified in the tailings [13]. The Smaltjärnen repository is classified as an open system because it is not surrounded by a dam and directly exposed to oxidising conditions [21]. The exposure of the tailings to oxidising conditions for approximately 6 decades has led to the establishment of 3 geochemical zonations, namely (i) oxidised (OZ), (ii) transition (TZ) and (iii) unoxidised zones (UZ), according to their pH, elemental concentrations and colour [21]. The OZ was characterised by a brownish-red colour, a low pH (3.6–4.5) and the depletion of elements such as Al, Be, Ca, Co, Cu, Mg, Na, S, Sr and Zn in the bulk tailings due to the combined effects of the oxidation of the sulphide minerals, silicate weathering and the depletion of calcite in this zone. Gypsum and clay minerals were also identified, especially in the lower part of the OZ [21]. The TZ, which was directly located beneath the OZ, had a brownish-grey colour and a pH range of 5.3 to 6.3. The sulphide and silicate minerals in this zone showed no signs of oxidation/weathering, resulting in little or no depletion of Al, Be, Co, Cu, S and Zn relative to the OZ [21]. However, calcite was weathered in this zone, resulting in an elevated recorded pH relative to the OZ. This zone also showed the enrichment of Al and, to a lesser extent, Fe in the bulk tailings due to the precipitation of Al and Fe (III)-(oxy)-hydroxides, resulting from the increased pH [21]. Underneath the TZ was the UZ, with a dark-grey colour and a relatively high pH (6.2–7.9) compared to the overlying OZ and TZ. All the sulphide minerals, including pyrite, pyrrhotite, and chalcopyrite, were not affected by oxidation and hence were intact in this zone, resulting in no depletion of S and its related elements in the solid phase. The Morkulltjärnen repository, on the other hand, was deposited during mining from 1969 to 1989. The Morkulltjärnen repository is the younger of the two abandoned tailings, is confined by a dam and is water saturated. This has resulted in limiting sulphide oxidation [10]. The annual average precipitation and temperature values for the Yxsjöberg area are 730 mm and 11 °C, respectively [23].

## 2.2. Sampling

### 2.2.1. Tailings and Ore Minerals (Calcite)

Four drill cores were collected at different locations (A1, A2, A3 and A4) in the Smaltjärnen tailings repository (Figure 1) in Plexiglas tubes by percussion drilling using a geoprobe in September 2016. Groundwater pipes were then installed in A1 and A3, with depths of 6.0 and 2.84 m, respectively. In general, the drill cores exhibited similarities in terms of their mineralogy, chemical composition and pH across profiles [13]. In light of this, one drill core (A1) was chosen to further focus on stable C isotopes ( $\delta^{13}\text{C}$ ), chemical composition and mineralogy. The chosen drill core was divided into 18 subsamples of 8–120 cm intervals and kept in properly sealed polyethylene bags, prior to analyses. The pH of the tailings was measured as a paste pH using a 1:1 solid to liquid (MilliQ water) ratio [24] with a Van Waters and Rogers (VWR) multiparameter instrument (MU 6100H). Calcite was extracted from a diamond drill core belonging to one of the three orebodies from which the tailings originated, through crushing and hand picking under a binocular microscope. The diamond drill core was obtained from the mineral resources information office of the Swedish Geological Survey (SGU) located in Malå, Sweden. The purity of the extracted calcite was optically checked and estimated to be, at a minimum, 97%. The tailings and extracted calcite were homogenised by grinding with an agate mortar to obtain powdered fractions prior to chemical and isotopic ( $\delta^{13}\text{C}$ ) analyses.



**Figure 1.** A modified map (based on [25]) of the study area showing the sampling points used for this study.

### 2.2.2. Groundwater and Surface Water

Between the period of May and October 2018, 6 sampling campaigns were carried out during which the 2 groundwater wells (i.e., A1 and A3) located in the Smaltjärnen repository and 6 surface waters (C7, C9, C11, C13, C14 and the reference) were sampled (Figure 1). Two of the surface water sampling points, namely C7 and C11, were located downstream of the Smaltjärnen repository, whereas C13 was located downstream of the Morkultjärnen repository. Sampling point C14 was located downstream of both the Smaltjärnen and Morkultjärnen repositories. Sampling site C9 served as a tributary to C7, whereas the reference point (Ref) was considered pristine by virtue of its low dissolved

ion concentrations and therefore represented the background surface water chemistry in the area. Prior to each groundwater sampling, a 10-min minimum period of purging was executed to flush stagnant water to ensure that representative samples were taken. Further and detailed information regarding the ground and surface water sampling procedures are reported by [15]. Ground and surface water samples for  $^{13}\text{C}_{\text{DIC}}$  measurements were injected (aliquots of 1–6 mL) into 12-mL sealed glass vials (from Labco Limited), which were flushed with helium gas ( $75 \text{ mL} \cdot \text{min}^{-1}$ ) for 5 min. To each vial, 100  $\mu\text{L}$  of 85.5 %  $\text{H}_3\text{PO}_4$  was added to act as a preservative and to transform all the inorganic carbonate to  $\text{CO}_2(\text{g})$ . The samples were stored cold ( $+4^\circ\text{C}$ ) and in the dark before analysis. Ground and surface samples were then selected for hydrochemical (major and trace elements), dissolved organic carbon (DOC) and  $^{13}\text{C}_{\text{DIC}}$  analyses.

### 2.3. Analyses

Determinations of total S and C as well as the organic C contents of the tailings were executed by ALS Vancouver, Canada. Total S and C were analysed using a Laboratory Equipment Corporation (LECO) induction furnace melt, whereas organic C was analysed by combustion with dilute hydrochloric acid (HCl). Inorganic C was calculated as the difference between total C and organic C. Chemical (Al, Be, Fe, Ca, Mg, Na, W) analyses of ground and surface water samples were carried out at ALS Scandinavia AB, Luleå, Sweden, using inductively coupled plasma-sector field mass spectrometry (ICP-SFMS). Sulphate ( $\text{SO}_4^{2-}$ ) was analysed using ion chromatography. Determinations of the  $\delta^{13}\text{C}$  of calcite, bulk tailings, organic C and carbonate fractions of the tailings as well as the  $\delta^{13}\text{C}_{\text{DIC}}$  and DOC concentrations of ground and surface waters were carried out at the Stable Isotope Laboratory (SIL), Department of Environmental Sciences, Stockholm University, Sweden. Concentrations of DOC were determined by high-temperature catalytic combustion with a Shimadzu Total Organic Carbon (TOC-VCPH). Inorganic C was removed by adding 2 M of hydrochloric acid (HCl) to a pH of 2 and sparging the samples before analyses. The precision of the DOC analysis was better than 0.8% (coefficient of variation, CV) and the total uncertainty interval based on laboratory intercomparisons was  $\pm 5\%$ . Analyses of the  $\delta^{13}\text{C}$  of calcite, bulk tailings, organic C and carbonate fractions of the tailings as well as the  $\delta^{13}\text{C}_{\text{DIC}}$  of ground and surface waters were carried out using a GasBench II (Thermo Fisher Scientific, Waltham, MA, USA) coupled to a Finnigan MAT 253 mass spectrometer. From repeated measurements of standards, the reproducibility was better than  $\pm 0.1\text{‰}$ . The stable C isotope ( $^{13}\text{C}$ ) composition was expressed in the delta ( $\delta$ ) notation as per mil (‰) versus Vienna Pee Dee Belemnite (V-PDB) according to Equation (1):

$$\delta^{13}\text{C} (\text{‰}) = [(R_{\text{sample}}/R_{\text{standard}}) - 1] \times 1000 \quad (1)$$

where  $R$  is the ratio of the heavy ( $^{13}\text{C}$ ) to light ( $^{12}\text{C}$ ) isotope.

## 3. Results

### 3.1. Chemical and Stable Carbon Isotope ( $\delta^{13}\text{C}$ ) Composition of the Tailings

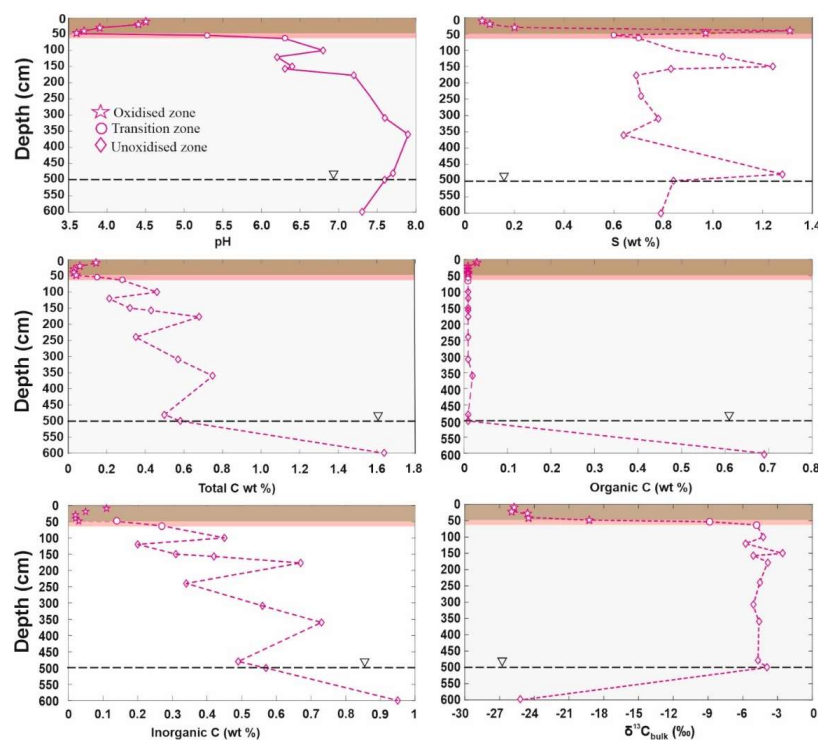
The chemical and stable carbon isotope ( $\delta^{13}\text{C}$ ) composition of the bulk tailings, organic and inorganic C fractions of the tailings and their depth distribution are shown in Table 1 and Figure 2, respectively. The total S content of the OZ ranges from 0.07 to 1.31 wt %, whereas values ranging between 0.60 and 0.70 wt % are reported for the TZ. The high S values of 0.97 and 1.31 wt % recorded in the lower part of the OZ (Table 1), despite sulphide oxidation, are most likely due to its (i.e., S) capture by gypsum formed in this section, as reported by [21]. The UZ also has a total S content in the range of 0.64–1.28 wt %. The total C content of the tailings in the OZ, TZ and UZ ranges from 0.03 to 0.14 wt %, 0.15 to 0.28 wt % and 0.21 to 1.64 wt %, respectively. Very low organic C contents are recorded in the tailings except for a relatively elevated value of 0.69 wt % at the bottom of the tailings, which reflects the influence of the underlying peat on which the tailings are deposited. The uppermost

part of the tailings also recorded slightly elevated C contents (0.03 wt %), albeit low compared to the lowermost sample. For inorganic C, the OZ exhibit very low contents, with 0.11 wt % as the highest concentration. The TZ and UZ, however, show elevated concentrations ranging from 0.14 to 0.27 wt % and 0.20 to 0.95 wt %, respectively. The bulk (total)  $\delta^{13}\text{C}$  values of the tailings range from  $-26\text{‰}$  to  $-19\text{‰}$  in the OZ,  $-9\text{‰}$  to  $-5\text{‰}$  in the TZ and  $-25\text{‰}$  to  $-3\text{‰}$  in the UZ. The  $\delta^{13}\text{C}$  of the organic carbon ( $\delta^{13}\text{C}_{\text{org}}$ ) contents of the tailings varies between  $-31\text{‰}$  and  $-25\text{‰}$ , whereas that of the carbonates ( $\delta^{13}\text{C}_{\text{carb}}$ ) ranges from  $-5\text{‰}$  to  $+1\text{‰}$ . In the OZ,  $\delta^{13}\text{C}_{\text{carb}}$  could not be measured due its very low carbonate contents.

**Table 1.** Chemical and isotopic ( $\delta^{13}\text{C}$ ) composition of the drill core (A1) from the Smaltjärnen tailings at Yxsjöberg. Bulk carbon ( $\text{C}_{\text{bulk}}$ ) and S data are from [21].

| Sample     | Depth (cm) | pH  | $\text{C}_{\text{bulk}}$ | S    | Organic C ( $\text{C}_{\text{org}}$ ) | Inorganic C | $\delta^{13}\text{C}_{\text{bulk}}$ | $\delta^{13}\text{C}_{\text{org}}$ | $\delta^{13}\text{C}_{\text{carb}}$ | Remarks |
|------------|------------|-----|--------------------------|------|---------------------------------------|-------------|-------------------------------------|------------------------------------|-------------------------------------|---------|
|            |            |     | (%)                      | (%)  | (%)                                   | (%)         | (‰)                                 | (‰)                                | (‰)                                 |         |
| MS 1_BT    | 10         | 4.5 | 0.14                     | 0.07 | 0.03                                  | 0.11        | $-25.78$                            | $-25.85$                           | -                                   |         |
| MS 2_BT    | 20         | 4.4 | 0.06                     | 0.1  | 0.01                                  | 0.05        | $-25.96$                            | $-25.79$                           | -                                   |         |
| MS 3_BT    | 30         | 3.9 | 0.03                     | 0.2  | 0.01                                  | 0.02        | $-24.58$                            | $-24.73$                           | -                                   | OZ      |
| MS 4_BT    | 40         | 3.7 | 0.03                     | 1.31 | 0.01                                  | 0.02        | $-24.15$                            | $-25.37$                           | -                                   |         |
| MS 5_BT    | 48         | 3.6 | 0.04                     | 0.97 | 0.01                                  | 0.03        | $-19.15$                            | $-25.57$                           | -                                   |         |
| MS 6_BT    | 49         | 5.3 | 0.15                     | 0.6  | 0.01                                  | 0.14        | $-8.86$                             | $-26.44$                           | 0.7                                 |         |
| MS 7_BT    | 63         | 6.3 | 0.28                     | 0.7  | 0.01                                  | 0.27        | $-4.8$                              | $-25.59$                           | $-2.81$                             | TZ      |
| MS 8_BT    | 100        | 6.8 | 0.46                     | 0.85 | 0.01                                  | 0.45        | $-4.22$                             | $-28.34$                           | $-2.42$                             |         |
| MS 9_BT    | 120        | 6.2 | 0.21                     | 1.04 | 0.01                                  | 0.2         | $-5.78$                             | $-29.48$                           | $-2.06$                             |         |
| MS 10_BT   | 150        | 6.4 | 0.32                     | 1.24 | 0.01                                  | 0.31        | $-2.54$                             | $-30.54$                           | $-0.97$                             |         |
| MS 11_BT   | 157        | 6.3 | 0.43                     | 0.83 | 0.01                                  | 0.42        | $-5.05$                             | $-30.7$                            | $-2.12$                             |         |
| MS 12_BT   | 177        | 7.2 | 0.68                     | 0.69 | 0.01                                  | 0.67        | $-3.85$                             | $-30.63$                           | $-2.86$                             |         |
| MS 13_BT   | 240        | 7.4 | 0.35                     | 0.71 | 0.01                                  | 0.34        | $-4.54$                             | $-30.91$                           | $-3.92$                             | UUZ     |
| MS 14_BT   | 309        | 7.6 | 0.57                     | 0.78 | 0.01                                  | 0.56        | $-5.09$                             | $-30.11$                           | $-4.58$                             |         |
| MS 15_BT   | 360        | 7.9 | 0.75                     | 0.64 | 0.02                                  | 0.73        | $-4.61$                             | $-28.92$                           | $-4.25$                             |         |
| MS 16_BT   | 480        | 7.7 | 0.5                      | 1.28 | 0.01                                  | 0.49        | $-4.69$                             | $-28.43$                           | $-4.16$                             |         |
| MS 17_BT   | 500        | 7.6 | 0.58                     | 0.84 | 0.01                                  | 0.57        | $-3.88$                             | $-27.9$                            | $-3.23$                             |         |
| MS 18_BT * | 600        | 7.3 | 1.64                     | 0.79 | 0.69                                  | 0.95        | $-25.22$                            | $-25.56$                           | -                                   |         |

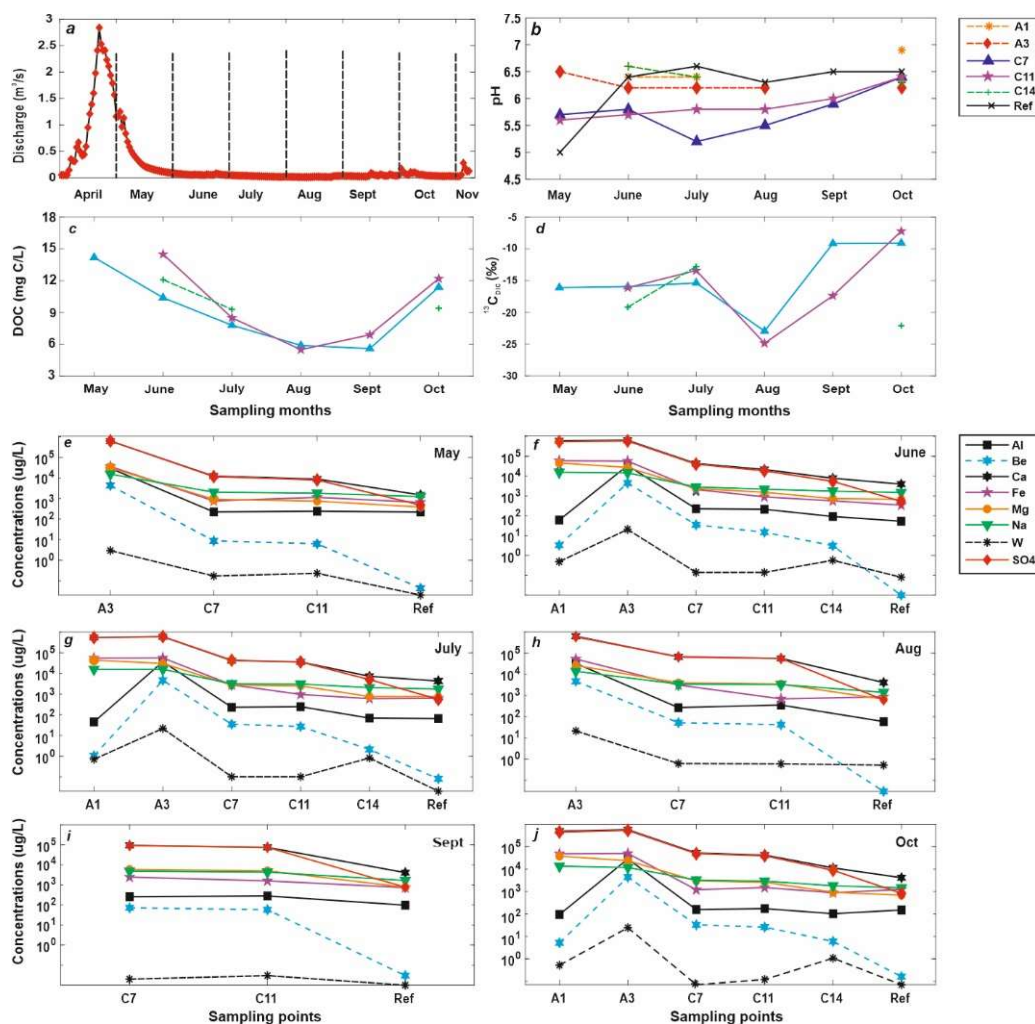
Oxidised zone (OZ); transition zone (TZ); unoxidised zone (UZ). Bulk carbon ( $\text{C}_{\text{bulk}}$ ); carbonate fraction of C ( $\text{C}_{\text{carb}}$ ); organic C ( $\text{C}_{\text{org}}$ ). \* The bottom of the tailings, consisting of a mixture of tailings and peat.



**Figure 2.** Vertical distribution of the chemical and isotopic ( $\delta^{13}\text{C}$ ) composition of the tailings.

### 3.2. Hydrochemical and $\delta^{13}\text{C}_{\text{DIC}}$ Composition of Ground and Surface Waters

The hydrochemical and isotopic ( $\delta^{13}\text{C}_{\text{DIC}}$ ) dataset from the ground and surface water sampling campaigns are presented in Table 2, whereas their spatial and temporal distributions are shown in Figure 3. The pH of the groundwater samples ranges from 6.2 to 6.9 whereas the electrical conductivity (EC) varies between 2430 and 2670  $\mu\text{S}/\text{cm}$ . The surface waters, on the other hand, have pH and EC values ranging from 5.0 to 7.6 and 18–555  $\mu\text{S}/\text{cm}$ , respectively. The groundwater samples have higher concentrations of dissolved ions relative to that of the surface waters: Al (0.05–37 mg/L), Be (1–4671  $\mu\text{g}/\text{L}$ ), Fe (37–59 mg/L), Ca (498–642 mg/L), Mg (24–46 mg/L), Na (12–16 mg/L), W (0.5–24  $\mu\text{g}/\text{L}$ ) and  $\text{SO}_4^{2-}$  (455–639 mg/L). The relatively higher dissolved concentrations of Al, Be, Fe, Ca, Mg, Na and  $\text{SO}_4^{2-}$  are attributable to the oxidation of sulphides, the weathering of calcite and silicate minerals, as well as gypsum dissolution [15], whereas W reflects scheelite weathering [25]. The respective dissolved concentrations of Al, Be, Fe, Ca, Mg, Na, W and  $\text{SO}_4^{2-}$  in the surface waters range from 1.4–94 mg/L, 0.02–72  $\mu\text{g}/\text{L}$ , 0.3–3 mg/L, 1.4–94 mg/L, 0.4–6 mg/L, 1.2–4.3 mg/L, 0.01–1.72  $\mu\text{g}/\text{L}$  and 0.5–91 mg/L. Among the surface waters, the reference sample has the lowest dissolved ion concentrations, as shown in Table 2 and Figure 3, whereas those downstream of the Smaltjärnen repository, vis-à-vis C7, C11 and C14, have the highest concentrations.



**Figure 3.** (a) Time series data of surface water discharge in the study area from April to November 2018. (b–d) Temporal variations in pH, DOC and  $\delta^{13}\text{C}_{\text{DIC}}$  for A1, A3, C7, C11, C14 and the reference point (Ref) from May to October; (e–j) temporal and spatial variations in dissolved ion concentrations for A1, A3, C7, C11, C14 and Ref.

**Table 2.** Physicochemical, hydrochemical and isotopic data of ground and surface water samples. All data, except those for dissolved organic carbon (DOC) and the chemical and isotopic composition of primary calcite and dissolved inorganic carbon ( $\delta^{13}\text{C}_{\text{DIC}}$ ), are from [15,25].

| Sampling Site | EC ( $\mu\text{S}/\text{cm}$ ) | pH  | Al (mg/L) | Ca (mg/L) | Fe (mg/L) | Mg (mg/L) | Na (mg/L) | Be ( $\mu\text{g}/\text{L}$ ) | W ( $\mu\text{g}/\text{L}$ ) | $\text{SO}_4^{2-}$ (mg/L) | DOC (mg·C/L) | $\delta^{13}\text{C}_{\text{DIC}}$ (‰) |
|---------------|--------------------------------|-----|-----------|-----------|-----------|-----------|-----------|-------------------------------|------------------------------|---------------------------|--------------|----------------------------------------|
| <b>May</b>    |                                |     |           |           |           |           |           |                               |                              |                           |              |                                        |
| A3            | 2500                           | 6.5 | 29.83     | 635       | 36.62     | 31.33     | 15.45     | 4367                          | 2.94                         | 639                       | 7.4          | −4.43                                  |
| C7            | 100                            | 5.7 | 0.22      | 12.42     | 0.77      | 0.93      | 2.05      | 8.7                           | 0.17                         | 11.76                     | 14.2         | −16.09                                 |
| C9            | 18                             | 5.2 | 0.22      | 1.39      | 0.81      | 0.35      | 1.18      | 0.09                          | 0.14                         | 0.55                      | 18.4         |                                        |
| C11           | 73                             | 5.6 | 0.24      | 8.95      | 1.15      | 0.75      | 1.82      | 6.30                          | 0.23                         | 8.09                      |              |                                        |
| C13           | 27                             | 6.1 | 0.11      | 2.52      | 0.32      | 0.37      | 1.75      | 0.04                          | 0.38                         | 0.91                      | 13.2         |                                        |
| Ref           | 18                             | 5.0 | 0.22      | 1.50      | 0.65      | 0.39      | 1.25      | 0.04                          | 0.02                         | 0.48                      | 15.4         | −20.23                                 |
| <b>June</b>   |                                |     |           |           |           |           |           |                               |                              |                           |              |                                        |
| A1            | 2660                           | 6.4 | 0.06      | 607       | 59.38     | 46.19     | 15.72     | 3.28                          | 0.49                         | 547                       | 18.9         | −12.64                                 |
| A3            | 2670                           | 6.2 | 34        | 642       | 57.35     | 27.45     | 14.58     | 4512                          | 20.60                        | 590                       | 10.6         | −7.92                                  |
| C7            | 256                            | 5.8 | 0.23      | 43.30     | 2.13      | 2.36      | 2.84      | 35.10                         | 0.14                         | 40.20                     | 10.4         | −15.94                                 |
| C9            | 33                             | 5.6 | 0.21      | 3.11      | 0.99      | 0.73      | 1.67      | 0.10                          | 0.20                         | 1.09                      | 21.1         | −22.15                                 |
| C11           | 163                            | 5.7 | 0.21      | 21.61     | 0.90      | 1.54      | 2.19      | 15                            | 0.14                         | 18.54                     | 14.5         | −16.1                                  |
| C13           | 27                             | 6.5 | 0.08      | 2.86      | 0.52      | 0.38      | 1.57      | 0.03                          | 0.85                         | 0.83                      | 12           | −17.52                                 |
| C14           | 66                             | 6.6 | 0.09      | 7.83      | 0.57      | 0.74      | 1.75      | 3.10                          | 0.57                         | 5.46                      | 12.1         | −19.17                                 |
| Ref           | 37                             | 6.4 | 0.05      | 3.95      | 0.35      | 0.68      | 1.51      | 0.01                          | 0.08                         | 0.53                      | 10.2         | −14.03                                 |
| <b>July</b>   |                                |     |           |           |           |           |           |                               |                              |                           |              |                                        |
| A1            | 2430                           | 6.4 | 0.05      | 545       | 55.39     | 44.02     | 15.80     | 1.04                          | 0.70                         | 542                       | 13           |                                        |
| A3            | 2590                           | 6.2 | 36.87     | 594       | 56.10     | 30.45     | 15.80     | 4610                          | 21.70                        | 606                       | 3.6          | −4.96                                  |
| C7            | 306                            | 5.2 | 0.23      | 41.72     | 2.81      | 2.72      | 3.14      | 35                            | 0.10                         | 43.53                     | 7.8          | −15.36                                 |
| C9            | 41                             | 6.4 | 0.15      | 4.37      | 1.20      | 1.01      | 2.14      | 0.12                          | 0.28                         | 0.46                      | 16.2         | −14.28                                 |
| C11           | 259                            | 5.8 | 0.25      | 35.95     | 0.96      | 2.50      | 3.08      | 27                            | 0.10                         | 35.86                     | 8.5          | −13.4                                  |
| C13           | 29                             | 7.6 | 0.08      | 2.87      | 0.59      | 0.41      | 1.86      | 0.07                          | 1.04                         | 0.81                      | 10.5         | −10.76                                 |
| C14           | 63                             | 6.4 | 0.07      | 7.26      | 0.60      | 0.76      | 2.06      | 2.10                          | 0.81                         | 5.03                      | 9.3          | −12.78                                 |
| Ref           | 38                             | 6.6 | 0.07      | 4.29      | 0.63      | 0.75      | 1.76      | 0.08                          | 0.02                         | 0.56                      | 9.3          | −14.04                                 |
| <b>Aug</b>    |                                |     |           |           |           |           |           |                               |                              |                           |              |                                        |
| A3            | 2640                           | 6.2 | 32.29     | 621       | 52.03     | 26.15     | 13.74     | 4671                          | 21.34                        | 577                       | 3.3          |                                        |
| C7            | 460                            | 5.5 | 0.27      | 65.63     | 3.12      | 3.93      | 3.44      | 52                            | 0.62                         | 66.50                     | 5.9          | −22.95                                 |
| C9            | 45                             | 6.5 | 0.11      | 4.55      | 0.79      | 1.00      | 2.08      | 0.07                          | 0.82                         | 0.83                      | 13.3         | −15.91                                 |
| C11           | 402                            | 5.8 | 0.35      | 55.77     | 0.69      | 3.44      | 3.27      | 42                            | 0.60                         | 55.37                     | 5.5          | −24.86                                 |
| C13           | 29                             | 6.7 | 0.05      | 12.85     | 0.37      | 1.18      | 2.06      | 3.00                          | 0.98                         | 0.75                      | 10.1         | −16.18                                 |
| Ref           | 40                             | 6.3 | 0.06      | 4.08      | 0.86      | 0.67      | 1.40      | 0.03                          | 0.52                         | 0.62                      | 8.9          | −19.98                                 |

Table 2. Cont.

| Sampling Site | EC<br>( $\mu\text{S}/\text{cm}$ ) | pH  | Al (mg/L) | Ca (mg/L) | Fe (mg/L) | Mg (mg/L) | Na (mg/L) | Be ( $\mu\text{g}/\text{L}$ ) | W ( $\mu\text{g}/\text{L}$ ) | $\text{SO}_4^{2-}$<br>(mg/L) | DOC<br>(mg·C/L) | $\delta^{13}\text{C}_{\text{DIC}}$<br>(‰) |
|---------------|-----------------------------------|-----|-----------|-----------|-----------|-----------|-----------|-------------------------------|------------------------------|------------------------------|-----------------|-------------------------------------------|
| <b>Sept</b>   |                                   |     |           |           |           |           |           |                               |                              |                              |                 |                                           |
| C7            | 555                               | 5.9 | 0.26      | 94.41     | 2.46      | 5.92      | 4.86      | 72                            | 0.02                         | 91.21                        | 5.6             | −9.15                                     |
| C11           | 400                               | 6.0 | 0.28      | 74.66     | 1.59      | 5.06      | 4.33      | 58                            | 0.03                         | 74.54                        | 6.9             | −17.37                                    |
| C13           | 30                                | 6.6 | 0.06      | 3.20      | 0.62      | 0.48      | 1.99      | 0.08                          | 1.02                         | 0.98                         | 9.5             | −10.54                                    |
| Ref           | 35                                | 6.5 | 0.10      | 4.09      | 0.74      | 0.77      | 1.67      | 0.03                          | 0.01                         | 0.77                         | 9.1             |                                           |
| <b>Oct</b>    |                                   |     |           |           |           |           |           |                               |                              |                              |                 |                                           |
| A1            | 2500                              | 6.9 | 0.10      | 498       | 48.60     | 38.14     | 13.62     | 5.2                           | 0.52                         | 455                          | 16.4            |                                           |
| A3            | 2690                              | 6.2 | 28.59     | 576       | 49.93     | 23.85     | 11.82     | 4406                          | 24.47                        | 535                          | 4.4             |                                           |
| C7            | 396                               | 6.4 | 0.16      | 52.61     | 1.213     | 3.01      | 3.26      | 33                            | 0.07                         | 49.03                        | 11.4            | −9.09                                     |
| C9            | 36                                | 6.0 | 0.17      | 3.29      | 1.23      | 0.79      | 1.64      | 0.18                          | 0.24                         | 1.18                         | 17.6            |                                           |
| C11           | 220                               | 6.4 | 0.17      | 42.49     | 1.51      | 2.61      | 2.93      | 26                            | 0.12                         | 39.79                        | 12.2            | −7.21                                     |
| C13           | 29                                | 6.6 | 0.07      | 2.87      | 1.11      | 0.39      | 1.54      | 0.10                          | 1.74                         | 0.78                         | 9.4             |                                           |
| C14           | 99                                | 6.3 | 0.10      | 11.37     | 0.89      | 0.94      | 1.82      | 6.00                          | 1.07                         | 8.87                         | 9.4             | −22.09                                    |
| Ref           | 38                                | 6.5 | 0.15      | 4.17      | 1.24      | 0.69      | 1.47      | 0.16                          | 0.07                         | 0.84                         | 11.7            |                                           |

The groundwater samples exhibit similar average DOC concentrations (10 mg C/L;  $n = 8$ ) as that of the reference sample (11 mg C/L;  $n = 6$ ). The mixed surface waters downstream of the tailings have DOC concentrations ranging between 6–15 mg C/L (average = 10 mg C/L), with C11 recording the highest concentrations. The high DOC concentrations of C11 reflect the contributions of C9, which has DOC concentrations ranging between 13 and 21 mg C/L (average = 17 mg C/L;  $n = 5$ ) and the highest among all the surface waters (Table 2). The  $\delta^{13}\text{C}_{\text{DIC}}$  of ground and surface waters ranges from  $-12.64\text{‰}$  to  $-4.43\text{‰}$  and  $-24.86\text{‰}$  to  $-7.21\text{‰}$ , respectively. The measured data for daily surface water discharge in the study area (Figure 3) from April to November 2018 range from a peak value of  $2.84 \text{ m}^3/\text{s}$  in April, as a result of the snowmelt, to a minimum value of  $0.02 \text{ m}^3/\text{s}$  in August [23]. Although the sampling campaign began in May, relatively high discharge values, ranging between  $0.08$  and  $1.25 \text{ m}^3/\text{s}$ , were also recorded.

## 4. Discussions

### 4.1. Carbon Isotope ( $\delta^{13}\text{C}$ ) Systematics and Secondary Carbonate Formation in the Tailings

The  $\delta^{13}\text{C}$  values of the bulk tailings in the OZ ( $\delta^{13}\text{C}_{\text{bulk}} = -26\text{‰}$  to  $-19\text{‰}$ ) are far lower than those of the primary calcite ( $\delta^{13}\text{C} = +0.1\text{‰}$ ) found in the mineralisation from which the tailings originated, indicating the depletion of calcite in this zone, which is consistent with the mineralogical observations by [13] and the inorganic C contents in Figure 2. The  $\delta^{13}\text{C}$  values of the bulk tailings in this zone are typically within the range of  $\delta^{13}\text{C}$  of  $\text{C}_3$  terrestrial plants ( $-30\text{‰}$  to  $-24\text{‰}$ ) [26,27]. These signatures may represent a mixture of C sources from the degradation of organic matter from vegetation (plants and grasses) on the tailings and sewage sludge used to establish the vegetation cover on the tailings. In the TZ and UZ (excluding samples from the bottom of the tailings), the bulk  $\delta^{13}\text{C}$  signatures of the tailings show a shift towards higher values ( $\delta^{13}\text{C} = -8.9\text{‰}$  to  $-3.8\text{‰}$ ) compared to the OZ. The higher  $\delta^{13}\text{C}$  values correspond to an increase in pH (5.3–7.9), which is characteristic of calcite neutralisation and/or buffering of acidity [28]. Ironically, the  $\delta^{13}\text{C}$  of carbonates ( $\delta^{13}\text{C}_{\text{carb}}$ ) in these zones averages  $-2.7\text{‰}$  (range =  $-4.6\text{‰}$  and  $+0.7\text{‰}$ ), which is slightly lower than that of the  $\delta^{13}\text{C}$  of the primary calcite. Since isotopic fractionation between  $^{12}\text{C}$  and  $^{13}\text{C}$  during calcite dissolution by acidity is negligible [29], these lower  $\delta^{13}\text{C}_{\text{carb}}$  values are relative to those of the primary calcite signal in the addition of a C source or sources with lighter isotopic ( $\delta^{13}\text{C}$ ) signatures, most likely organic matter and/or atmospheric  $\text{CO}_2$ , which have a present  $\delta^{13}\text{C}$  value of  $\sim -8\text{‰}$  [30]. In fact, the lower  $\delta^{13}\text{C}_{\text{carb}}$  values are consistent with the range of reported values for secondary soil carbonates ( $\delta^{13}\text{C} = -10.3\text{‰}$  to  $+1.1\text{‰}$ ) especially within Europe and the Mediterranean areas [31,32], indicating their authigenic origin. This therefore indicates the formation of secondary carbonates, as suggested by [13]. The dissolution of primary calcite can increase the amount of carbonate in solution and promote the precipitation of secondary calcite in the presence of  $\text{Ca}^{2+}$  due to increased pH [33]. Thus, carbonate released from the dissolution of primary calcite in the OZ and TZ (particularly at MS 6) and mobilised to the underlying zones, as well as the availability of  $\text{Ca}^{2+}$  mobilised from the OZ via the weathering of the Ca-bearing minerals such as plagioclase, scheelite, fluorite and garnet, may have favoured the precipitation of the secondary carbonate in the TZ (specifically at MS 7) and the UZ. The recorded pH range of 6.3–7.9 recorded at MS 7 in the TZ and the UZ suggests  $\text{HCO}_3^-$  as the dominant carbonate specie [6]. Therefore, the lower  $\delta^{13}\text{C}_{\text{carb}}$  values may represent a mixture of isotopically light  $\text{CO}_2(\text{aq})$  from the atmosphere and the oxidation of organic matter (vegetation and sewage sludge) in the uppermost part of the tailings as well as isotopically heavy  $\text{HCO}_3^-$  mobilised downwards in the tailings from the dissolution of calcite in the OZ and TZ. This results in potentially higher DIC concentrations but lowers the  $\delta^{13}\text{C}_{\text{DIC}}$  values. The subsequent precipitation of these secondary carbonates from this mixture results in such negative  $\delta^{13}\text{C}$  values [34,35]. An interesting observation is the formation of secondary carbonates even in the UZ, as suggested by the  $\delta^{13}\text{C}_{\text{carb}}$  values (Table 1). This signals the extent to which the DOC produced in the uppermost part of the tailings has been mobilised in the tailings.

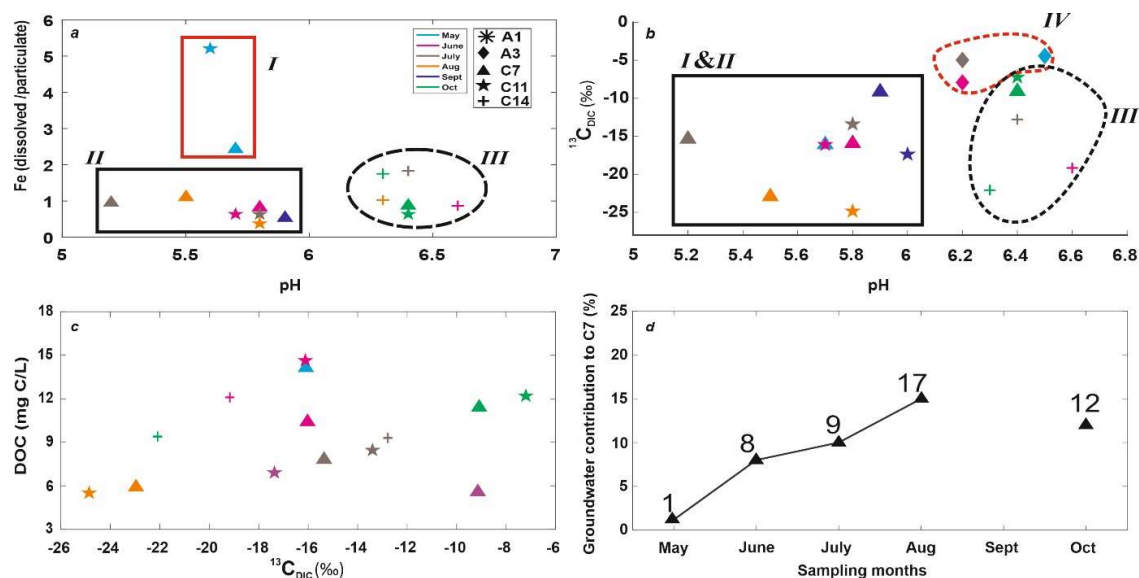
#### 4.2. Biogeochemical Processes Controlling $\delta^{13}\text{C}_{\text{DIC}}$ Signatures of the Groundwater and Downstream Surface Waters

The pH of the groundwater samples (pH = 6.2–6.9) are consistent with the dissolution of calcite [28] and suggests  $\text{HCO}_3^-$  as the main DIC specie [6]. Hypothetically, the dissolution of the primary calcite and the secondary carbonate in the tailings are expected to result in groundwater  $\delta^{13}\text{C}_{\text{DIC}}$  signatures ranging between  $-4.6\text{‰}$  and  $+0.7\text{‰}$ . However, very low groundwater  $\delta^{13}\text{C}_{\text{DIC}}$  values ranging from  $-12.6\text{‰}$  to  $-4.4\text{‰}$  are recorded. Coupled with these low  $\delta^{13}\text{C}_{\text{DIC}}$  signatures are relatively high DOC (3–19 mg C/L) concentrations, signalling the influence of a C source with a lighter ( $\delta^{12}\text{C}$ ) signature. Since the tailings are deposited into bogs and swamps [14], the lower  $\delta^{13}\text{C}_{\text{DIC}}$  signatures and high DOC concentrations suggest an organic source, which is supported by the elevated organic C content (0.69 wt %) at the bottom of the tailings (Figure 2). Furthermore, the study area is surrounded by vast forests, which can also contribute to the high DOC that lowers the  $\delta^{13}\text{C}_{\text{DIC}}$  signatures during groundwater recharge. Furthermore, the degradation of the plant and grass debris as well as sewage sludge in the upper part of the tailings may also contribute to the high DOC and lower  $\delta^{13}\text{C}_{\text{DIC}}$  values of the groundwater [36,37]. The recorded groundwater  $\delta^{13}\text{C}_{\text{DIC}}$  values are therefore assumed to represent a mixture of carbonate (calcite and secondary carbonate) dissolution in the tailings and the degradation of organic matter in the uppermost section of the tailings, underneath the tailings and/or from the surrounding forests.

Surface waters downstream of the Smaltjärnen tailings (C7, C11 and C14) have similar average DOC concentrations (9.7 mg-C/L) as that of the groundwater samples (9.6 mg-C/L) but lower  $\delta^{13}\text{C}_{\text{DIC}}$  signatures ( $-25\text{‰}$  to  $-7\text{‰}$ ) relative to that of the groundwater samples (Figure 3). Sampling point C7 was indirectly sourced from the Smaltjärnen lake and receives contributions from groundwater, whereas C11 consists of a mixture of C7 and C9 [15], as depicted in Figure 1. In addition, the DOC and discharge display a direct correlation with each other (Figure 3), with the highest values reported in May; these then decline from June to September for both parameters. The strong agreement between discharge and DOC suggests a high degree of allochthonous origin due to the erosion of the surrounding forests' soil organic matter [9] during the snowmelt and spring flood.

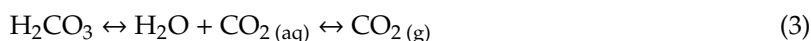
The mixed surface waters were previously categorised into three main groups (Figure 4a), namely Groups I, II and III [15], based on pH and dissolved/particulate Fe ratios. Group I is made up of C7 and C11 samples collected during the month of May, with high dissolved/particulate Fe ratios and low pH values (5.0–6.0). This group of samples have the highest DOC and discharge values (Figure 3) in addition to a relatively low  $\delta^{13}\text{C}_{\text{DIC}}$  ( $-16\text{‰}$ ; see Figure 4b). The high DOC and discharge coupled with the low pH reflects the large contribution of drainage ( $\sim 99\%$ ) from the wash out of the mires and forests (with significant soil organic matter) during the snowmelt and spring flood [15]. The low  $\delta^{13}\text{C}_{\text{DIC}}$ , on the other hand, suggests the introduction of isotopically light ( $\delta^{12}\text{C}$ )  $\text{CO}_2$  from the degradation of the DOC, which may contribute to an increased DIC pool [9].

Group II samples, consisting mainly of C7 and C11 samples from June to September, have low pH values (5.2–5.9) and dissolved/particulate Fe ratios. The particulate Fe contents and pH at C11 are considered as merely artefacts or remnants of C7 as it flows downstream [15]. During this period, the contribution of groundwater to C7 ranges between 8% and 17% (Figure 4d) [15]. These observed trends in the pH and dissolved/particulate Fe ratios are attributed to the hydrolysis of  $\text{Fe}^{3+}$  and the subsequent formation of Fe (III)-oxyhydroxides [16], resulting from the coupled effect of the mixing of the  $\text{Fe}^{2+}$ -rich groundwater with the oxygenated surface water in the Smaltjärnen lake (Figure 1) or merely the exposure of the groundwater to atmospheric oxygen. The formation of the Fe (III)-oxyhydroxides is reported to partially account for the low dissolved concentrations of elements such as Be, Fe, and W in these waters (Figure 3) relative to the groundwater samples [15].



**Figure 4.** (a) pH versus dissolved/particulate Fe ratios of mixed surface waters: C7, C11 and C14 (from [15]). (b) pH versus  $\delta^{13}\text{C}_{\text{DIC}}$  of ground water and mixed surface waters. (c) DOC versus  $\delta^{13}\text{C}_{\text{DIC}}$  of the mixed surface waters. (d) Estimated monthly groundwater contribution to C7.

Since  $\text{HCO}_3^-$  is assumed as the main DIC specie in the groundwater (based on its prevailing pH), the resulting low pH in the Group II samples will dehydrate the  $\text{HCO}_3^-$  to ultimately produce  $\text{CO}_2(\text{g})$ , which may be lost to the atmosphere [38], as shown in Equations (2) and (3).



Although this study is limited by the unavailability of data regarding DIC concentrations, the loss of  $\text{CO}_2(\text{g})$  is expected to result in a decrease in the DIC pool and an enrichment of the  $\delta^{13}\text{C}_{\text{DIC}}$  of the surface waters compared to that of the groundwater. Furthermore, the high temperatures recorded, especially during these months, can enhance photosynthetic activities in the surface waters, which may lead to a reduction in the net DIC concentrations but an enriched  $\delta^{13}\text{C}_{\text{DIC}}$  concentration [39,40].

Despite the potential occurrence of these aforementioned processes and their overall contribution to the enrichment of the  $\delta^{13}\text{C}_{\text{DIC}}$ , very low  $\delta^{13}\text{C}_{\text{DIC}}$  signatures ( $\delta^{13}\text{C}_{\text{DIC}} = -25\text{‰}$  to  $-9\text{‰}$ ) are recorded for this group of samples. These low  $\delta^{13}\text{C}_{\text{DIC}}$  signatures indicate inputs from isotopically light ( $\delta^{12}\text{C}$ ) C source(s). This suggest that potentially multiple biogeochemical processes may be occurring simultaneously within these surface waters as indicated by the undefined pattern between DOC and  $\delta^{13}\text{C}_{\text{DIC}}$  (Figure 4c). For example, the oxidation of the DOC and aquatic respiration in these surface waters will result in an increased DIC pool through the addition of isotopically light  $^{12}\text{CO}_2$ . However, this may cause a shift in the  $\delta^{13}\text{C}_{\text{DIC}}$  of the surface waters toward lower values [41]. In addition, the high DOC and low pH of these surface waters may enhance photooxidation [42], leading to an increase in the DIC concentrations but lower  $\delta^{13}\text{C}_{\text{DIC}}$  values. These are all likely processes that can contribute to such lower  $\delta^{13}\text{C}_{\text{DIC}}$  signatures recorded in Group II samples.

All C14 samples, as well as C7 and C11 samples, for the month of October constitute Group III, with low dissolved/particulate Fe ratios and a high pH (6.3–6.4). This group of samples also have high DOC concentrations relative to those of Group II (Figure 3), as well as reduced groundwater contribution to C7 (12%). The low dissolved/particulate Fe ratios for C14 are due to dilution from C13, autumn rainfall and the influence of the high particulate contents from C7 and C11, whereas the high pH is from the carbonate buffer of C13 [15]. Of particular interest in this group is the increased pH (6.4) and  $\delta^{13}\text{C}_{\text{DIC}}$  ( $-9\text{‰}$  to  $-7\text{‰}$ ) values of C7 and C11, which show close association with those

of the groundwater samples (Group IV) (Figure 4b). This shift in  $\delta^{13}\text{C}_{\text{DIC}}$  signatures towards higher values is hypothesised to represent a period of photosynthetic activity in the surface waters and/or potential  $\text{CO}_2(\text{g})$  loss from these surface waters due to their high partial pressure ( $P_{\text{CO}_2}$ ) relative to the atmosphere.

## 5. Conclusions

- Lower  $\delta^{13}\text{C}$  values of carbonates in the deeper tailings relative to those of the primary calcite indicate the precipitation of secondary carbonates. The  $\delta^{13}\text{C}$  signatures of these secondary carbonates reflect a mixture of three C sources involving atmospheric  $\text{CO}_2$  ( $\delta^{13}\text{C} = -8\text{‰}$ ), degraded organic matter ( $\delta^{13}\text{C} = -26\text{‰}$ ) and primary calcite ( $+0.1\text{‰}$ ) dissolution in the tailings.
- The recorded  $\delta^{13}\text{C}_{\text{DIC}}$  signatures of the groundwater represent a mixture of C signals from calcite and secondary carbonate dissolution in the tailings, as well as the degradation of organic matter (vegetation and sewage sludge) in the uppermost section of the tailings, peat underneath the tailings and the surrounding forests.
- The lower  $\delta^{13}\text{C}_{\text{DIC}}$  values of the mixed surface waters (i.e., C7 and C11) downstream of the Smaltjärnen repository in May are regulated by the degradation DOC from the mires and forests during the high discharge from the snowmelt.
- The myriad of potential in-stream biogeochemical processes regulating the  $\delta^{13}\text{C}_{\text{DIC}}$  signatures of the downstream surface waters from June to September and the lack of DIC concentrations makes it difficult to decipher the dominant process. In view of this limitation, other isotopic systems and elemental concentrations may be helpful in unravelling the dominant biogeochemical process or source.

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