School of Civil Engineering and Geosciences

BIOGEOCHEMICAL PROCESSES IN REDUCING AND ALKALINITY PRODUCING SYSTEMS, BOWDEN CLOSE, UK

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DECLARATION

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Abstract

A study was undertaken on the Bowden Close (BCl) Passive mine water Treatment System (PTS). BCl consists of two parallel working Reducing and Alkalinity Producing Systems (RAPS, reactive substrate = limestone, compost, manure) that are followed by a polishing wetland. Thereafter, the water is discharged into a local burn. The main purpose of the PTS is to decrease metal concentrations (Fe ($\leq$177mgL^{-1}), Al ($\leq$85mgL^{-1}), Zn ($\leq$2.8mgL^{-1}), Mn ($\leq$20.5mgL^{-1})) and increase alkalinity ($\geq$0mg L^{-1} $CaCO_3$ eq) and pH ($\geq$3.2) in two coal mine drainages. The aim of this study was to assess the treatment performance and the dominant (bio)geochemical processes promoting metal removal and alkalinity generation, particularly in the RAPS. Over nearly six years of operation, BCl performed well with regards to the removal of iron (-84%) and aluminium (-87%) and the generation of alkalinity (+74%). Zinc (-51%), manganese (-23%) and sulfate (-29%) were partially removed. The effluent pH was raised to ~6.9. However, a long-term decrease in alkalinity generation has been observed, which could threaten the treatment performance over the short term and might eventually lead to metal remobilization. Against expectations, Bacterial Sulfate Reduction (BSR) is not a driving process in the removal of the main contaminant, iron. Only ~5% of iron was removed as di-sulfide mineral (i.e. pyrite). Rather, removal processes such as observed in aerobic treatment systems predominate (i.e. retention in (hydr)oxides). It is suggested, that the reoxidation of hydrogen sulfide by Fe(III)hydroxides is limiting the generation of mineral sulfides. Carbon isotope ratios of total dissolved inorganic carbon indicate that anaerobic microbial respiration, including BSR, has considerable influence on the generation of alkalinity. Two mass balances suggest, that more than 52% of bicarbonate generated by the RAPS derives from the oxidation of organic matter, thereby safeguarding the limestone in the reactive substrate and increasing the overall lifetime of the RAPS. Analyses of sulfur and oxygen isotope ratios of dissolved sulfate and sulfide, together with solid phase sulfur and water isotopes suggested: i) mine waters are of meteoric origin, ii) and have one single sulfate sulfur source (potentially oxidation of coal derived iron sulfide), iii) sulfide oxidation in the mine waters is dominated by anaerobic oxidation, iv) in both RAPS, BSR is occurring year round, v) sulfate concentrations might be limiting BSR in RAPS 1 during the summer months and vi) pyrite seemed to form via the hydrogen sulfide pathway without solid phase iron mono-sulfide intermediate. Overall, sulfur and oxygen isotope fractionation suggest that BSR kinetics are slow and bi-directional. Detailed studies, including the microbial ecology in the RAPS are proposed to enhance understanding about the functioning of the system.

Key words: coal mine drainage, microbial sulfate reduction, alkalinity generation, isotopes

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Abbreviations

ALD	Anoxic limestone drains
Alk	Alkalinity
AMD	Acid mine drainage
ARD	Acid rock drainage
a.s.l.	Above sea level
AVS	Acid volatile sulfur
BCl	Bowden Close passive mine water treatment site
bdl	Below detection limit
bs	Below surface
BSR	Bacterial sulfate reduction
COD	Chemical oxygen demand
CRS	Chromium reducible sulfur
DCM	Dichloromethane
DIC	Dissolved inorganic carbon
DO	Dissolved oxygen
DOC	Dissolved organic carbon
EC	Electrical conductivity
Eh	Redox potential
EQS	Environmental quality standard
ES	Elemental sulfur
FAAS	Flame atomic absorption spectrometry
HDPE	High-density polyethylene
IC	Ion chromatography
ICP-AES	Inductively coupled plasma – atom emission spectrometry
ICP-OES	Inductively coupled plasma – optical emission spectrometry
ICP-MS	Inductively coupled plasma – mass spectrometry
IRMS	Isotope ratio mass spectrometer
IS	Ionic strength
ISS	Inorganic sulfur species
L	Load
pH	Negative logarithm of the concentration of hydrogen ions
PRB	Permeable reactive barrier
PTFE	Polytetrafluorethylene
PTS	Passive treatment system
QA/QC	Quality assurance and quality control procedures
r, R, R^2, R_{adj}^2	Correlation coefficients
RAPS	Reducing and alkalinity producing system
RIS	Reduced inorganic sulfur
rpm	Revolutions per minute
rps	Revolutions per second
SI	Saturation index
SRB	sulfate reducing bacteria
Stdev, σ	Standard deviation
T	Temperature
TDIC	Total dissolved inorganic carbon
TC	Total carbon
TIC	Total inorganic carbon
TOC	Total organic carbon
TS	Total sulfur
V-CDT	Vienna canyon diablo troilite
V-PDB	Vienna pee dee belemnite
VIF	Variance inflation factor, measure of multicollinearity (optimal value near 1.0)

Introduction

Mine drainage is considered to be the main environmental concern caused by the mineral extracting and processing industry (Jarvis and Younger 1997) and one of the main sources of the pollution of surface water bodies in the UK (Younger 1997, Mayes et al. 2010) and abroad (Cravotta 2008a, Cravotta 2008b). Mine waters are often metalliferous and acidic (acid mine drainage, AMD) (Barnhisel et al. 1982, Wagner et al. 1982, Nordstrom and Alpers 1999b, Ávila et al. 2008, Kelm et al. 2009). Uncontrolled discharge of these waters can lead to severe environmental impacts on a number of receptors including soils, sediments, water bodies, biosphere, humans and infrastructure (Jarvis and Younger 1997, Bigham and Nordstrom 2000, Sanchez España et al. 2005, Peplow and Edmonds 2006, Canovas et al. 2007, Mäkinen and Lerssi 2007, van Damme et al. 2008, Åberg and Satake 2009, Casiot et al. 2009, Kim et al. 2009, Li et al. 2009, Asta et al. 2010, Bird et al. 2010, Liu et al. 2010, Saunders et al. 2010).

Coal mine drainage can be enriched in iron, aluminium, manganese, trace metals (e.g. Pb, Cu, Ni, U, As, Zn and rare earth elements), sulfate and proton acidity (Kepler and Mc Cleary 1994, Yu and Heo 2001, Younger et al. 2002, Buil et al. 2007, Jena et al. 2007, Cravotta 2008a, Botha et al. 2009, Janson et al. 2009, Wu et al. 2009). Iron can have potentially suffocating effects on gilled organisms (Dent and Pons 1995) and cause sediment smothering and decrease abundance and diversity of bottom dwelling organisms (Younger 1997). Neurological diseases (Rondeau et al. 2000, Campbell et al. 2001, WHO 2003b, Becaria et al. 2006) have been reported as a result of elevated aluminium concentrations along with fish and zooplankton toxicity (Baker and Schofield 1982, Havas and Likens 1985, Havens and Heath 1989, Mihaljevic et al. 2009). The precipitation of Al-hydroxide onto gills hampers ion-regulatory and respiratory organs (Havens and Heath 1989). Manganese can cause discoloration of the waters, bioaccumulation and neurological effects upon inhalation and ingestion (WHO 2003a, Zeng et al. 2009).

AMD is generated through atmospheric weathering of sulfide minerals (e.g. pyrite, pyrrhotite, bornite, chalcopyrite, arsenopyrite) that are exposed to water and oxygen (e.g. summary equation for pyrite oxidation: $FeS_2 + 2O_2 + 2H_2O \rightarrow 2Fe^{2+} + 4SO_4^{2-} + 4H^+$; summary equation for pyrrhotite oxidation: e.g. pyrrhotite: $FeS + O_2 + 2H_2O \rightarrow Fe^{2+} + SO_4^{2-} + 4H^+$).

These highly complex processes include both abiotic and biotic pathways and occur under aerobic (pyrite: $FeS_2 + 3.5O_2 + H_2O \rightarrow 2SO_4^{2-} + 2Fe^{2+} + 2H^+$) and anaerobic (pyrite: $FeS_2 +$

$14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+$) conditions (Silverman 1967, Nordstrom 1982a, Silver 1989, Nordstrom and Southam 1997, Nordstrom and Alpers 1999a, Bigham and Nordstrom 2000, Kazadi and Petersen 2008, Tan et al. 2009). Microorganisms potentially enhance reaction rates by up to six orders of magnitude (Singer and Stumm 1970) through direct and indirect mechanisms (Nordstrom 1982a, Ehrlich 1996).

The generation of AMD is naturally occurring (Bigham and Nordstrom 2000, Rüde 2004, Eppinger and Fuge 2009, Hinman et al. 2009, Kwong et al. 2009, Lavergren et al. 2009, Verplanck et al. 2009). However, mineral extraction and processing cause an enhancement of AMD generation through i) the increase of reactive surface areas of potentially acid generating rock, ii) enhanced exposure to atmospheric conditions and iii) concentration of acid generating minerals in waste rock (Nordstrom and Alpers 1999a). Metalliferous drainage has been reported from tailing impoundments, waste rock dumps, underground and open pit mines and heap leach pads (Kuyucak 1999).

Despite the potentially adverse effects of AMD which have been known for centuries (Agricola 1556), its remediation has only fairly recently gained attention due to increased public pressure and introduction of environmental legislation (e.g. European Water Framework Directive 2000/60/EC; EU Mine Waste Directive 2006/21/EC). Often, responsibilities for the remediation are unclear, particularly for closed or abandoned mines. In such cases, (UK) government funds are necessary to limit the environmental damage for which economic remediation options are needed. In the past, active (chemical) treatment of AMD has been the most reliable form of treatment (Lenter et al. 2002, Bowell 2004, Bologo et al. 2009, Howard et al. 2009) despite being highly labour intensive and expensive (Younger et al. 2002, Kalin et al. 2006). In many cases, AMD generation proceeds for decades or even centuries (Younger 1997, Kalin 2001, Bryan et al. 2004) so that active treatment is unfeasible.

Natural attenuation of metal pollution in natural wetlands (Wieder and Lang 1984, Huntsman and Brehm Laboratory 1986, Wieder and Lang 1986, Spratt et al. 1987, Eger et al. 1993, Witthar 1993, Brown et al. 1994) and experiences gained from the passive municipal and industrial waste water treatment (Mingee and Crites 1989, Watson and Danzig 1993, Robertson et al. 1995) have led to the development of a passive form of AMD treatment system (i.e. passive treatment systems, PTS) (Brodie et al. 1989, Hammer and Bastian 1989, Howard et al. 1989, Klusman and Machemer 1991, Frostman 1993, Machemer et al. 1993).

Compared to active treatment systems, PTS require less financial investment and limited supervision and maintenance. Therefore, PTS have found global application, particularly in the remediation of coal mine derived drainage (Hedin et al. 1994, Ziemkiewicz et al. 2003, Ji et al. 2008). In the UK, to date more than 50 passive treatment schemes are in operation, mostly for the remediation of net-alkaline coal mine drainage (Edwards et al. 1997, Younger 1998a, Banks 2002, Parker 2002, Amos and Younger 2003, Hancock 2005, Batty et al. 2008, Morrison and Aplin 2009, Watson et al. 2009). Many more are reported from Europe, North America, South Africa and some Asian countries (e.g. Hedin et al. 1994, Bhattacharya et al. 2008, Ji et al. 2008).

Passive treatment systems are categorised into aerobic and anaerobic schemes (Hedin et al. 1994, Younger et al. 2002). Whilst the former are applied to treat net-alkaline metalliferous waters, the latter are aimed at the treatment of net-acidic waters.

For the passive treatment of the latter, a variety of chemically and biologically based PTS exist (Brown et al. 2002, Younger et al. 2002). One of them, first cited by Kepler and Mc Cleary (1994), are Reducing and Alkalinity Producing Systems (RAPS) (named Successive Alkalinity Producing Systems (SAPS) by those authors). RAPS are essentially combinations of anoxic limestone drains (ALD) and compost wetlands (Kepler and Mc Cleary 1994), but are vertical (downward) rather than horizontal flow systems. RAPS therefore have a significantly lower footprint than other systems and require less financial investment for the purchase of land, one of the principal limiting factors for the application of passive treatment. RAPS are commonly combined with other PTS, both aerobic and anaerobic (Norton et al. 1998, Demchak et al. 2001).

The principal aims of anaerobic organic-rich treatment systems are to increase the pH and alkalinity and decrease metal and sulfate loads. Therefore, oxygen is stripped from the waters by aerobic microbial respiration ($CH_2O + O_2 \rightarrow CO_2\uparrow + H_2O$; CH_2O=organic matter). Due to the high energy gains ($-241.6\ \mathrm{kJ}\ H_2\ \mathrm{mol}^{-1}$) (Zinder and Brock 1978) aerobic respiration is the preferred mineralization process under oxidizing conditions. Oxygen consumption in organic rich substrate, however, generally occurs fast and leads to oxygen depleted conditions a few centimetres below the air-sediment or water-sediment interface. Upon consumption of oxygen, other electron acceptors (e.g. $NO_3^- > Mn^{4+} > Fe^{3+} > SO_4^{2-} > CO_2$) can be used by microorganisms to gain energy from the oxidation of organic matter, however with declining energy yields. It is commonly believed, that due to the elevated concentrations of sulfate in mine waters, bacterial sulfate reduction ($2CH_2O + SO_4^{2-} \rightarrow H_2S + 2HCO_3^-$, CH_2O=organic matter) is a dominant process in PTS. The main reaction products, bicarbonate and hydrogen sulfide, contribute to the increase in alkalinity, buffering of pH ($HCO_3^- + H^+ \leftrightarrow H_2CO_3$) and the removal of chalcophilic elements as sulfide minerals ($M^{2+} + H_2S \rightarrow MS\downarrow + 2H^+$, M=metal).

The Bowden Close Treatment Scheme

The Bowden Close passive treatment scheme (2103.9-2304.8 m Easting, 2177.5-2249.4 m Northing, 70–77 m a.s.l, Figure 1), that has been studied as part of this dissertation, is located 12 km South West of Durham, North East England, and treats uncontrolled discharges of the Durham coalfield (Younger 1998b). The three individual mine waters are characterised by elevated concentrations of iron and aluminium, considerable amounts of zinc, manganese and acidic pH. Trace amounts of arsenic, lead, nickel, chromium, cobalt, cadmium and copper have also been detected (Fabian et al. 2006a).

Discharges 1 and 2 (discussed together as influent 1, Figure 1) derive from an abandoned flooded drift mine of the Harvey and Hutton coal seams (total sulfur=~1-5%), (Younger 1998b). Discharge 3 (influent 2, Figure 1) emerges from a waste rock dump of the former Bowden Close colliery (Younger et al. 2003). During closure of the colliery in the 1960s, buildings were dismantled and the waste rock dump revegetated. However, no attempt was made to prevent the generation of acid mine drainage. Three decades later, it became apparent that the generated mine water had a severe impact on the water quality of the Willington Burn (a tributary of the River Wear) to which the drainage was discharged without prior treatment. The main effects were the decrease in diversity and abundance of invertebrates (Jarvis and Younger 1997).

After the successful operation of a pilot-scale treatment plant between 1999 and 2001 (Younger et al. 2004), a full scale treatment system was installed in 2003 (Figure 1). It consists of two parallel working RAPS (RAPS 1: designed area=1728 m^2, actual area=1511 m^2, length / width / depth=86.3/4.5-22.5/0.8 m; RAPS 2: designed area=4350 m^2, actual area=1124 m^2, length / width / depth=83.7/5-16.3/0.8 m) that are filled with blended limestone gravel, horse manure and straw compost. The RAPS discharge into an aerobic wetland colonised with *Typha latifolia* and *Juncus effusus* (designed area=1300 m^2, actual area=990 m^2, length/width/depth=88.8/5.3-19.5/0.9-1.0 m). From the wetland outlet chamber, the treated water is discharged into the Willington Burn.

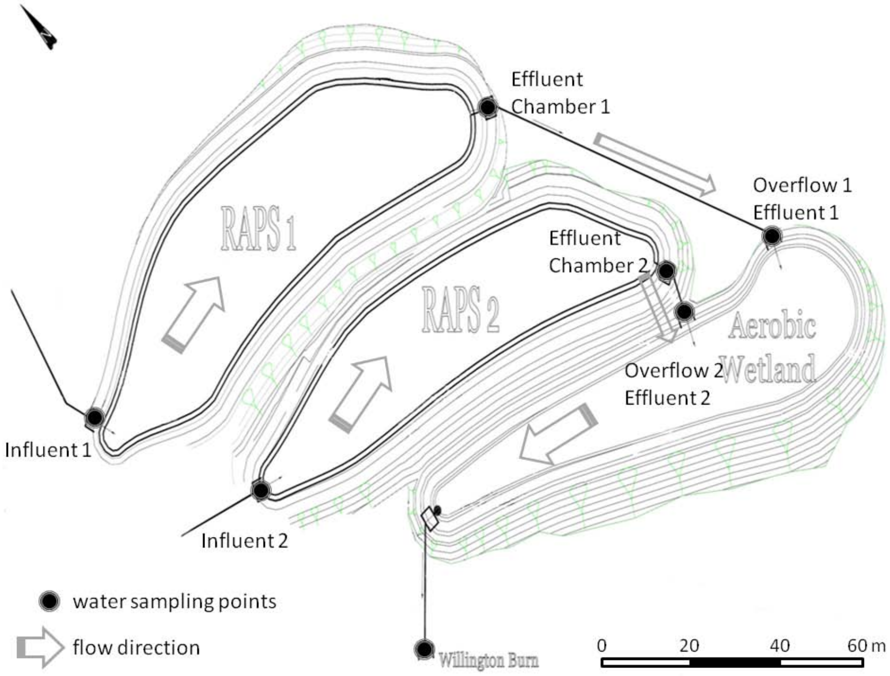


Figure 1 The Bowden Close treatment scheme is composed of two parallel working Reducing and Alkalinity Producing Systems (RAPS) and one aerobic reed wetland. During the historical monitoring, samples from influents (mine waters), effluents (at the point of discharge into the aerobic wetland) and the final effluent (at the discharge point into Willington Burn) were taken. During this study, influents and RAPS effluents (from the effluent chamber) and overflow waters of the RAPS (at discharge point into the aerobic wetland) were sampled.

RAPS 1 is fitted with an artificial HDPE liner (2 mm) protected by 50 mm sand layers above and below. RAPS 2 is underlain by a natural layer of compacted clay. The RAPS have a perforated outlet pipe system with granular fill surround. This runs under the reactive compost-limestone substrate to discharge the treated water (effluent, i.e. water that has percolated through the sediment) to underground aeration pipes via an outlet chamber into the wetland. The RAPS are also equipped with overflow pipes to allow a controlled discharge of surplus water (overflow, i.e. water that is short-circuiting over the RAPS substrate) from the freeboard during high flow events and to prevent erosion and potential failure of retaining embankments. Influent 1 is directed into RAPS 1 and influent 2 is directed into RAPS 2. Due to land restrictions, the three treatment ponds, but particularly RAPS 2, had to be downsized as shown above (compare designed and actual areas).

After about 20 years experience with PTS for AMD remediation, many claims over their functioning and dominant (bio)geochemical processes remain little explored. One of them is the quantitative understanding of bacterial sulfate reduction (BSR; $2CH_2O + SO_4^{2-} \rightarrow H_2S + 2HCO_3^-$) and its influence on the treatment performance of anaerobic PTS composed of organic-rich substrate (Machemer et al. 1993).

Bicarbonate derived from organic matter safeguards limestone in the reactive substrate and thereby prolongs the overall lifetime of the treatment system (Younger et al. 2002). It is believed that under the reducing, oxygen depleted conditions, iron oxidation ($Fe^{2+} + 0.25O_2 + H^+ \rightarrow Fe^{3+} + 0.5H_2O$) is prevented. Consequently, no hydrolysis of Fe^{3+} occurs that would otherwise generate proton acidity and enhance iron(III)hydroxide precipitation ($Fe^{3+} + 3H_2O \rightarrow Fe(OH)_3\downarrow + 3H^+$). The latter has been reported to cause clogging of the reactive substrate, armouring of the limestone and ultimately failure of the treatment system due to the low density of this “ochre” sludge.

The removal of iron and other chalcophilic elements in form of sulfide minerals in the anaerobic PTS decreases the ecotoxicity of the mine waters. Due to their high densities in comparison to most iron (oxyhydr)oxides and their high stabilities under permanently reducing conditions, a long-term stabilization of these metals is thought to be guaranteed.

The theoretical background explained in the previous section is often only assumed without supporting data of BSR occurrence. However, only if we gain confidence of the dominant processes in the treatment process can we develop and improve these systems, enhance their performance and prolong their longevities.

The aim of this study was therefore to assess the treatment performance of the Bowden Close treatment scheme. Nearly six years of monthly surface water data in combination with sediment analyses and stable isotope studies are used to examine the following questions:

- How did the Bowden Close treatment scheme perform over the first six years of operation with regard to iron, aluminium, zinc, manganese and sulfate removal and the increase in pH and alkalinity? What can seasonality and annual trends of the removal process tell us about the long-term performance?
- Based on the surface water geochemistry, what are the dominant sinks of iron, aluminium, zinc, manganese and sulfate in the RAPS?
- Is bacterial sulfate reduction occurring in the RAPS and to what degree does this process influence the removal of iron, the main pollutant in the mine waters?

- How do limestone dissolution and anaerobic microbial respiration relate to the bicarbonate generated by the RAPS and what are the implications for the long-term performance of these systems?

To answer these research questions the dissertation is divided into four chapters; an introduction and a conclusions / recommendations section. The latter two outline research needs, research questions and the main outcomes of the thesis. Field and laboratory methods are explained in Appendix 2 and are summarized in each chapter.

Chapter 1 – Treatment Performance. This chapter focuses on the performance of the Bowden Close treatment scheme in removing iron, aluminium, manganese, zinc and sulfate and increasing pH and alkalinity over a period of 5.5 years (2003-2009). Seasonal and annual changes of the treatment performance are assessed to estimate the lifetime of the treatment scheme. The data presented in this chapter were obtained by staff of Newcastle University, whilst the data in Chapters two to four were obtained by myself.

Chapter 2 – Geochemistry of RAPS Waters. This chapter evaluates an 18 month monitoring of RAPS influents, effluents and overflows. Besides the assessment of the performance of the RAPS, the main focus is on potential geochemical reactions controlling metal and proton concentrations. In addition, stable carbon isotope ratios were measured to discriminate between the main sources of alkalinity (i.e. limestone and organic matter).

Chapter 3 – Iron and Sulfur Speciation in RAPS Sediments. In this chapter, the main inorganic sinks of iron and sulfur in four sediment cores of the RAPS are presented in order to assess the dominant removal processes of iron and the influence of bacterial sulfate reduction on the retention of iron.

Chapter 4 – S, O and H Isotope Ratios in RAPS Waters and Sediments. Sulfide and sulfate stable isotopes ($\delta^{18}O$, $\delta^{34}S$) and water isotopes (δD, $\delta^{18}O$) were analysed during 18 months of water monitoring and compared to $\delta^{34}S$ of the inorganic sulfur sinks in the reactive substrate. The purpose of these analyses was to i) assess the origin of the mine water and its principal sulfur source; ii) outline the oxidation mechanism of the sulfide minerals that lead to the generation of AMD; iii) assess the occurrence of BSR in the RAPS and iv) link water and sediment isotopes in order to explain which process is likely to be responsible for the low pyrite generation observed.

Supporting information about the treatment scheme (i.e. images from the treatment site, Appendix 1), methodologies (Appendix 2), raw data obtained during preliminary investigations (Appendix 3, electronic) and during this study (Appendix 4, electronic) are presented in the appendices.

Results presented in Chapters 1 to 4 have been presented at international conferences (Matthies et al. 2009a, Matthies et al. 2009b, Matthies et al. 2010b, Matthies et al. 2010a). Chapter 1 has recently been accepted for publication (Matthies et al. in press).

1. TREATMENT PERFORMANCE

The aim of this chapter was to evaluate influent and effluent water qualities of the Bowden Close treatment system (collected by staff of Newcastle University) in order to assess its treatment performance with respect to Fe, Al, Mn, Zn, SO_4^{2-}, pH and alkalinity over the course of 5.5 years. Seasonal and annual trends have been assessed with a view to identifying the influence of changing influent concentrations and loads on treatment performance and making a preliminary evaluation of the likely overall lifetime of the system.

Methods

Monthly surface water monitoring data from December 2003 to May 2009 were assessed. During each sampling event, pH, electrical conductivity (EC), temperature (T), alkalinity (Alk), dissolved oxygen (DO since January 2008) and flow rates (Q) were determined, along with total cation and anion concentrations. Filtered (<0.45 µm, cellulose nitrate filter) samples for cation analysis were only sampled sporadically during this time and are not reported here. A Myron 6P Ultrameter was calibrated with pH 4, 7 and 10 and EC 1214 µS cm^{-1} standard solutions. Dissolved oxygen was analysed with an YSI 550A dissolved oxygen meter calibrated against atmospheric oxygen. Redox potentials were corrected to the standard hydrogen electrode. Alkalinity was determined by colorimetric titration (HACH AL-DT test kit) and total acidity was calculated (Hedin et al. 1994). Flow rates were determined in triplicate by the bucket and stop watch method.

Acid-washed polyethylene bottles used for sampling were completely filled and stored at 4°C in the absence of light. Samples for the determination of cations (Mg, Ca, Na, K, Fe, Al, Mn, Zn, S; since July 2005: Si) were preserved with reagent grade nitric acid (1% v/v) and analysed within one month. Samples for sulfate and chloride determination were filtered (<0.45 µm, cellulose nitrate filters) and analysed within two weeks.

Anions were determined with an ion chromatograph (IC, type IC25 Dionex equipped with an AG16 guard column and an AS17 analytical column). The IC was one-point calibrated (10 mg L^{-1} Cl^-, 20 mg L^{-1} SO_4^{2-}; detection limits=0.1 mg L^{-1} Cl^-, 0.5 mg L^{-1} SO_4^{-2}). Cation concentrations were quantified with an Inductively Coupled Plasma – Optical Emission Spectrometer (Vista MPX, CCP Simultaneous ICP-OES, Varian; detection limits=0.01 mg L^{-1} except Al=0.1 mg L^{-1} and K=1 mg L^{-1}). Blanks, standard checks, replicates and standard reference materials (Thames river water: LGC6019, landfill leachate: LGC6175 and riverine water SLRS-3: National Research Council, Canada) were run alongside.

Statistical analyses were undertaken with SPSS 17.0. Statistical significance was assumed if $p<0.05$. Data were converted to a normal distribution by Blom's transformation. Missing data or data where $Q_{inf} \neq Q_{eff}$ were estimated by the median of the immediately previous and subsequent months. In order to assess the importance of predictor variables on the removal of metals, multiple regression was applied.

Results and Discussion

The raw data of the water monitoring are presented in Appendix 4 and are summarized in Table 1. Sequence charts for total concentrations of pH, net-acidity (acidity-alkalinity), treatment targets and flow rates in influents and the effluent of the PTS are shown in Figure 2. Correlation coefficients of concentrations and loads from each sampling point are presented in Appendix 4-Chapter 1.

Flow Rates and Retention Times

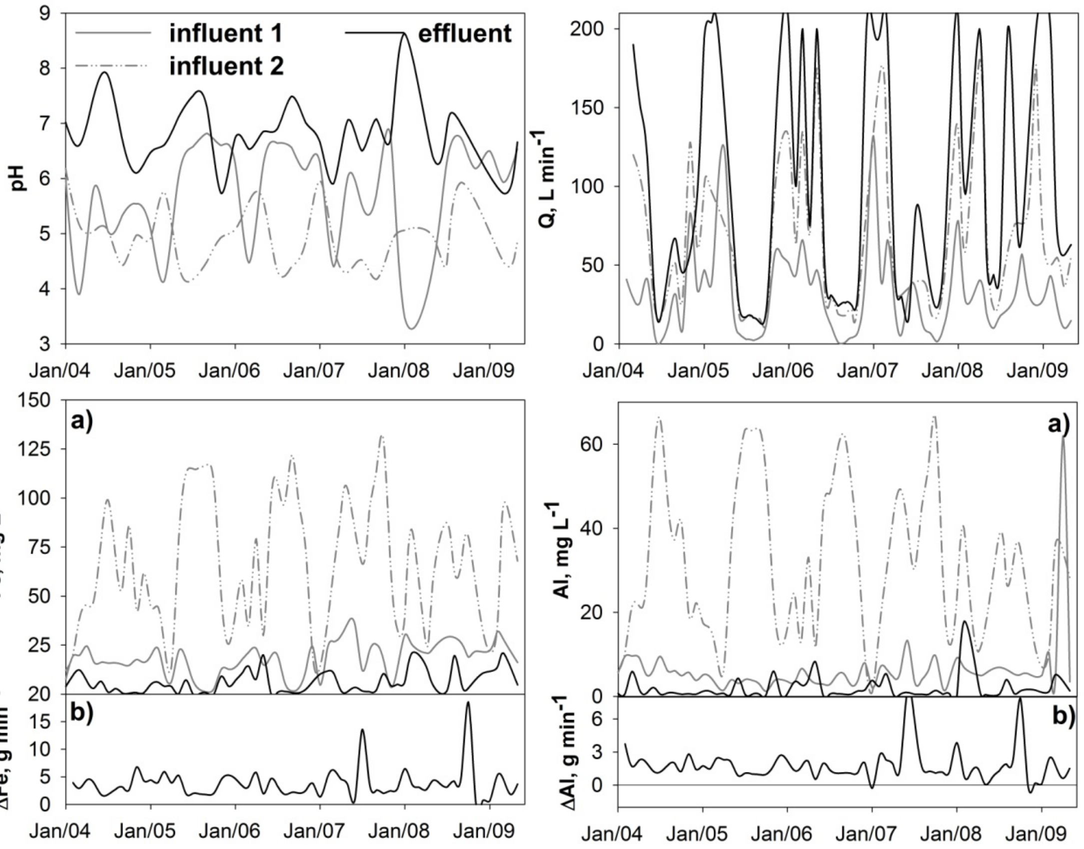
Three-fold higher average flow rates were measured in influent 2 compared to influent 1 (Table 1). The highest flow rates were observed in late autumn to spring with maximum flow rates in December to February exceeding detection limits (~200 L min^{-1}) in influent 2 ($\bar{x}_{inf1}$=45 L min^{-1}, $\bar{x}_{inf2}$=125 L min^{-1}). Lowest flow rates ($\bar{x}_{inf1}$=9 L min^{-1}, $\bar{x}_{inf2}$=33 L min^{-1}) were measured during July to September.

Flow rates are linked to treatment performance in that they control hydraulic retention times, mixing and diffusional mass transfer (Jarvis and Younger 2000, Kadlec 2000, Giraldi et al. 2009). Tracer tests using bromide and sodium fluorescein indicated retention times varying from four to eight days for RAPS 1 and from four to six days for RAPS 2, with effective velocities of ~0.01 m h^{-1} (Wolkersdorfer et al. 2005). The mean residence time of water within the aerobic wetland was one to two days (Wolkersdorfer et al. 2005). Tracer concentration peaks were recorded at between 90-140 h (RAPS 1) and 120 h (RAPS 2).

Table 1 Arithmetic averages of physicochemical parameters and total element concentrations (2003-2009)

Parameter	Influent 1	Influent 2	Wetland Effluent
T	9.6 ± 2.2	9.5 ± 1.7^{63}	10.1 ± 5.2^{63}
pH	5.77 ± 0.98	$\underline{5.0\pm0.6}^{63}$	6.89 ± 0.49^{63}
EC	845 ± 129	1617 ± 570^{63}	1430 ± 517^{63}
Eh	330 ± 120	360 ± 80^{63}	220 ± 66^{63}
Alk	25 ± 23	12 ± 20^{63}	115 ± 79^{63}
Acd	73 ± 81	315 ± 173	30 ± 24
DO*	8.3 ± 1.6^{10}	7.6 ± 0.6^{10}	n.m.
Q	33 ± 28^{61}	100 ± 89^{65}	124 ± 125^{61}
SO_4^{2-}	370 ± 106^{63}	$\underline{1075\pm553}^{62}$	$\underline{670\pm332}^{62}$
Ca	102 ± 19^{63}	174 ± 60^{62}	218 ± 112^{62}
Fe	$\underline{19.7\pm22}^{63}$	$\underline{71\pm49}^{62}$	$\underline{5.9\pm5.5}^{62}$
Al	6.1 ± 7.5^{63}	33 ± 19^{61}	1.9 ± 2.7^{62}
Mn	$\underline{1.1\pm0.4}^{63}$	$\underline{7.4\pm4.5}^{62}$	$\underline{4.4\pm3.0}^{62}$
Zn	$\underline{0.2\pm0.1}^{63}$	$\underline{1.2\pm0.7}^{62}$	$\underline{0.3\pm1.3}^{62}$

Average±standard deviation^n, concentrations=mg L^{-1} except pH, Eh=mV (raw data corrected for the standard hydrogen electrode), Q=flow L min^{-1}, EC=µS cm^{-1}, T=°C, Alk, alkalinity and Acd, acidity=mg $CaCO_3$ eq L^{-1}), DO, dissolved oxygen=mg L^{-1} measured between 2008-2009, n=sample size: 64 unless otherwise indicated, n.m.=not measured; underlined values indicate exceedance of guideline limits for UK environment guidelines (compiled from Environmental Quality Standards, Dangerous Substances Directive-List II (76/464/EC), Drinking Water Directive (98/83/EC), Freshwater Fish Directive (78/659/EEC) and Surface Water (River Ecosystem) Regulation (1994/1057))


influent 1
influent 2
effluent
pH
9
8
7
6
5
4
3
Q, L min^{-1}
200
150
100
50
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Fe, mg L^{-1}
150
125
100
75
50
25
20
a)
b)
ΔFe, g min^{-1}
15
10
5
0
Al, mg L^{-1}
60
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Jan/08
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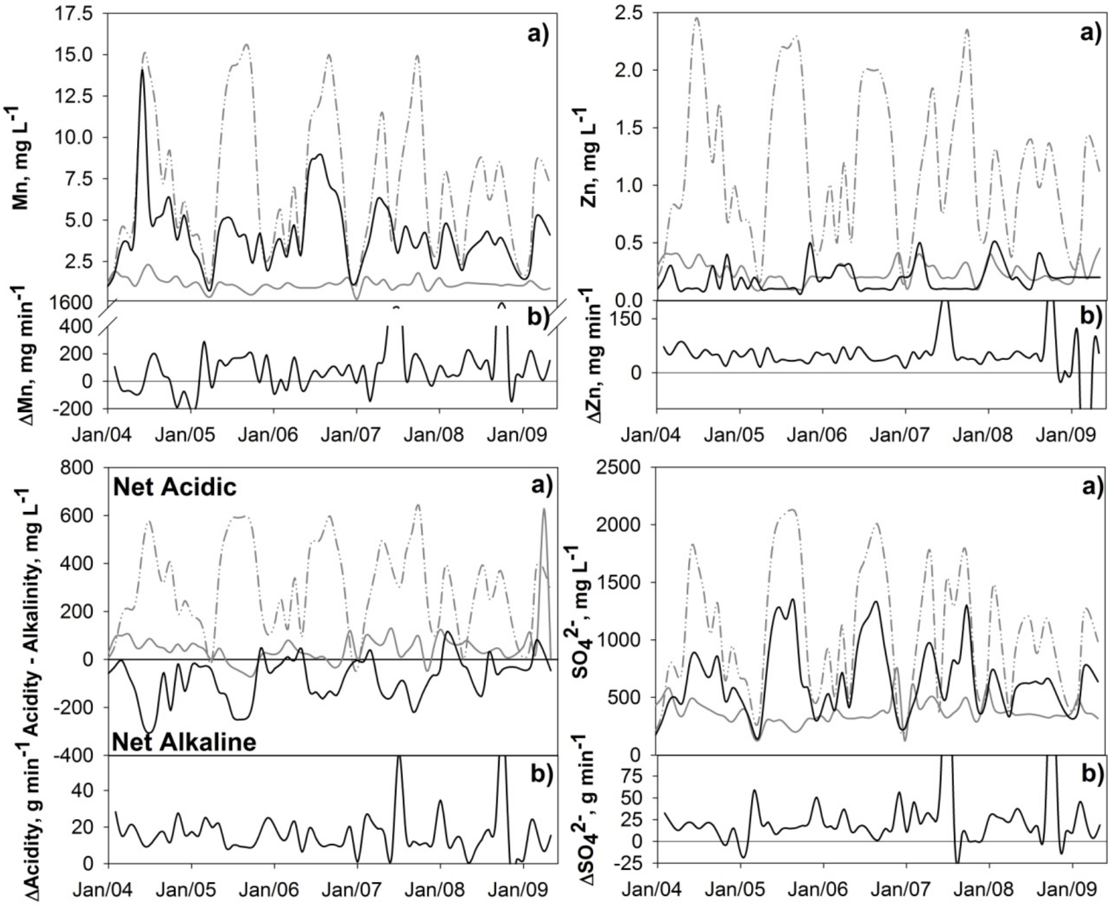

Figure 2 Sequence charts of pH, flow rates and total concentrations of iron, aluminium, manganese, zinc, sulfate and acidity in influents and the wetland effluent (a); element removal rates of iron, aluminium, manganese, zinc, net-acidity and sulfate in g min^{-1} (alkalinity, acidity=$CaCO_3$ eq (b))

The first bromide was detected in the wetland effluent just one day after tracer injection (Wolkersdorfer et al. 2005), but dispersion effects resulted in tracer concentrations remaining above baseline concentrations even up to one month after tracer injection. This suggests that at least a fraction of the mine water may short-circuit via surface flow across the RAPS substrate, while another portion appears to stagnate within the substrate. Preferential pathways are likely decreasing overall retention times (Amos and Younger 2003).

Short-circuiting was confirmed by measurements of the RAPS overflow. Although the overflow pipes were installed for occasional use only, in 49% and 77% of all sampling events, overflow was recorded in RAPS 1 and 2, respectively. On average, 50% (RAPS 1) and 65% (RAPS 2) of the influent water short-circuited over the RAPS substrate and was directly discharged via overflow pipes into the aerobic wetland. During the first five years of the treatment, overflows were quantified only in terms of flow rates. Water qualities were not determined. However, recent measurements showed (Chapter 2), that high but variable amounts of iron (>73% of total Fe), aluminium (>60% of total Al) and sulfate (>54% of total SO_4^{2-}) are removed in the freeboard of the RAPS, leading to overflow concentrations being different to those of the influents. Thus, the treatment performance of the individual ponds of the Bowden Close treatment scheme could not be estimated for the first years of treatment within an acceptable margin of error. Therefore, this Chapter reports the performance of the entire PTS (i.e. RAPS 1 + 2 plus the aerobic wetland).

Overall, tracer tests showed that retention times largely exceeded the recommended minimum of 14 hours (Younger et al. 2002, Wolkersdorfer et al. 2005) which were set as design criteria for Bowden Close RAPS (Fabian et al. 2005).

Influent Water Chemistry

The data are similar to historic, pre-treatment mine water data (Younger 1998b). Influent 2 was net acidic (acidity > alkalinity) (Figure 2). Influent 1 was largely net-acidic with about four-fold lower acidity compared to influent 2 (Table 1, Figure 2). The average alkalinity in influent 1 was two-fold higher than in influent 2 and likely originated from the dissolution of Ca-(Mg)-carbonates (Hedin et al. 1994), siderite (Younger 1998b) and ankerite (Prieto and Mery Duitama 1999). Redox potentials and dissolved oxygen concentrations indicated oxidizing conditions (Table 1).

Major ions were predominantly present in the filtered fraction (< 0.45 µm filter pore size, Chapter 2) which made it reasonable to use total concentrations for the assessment of water types. The mine drift water (influent 1, Figure 3) is a calcium-magnesium-sulfate water, similar to other uncontrolled discharges of the Durham coalfield (Younger 1998b). In influent 2, iron and aluminium showed average concentrations similar to Ca, Mg and SO_4^{2-} (i.e. Ca-Mg-Fe-Al-SO_4^{2-} water type).

Correlations between total concentrations and physicochemical parameters were poor in influent 1 except for the pH-alkalinity and sodium-chloride couples (r>0.8, Appendix 4-Chapter 1). The pH and alkalinity are closely linked through the carbonate system ($CO_{2(aq)} + H_2O \leftrightarrow HCO_3^- + H^+ \leftrightarrow CO_3^{2-} + 2H^+$).

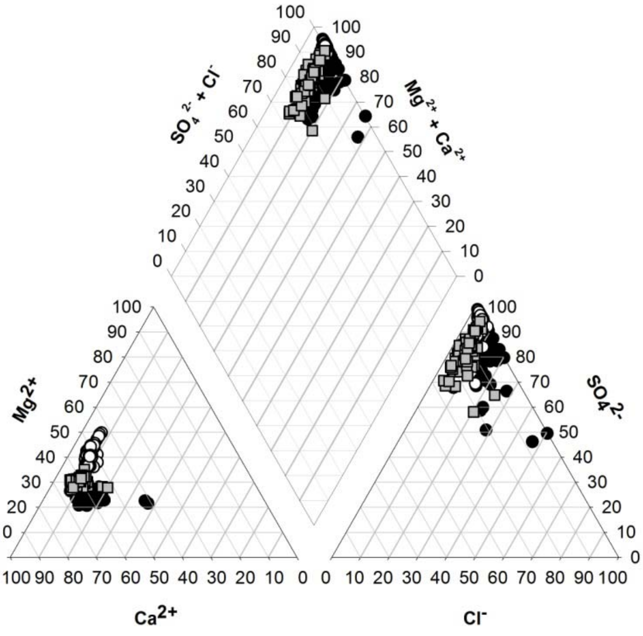

Figure 3 Piper plot of influents 1 (black) and 2 (white) and the wetland effluent (grey) (Ca, Mg, Na+K; Cl^-, SO_4^{2-},CO_3^{2-}+HCO_3^-)

Element concentrations in influent 2 are positively correlated to each other and inversely to flow rates (Figure 4), indicating dilution processes, probably by infiltrating meteoric water into the waste rock dump. Alkalinity and pH showed negative correlations compared to other element concentrations ($r<-0.5$) in influent 2. This could be related to the increasing instability of the metals (e.g. Al, Fe) at higher pH which causes increased hydrolysis and precipitation as (hydr)oxides.

Compared to influent 1, total concentrations of sulfate, iron, manganese, aluminium and zinc are enriched in influent 2, typically by three to six times. Compared to world average stream concentrations (Reimann and de Caritat 1998) and north east England average stream concentrations (Salminen 2005, de Vos and Tarvainen 2006) mine water contaminants (Fe, Al, Zn, Mn, S) are enriched by 17 to 1800 times (Table 2). Average, minimum and maximum concentrations of influents and the effluent were compared to several UK environmental guidelines (Table 1).

Table 2 Enrichment factors of mine water contaminants in comparison to world average stream concentrations and north east England average stream concentrations

	Fe	Mn	Al	Zn	S
Influent 1	395* 80**	300* 70**	17* 90**	13* 75**	90* 23**
Influent 2	1690* 250**	1800* 465**	105* 470**	80* 450**	260* 70**

** average enrichments compared to world average stream concentrations (Reimann and de Caritat 1998); ** average enrichments compared to north east England average stream concentrations (Salminen 2005, de Vos and Tarvainen 2006); both values describe how many times more the contaminant can be found in the mine waters as compared to the world or north east England average*

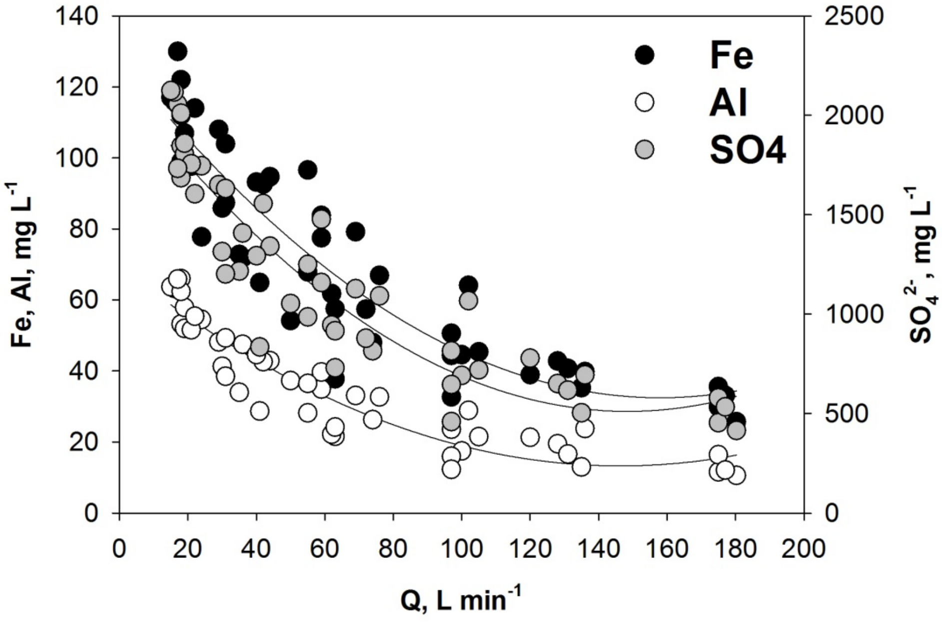

Figure 4 Iron, aluminium and sulfate concentrations (and second order regression curves) in influent 2 compared to flow rates (Q)

Although these guidelines are not directly applicable to mine water but rather to the receiving surface water bodies, the comparison indicates the degree of contamination encountered at Bowden Close. In the influents, iron, zinc and manganese (all filtered fraction) exceeded aquatic life guidelines. Additionally, the average and 95th percentile of sulfate in influent 2 exceeded the guideline limit of 400 mg L^{-1}. The pH did not comply with the minimum level of 6 in influent 2 (Q_{95}=5.8). Iron, manganese, zinc, sulfate and pH were identified as main treatment targets. No guideline limit exists for aluminium. Nonetheless, due to its toxicity and potentially suffocating effects on aquatic biota (Nordstrom 1982b, Havas and Likens 1985, Havens and Heath 1989, Havens and Heath 1990) it was included in the list of treatment targets.

Effluent Water Chemistry

Bowden Close effluent is characterized by circum-neutral pH (>5.7, Figure 2, Table 1), and most waters are net-alkaline. The effluent water is characterised as a Ca-Mg-SO_4^{2-}(-HCO_3^-) water type (Figure 3). Compared to influents, acidity, iron, aluminium and sulfate are significantly depleted. Zinc and manganese are significantly depleted compared to influent 2 only. Alkalinities and pH are increased. Effluent element concentrations and electrical conductivities in the effluent are inversely correlated to flow rates (Appendix 4-Chapter 1). However, this was not the case for iron, aluminium and zinc (r<0.27), which could be an effect of the overflow and flushing of hydrous oxides in the surface sediment. As discussed earlier, increased flow rates favour horizontal flow over the RAPS which could lead to resuspension of the surface ochre sludge during high flow events. Despite the considerable improvement of the mine water quality by the passive treatment, concentrations of some contaminants still exceeded guideline limits. This was particularly the case for sulfate and manganese, and occasionally for iron and zinc.

Treatment Performance

Evaluating pollutant concentrations in mine water is an essential part of the assessment of toxicity effects to environmental receptors. However, to discuss the performance of the treatment system, element loads (g d^{-1}) have to be calculated to assess element mass balances. Overall, the Bowden Close PTS received a mean acidity load of 30.2 kg acidity $CaCO_3$ eq per day (range: 2.2-118 kg). The waste rock dump drainage (influent 2) contributed more than 88% of the total acidity load. Influent loads of major contaminants are positively correlated (Appendix 4-Chapter 1), as are effluent loads. However, correlation between influent loads and loads removed are generally below r<0.7 or not significant (e.g. Mn).

Treatment efficiencies are calculated based on the differences in concentration between the influent and effluent sampling points (Wieder 1993). This approach has the disadvantage that flow rates, element loads, area and volume of the treatment system are not considered. Hence, outcomes are relative and not comparable to other treatment facilities. Here, I calculated:

i. Load efficiencies ($\Delta L\%=100(L_{inf}-L_{eff})L_{inf}^{-1}$; L_{inf}=influent load including influent 1 and influent 2 (g d^{-1}), L_{eff}=effluent load (g d^{-1})) and

ii. Average load removal rates ($\Delta L=L_{inf}-L_{eff}$, g d^{-1}).

Area adjusted removal rates (AR, g d^{-1} m^{-2}) are most commonly used for the assessment of the treatment performance. Thus, the average load removal is adjusted to the surface area of the system ($AR=\Delta LA^{-1}$; A=surface area). However, because RAPS are vertical flow systems and because of the increased depths compared to aerobic PTS, it is logical to evaluate treatment performance on a volume-adjusted basis (Mayes et al. 2009), which has been done here as well ($VR=AR*d*n_e$, d=depth, n_e=effective porosity (0.3-0.5)). These metrics of treatment performance assume zero-order removal kinetics.

Treatment performance and total mass removal since system commissioning are summarized in Table 3. Overall, the effectiveness of contaminant removal is in the order: aluminium > iron > (acidity) > zinc > sulfate> manganese.

Table 3 Removal rates of treatment parameters and total amounts removed

Parameter	Load Efficiency	Load Removal	Total Removal	Area adj. Removal	Volume adj. Removal
Acidity	83	24±18	48.6	6.7±4.9	17±13
Iron	84	5.41±2.4	10.6	1.5±0.7	3.8±3
Aluminium	87	2.5±1.3	4.9	0.69±0.35	1.9±2
Manganese	23	0.11±0.18	0.22	0.03±0.05	114±274
Zinc	51	48.3±138	0.94	13±38	43±101
Sulfate	29	29±24	57	8.0±6.5	27 ±44

Average±standard deviation, load efficiency=%, load removal=kg d^{-1} except Zn (g d^{-1}), total removal=tons (December 2003-May 2009), area adjusted removal rates=g d^{-1} m^{-2} except Zn (mg d^{-1} m^{-2}), volume adjusted removal rates=g d^{-1} m^{-3} except Zn, Mn (mg d^{-1} m^{-3})

Average acidity removal rates (6.7 g d^{-1} m^{-2}) were low compared to literature sizing criteria for RAPS treatment schemes of 20-30 g d^{-1} m^{-2} (Nairn and Mercer 2000, Demchak et al. 2001, Watzlaf et al. 2002, PIRAMID Consortium 2003, Ziemkiewicz et al. 2003, Riefler et al. 2008) and also compared to removal rates reported from other RAPS (0-293 g d^{-1} m^{-2}); (Nairn and Mercer 2000, Danehy et al. 2001, Demchak et al. 2001, Ziemkiewicz et al. 2003, Bhattacharya et al. 2008). Nairn and Mercer (2000) measured mean iron removal rates of 17 g d^{-1} m^{-2} compared to 1.5 g d^{-1} m^{-2} in Bowden Close. Hedin et al. (1994) reported average sulfate removal rates of

5.2 g d^{-1} m^{-2} for compost wetlands; lower than those observed in Bowden Close (8.0 g d^{-1} m^{-2}). Expressed as mass removal per litre and day, Bowden Close ($\bar{x}$=291±249 mg d^{-1} L^{-1}) removed sulfate in the same order of magnitude as obtained from column and batch experiments reported by Cruz Viggi et al. (2010) and citations therein. Average area adjusted removal rates of manganese were about one order of magnitude lower than those measured in aerobic wetlands monitored by Hedin et al. (1994). Zinc removal rates are low compared to those reported by Mayes et al. (2009) and to most references cited therein.

Seasonality and Annual Trends

To assess seasonal changes and trends in the treatment performance it is necessary first to address variations in influent water characteristics. Both influents showed significant seasonality both in terms of concentrations and loads (e.g. Fe; Figure 2). Flow rates varied significantly over the course of a year and were negatively correlated to electrical conductivities ($r_{inf1/inf2}$ = -0.39/-0.79), suggesting that changes in concentrations are primarily driven by dilution effects (Mac Causland and Mc Tammany 2007). The non-linear correlation of Q and EC and the major ions in influent 2 (Figure 4) suggests additional factors, such as mineral precipitation and dissolution, may also influence element concentrations. Despite the considerably lower concentrations for most parameters over the winter and early spring period, highest element loads were recorded during February to April due to the significantly higher flow rates.

Physicochemical parameters and element loads showed significant seasonal variations in influents (except alkalinity, EC (influent 1), Mn, Al, Zn (influent 2)). However, annual means showed no significant changes throughout the five years, i. e. there was no long term trend (tested with moving average (span=12) and seasonal decomposition). This indicates that AMD generation in the waste rock dump and the mine processes have stabilised and are largely controlled by *juvenile* acidity formation (i.e. acidity that is generated during the oxidation of sulfide minerals as opposed to *vestiginal* acidity which is the resuspension and redissolution of secondary acidity producing minerals - products of sulfide oxidation) (Younger 1998b).

Despite the seasonality in influent chemistry, removal rates did not show clear temporal patterns and were characterized by non-stationarity and heteroscedastisity. This is possibly a combined effect of the two influents, dispersion and short-circuiting but could here not be unravelled.

On 6 out of 66 occasions, respectively, a net increase of manganese was observed across the treatment system, i.e. effluent loads exceeded influent loads. In 27 occasions, a net sulfate increase was observed. This could be related to increased exchange of interstitial waters at higher flow rates or remobilization via desorption, redissolution and ion exchange or an artefact of sampling time.

The removal of the seasonality by running median (span=12) did not lead to any clear trends. Annual average removal rates and seasonal average removal rates were not significantly different for any treatment performance parameter. Cumulative curves of removal rates (Figure 5) suggest that, despite the time dependent increasing variance and occasional remobilisation of manganese and sulfate, no indication was found for a change in the treatment performance of Bowden Close for the principal treatment parameters (Al, Fe, Zn, SO_4^{2-}). The parameters plot on linear cumulative curves, except for manganese, indicating that removal rates were approximately constant over the time of monitoring.

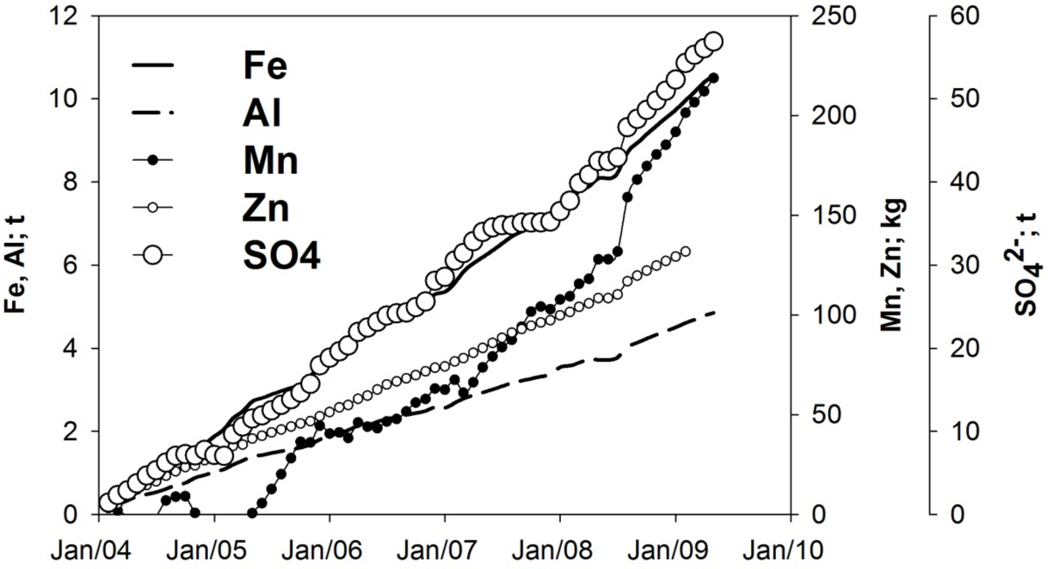

Figure 5 Cumulative curves of iron, aluminium, zinc, manganese and sulfate removal in Bowden Close over 5.5 years of passive treatment

Removal trends observed in Bowden Close differed from similar treatment systems (e.g. Wieder 1993, Hedin et al. 1994, Woulds and Ngwenya 2004). In the latter, the lowest acidity removal rates occurred during winter months whereas highest removal rates occurred in summer. This was not the case in Bowden Close, where the highest removal rates coincided with the highest influent loads (February, March). A comparison of loads of influent acidity and acidity removal rates (Figure 6) revealed significant positive correlation (r>0.6, without outliers: r>0.88). This indicates that acidity removal was mostly load limited (particularly at influent acidity loads <25 g min^{-1} $CaCO_3$ eq), of first order and the reason why seasonal removal patterns of other PTS were not repeated in Bowden Close.

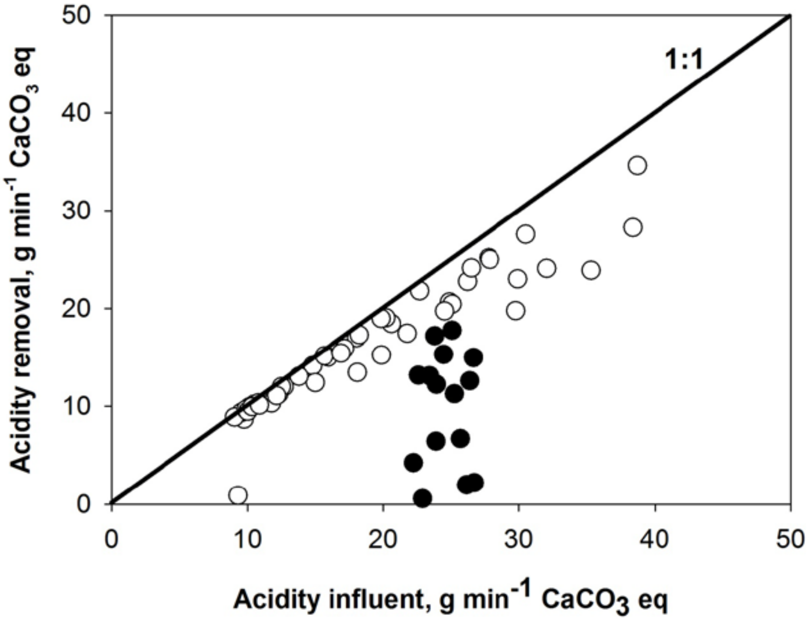

Figure 6 Acidity influent load versus acidity removal, samples represented by filled circles are possibly caused by short-circuiting of the water during high flow events; regression equation of the remaining samples: $\Delta acidity_{rem}=1.7+0.8 acidity_{inf}$; r = 0.79

During high flow events (filled circles in Figure 6), increased horizontal flow in the RAPS probably led to increased short-circuiting of the water over the RAPS and an overall decrease in retention time in the treatment scheme. Treatment performance seemingly declined during these periods. This assumption is supported by the fact that these “outliers” occurred at average overflow 2: effluent 2 flow ratios of 4.6 (in RAPS 2), i.e. four times more water was short-circuited over the reactive RAPS substrate than infiltrated into it.

Removal Processes for Main Contaminants

Potential sinks for metals in PTS have been widely discussed (Kepler and Mc Cleary 1994, Younger et al. 2002). Due to the lack of filtered element concentrations, potential removal processes were estimated based on removal ratios, correlation coefficients (Appendix 4-Chapter 1) and multiple regression.

Redox sensitive iron and sulfur are often believed to be preferentially removed as sedimentary sulfide minerals (FeS, FeS_2) in anaerobic PTS (Younger et al. 2002). From the average S:Fe removal ratio of 3.6±2.4 (range: -1.8-11.3; Figure 7) it is apparent that a number of removal processes are potentially occurring in parallel within the system including the removal of sulfides (S:Fe=1 (FeS), =2 (FeS_2)) and oxyhydroxysulfates (S:Fe=0.125-0.167, e.g. schwertmannite (Bigham et al. 1996b)). However, despite the strong correlation between iron and sulfur removal rates (r=0.81), the excess sulfur removed by the PTS over iron suggests that a significant fraction of sulfur is removed independently of iron. The dominant sulfur and iron sinks in the RAPS substrate are presented in Chapter 3.

The principal aluminium sinks in this kind of treatment system are oxyhydroxysulfates and (hydr)oxides (Younger et al. 2002). Manganese was net removed in the substrate during May to October whilst in November to April it was potentially net-released. Temperature, iron removal, effluent pH and the mobilization of calcium appeared to have a significant impact on the removal of manganese (multiple regression, equation (1)) with calcium having the highest importance (highest standardized β=-0.69) of all predictor variables (T, Ca, Fe, H^+):

(1)

$$\Delta Mn = -214 + 25.6T - 0.023Ca + 0.032Fe - 6.3*10^{5}H^{+}$$

ΔMn=manganese removal rates (mg min^{-1}*), T=temperature in ℃ determined in influents, Ca=calcium mobilization (mg* min^{-}*), Fe=iron removal (mg* min^{-1}*),* H^+*=effluent pH (in* H^+*), standard errors (*$stderr_{const}=50.8$*,* $stderr_T=4.6$*,* $stderr_{Ca}=0.001$*,* $stderr_{Fe}=0.005$*,* $stderr_H=2.07*10^5$*; standardized β (*$\beta_T=0.21$*,* $\beta_{Ca}=-0.69$*,* $\beta_{Fe}=0.327$*,* $\beta_{pH}=-0.124$*)*

No multicollinearity (i.e. linear relationship) between the predictor variables was observed. It is apparent that most manganese was removed at higher temperatures and circum-neutral to alkaline effluent pH. More manganese was removed when iron removal was high, suggesting co-precipitation. It is unclear, however, how the negative relation between calcium mobilization (potentially caused by limestone dissolution) and manganese removal can be interpreted. Sequential extractions of the RAPS substrates (unpublished data) indicated that more than 50% of the total manganese was bound to carbonates. Whether the precipitation of calcium carbonate, supersaturated in RAPS effluents, could favour the coprecipitation of manganese has to be assessed further.

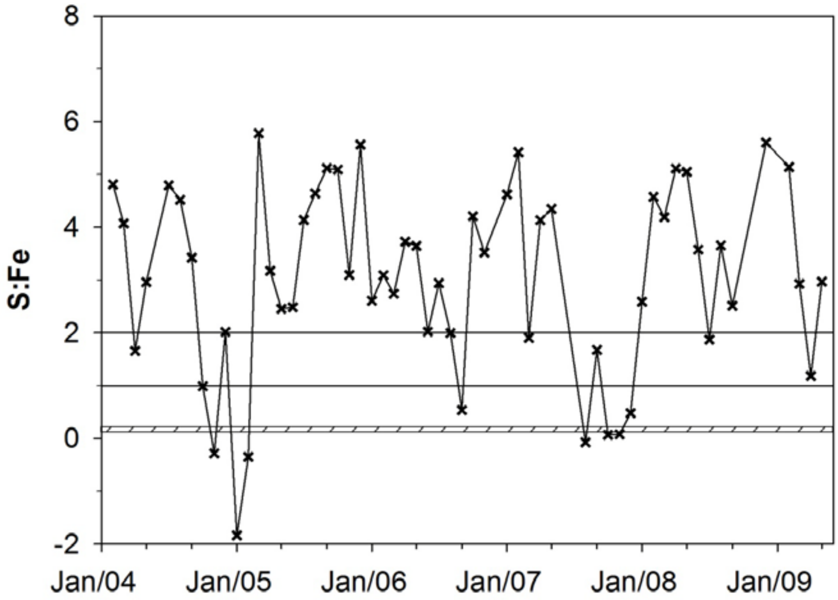

Figure 7 Sulfur versus iron removal ratios in Bowden Close; S:Fe=1: FeS; S:Fe=2: FeS_2; the shaded area indicates S:Fe ratios (0.125-0.166) of oxyhydroxysulfates (Bigham et al. 1996b); S:Fe<0: remobilization of either sulfur or iron; outliers excluded

Zinc removal was poorly correlated to other parameters (Appendix 4-Chapter 1). Unpublished data of sequential extractions of RAPS sediments indicated that more than 40% of zinc is remobilised from the substrate upon treatment with 6N HCl and could represent both zinc in sulfides or coprecipitated zinc onto hydroxides.

Alkalinity Generation

The longevity of the treatment system depends on two principal factors: the generation of bicarbonate alkalinity and the pore volume available for the accumulation of metal sludge which crucially influences substrate permeability.

The increase in net-alkalinity in the PTS is a complex process driven by the sum of alkalinity generating processes (e.g. limestone dissolution and anaerobic respiration processes), metal acidity generating processes (precipitation of hydroxide minerals, e.g.: $Fe^{3+} + 3H_2O \rightarrow Fe(OH)_3 + 3H^+$) and proton acidity consuming processes (e.g. $CaCO_3 + H^+ \rightarrow Ca^{2+} + HCO_3^-$). The net-alkalinity generated by a PTS is often estimated (equation (2)) by the sum of metal and proton removal expressed in calcium carbonate equivalent) and the *surplus alkalinity* (i.e. the increase in bicarbonate alkalinity generated by the PTS from limestone dissolution and anaerobic respiration).

(2)

$$\text{Net alkalinity} = \text{Acidity Removal} + \text{Surplus Alkalinity}$$

Acidity removal=Influent – Effluent acidity loads; Surplus alkalinity=Effluent – Influent Bicarbonate Alkalinity Loads

The equation is based on two principal statements: (i) the release of calcium from the PTS is an indicator for the dissolution of limestone, i.e. limestone alkalinity (e.g. Kepler and Mc Cleary 1995, Riefler et al. 2008), and (ii) the unaccounted bicarbonate generation is a product of the removal of sulfate by microbial reduction (BSR, $2CH_2O + SO_4^{2-} \rightarrow H_2S + 2HCO_3^-$) (Hedin et al. 1994, Kepler and Mc Cleary 1994, Jarvis and England 2002).

This approach may be complicated by the following reasons:

I) Organic substrates can function as a net source of calcium (total Ca concentration ≈ 9.4-65.2 g kg^{-1}) during degradation (Stewart et al. 2000, Guo et al. 2001, Ji and Kim 2008). However, compared to the 50% limestone in the substrate, I expect this is likely to be a minor calcium source.

II) Calcium can be retained in the substrate by precipitation as carbonate or sulfate (e.g. calcite and gypsum) (e.g. Barton and Karathanasis 1999, Herbert et al. 2000), and by assimilation, sorption and ion-exchange.

III) Analysis of PTS sediments (e.g. Herbert et al. 2000, Neculita et al. 2008) showed that the removal of sulfate largely occurs as organic sulfur or oxyhydroxysulfates and only minor amounts of chalcophilic elements were retained in sulfides.

IV) Non-BSR anaerobic respiration processes (e.g. anaerobic NO_3^-, Fe^{3+}, Mn^{4+} reduction and methanogenesis) are sources of CO_2 but are mostly neglected in the treatment performance discussion.

V) Sequential extractions of RAPS sediments showed that a minimum of 72% of iron and aluminium were recovered in the (hydr)oxide phase (e.g.: $Al^{3+} + H_2O \rightarrow Al(OH)_3 + 3H^+$). In consequence, other iron and aluminium removal processes might not have contributed to the generation of proton acidity and hence Al and Fe removal rates overestimated proton acidity generation.

As a consequence of these limitations, limestone alkalinity can be both over- or underestimated (points (I) and (II), respectively); biologically derived alkalinity can be over- and underestimated (points (III) and (IV), respectively) and the alkalinity that is consumed based on the removal of metal acidity can be overestimated (point (V)). These potentially complicating factors need to be borne in mind when interpreting the mechanisms of alkalinity generation in PTS.

It was shown in previous sections that pH and alkalinity of the mine water were raised by the PTS throughout the more than five years of treatment, with effluent values exceeding 5.7 and 9 mg L^{-1} $CaCO_3$ eq, respectively. One way analysis of variance on alkalinity loads showed that increases were significantly different both seasonally and annually. Multiple regression (equation

3) did not lead to a clear identification of the main processes influencing the increase in pH and release of alkalinity. However, calcium mobilisation accounts for only 17% of the variation in alkalinity, suggesting that a considerable portion of alkalinity derives from processes other than limestone dissolution, e.g. anaerobic microbial respiration. Furthermore, bicarbonate was generated even in circumstances in which there was no net-generation of calcium in the treatment system. The cumulative curve of the net-alkalinity generation (multiple regression, equation (3)) was constant throughout the time of monitoring (Figure 8). This indicates a constant overall treatment performance of the system. About 87% (R_{adj}^2) of the variation of the net-alkalinity was explained by the removal of iron (β=0.88), the increase in calcium (β=0.40) and the decrease in aluminium (β=0.35).

(3)

$$\text{Net-alkalinity} = -1.67*10^3 + 0.67\text{Ca} + 4.49\text{Fe} + 3.19\text{Al}$$

*Net-alkalinity=generation of alkalinity (mg min^{-1}), Ca=calcium remobilization rate (mg min^{-1}), Fe=iron removal (mg min^{-1}), Al=aluminium removal (mg min^{-1}), standard errors (stderr$_{const}$=1.44*10^3, stderr$_{Ca}$=0.10, stderr$_{Fe}$=0.33, stderr$_{Al}$=0.62*

There was no significant long term change in effluent pH. However, the cumulative curve of surplus alkalinity and calcium (Figure 8) follow first order logarithmic behaviour. Significant decreases in annual bicarbonate generation and calcium mobilization were observed. Two main reasons have been identified as possible causes. If the bulk of calcium mobilized is potentially derived from limestone dissolution, a decrease in calcium concentrations in the effluent could be caused by armouring of the limestone gravels with secondary mineral precipitates (Huminicki and Rimstidt 2008). Secondly, since calcium carbonate is supersaturated in RAPS effluents (Chapter 2), carbonate precipitation could partially account for the decrease in alkalinity and calcium. In addition, the apparent decrease in bicarbonate generation could also be related to a deceleration of anaerobic respiration processes. It has been widely reported that the ageing organic substrate of PTS is increasingly depleted in short chained organic molecules, essential for heterotrophic sulfate reducing bacteria (SRB) (Cocos et al. 2002).

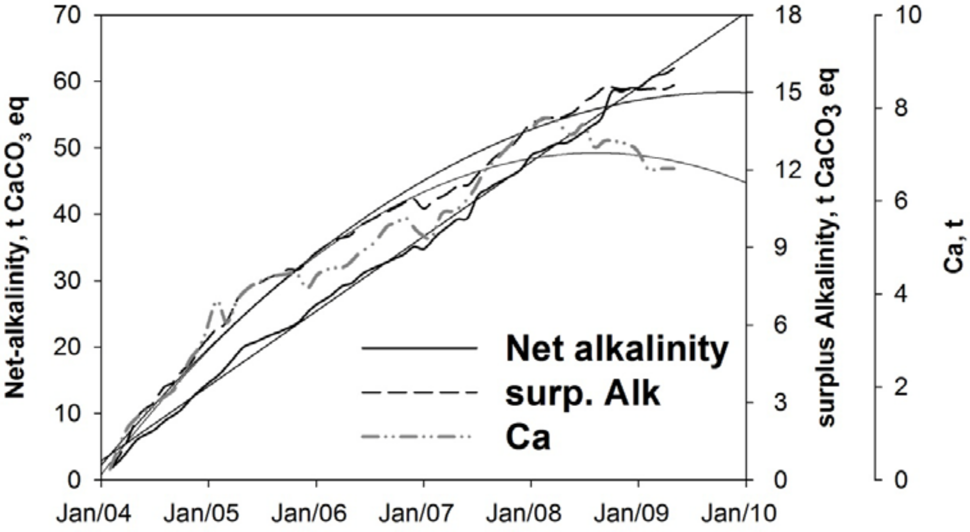

Figure 8 Cumulative curves (and regression curves) of the generation of net-alkalinity, surplus alkalinity and mobilization of calcium over 5.5 years of passive treatment

The remaining organic matter is increasingly enriched in lignin that have to be pre-digested, e.g. by fermentative bacteria and converted into lower molecular weight compounds which can be utilised by SRB (Tsukamoto et al. 2004, Zagury et al. 2006). More work is necessary to unravel the principal cause of the decrease in alkalinity generation. In the following Chapter, I present carbon isotope data that potentially will help to unravel the principal source of total dissolved inorganic carbon.

Summary

- The Bowden Close treatment system was monitored by staff of Newcastle University over 5.5 years;
- Physicochemical and total element concentrations of two mine waters and the final effluent of the PTS were sampled in monthly intervals;
- Mine water influents showed maximum concentrations of 177 mg L^{-1} (iron), 85 mg L^{-1} (aluminium), 2.8 mg L^{-1} (zinc), 20.5 mg L^{-1} (manganese) and 2120 mg L^{-1} (sulfate);
- pH and alkalinities in the mine waters were as low as 3.2 and 0 mg L^{-1} CaCO$_3$ eq, respectively;
- Over nearly six years of treatment, the main contaminants were removed by on average: 84% Fe, 87% Al, 83% acidity, 51% Zn, 23% Mn and 29% SO$_4^{2-}$;
- Alkalinity and pH were increased by 74% and 95% (as H$^+$), respectively;

- Due to load limitations, area adjusted removal rates (Fe=1.49±0.66 g d^{-1} m^{-2}; acidity=6.7±4.9 g $d^{-1}m^{-2}$) were relatively low compared to similar treatment systems and design criteria;
- Acidity removal and effluent pH were stable over the time of monitoring;
- A decrease in calcium and alkalinity generation has been observed during years 5 and 6 of the treatment but has so far not affected the pH of the effluent.

2. GEOCHEMISTRY OF RAPS WATERS

The treatment performance of the overall Bowden Close treatment scheme including RAPS 1 and 2 and the aerobic wetland for the years 2003-2009 was presented in Chapter 1. The assessment of the treatment performance and principal geochemical removal processes within the RAPS was limited by the lack of water chemical data for RAPS overflows and insufficient data of filtered element concentrations. During 2008 and 2009, I collected monthly surface water from influents, effluents and overflows of both RAPS.

The principal sources of bicarbonate in the RAPS are mineral carbonate dissolution (e.g. calcite: $CaCO_3 + H^+ \rightarrow Ca^{2+} + HCO_3^-$) and the oxidation of organic matter through anaerobic respiration (e.g. bacterial sulfate reduction: $2CH_2O + SO_4^{2-} \rightarrow H_2S + 2HCO_3^-$; CH_2O=organic matter; bacterial iron reduction: $4Fe(OH)_3 + CH_2O + 7H^+ \rightarrow 4Fe^{2+} + HCO_3^- + 10H_2O$). Carbon isotope ratios of total dissolved inorganic carbon (TDIC), used as tracers, aim to discriminate between these alkalinity sources. Anaerobic respiration and the resultant bicarbonate generation can help to safeguard the dissolution of limestone and prolong lifetimes of the RAPS.

The aim of this Chapter was to assess i) the treatment performance of the RAPS, ii) the metal removal processes of the main treatment targets (Fe, Al, Zn, Mn) and, by analyses of stable carbon isotopes, iii) to discriminate the principal alkalinity sources in the treatment systems (i.e. limestone dissolution vs. oxidation of organic matter).

Methods

Since April 2008, monthly water samples were taken from influents of both RAPS, effluents (i.e. water that has drained through the reactive substrate) and overflows (water that has short-circuited over the reactive substrate and is discharged via overflow pipes into the aerobic wetland). During each sampling event, physicochemical parameters (pH, temperature (T), redox potential (Eh), electrical conductivity (EC), dissolved oxygen (DO), alkalinity (including HCO_3^-, CO_3^{2-}) and flow (Q, by bucket and stop watch)) were measured along with total and 0.45 µm filtered element concentrations of cations (Ca, Mg, Na, K Fe, Al, Zn, Mn, Si, S) and filtered concentrations of anions (SO_4^{2-}, Cl^-). Sulfide and ferrous iron in the filtered fraction (<0.45 µm, Cellulose nitrate filter) were analysed after Cline (1969) and Viollier et al. (2000), respectively. Flow rates of influent 1 were estimated from the combined flow rates of overflow and effluent because the surface sludge was increasingly covering the influent pipe making flow measurements impossible.

Sampling, storage and analysis of the above parameters were undertaken as to recommendations of the APHA (Clesceri et al. 1992). Dissolved oxygen was analysed by an YSI 550A dissolved oxygen meter which was calibrated against air. A Myron Ultrameter II, calibrated with pH 4, 7 and 10 and EC 1214 µS cm^{-1} standard solutions, was used to analyse for pH, Eh, EC and T. Alkalinity was determined in 0.45 µm filtered water samples by colorimetric titration (HACH AL-DT test kit). Cation concentrations were analysed using an Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES, Vista MPX, Varian) calibrated with three matrix matched standards and a blank. Detection limits for all elements were 0.01 mg L^{-1} except for aluminium (0.1 mg L^{-1}) and potassium (1 mg L^{-1}). Anion concentrations were determined with an Ion Chromatograph (IC, type IC25 Dionex equipped with an AG16 guard column and an AS17 analytical column) which was one-point calibrated (10 mg L^{-1} Cl^{-}, 20 mg L^{-1} SO_4^{2-} standard solution, detection limits: 0.1 mg Cl^{-} L^{1}, 0.5 mg SO_4^{2-} L^{-1}). Acidity was calculated after Hedin et al. (1994) considering proton and metal (Fe, Al, Mn) acidity. Carbonic acid was not considered, but might have contributed to the overall acidity particularly in the mine waters with pH<4.5 (Kirby and Cravotta 2005a, Kirby and Cravotta 2005b, Mc Allan et al. 2009).

Quality Assurance and Quality Control

All flow measurements were undertaken in triplicate. Between 5-10% of all field parameters were run in duplicate (coefficient of variance $V=100\sigma\bar{x}^{-1}$: ±6%, σ=standard deviation, $\bar{x}$=arithmetic average). Dilutions for ICP-OES and IC were undertaken using standardized volumetric flasks and deionised water (MilliQ purification system, Elga Purelab Ultra, Ultra Scientific). For the ICP-OES, every 15 samples one blank, one standard check, one replicate and one water reference material (Thames river water: LGC6019, landfill leachate: LGC6175 and riverrine water SLRS-3: National Research Council, Canada) were run alongside. The ICP-OES was recalibrated when the standard check differed by more than ±5% from its original value. The quality control procedure for the IC included the analysis of one duplicate, one replicate and one blank after each 10 samples and standard checks after three samples. If standard checks exceeded differences of ±5% with respect to the original value, the IC was recalibrated. Duplicates of anions and cations lay within ±7%. Ion balances ($IA=100(c-a)(c+a)^{-1}$, a=sum of anion concentrations, c=sum of cation concentrations in meq L^{-1}) ranged within 5±7.5%.

Carbon Isotopes

Stable carbon isotope ratios of total dissolved inorganic carbon (TDIC, including CO_{2aq}, CO_{2g}, HCO_3^{-}, CO_3^{2-}) were determined after a modified approach of Atekwana and Krishnamurthy

(2004). Water (12 mL, glass exetainers) was sampled in triplicate, preserved with 240 µL formaldehyde to inhibit microbial activity, filled to the top, sealed with parafilm and stored until analysis upside down in the absence of light at 4°C. For analysis, 6 mL of sample was transferred via syringe fittings into helium-purged exetainers. About 200 µL hot deaerated concentrated phosphoric acid was added and the sample vortexed. After equilibration (~48 h), carbon isotopes were analysed on a Prism3 (Fisons Instruments) calibrated with marble standards (MARB, medium marble 85/160, δ^{13}C=2.48‰), internal sodium bicarbonate (δ^{13}C=-4.67‰) and calcium carbonate (δ^{13}C=-24.23‰)). Standards (n=16) in the alkalinity range of 6.7-300 mg L^{-1} $CaCO_3$ eq were set up in 6 mL 10% hot deaerated phosphoric acid. The international standards IAEA CO-1 (calcite, δ^{13}C=2.48‰, stdev=±0.025‰), and NBS 18 (calcite, δ^{13}C=-5.029‰, stdev=±0.049‰), IAEA CO-8 (δ^{13}C=-5.749‰, stdev=±0.063‰) and IAEA CO-9 (barium carbonate, δ^{13}C=-47.119‰, stdev=±0.149‰) were used to calibrate the mass spectrometer and check for accuracy on a monthly basis. Standard deviations of replicates and duplicates ranged within ±5‰.

Surface acid leached specimens of limestone grains (n=4) from the reactive substrate were ground and digested with phosphoric acid in helium purged rubber septum sealed glass exetainers. After three days of reaction at 70°C, δ^{13}C are determined on an Analytical Precision AP 2003 mass spectrometer (AP-MS) that was calibrated as the Prism3.

Bulk carbon isotope ratios of air dried and ground inorganic carbon-free organic matter (n=11) were analysed on a Thermo Finnigan-Delta plus XP coupled to a Costech Elemental Combustion System. In addition, a sample of the most abundant plant species populating RAPS 1, *Typha latifolia,* was analysed in parallel (n=4) to determine δ^{13}C of roots and leave samples. The apparatus was calibrated daily against internal standards (14N Alanine=-10.65‰ (stdev=±0.03‰), 15N Alanine=-23.25‰ (stdev=±0.03‰), Gelatine=-20.17‰ (stdev=±0.03‰) and Tryptophans=-10.51‰ (stdev=±0.04‰)) and is also checked against international standards once per month (IAEA N1=0.3‰ (stdev=0.02‰); IAEA N2=20.4‰ (stdev=±0.19‰), USGS 25=-30.2‰ (stdev=±0.08‰), USGS 24=-15.91 (stdev=±0.03‰), IAEA PEF CH 7=-31.85 (stdev=±0.04‰), IAEA Surcose CH6=-10.49‰ (stdev=±0.05‰)). Standard deviation averaged ±0.4‰ for isotope ratios and ±0.8% for carbon concentrations. Concentrations and isotope ratios were undetectable in the blanks. Isotope ratios are presented in standard delta notation in per mill compared against primary reference material Vienna-Peedee Belemnite.

Carbon isotope ratios of atmospheric carbon dioxide were obtained from an Irish monitoring station (Mace Head, Galway, Ireland; 53.3260°N, 9.899°W, 25 m a.s.l., Earth System Research

Laboratory, Global Monitoring Division, www.cmdl.noaa.gov/ccgg.iadv/, n=126, June 1991-November 1992).

Equilibrium modelling was undertaken with PhreeqC (Version 2.15.07) accepting that equilibrium might not have been achieved in the waters. The Wateq4f database was amplified with stability constants of ferrihydrite, schwertmannite, green-rust, lepidocrocite and (pseudo)kutnahorite (Bigham et al. 1996a, Bigham et al. 1996b, Parkhurst 1997, Bourrié et al. 1999, Majzlan et al. 2004, Mucci 2004, Bonneville et al. 2009). Aqueous species and element activities presented in this work were obtained from the model output.

Data were assessed statistically by SPSS 17.0. Normality and homogeneity of variance were tested with Kolmogorov-Smirnov and Levene's tests. Statistical significance was assumed at $p<0.05$.

Results

The raw data set of physicochemical parameters, total and filtered element concentrations over a monitoring period of 18 months (April 2008-October 2009) are presented in Appendix 4 and are summarized in Table 4.

Water Chemistries

Mine waters (influent 1 and 2) were moderately net-acidic (acidity>alkalinity, pH_{inf1}~6.02, pH_{inf2}~5.11, Figure 9). The waters were oxidizing (Eh~280-340 mV), of low alkalinity (<125 mg L^{-1} $CaCO_3$ eq, Figure 9), elevated electrical conductivity (<2400 µS cm^{-1}) with distinct seasonal trends that were governed by dilution processes (Figure 10 and Figure 11). Both drainages were dominated by Ca-Mg-SO_4^{2-} water types (Figure 12) and enriched in iron (<177 mg L^{-1}), zinc (<2.22 mg L^{-1}), manganese (<13.1 mg L^{-1}) and aluminium (<62 mg L^{-1}).

Overflow occurred in 3 and 17 out of 18 sampling events in RAPS 1 and 2, respectively. Overflows were commonly more acidic than influents (ΔpH=0.2, range: -1.2-1.1), more oxidising (ΔEh=80mV, ΔDO=13%, ΔDO=2.5 mg L^{-1}) and less alkaline (Δalkalinity=10 mg $CaCO_3$ eq L^{-1}). Particularly iron and aluminium, were depleted by in average 50% and 32%, respectively, (range Fe: -10-83%, Al:-182-99%). Paired t-test and Wilcoxon Signed Rank test, however, indicated no significant differences between influent 1 and overflow 1 whilst physicochemical parameters (Eh, alkalinity, DO) and concentrations of sulfate, iron, magnesium, manganese, silicon (total and filtered) and aluminium and zinc (total fraction) in RAPS 2 were significantly different.

Effluents were characterized by increased pH and alkalinities and were depleted in iron, aluminium, zinc and dissolved oxygen. The latter three were often close to detection limits (Table 4). Acidities were considerably lower ($\Delta_{inf-eff}$=59-345 mg L^{-1} $CaCO_3$ eq) than in influents, whilst pH ($\Delta_{eff-inf}$=1.76-2.10) and alkalinities ($\Delta_{eff-inf}$=247-201 mg L^{-1} $CaCO_3$ eq) were consistently higher than in influents.

Redox potentials decreased from oxidizing in the influents to ~0 mV in the effluents. Sulfide reached 0.88 mg L^{-1} ($\bar{x}$=0.55±0.23 mg L^{-1}, n=10) and 1.15 mg L^{-1} ($\bar{x}$=0.65±0.27 mg L^{-1}, n=10) in effluents 1 and 2, respectively. Water types varied seasonally between Ca-Mg-SO_4^{2-} (winter-spring) and Ca-Mg-HCO_3(-SO_4^{2-}) (summer) (Figure 12). Lowest alkalinity generation in the RAPS coincided with highest flow rates of influents potentially caused by reduced retention times (r_{RAPS1}=-0.63- -0.72, $p<0.05$; r_{RAPS2}=-0.57- -0.52, $p<0.05$). There was a positive correlation between pH and alkalinities in effluent 1 (r=0.67, $p<0.05$) whilst a poor or no correlation was observed in effluent 2 (r=-0.27). Weak positive correlations existed between acidities and alkalinities in both effluents (r_{eff1}=0.54; r_{eff2}=0.57, $p<0.05$).

Filtered element concentrations (<0.45 µm) accounted for more than 98% (Ca, Mg, Na, K, S) and more than 92% (Zn, Mn, Si) of the total concentrations. Filtered iron accounted for 70 to 97% of the total fraction whilst filtered aluminium made up 50±6.2% (influent 1), >72% (overflow 1), ≈99% (influent 2) and 69% (overflow 2) of the total fraction. Any aluminium determined in effluent 2 occurred largely in the particulate fraction (>95%).

Table 4 Averages of physicochemical parameters and total element concentrations of RAPS influents, effluents and overflows (2008-2009)

Parameter	Inf 1	Eff 1	Ov 1	Inf 2	Eff 2	Ov 2
T	10.0±1.7^{17}	10.2±4.1^{17}	9.13±6.8^{3}	10.0±1.0^{17}	12.2±4.3^{17}	11.3±4.2^{16}
pH	6.02±0.76^{17}	7.21±0.20^{17}	6.58±0.77^{3}	5.11±0.66^{17}	6.91±0.26^{17}	4.78±1.30^{15}
EC	775±50^{17}	892±95^{17}	526±239^{3}	1757±427^{17}	1865±275^{17}	1699±411^{16}
Eh	280±80^{17}	-2±40^{17}	273±40^{3}	340±50^{17}	3±30^{17}	435±180^{16}
Alk	31±20^{17}	202±78^{17}	30±26^{3}	24.5±33.6^{17}	185±27^{17}	21.9±39^{16}
DO	7.9±2.4^{15}	0.1±0.1^{13}	9.4±3.3^{2}	7.6±0.8^{14}	0.1±0.1^{14}	9.1±1.1^{14}
Q	30±26^{15}	24±15^{16}	27±26^{3}	69±64^{16}	17±4^{16}	54±72^{15}
Cl^-	27.7±8.2^{16}	24.8±5.8^{15}	32.7±31^{3}	22.9±6.6^{16}	24.9±7.7^{16}	22.9±6.5^{15}
SO_4^{2-}	352±50^{16}	218±78^{15}	292±272^{3}	1212±498^{16}	934±241^{16}	1109±462^{15}
Ca	97±13^{16}	139±17^{16}	69±39^{3}	203±45^{17}	318±53^{17}	195±44^{16}
Mg	25.8±2.0^{16}	27.1±3.7^{16}	17.4±9.4^{3}	98±27^{17}	95±21^{17}	91±24^{16}
Na	19.1±3.3^{16}	18.2±3.5^{16}	12.4±6.3^{3}	26.7±4.8^{17}	27.6±3.6^{17}	26.2±4.5^{16}
K	6.6±0.9^{16}	16.9±6.5^{16}	8.0±2.6^{3}	10.9±1.8^{17}	11.7±1.6^{17}	11.0±2^{16}
Fe	32.1±39.3^{16}	1.35±0.5^{16}	3.20±2.9^{2}	74.2±298^{17}	4.09±1.8^{16}	29.9±21^{16}
Al	8.95±14.3^{16}	0.44^{1}	3.29±4.4^{3}	25.0±18^{17}	bdl	24.6±20^{15}
Mn	1.04±0.19^{16}	1.75±0.59^{16}	0.90±0.70^{3}	7.46±3.16^{17}	6.75±2.03^{17}	6.81±2.8^{16}
Zn	0.2±0.11^{16}	bdl	0.23^{1}	1.41±0.64^{17}	0.07^{1}	1.17±0.5^{16}
Si	14.3±4.7^{16}	11.3±1.1^{16}	12.5±2.8^{3}	15.6±3.2^{17}	8.6±1.5^{17}	14.9±3.5^{16}

Average±standard deviation^{n}*; n=sample number, Inf=influent, eff=effluent, ov=overflow, T, temperature=℃; EC, electrical conductivity=μS cm*$^{-1}$*; Eh, redox potential compared to standard hydrogen electrode=mV; Alk, alkalinity=mg L*$^{-1}$ *$CaCO_3$ eq; DO, dissolved oxygen=mg L*$^{-1}$*; Q=flow rate in L min*$^{-1}$*; total element concentrations=mg L*$^{-1}$*, bdl=below detection limit*

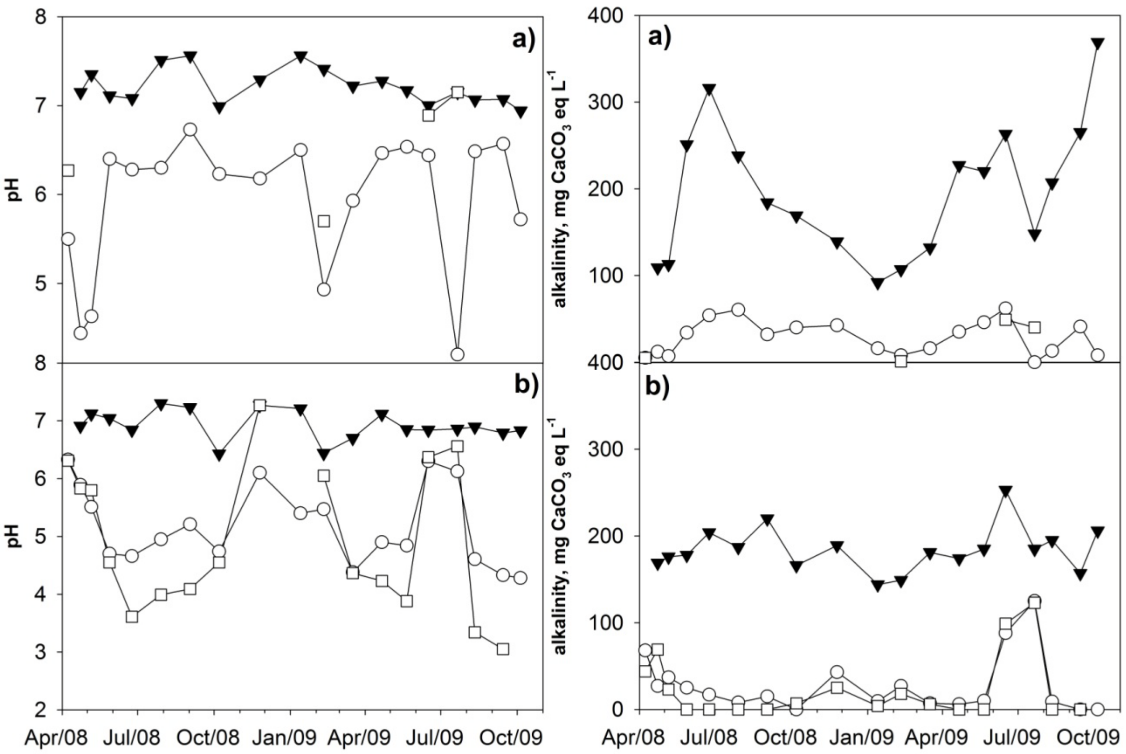

Figure 9 pH and alkalinities in influents (white circle), effluents (black) and overflows (white square) of RAPS 1 (a) and 2 (b)

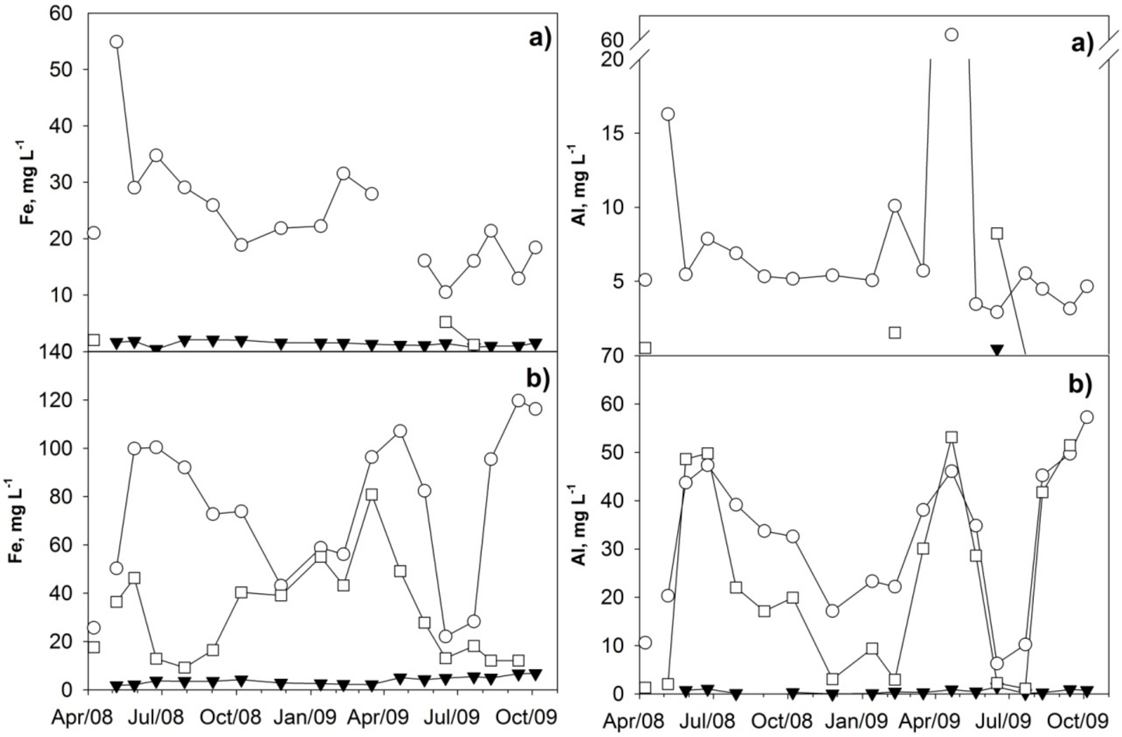

Figure 10 Total iron and aluminium concentrations in influents (white circle), effluents (black) and overflows (white square) of RAPS 1 (a) and 2 (b)

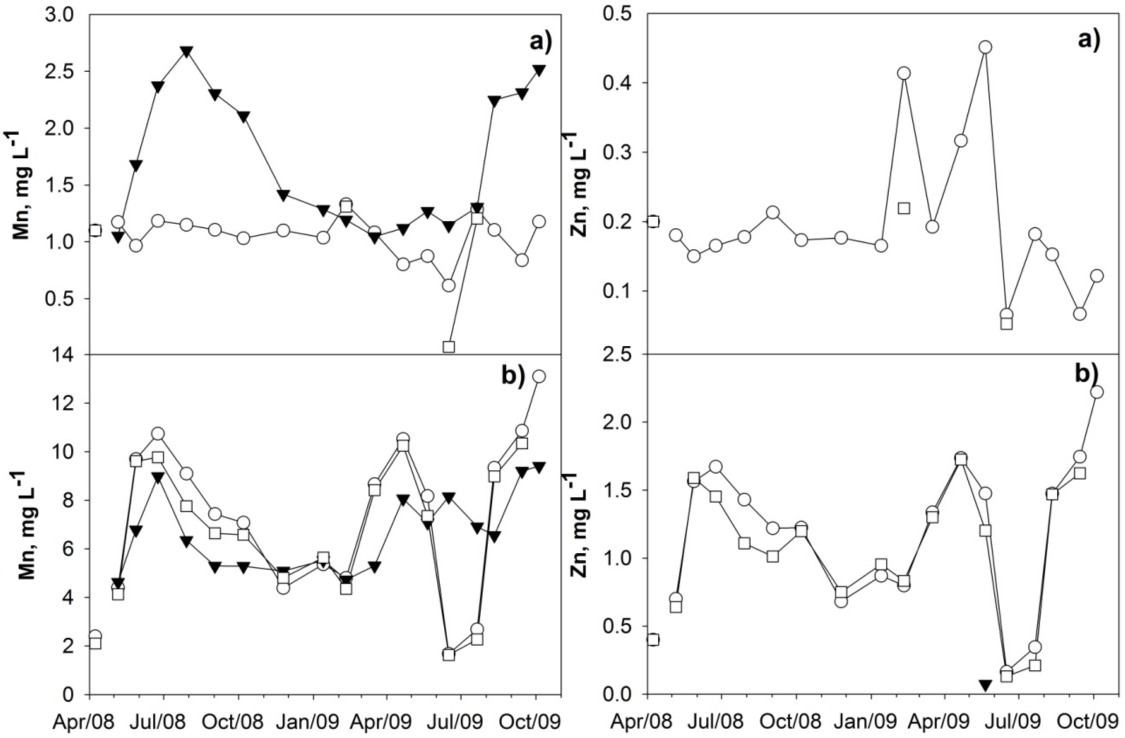

Figure 11 Total manganese and zinc concentrations in influents (white circle), effluents (black) and overflows (white square) of RAPS 1 (a) and 2 (b)

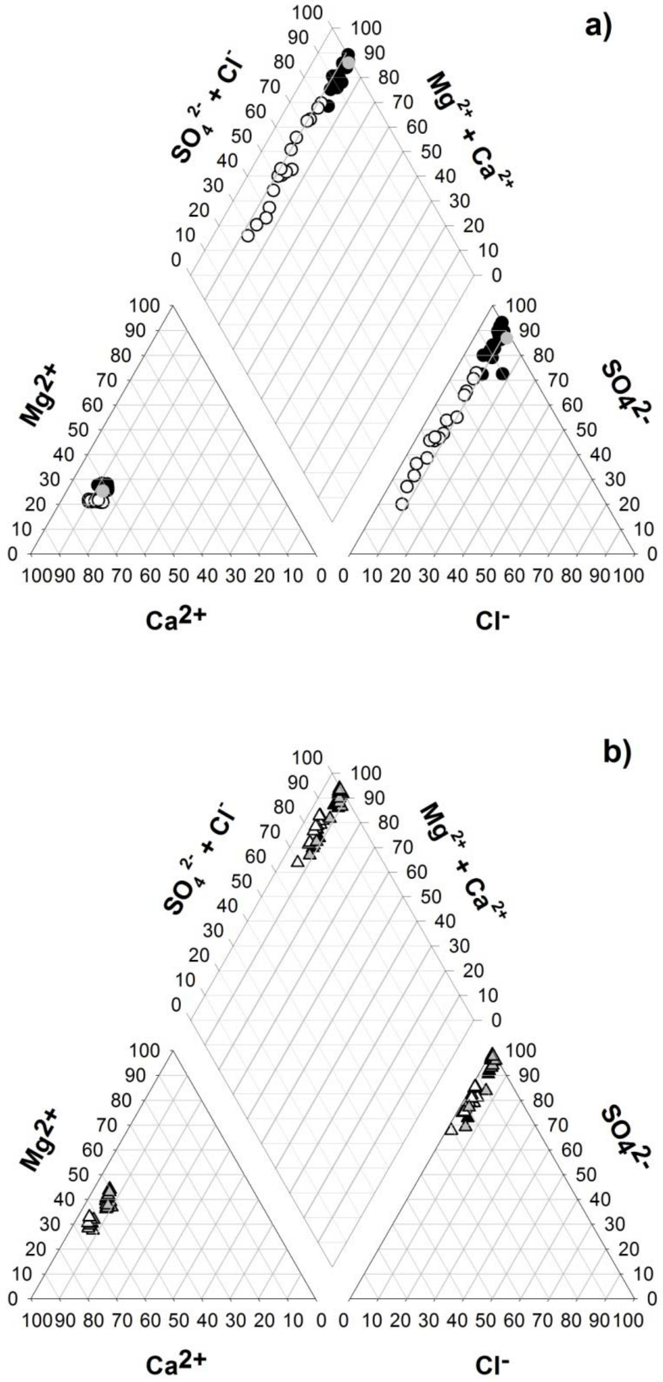

Figure 12 Piper plots of RAPS 1 (a) and 2 (b); influents (black), effluents (white), overflows (grey)

Carbon Isotopes

Principal end-members influencing the stable isotope composition of total dissolved inorganic carbon in the mine waters are atmospheric carbon ($CO_{2(atm)}$), marine carbonates and coal derived carbon. Marine carbonates have commonly carbon isotope ratios ranging between -6‰ and 3‰. The organic carbon component of coal is significantly depleted in ^{13}C, (-23.7 to -20.6‰) (Pezdic 1998, Hoefs 2004). Carbon isotope ratios of TDIC in the waters showed some scatter for RAPS influents (RAPS 1: -8±7‰ n=14; RAPS 2: -16±2‰, n=12) and overflows (RAPS 1: -14±3‰, n=3; RAPS 2: -19±6‰, n=11, Figure 13) with carbon isotopes plotting between the end members.

The principal alkalinity generating processes in the RAPS are the dissolution of limestone gravel and the microbial oxidation of compost. In addition, interaction (dissolution, exsolution, exchange) with atmospheric CO_2 is likely to occur. Limestone had an isotopic value of 1.8±0.3‰ (n=4), typical for marine carbonates (Anderson et al. 1992, Hoefs 2004, Wadham et al. 2004). Inorganic carbon-free organic matter had an average carbon isotope ratio of -28.5±2.4‰ (n=12) indicative of C3 plants that use the Calvin cycle for photosynthesis (Smith and Epstein 1971b, Farquhar et al. 1989, Yanes et al. 2008).

Similar to other investigations (Forsberg et al. 1993, Stern et al. 2007), fresh *Typha* roots and leaves had $\delta^{13}C$ of -27.5±0.3‰ (n=2) and -28.0±0.0‰ (n=2), respectively. The original reactive substrate of the RAPS (50 vol.% horse manure and straw compost; 50 vol.% limestone gravel) had a total carbon concentration of 8.9% to 27.9% (dry weight). Total organic carbon (TOC) accounted for 79±13% of TC (74.7-258.3 g kg^{-1}). Average global atmospheric $\delta^{13}C_{CO2}$ range at -6.4‰ (Clark and Fritz 1997) but might change locally based on increased emissions due to burning of fossil fuels. Carbon isotopic ratios of atmospheric carbon dioxide of a monitoring site of western Ireland (www.cmdl.noaa.gov) ranged between -6.77‰ to -11.9‰ (-7.89±0.48‰, n=126).

A distinct seasonality with highest alkalinity additions was observed in RAPS 1 during the summer months ($\Delta alkalinity_{inf-eff}$=160±55 mg L^{-1} $CaCO_3$ eq, range: 75-260 mg L^{-1} $CaCO_3$ eq; Figure 9). In RAPS 2 average alkalinity additions were similar ($\Delta alkalinity_{inf-eff}$ =160±35 mg L^{-1} $CaCO_3$ eq, 60-205 $CaCO_3$ eq), however, the distinct seasonality was not observed.

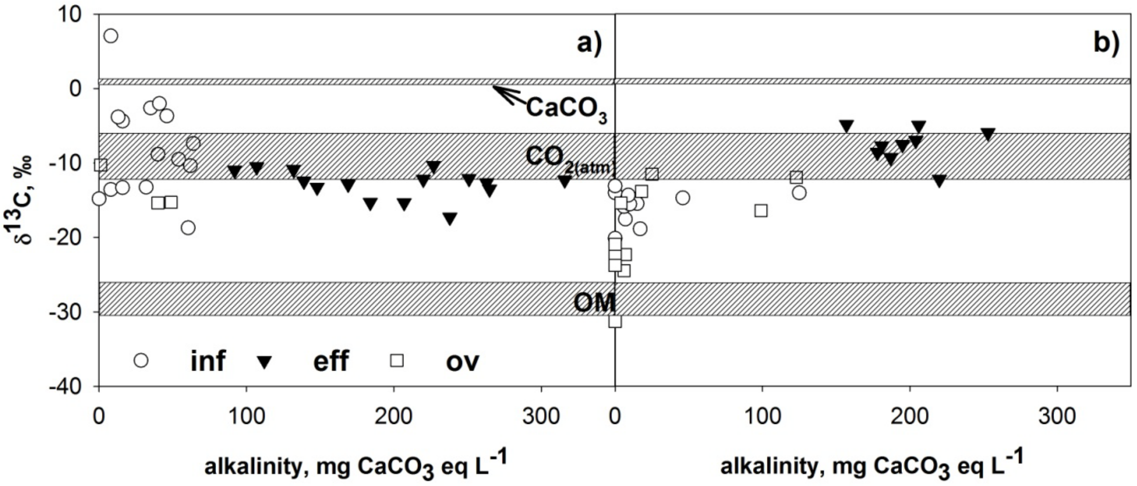

Figure 13 Alkalinity concentrations and carbon isotope ratios in waters of RAPS 1 (a) and 2 (b), shaded areas=$\delta^{13}C$ of organic matter (OM), limestone ($CaCO_3$) and atmospheric carbon dioxide ($CO_{2(atm)}$)

Isotopic ratios of TDIC in effluent 1 (-13±2‰, n=14) varied only marginally from those measured in influent 1 ($\Delta^{13}C_{inf\text{-}eff}$~4±5‰, n=14). Effluent 2 (-8±2‰, n=9) was significantly more enriched in ^{13}C compared to influent 2 by in average 8±3‰ (n=5, Figure 13). Alkalinity enrichments and fractionation of $\delta^{13}C$ in both effluents were uncorrelated ($p>0.05$).

Treatment Performance

Iron, aluminium and zinc were close to quantitatively removed in RAPS 1 (Table 5). Considerably lower percentage removal in RAPS 2 was mainly related to the about 9 times higher acidity influent loads by equal volumes of reactive substrate (Chapter 1). Land restrictions required undersizing RAPS 2 by four-times in surface area. Consequently, theoretical retention times were at least 4 times lower in this RAPS than those defined by the design criteria (Younger et al. 2004, Fabian et al. 2005) which adversely influenced the treatment performance.

The removal of manganese is notoriously difficult (Hedin et al. 1994, Mataix Gonzalez 1999, Younger et al. 2002). It was therefore no surprise that the removal rates of manganese in RAPS 2 were low (~23%). In RAPS 1, a constant (re-)mobilization of manganese was observed at the beginning of the treatment, similar to other treatment systems (Gammons and Frandsen 2001, Bhattacharya et al. 2008, Kröpfelová et al. 2009).

Table 5 Percentage and load removal rates of contaminants in RAPS (2008-2009)

	RAPS 1		RAPS 2	
	%	LRR	%	LRR
Fe	93 (67-99)	871 (-51-2564)	78 (29-97)	3.8 (1.6-6.6)*
Al	~100 (-59-100)	189 (-256-904)	76 (48-95)	1.6 (1.1-2.7)*
Zn	>98 (80-100)	6.7 (0-21)	55 (11-93)	45 (12-97)
Mn	-45 (-176-5)	-12.1 (-89-5)	23 (-1-54)	115 (-6.6-363)

*%=median percentage removal (min-max); LRR=median load removal rates=g d^{-1} (min-max), *kg d^{-1}*

However, elevated manganese concentrations in the effluent were also reported for the nearly seven year old system. The highest concentration increases were observed during low-flow occasions in summer months (Figure 11).

Discussion

Geochemical Attenuation

Iron

Analytical results paired with geochemical modeling suggested that more than 79% of the filtered iron fraction occurred in divalent ionic form (Figure 14). An increase in Fe(III) by up to 20% in the water cover (and overflow) of the systems suggest iron oxidation ($Fe^{2+} + 0.25O_2 + H^+ \rightarrow Fe^{3+} + 0.5H_2O$) occurred fast. Under moderate acidic to circum-neutral pH, ferric iron is highly unstable ($Fe^{3+} + H_2O \rightarrow Fe(OH)^{2+} + H^+$, log k=-2.2), which explains the high concentrations of ferrous iron in dissolved phase. Upon hydrolysis of ferric iron in sulfate rich medium (e.g. $Fe^{3+} + 3H_2O \rightarrow Fe(OH)_3 + 3H^+$; $8Fe^{3+} + SO_4^{2-} + 14H_2O \rightarrow Fe_8O_8(SO_4)(OH)_6 + 22H^+$) the precipitation of Fe(III)-rich mineral phases is promoted.

Despite oxygen consumption during ferrous iron oxidation ($O_2 + 4Fe^{2+} + 4H^+ \rightarrow 4Fe^{3+} + 2H_2O$), overflows were enriched in oxygen compared to influents suggesting dissolution rates of atmospheric oxygen in the waters exceeded oxygen consumption rates. Hence, I assume that the removal of iron in the water-sediment interface was limited by pseudo-first order oxidation rates of ferrous iron (Pham and Waite 2008). Nordstrom (1985) showed, that under net-acidic conditions iron oxidation rates occur in the order of $5*10^{-7}$ mol L^{-1} s^{-1} which is several orders of magnitude slower than the average influent load of Fe^{2+} (~9.189 mol s^{-1}, RAPS 2). In addition, low reactive zero-valent iron sulfate and hydroxide complexes (Figure 14) potentially hampered iron removal. Positive correlation of Fe^{3+} with temperature ($r=0.72$), DO ($r=0.70$) and negative correlation with flow rate ($r=-0.72$) suggest, that oxygen was the dominant oxidizing agent of Fe^{2+}. Ferrous iron oxidation is potentially enhanced by heterogeneous oxidation with solid state Fe(III) (Barnes et al. 2009).

Influent and overflow iron concentrations were potentially controlled by hydroxide, oxide and oxyhydroxysulfate mineral species (Figure 15). Jarosite, schwertmannite and ferrihydrite form at pH ranges of 2.7-5.9; 2.8-5.8 and >5.7, respectively, (Bigham et al. 1990, Bigham et al. 1996b, Williams et al. 2002, Desborough et al. 2010). Goethite, hematite and lepidocrocite were also supersaturated in the waters and are thermodynamically more stable under ambient conditions (Cornell and Schwertmann 2003). However, it is believed that due to their slow reaction kinetics, they do not precipitate directly but form through dehydration of meta-stable hydroxides (Dutrizac and Jambor 2000, Williams et al. 2002, Peretyazhko et al. 2009).

Schwertmannite (formerly glockerite (Glocker 1853)) seemed to be the most stable iron phase over the whole sampling period (based on geochemical modelling) and was also found by Transmitted Electron Microscopy (Figure 18). Fe:S ratios (analysed by EDS) ranged above 11 which is higher than ideal Fe:S ratios for this mineral (~8) (Bigham and Nordstrom 2000)). The low potassium concentrations in the surface sludge (~0.06 mol kg^{-1}), suggests only little iron (~3.3%) is retained in jarosites (ideal K:Fe:S ratios=1:3:2).

Measured redox potentials (converted to pE with Nernst equation) were well correlated to calculated $p\varepsilon_{Fe}$ ($Fe^{2+} \rightarrow Fe^{3+} + e^-$; $p\varepsilon_{Fe}=-\log K_{Fe2+/Fe3+} + \log(aFe^{3+})-\log(aFe^{2+})$, $r>0.82$, $p<0.05$). However, calculated $p\varepsilon_{Fe}$ were in average 2.1 units higher than measured pE suggesting a lack of redox equilibrium.

Under the pH/pE conditions encountered in the freeboard, ferrous iron is highly mobile (Hem 1985). Whilst highest Fe^{2+} activities (aFe^{2+}) were observed at pH 4.5-6.5 (Figure 16). A decrease in aFe^{2+} at pH<4.5, mostly observed in overflow 2, could be explained by ion exchange and sorption processes. The increasing oxidation, hydrolysis and precipitation of Fe(III)hydroxides in the freeboard, create increasing surface charge and sorption sites. Despite the high mobility of ferrous iron, a significant amount seems to be retained by sorption onto Fe(III)hydroxides.

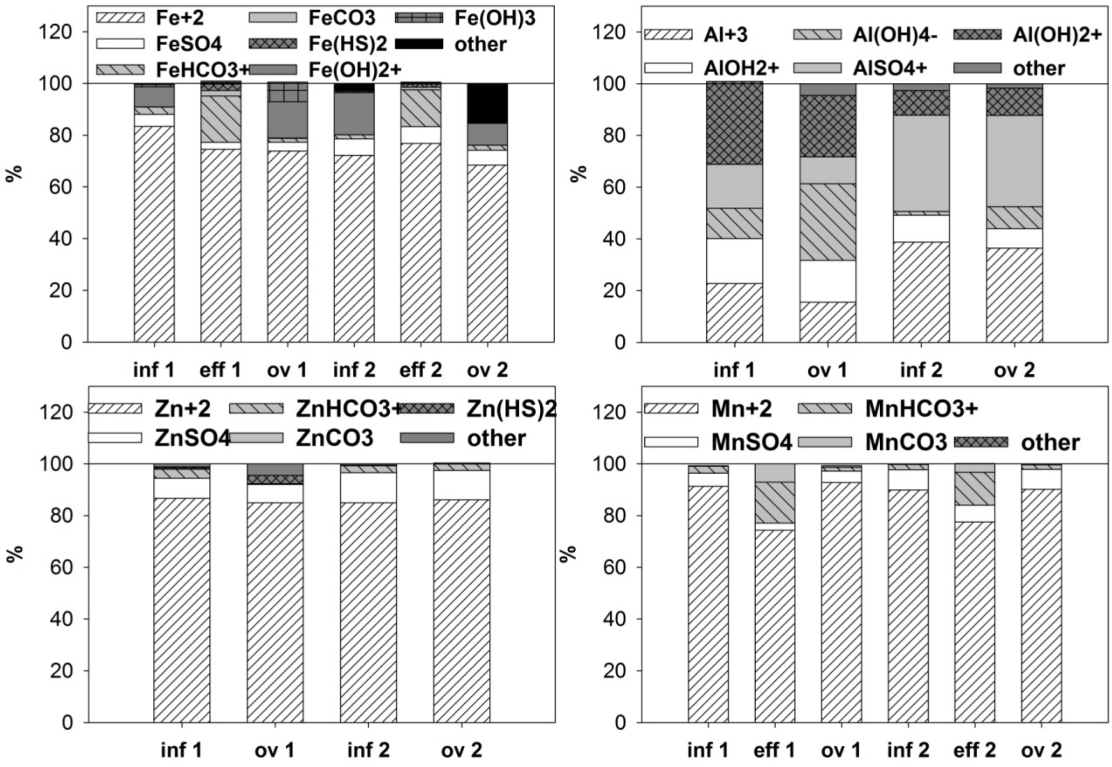

Figure 14 Dominant aqueous species of iron, aluminium, zinc and manganese in RAPS influents, overflows and (when detectable) effluents

As to the significant increase in pH, alkalinity and hydrogen sulfide and the concomitant decrease in redox potentials, iron in effluents was potentially controlled by carbonate species (e.g. siderite $SI_{eff1}=0.14\pm0.26$, $SI_{eff2}=0.23\pm0.33$, and solid solutions) and mono- and di-sulfides (mackinawite $SI_{eff1}=1.5\pm0.7$, $SI_{eff2}=1.5\pm1.0$, pyrite: $SI_{eff1}=17.5\pm2.4$, $SI_{eff2}=17.2\pm2.2$; $FeS_{(amph)}$: $SI_{eff1}=0.8\pm0.7$, $SI_{eff2}=0.7\pm1.0$). Incomplete iron removal seems to be partially an effect of complexation of iron in zero-valent carbonate, hydroxide and sulfate complexes, in addition to a limited filtration potential of the reactive substrates for nano-and microscale particles.

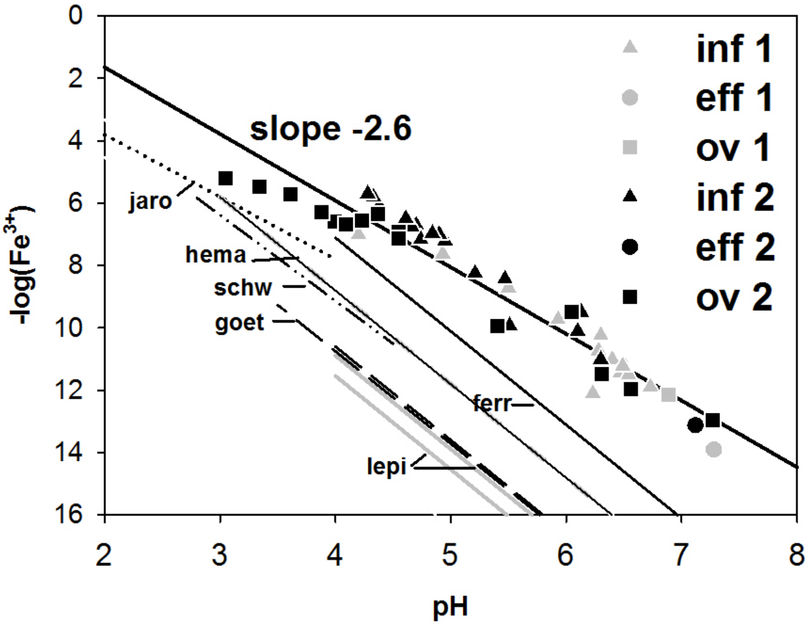

Figure 15 pH versus ferric iron activity in RAPS waters; solubility lines: goethite: $-\log(Fe^{3+})=-\log k+3pH$; ferrihydrite: $-\log(Fe^{3+})=-\log k+3pH$; schwertmannite: $-\log(Fe^{3+})=-0.125\log k + 2.75pH - 0.125\log(SO_4^{2-})$; K-jarosite: $-\log(Fe^{3+})=-0.33\log k +2pH +0.33\log(K^+) + 0.66\log(SO_4^{2-})$, lepidocrocite: $-\log(Fe^{3+})=-\log k + 3pH$; average log. activity of potassium=-3.6 and sulfate=-3.1; $\log k_{goet}=-1.4$, $\log k_{ferr}=4.81$, $\log k_{schw}=18.0$, $\log k_{jaro}=-9.2$, $\log IAP_{lepi}=0.46$-1.11

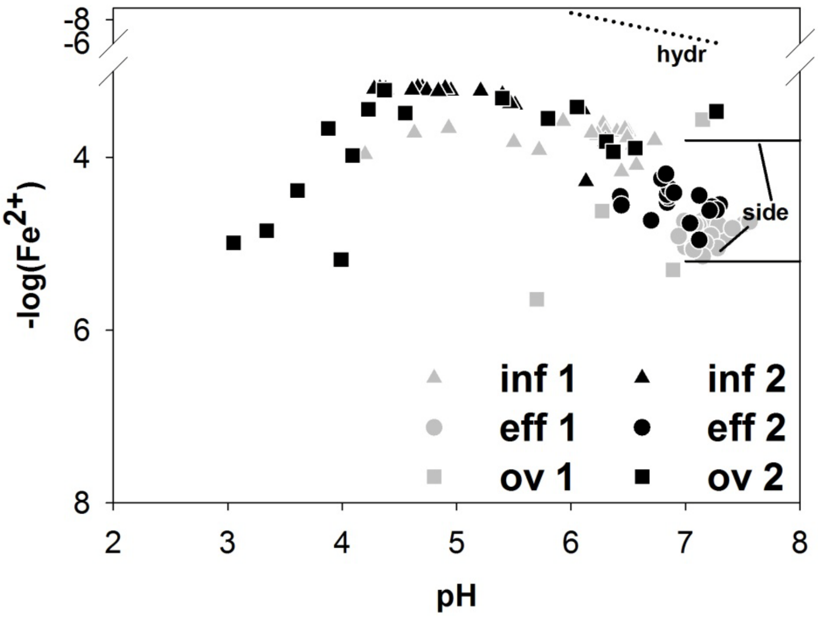

Figure 16 pH versus ferrous iron activities in RAPS waters; solubility lines: siderite: -log(Fe^{2+})=-log k +log(CO_3^{2-}),
amorphous iron hydroxide: -log(Fe^{2+})=-log k +2pH; assumed carbonate activity=-5.3 to -6.7, log k_{side}=-10.45, log k_{amph}=20.57

Aluminium

Geochemical modelling suggests that most aluminium in influents and overflows was complexed in charged hydroxide or sulfate species (Figure 14). The strong seasonality observed in the distribution of the dominant aluminium aqueous species was mostly dependent on sulfate concentrations (r=0.87-0.92) and pH (r>0.74).

The first hydrolysis reaction of aluminium (($Al^{3+} + H_2O \rightarrow Al(OH)^{2+} + H^+$); solubility constant: log k=-5.00 to -4.6 (Nordstrom and Ball 1986)) causes an increasingly non-conservative behaviour of aluminium at pH>5 followed by a removal in form of poorly crystalline (hydro)basaluminite and amorphous aluminium oxyhydroxide (Figure 17) (Nordstrom 1982b, Hem 1985, Blowes and Jambor 1990), potentially accompanied by other oxyhydroxysulfates (Bigham and Nordstrom 2000). Also the incorporation of hydrolysed aluminium ($AlOH^{2+}$, $Al(OH)_2^+$,$Al(OH)_4^-$) into iron hydroxides has been reported (Cornell and Schwertmann 2003).

Upon ageing, these meta-stable phases transform into more crystalline hydroxides such as gibbsite, boehmite, alumina and alunite (Bigham and Nordstrom 2000). The occurrence of jurbanite has rarely been observed under ambient conditions and its saturation (jurbanite: $SI_{inf1}=0\pm0.6$, $SI_{inf2}=1\pm0.5$) might be a result of an erroneous solubility product (Bigham and Nordstrom 2000).

Hydrolysis and precipitation of Al-hydroxides caused a decrease in total aluminium concentrations in the water/sediment interface by >85% in RAPS 1 and ~44% in RAPS 2. A significant increase in the particulate fraction from 6% to 67% of the total aluminium fraction between influent 1 and overflow 1 (from 4% to 31% in RAPS 2) suggests that coagulation and precipitation is limiting complete aluminium removal.

Poorly crystalline aluminium oxyhydroxysulfate in form of spherical aggregates have been observed (Figure 18). EDS indicated Al:S ratios between 2.75-7.75 with trace amounts of iron (Figure 19). The low concentrations of silicon in the ochre (~40 mg kg^{-1} dry wt.) indicate alumosilicates (e.g. kaolinite) were of minor importance in the removal of aluminium.

The conservative behaviour of aluminium in the waters at pH below 5 are commonly observed in waters of low to moderate ionic strength with limited effects through complexation (Bigham and Nordstrom 2000). Particularly for RAPS 2, I observed that mineral phases supersaturated in influents became increasingly undersaturated in the overflow (freeboard) due to the increasing proton acidity, a product of hydrolysis. The coupled decrease in alkalinity might have been caused by dehydration of bicarbonate ($HCO_3^- + H^+ \rightarrow CO_{2(aq)} + H_2O$; $CO_{2(aq)} \leftrightarrow CO_{2(g)}$). Consequently, these processes led to a partial redissolution of aluminium precipitates at pH<5.

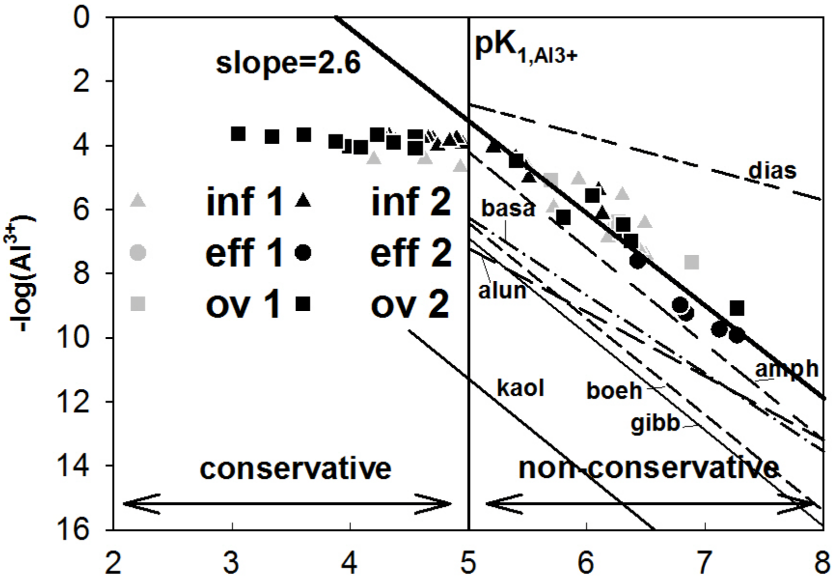

Figure 17 pH versus aluminium activities in RAPS waters; solubility lines: basaluminite: $-\log(Al^{3+})=-0.25\log k+2.5pH+0.25\log(SO_4^{2-})$; alunite: $-\log(Al^{3+})=-0.33\log k+2pH+0.33\log(K^+)+0.66\log(SO_4^{2-})$; boehmite: $-\log(Al^{3+})=-\log k+3pH$; gibbsite: $-\log(Al^{3+})=-\log k+3pH$; diaspore: $-\log(Al^{3+})=-0.33\log k+pH$; amorphous $Al(OH)_3$: $-\log(Al^{3+})=-\log k+3pH$, kaolinite: $-\log(Al^{3+})=-0.5\log k+3pH$; assumed sulfate activity=$\log(SO_4^{2-})=-3.1$, $\log(K^+)=-3.6$; $\log k_{basa}=22.7$, $\log k_{alun}=-1.4$, $\log k_{boeh}=8.584$, $\log k_{gibb}=8.11$, $\log k_{dias}=6.879$, $\log k_{amph}=10.8$, $\log k_{kaol}=7.435$, pK=first hydrolysis constant

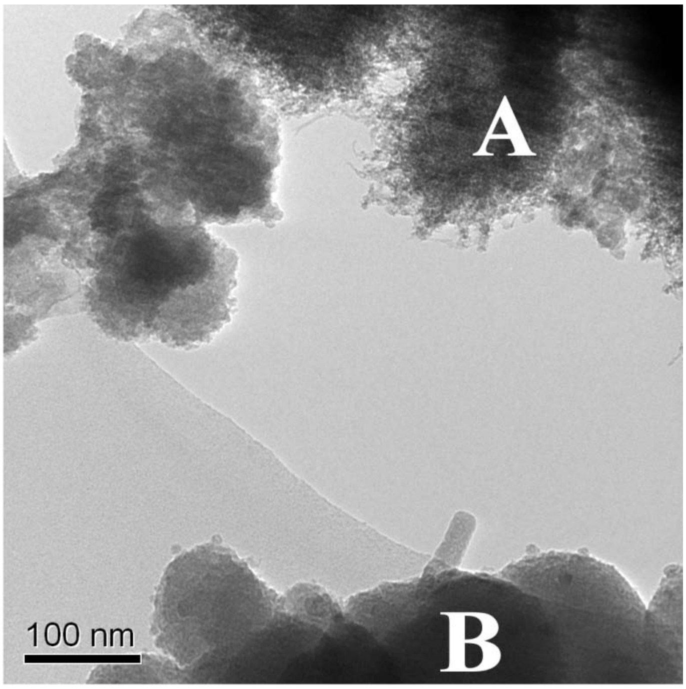

Figure 18 TEM image of pin-cushion like schwertmannite (A; Fe:S~11.5) and poorly crystalline aluminium oxyhydroxysulfate (B; Al:S~6) in RAPS 2 (15 cm below surface)

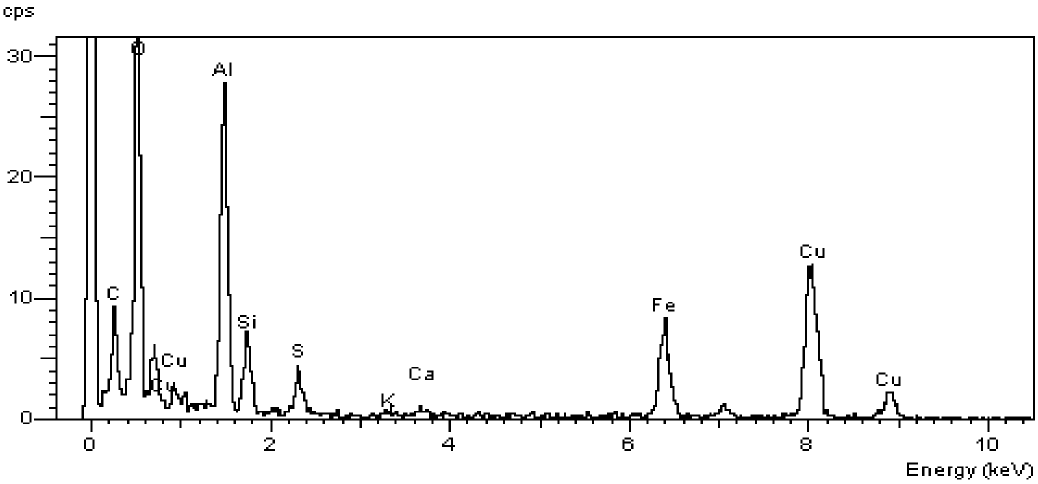

Figure 19 EDS diagram of aluminium-, iron- and sulfur-rich hydroxide (area B of previous figure)

Zinc

Changes in zinc concentrations in influents and overflows were small or negligible and zinc activity was independent of pH. No mineral phase controlled zinc concentrations, with exception of $ZnSiO_3$ (SI= -5.4-2.1). The high mobility of this element in the surface waters was confirmed by the modelling of principal aqueous species that were dominated by ionic Zn^{2+} whilst complexed zinc accounted for less than 15% of the dissolved zinc fraction (Figure 14). Similarly, Sanchez España et al. (2006) observed little pH dependent sorption capacities of iron and aluminium oxyhydroxysulfates for zinc.

In the effluents, zinc concentrations were commonly below detection limit. Geochemical modelling suggested that trace amounts of zinc in the effluents could potentially be bound in hydrogen sulfide complexes ($Zn(HS)_2$). Zinc sulfide minerals (e.g. sphalerite, wurzite) were supersaturated (SI>3). The association of zinc with iron sulfides (Johnson et al. 2004, van Hille et al. 2004, Peltier et al. 2005), sorption onto organic matter or ion-exchange processes (Kinniburg et al. 1976, Hem 1985, Blowes and Jambor 1990, Scheffer and Schachtschabel 2002) are also likely controlling processes for zinc concentrations in the interstitial waters. Traces of zinc bicarbonate and carbonate complexes in effluents suggest that a minor amount of zinc could also be retained as carbonate (smithonite) or in carbonate solid solutions (Billon et al. 2002).

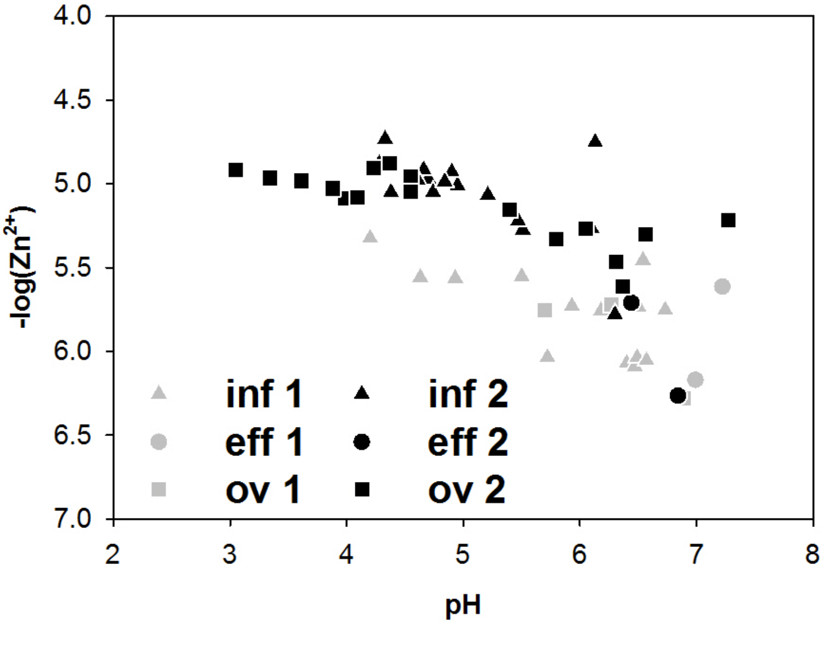

Figure 20 pH versus zinc activities in RAPS waters

Manganese

Manganese was not removed in the freeboard (Figure 11). Under measured pH/Eh conditions, divalent manganese dominates (Figure 14) and is highly mobile. Abiotic autooxidation to Mn^{4+} is slow at pH<8.5 (Hem 1985, Henrot and Wieder 1990, Johnson and Hallberg 2002, Younger et al.

2002). Manganese activity was largely disconnected from pH and no discrete mineral species controlled manganese in influents and overflows (Figure 21).

Under the anoxic conditions encountered in effluents, manganese sulfide (MnS) is commonly soluble at circum-neutral pH due to its high solubility product (Diaz et al. 1997). However, pyritisation of manganese is possible (Jacobs et al. 1985, Billon et al. 2001). The removal of manganese as a carbonate (e.g. rhodochrosite or manganoan carbonates (Mucci 2004), Figure 22) has been reported for pH exceeding 9 (Hem 1985), and might also partly have influenced the retention of manganese under moderately alkaline conditions within the substrates (SI_{eff1}=0.4±0.3, SI_{eff2}=0.7±0.3). Dissordered rhodochrosite commonly ranged below or close to saturation (SI~0). Sorption and co-precipiation on calcite surfaces was reported to be the dominant manganese controlling process in calcite-rich environment (Mucci 2004). Removal by co-precipitation and sorption onto newly formed Fe/Al hydroxides might also have led to some manganese removal.

Ion exchange processes (Machemer and Wildeman 1992, Wieder 1993), dissolution of limestone (Hem 1985, Mason and Moore 1985, Reimann and de Caritat 1998) (total Mn concentration in limestone=91-111 mg kg^{-1}) and mineralization of the organic substrate (Wieder 1993, van der Watt et al. 1994, Hsu and Lo 2001, Ji and Kim 2008) could be responsible for the manganese mobilization observed in RAPS 1. Why both RAPS, however, behaved so differently with respect to manganese, cannot be fully explained. Besides the different influent loads, the only noticeable difference between the systems is that RAPS 1 is populated by wetland species (e.g. grasses, *Typha*). The microbial niche in the root zone has been shown to promote bacterial reduction of Mn(IV)oxides and manganese bound to organic matter (Ji and Kim 2008) and might explain the enhanced manganese mobilization in RAPS 1.

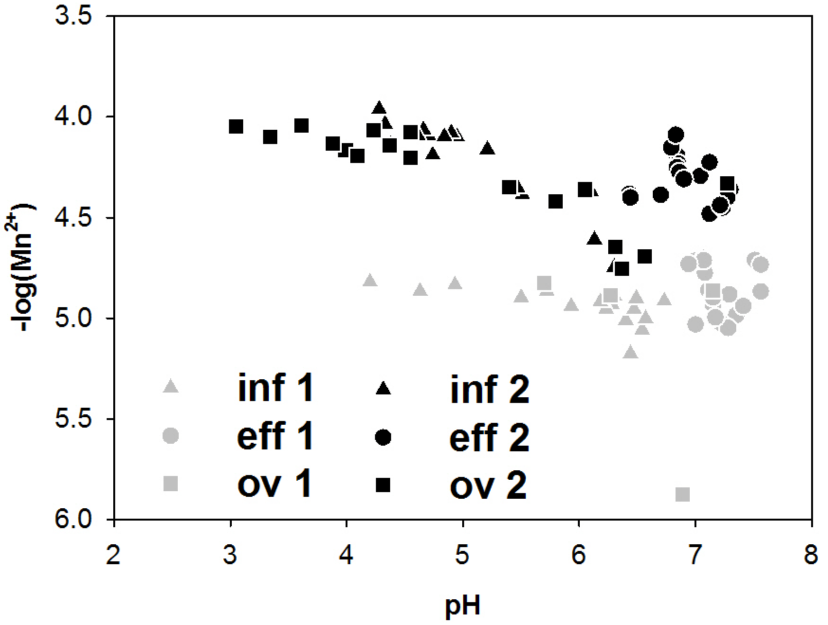

Figure 21 pH versus manganese(II) activities in RAPS waters

Alkalinity Sources

Mass Balance based on Acidity Removal and Alkalinity Generation

In order to discriminate the potential bicarbonate sources in the reactive substrate, total alkalinity generation and total acidity consumption were compared (equation (4)):

- The alkalinity generated (i.e. acidity neutralized) by limestone dissolution (Acd_{lst}) was calculated from the net mobilization of calcium assuming one mole of calcite dissolved neutralizes one mole of proton acidity ($CaCO_3 + H^+ \rightarrow Ca^{2+} + HCO_3^-$).
- The total acidity consumed was calculated as the sum of i) proton, iron and aluminium removal and ii) the surplus bicarbonate (assuming one mole of bicarbonate neutralizes one mole of proton acidity ($HCO_3^- + H^+ \rightarrow CO_{2(aq)} + H_2O$).

This approach assumes that bicarbonate consuming processes in the substrate are dominated by hydrolysis of iron and aluminium to the dominant mineral species: schwertmannite ($8Fe^{3+} + SO_4^{2-} + 14\ H_2O \rightarrow Fe_8O_8(OH)_6SO_4 + 22H^+$) and basaluminite ($4Al^{3+} + SO_4^{2-} + 10H_2O \rightarrow Al_4(OH)_{10}SO_4 + 10H^+$) in which 22 and 10 moles of H^+ are released, respectively, per mole of mineral generated. In addition, one mole of H^+ is consumed during the oxidation of ferrous iron to ferric iron. Overall, therefore, for each mole of iron and aluminium removed, 1.75 and 2.5 moles of protons, respectively, are liberated.

The acidity neutralized by the mineralization of organic matter (Acd_{OM}) was calculated as a difference between Acd_{tot} and Acd_{lst}.

(4)

$$Acd_{tot} = 1.75\Delta Fe + 2.25\Delta Al + \Delta H^{+}_{bic} + \Delta H^{+} + \Delta H^{+}_{DO}$$

Acd=total acidity consumed in mol min^{-1}*, Fe=total iron consumed assuming removal as hydroxide (schwertmannite), Al=total aluminium removed assuming removal as hydroxide (basaluminite),* H^{+}_{bic}*=proton acidity consumed by carbonate dissolution,* H^{+}*=proton acidity consumed,* H^{+}_{DO}*=proton acidity consumed that was generated through aerobic respiration and consumption of dissolved oxygen*

Sulfate removal rates are often assumed to indicate bacterial sulfate reduction ($2CH_2O + SO_4^{2-} \rightarrow H_2S + 2HCO_3^{-}$) (Riefler et al. 2008). However, a significant part of the sulfate is removed as oxyhydroxysulfate (Chapter 3). Consequently, this approach would significantly overestimate the bicarbonate generation deriving from BSR.

Further, about 90% of hydrogen sulfide in natural sediments is partially or fully reoxidised ($H_2S + Fe^{3+} \rightarrow S^0 + Fe^{2+} + 2H^+$; $H_2S + O_2 \rightarrow SO_4^{2-} + 2H^+$) (Jørgensen 1988, Canfield and Thamdrup 1993). Accordingly, assuming similar degrees of reoxidation are occurring in the RAPS, the BSR should be considered as a largely non-acidity removing process.

On one and six occasions in RAPS 1 and 2, respectively, limestone derived alkalinity was negative because effluent calcium loads were lower than influent calcium loads, suggesting calcium is net-retained in the substrate, possibly by supersaturation of mineral carbonates (Figure 22). By only considering those events were calcium release rates were positive (i.e. $eff_{Ca} > inf_{Ca}$), the mass balance suggests that 21±11% (RAPS 1, n=15) and 15±15% (RAPS 2, n=16) of the alkalinity generated (i.e. acidity consumed) derives from limestone dissolution, whilst the reminder derives from microbial oxidation of organic matter.

Mass Balance based on Carbon Isotope Fractionation in TDIC

In a second approach, carbon isotope ratios of the two end members (limestone and organic matter) were used to explain the isotope carbon ratios measured in TDIC (equation (5). Alkalinity concentrations encountered in the influents were generally low or undetectable and were therefore not included in the assessment.

(5)

$$\delta^{13}C_{TDIC} = x(\delta^{13}C_{lst} + \varepsilon_{bic}) + (1-x)(\delta^{13}C_{OM} + \varepsilon_{OM} + \varepsilon_{bic})$$

$\delta^{13}C$ in per mill, lst=limestone ($\delta^{13}C$~1.8‰), OM=organic matter ($\delta^{13}C$~-28.5‰), ε=enrichment factor during limestone dissolution and mineralization of organic matter

The enrichment factor for limestone (ε_{bic}) was assumed to be 7.9‰ based on the fractionation induced during CO_2 hydrolysis, ($CO_{2(aq)} + H_2O \rightarrow HCO_3^- + H^+$; 6.8-9.2‰ at T=30-0°C) (Deuser and Degens 1967, Smith and Epstein 1971a, Zhang et al. 1995). The fractionation factor of organic matter was assumed to be zero (Clark and Fritz 1997, Rees and Bowell 1999, Skidmore et al. 2004, Das et al. 2005). The transformation of organic matter derived CO_2 to bicarbonate was adjusted by addition of ε_{bic}.

After the mass balance, 26±6% of all alkalinity was generated by limestone dissolution in RAPS 1, whilst in RAPS 2 it was 43±8%. Due to the stable carbon isotope ratios measured in TDIC, the variation in the overall contribution of bicarbonate from oxidation of organic matter and limestone dissolution throughout the year of monitoring was relatively small.

Particularly for RAPS 2 significant differences in both mass balances are observed. Clearly, to some extent outgassing of carbon dioxide ($H_2O + CO_{2(aq)} \rightarrow H_2O + CO_{2(g)}\uparrow$) might have contributed to additional fractionation. However, it is assumed that the latter are only of minor importance compared to the differences here observed (3-5‰), (King 2004, Doctor et al. 2008). I suggest that the principal sources of error are:

- The re-precipitation of oversaturated carbonates which will have led to depletion in ^{13}C of TDIC and
- The assumption ε_{OM}=0‰.

Recent studies on sulfate reducing bacteria suggest, that significant fractionation of $\delta^{13}C$ occurs during BSR (Londry and des Marais 2003, Goevert and Conrad 2008, Goevert and Conrad 2010). The degree of carbon fractionation thereby depends on the mineral strain, its metabolic pathway, the organic reactant and on whether complete (CO_2=end product) or incomplete (acetate=end product) oxidation occurs. Using acetate as principal carbon source during these studies, isotope fractionation of acetate ranged between 1.5-19.3‰ (ε) and led to isotopically depleted dissolved inorganic carbon.

Further, Lovely and Phillips (1987b), Wieder (1993) and Morrison and Aplin (2009) showed, that bacterial iron reduction and methanogenesis are likely to contribute to bicarbonate generation (and consumption) in these types of treatment systems. Consumption of carbon dioxide, at least during the months between spring and early autumn, could also occur from the photosynthetic activity of the wetland plants growing on RAPS 1.

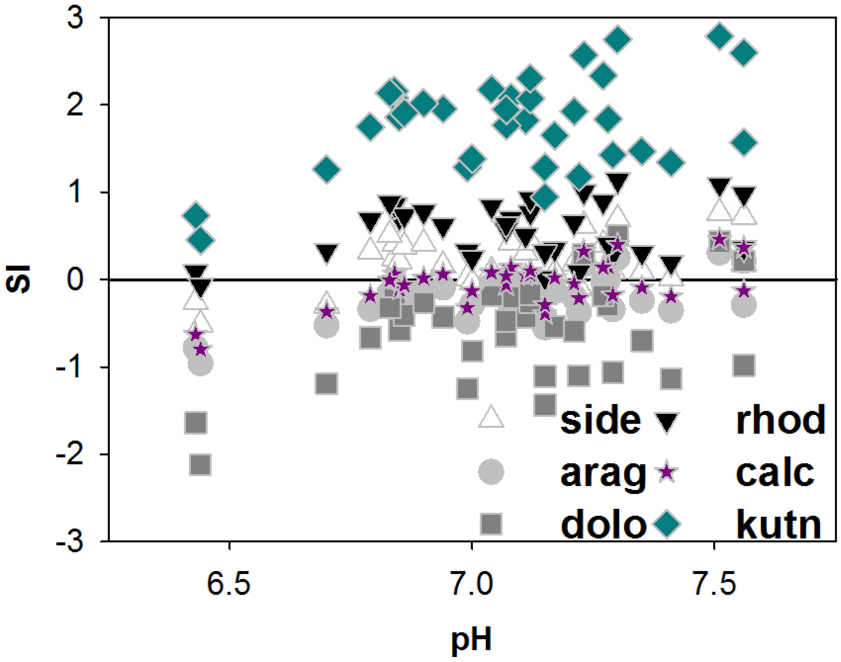

Figure 22 pH versus saturation indices of carbonate minerals in RAPS effluents, log k_{side}=-10.45, log k_{arag}=-8.336, log k_{dolo}=-16.54, log k_{calc}=-8.45, log k_{rhod}=-10.39, log k_{kutn}=-20.7, side=siderite, arag=aragonite, dolo=dolomite, rhod=rhodocrocite, calc=calcite, kutn=kutnahorite

Summary

- The two RAPS of the Bowden Close treatment system were monitored at monthly intervals over an 18 months period;
- From each RAPS, influents, effluents and overflows were analysed for physicochemical parameters, total and filtered element concentrations, sulfur and iron species and carbon isotopes of total dissolved inorganic carbon;
- Iron, aluminium and zinc were quantitatively removed in RAPS 1; in RAPS 2 they were removed by more than 55%;
- Manganese was removed by 23% in RAPS 2 but continuously mobilized from RAPS 1;
- Geochemical modelling suggested that iron and aluminium were removed as meta-stable hydroxides that are partially remobilized in the water/sediment interface upon increase of proton acidity as an effect of hydrolysis or upon flush out during high flow events;

- Manganese and zinc were potentially removed through sorption, ion exchange, in carbonate and sulfide minerals;
- Both, limestone dissolution and the microbial oxidation of organic matter contributed to the generation of alkalinity, however, the latter seems to be the dominant process in both RAPS.

3. IRON AND SULFUR SPECIATION IN RAPS SEDIMENTS

RAPS strive to reverse the AMD generation process by removing iron as sedimentary sulfides with the help of BSR (Tuttle et al. 1969a, Tuttle et al. 1969b, Hammack and Hedin 1989, Machemer et al. 1993, Kaksonen and Puhakka 2007). In comparison to most hydroxide minerals, sulfides are characterised by lower solubility constants, higher densities and lower mobilities in oxygen depleted environments (Gammons and Frandsen 2001, Kaksonen and Puhakka 2007). They therefore provide a long-term sink of potentially ecotoxic metals. Due to their higher densities, the removal of metals as sulfides generates less volumetric sludge. Thereby the lifetime of PTS, their sustainability and cost-efficiency is considerably enhanced in comparison to aerobic PTS or active (chemical) treatment.

The purpose of this Chapter is to present i) the solid phase geochemistry of sulfur and iron, ii) evaluate the principal inorganic sinks of iron and sulfur in the RAPS substrates, iii) assess the occurrence of BSR and iv) its importance on the overall removal of iron. Based on the results, the potential remobilisation of iron from the RAPS is discussed.

Methods

Sediment Sampling and Pre-Treatment

Two cores of reactive substrate were sampled from each RAPS one year after commissioning of the treatment system in November 2004 (RAPS1: core 3 close to influent, core 4 close to effluent; RAPS2: core 1 close to influent, core 2 close to effluent). The cores were sealed and transported on ice and frozen (-32°C) until further analysis. The cores were defrosted and extruded in a nitrogen-flushed glove box, partitioned into 3 cm sections and centrifuged (3000 rpm, 10 minutes) to separate aqueous and solid phases. The solid phase was freeze dried until a stable weight was attained, agate mortar ground and stored in a desiccator. The moisture content was calculated from the weight loss during freeze drying.

Total Element Concentrations

Total element concentrations of the freeze dried sediment were determined by multi-acid digestion (US EPA 3050B 1996). Total carbon (TC), total sulfur (TS) and total organic carbon

(TOC) were analysed (BS 7755-3.8 1995) using a Carbon-Sulfur Leco analyser (type CS-244). Duplicates varied within ±7%.

Sulfur Speciation

A sequential extraction procedure for six operationally defined inorganic sulfur species in the sediment was developed based on Duan et al*.* (1997) and Mayer et al*.* (2004): (WS=water soluble and easily mobilised sulfate, ES=elemental sulfur, AVS=acid volatile sulfur (mobilizes mackinawite and partially greigite), ASS=acid soluble sulfate (mobilizes oxyhydroxysulfates, gypsum, sulfate bound in surface complexes and acid soluble molecular weight organic sulfur compounds), CRS=chromium reducible sulfur (pyrite, marcasite, phyrrothite), AS=adsorbed sulfate). The acid volatile sulfur pool was extracted following the procedure of Cornwell and Morse (1987).

For each sample, at most five replicates were analysed (stdev_{ES}=0.22 g kg^{-1}, $\text{stdev}_{\text{AVS}}$=0.13 g kg^{-1}, $\text{stdev}_{\text{CRS}}$=0.42 g kg^{-1}). Between each extraction step the samples were washed with deionised water (except for the ES step: dichloromethane) and the aliquots of the respective extraction step pooled. Sulfur concentrations from ES, AVS and CRS were determined gravimetrically from recovered silver sulfide. No attempt was made to identify the organically bound sulfur fraction as it is unclear whether it originates from the compost or from the mine water. Residual sulfur concentrations (ResS) were calculated by difference between total sulfur and the sum of sequentially extracted sulfur.

Iron Speciation

Seven iron phases were sequentially extracted (WSS-Fe=water soluble bound, EXC-Fe=adsorbed and exchangeable, CARB-Fe=carbonate (partially siderite, ankerite, Fe solid solution carbonates, AVS-Fe), HYD-Fe=hydroxide (ferrihydrite, lepidocrocite, oxyhydroxysulfates, partially akaganeite), OX-Fe=oxide (goethite, hematite, akaganeite, partially magnetite and nontronite, AVS-Fe), AVS-Fe=acid volatile sulfide bound, CRS-Fe=chromium reducible sulfur) (Poulton and Canfield 2005). Magnetite bound iron (MAG-Fe) was analysed only in selected samples. Exchangeable iron was determined as the difference between the magnesium chloride and deionised water extracted iron. AVS and CRS bound iron were calculated from the recovered hydrogen sulfide (as Ag_2S) in the sulfur sequential extraction assuming S:Fe ratios of 1 and 2, respectively. Each sample was run in duplicate (precision: ±15%). Residual iron (ResFe) was determined by total acid digestion of sequentially extracted sediment. Difference of TFe and the sum of sequentially extracted iron and ResFe were within 3±18% difference.

Water and Aqueous Leachate Analysis

Aliquots of sequential extractions and total acid digestions were analysed by Inductively-Coupled Plasma-Optical Emission Spectrometry (Vista MPX, CCP Simultaneous ICP-OES, Varian). The apparatus was calibrated with matrix matched standards and blanks. Water reference materials were run alongside (Thames river water: LGC6019, landfill leachate: LGC6175 and riverine water SLRS-3: National Research Council, Canada). Anions were determined by Ion Chromatography (IC, type IC25 Dionex equipped with an AG16 guard column and an AS17 analytical column).

Mineralogy

Selected samples were analysed by Field Emission Gun - Scanning Electron Microscopy (FEG-SEM, LEO 1530) and Field Emission Gun - Transmission Electron Microscopy (FEG-TEM, Philips CM200). Elemental analyses on mineral species were undertaken by Energy Dispersive X-Ray Spectroscopy (EDS, Oxford Instruments INCA 350 and UTW ISIS, all LEMAS at Leeds University).

Statistical analyses were undertaken with SPSS 17.0. Statistical significance was assumed at $p<0.05$.

Results

Concentrations of total and sequentially extracted sediment sulfur and iron species are presented in Appendix 4, Figure 23 and Figure 24.

The sediment water content averaged 52±19%. Total carbon concentrations ranged between 8.9% to 27.9% (dry weight). Total organic carbon accounted for 79±13% of TC (74.7-258.3 g kg^{-1}), which is similar to other compost types (Guo et al. 2001, Hsu and Lo 2001, Ji and Kim 2008).

Sulfur

It has been suggested in Chapter 1 and 2 that sulfate is substantially removed by the treatment system (average of load efficiency~29%, average of load removal rate=30.9±42.7 kg SO_4^{2-} d^{-1}, range: -20.1-317 kg d^{-1}). Though concentrations of hydrogen sulfide in the RAPS effluents were low (<1.14 mg L^{-1}) at all times, they are a clear indicator of the occurrence of BSR, which was confirmed by the sediment extractions. An average of 37% (range: 15-59%) of total sediment sulfur occurred as Reduced Inorganic Sulfur (RIS=ES+AVS+CRS), a direct or indirect (reoxidation) reaction product of BSR. The dominant inorganic sulfur sinks were chromium reducible sulfur, possibly indicative of the occurrence of pyrite ($\bar{x}$=20.5%, range: 1-44%), and elemental sulfur ($\bar{x}$=14.7%, range: 3-28%), which is generated by partial oxidation of AVS and H_2S (Figure 23).

Acid volatile sulfur was only found in trace amounts ($\bar{x}$ =1.7%, range: 0-9%). In addition, sulfur was also removed in oxidized form: ASS: $\bar{x}$=10.3% (range: 4-32%) and WSS: $\bar{x}$=8.9% (range: 2-22%). The residual fraction (=TS-Σ sequentially extracted S) -possibly organic sulfur- contributed the biggest sulfur pool (44±13.5%). It has been shown that the uptake of sulfur as hydrogen sulfide in organic matter can occur in parallel to pyrite formation (Brüchert and Pratt 1996). However, because the original compost organic substrate is expected to contain organic sulfur (Machemer et al. 1993, Stewart et al. 1998, Herbert et al. 2000, Guo et al. 2001), the organic sulfur pool could either derive from the compost or through reactions of mine water sulfur with the organic matter. Organic sulfur concentrations, however, were two to three times higher than observed for similar composts used for mine water remediation elsewhere (~1.5 g kg^{-1}) (Machemer et al. 1993).

Despite the higher sulfate loads discharged into RAPS 2 (about nine times higher), no significantly increased sulfur concentrations were found in the sediment compared to RAPS 1. Only in the surface sediment layers were total sulfur concentrations higher, by 2-6 times, in cores 1 and 2 (RAPS 2) compared to cores 3 and 4 (RAPS 1). At depth, sulfur concentrations only differed marginally between the RAPS.

Water soluble and acid soluble sulfate were accumulated in upper sediment horizons and are possibly composed of occluded and adsorbed sulfate as well as sulfate bound to oxyhydroxysulfates like schwertmannite. Geochemical modeling suggested that schwertmannite was supersaturated in the mine waters and could therefore be a sink for sulfur. The presence of schwertmannite was confirmed by FEG-SEM and FEG-TEM (Figure 23).

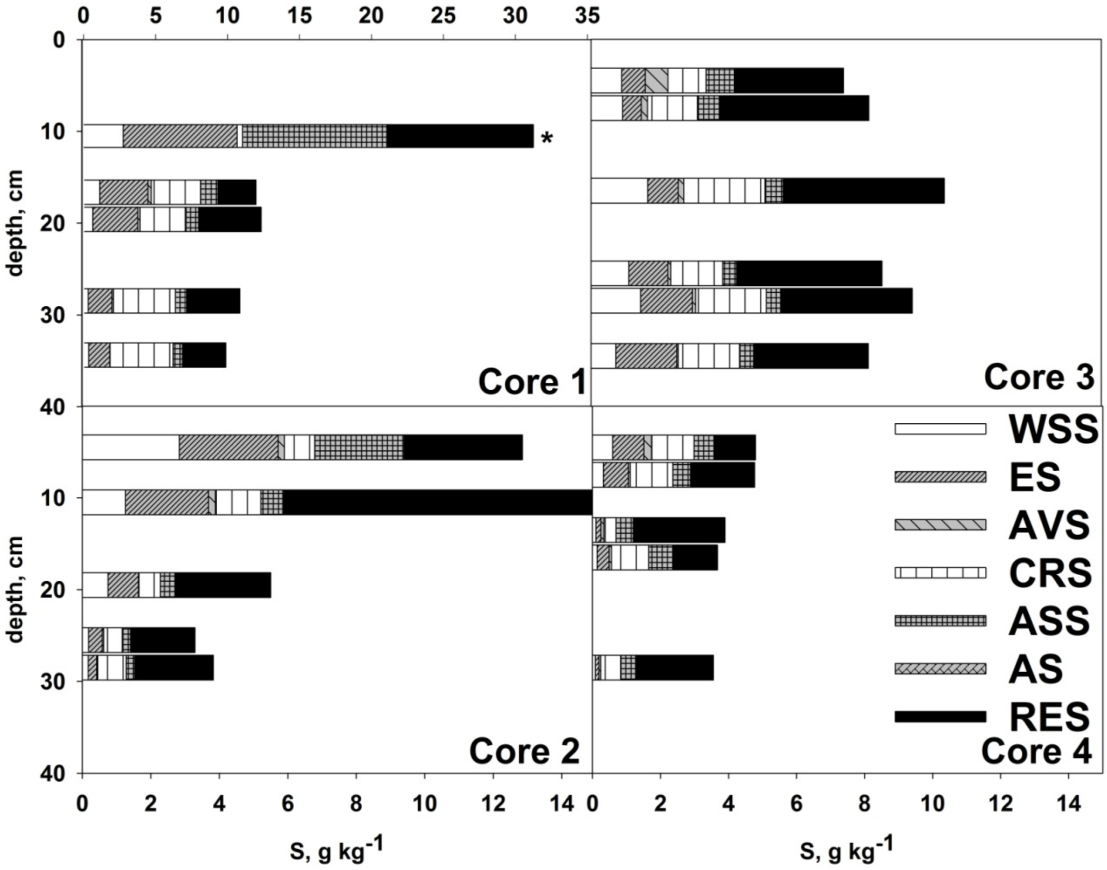

Figure 23 Sulfur concentrations in RAPS sediments (WS=water soluble, ES=elemental sulfur, AVS=acid volatile sulfur, CRS=chromium reducible sulfur, ASS=acid soluble sulfur, AS=adsorbed sulfur, RES=residual fraction (TS–Σ sequentially extracted sulfur), cores 1 and 2: RAPS 2, close to influent and effluent, respectively; cores 3 and 4: RAPS 1, close to influent and effluent, respectively; the upper x-axis is applicable to only the sample marked with "*" whilst the bottom x-axis describe all remaining samples in core 1

Schwertmannite is meta-stable and ages to more stable hydroxide and oxide phases (e.g. goethite, lepidocrocite) under both oxidizing and reducing conditions (Regenspurg et al. 2004, Jönsson et al. 2005, Burton et al. 2007). The occurrence of oxyhydroxysulfates in anaerobic subsurface horizons could be a result of physical displacement of particulates caused by the gravitational flow.

This is supported by the observation that during high flow events element concentrations in effluents occasionally exceeded those measured in influents (Chapter 1); an indication of exchange of pore waters, or flushing of mineral precipitates, or both.

The ratio of oxidized inorganic sulfur species and elemental sulfur (ASS+AS+WSS+ES) versus reduced sulfur species (CRS+AVS) decreased with depth in cores 1 and 4, and especially in core 2. In core 3 the inverse trend was observed. An inverse trend was also observed for the distribution of ES and CRS with highest elemental sulfur concentrations in upper horizons whilst CRS increased with depth. This indicates that any hydrogen sulfide that has been diffused or generated close to the water-sediment interface is at least partially reoxidised (ES) whilst sulfide in subsurface horizons is more likely to react with Fe^{2+} (or Fe-hydroxides) to precipitate as pyrite.

Acid volatile sulfur concentrations were up to two orders of magnitude lower than those of a two year old permeable reactive barrier treating mine water (Herbert et al. 2000). However, in this and other bioreactors (Neculita et al. 2008), AVS contributed less than 0.63% and 0.01% of total sulfur, respectively. It is unclear, whether the low concentration of meta-stable AVS in Bowden Close was caused by transformation to pyrite. AVS could also have been reoxidised to sulfate via intermediate sulfur oxidation products such as elemental sulfur. Though freezing is considered to be the best preservation method (de Lange et al. 2008), it cannot be ruled out that reoxidation occurred after sediment sampling (Prietzel et al. 2009). Burton et al. (2009) reported a quantitative oxidation of AVS to elemental sulfur at pH=7.3 within 3 hours (p_{O2}=0.2 atm) and an AVS half life of less than one hour (Burton et al. 2006b).

Iron

About 84% ($\bar{x}$=5.41±2.4 kg Fe d^{-1}, range: 0.9-26.7 kg d^{-1}) of all mine water iron that was discharged into the treatment system was removed (Chapter 1). Average molar S:Fe removal ratios ranged between -1.8-11.3 ($\bar{x}$=3.6±2.4, Figure 7), which suggests that pyrite (S:Fe=2) and monosulfide (S:Fe=1) might not be dominating iron and sulfate removal. Negative values were caused by remobilization and flushing of sulfate from the reactive substrate and pore waters and has been confirmed by the sediment analysis. Despite the expected elevated concentration of iron bound in the sulfide fraction (Younger et al. 2002), mackinawite and pyrite concentrations were low, and contributed only around 5% of the total iron (range: 0-9%).

The occurrence of trace amounts of framboidal pyrite and even fewer octahedral pyrite grains was confirmed by SEM-EDS (Figure 25). Grain sizes of framboids had a diameter of approximately 5 µm, similar to those observed in natural sediments (Wilkin et al. 1996). Thus, over the long-term, BSR seems not to be a driving process for the removal of iron as sedimentary sulfide in the RAPS. Despite the low percentage amount of iron bound in sulfides, pyrite removal in Bowden Close (15.2-102 µmol d^{-1} kg^{-1}) was similar to that observed for a permeable reactive barrier (Herbert et al. 2000), and was up to two orders of magnitude higher than in natural acid sulfate soils (Burton et al. 2007).

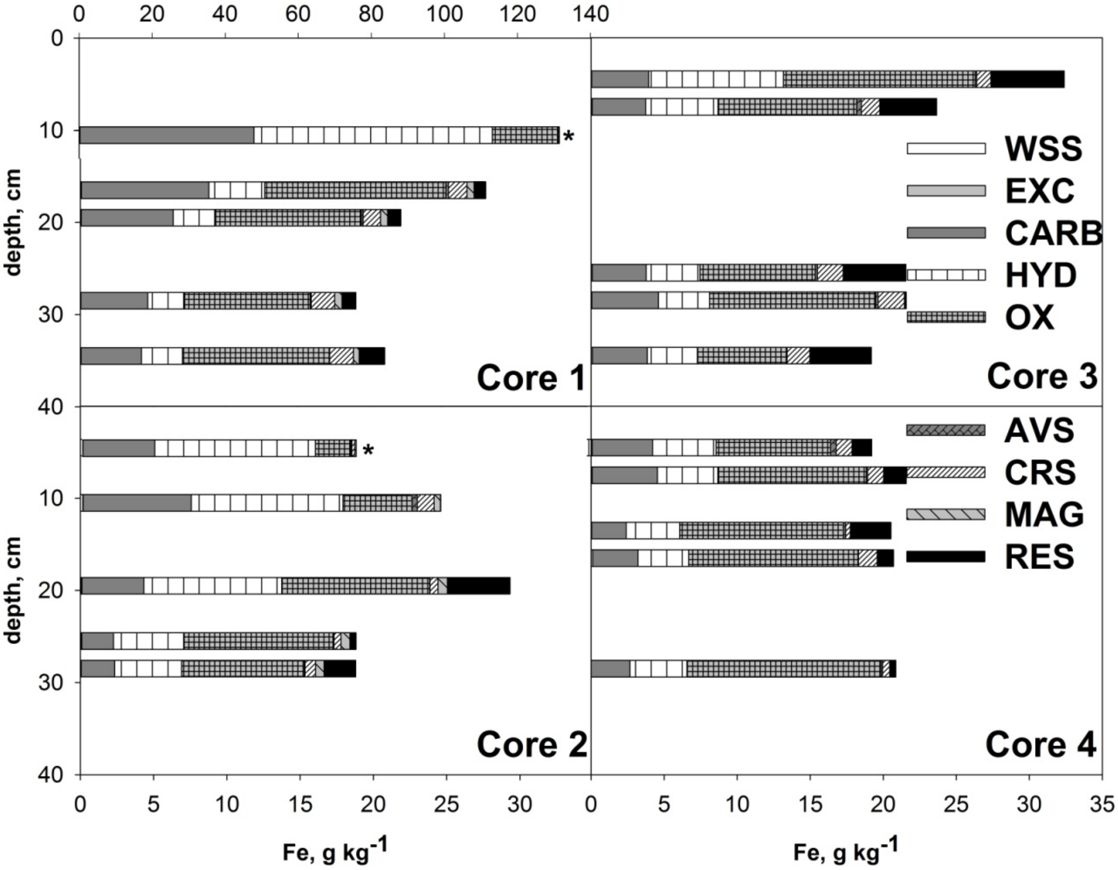

Figure 24 Iron concentrations in RAPS sediments (WS=water soluble, EXC=ion-exchangeable, CARB=carbonate bound, HYD=hydroxide bound, OX=oxide bound, AVS=acid volatile sulfur bound, CRS=chromium reducible sulfur, MAG=magnetite iron (only determined in core 1 and 2), RES=residual iron; cores 1 and 2: RAPS 2, close to influent and effluent, respectively; cores 3 and 4: RAPS 1, close to influent and effluent, respectively, the upper x-axis is applicable to only the samples marked with "*" whilst the bottom x-axis describe all remaining samples in cores 1 and 2

Nevertheless, 30% to 85% of total iron was bound in highly reactive iron phases. The most important iron phase was oxide, with a mean of 41% (OX-Fe, range: 14-64%), potentially comprising hematite and goethite and some magnetite (Poulton and Canfield 2005). Whilst akaganeite is potentially mobilised by the dithionite extraction (OX-Fe, Poulton and Canfield 2005), it is unlikely to occur in sulfate rich environments (Xiong et al. 2008). HYD-Fe ($\bar{x}$=24%, range: 13-62%) and CARB-Fe ($\bar{x}$=20%, range: 11-37%) were the second and third most abundant inorganic iron sinks, respectively. The labile hydroxide fraction (HYD-Fe) was dominated by ferrihydrite (Fabian et al. 2006b) and other Fe and Al hydroxides (Chapter 2).

The extraction with sodium acetate (CARB-Fe) can also remobilise AVS-Fe (Poulton and Canfield 2005). However, due to the low amounts of AVS-Fe, CARB-Fe is expected to be principally composed of carbonate phases such as siderite and ankerite (Poulton and Canfield 2005) and solid solutions of Fe-Ca-Mn carbonates. Siderite (CARB-Fe) was found to be a dominant reaction product from reductive dissolution of schwertmannite in water-logged acid sulfate soils (Burton et al. 2007). Nevertheless, since the extraction was performed at a pH of 4.5, I assume that a substantial amount of the Carb-Fe fraction is in fact iron bound in easily mobilisable hydroxide phases. This requires confirmation by further investigation.

Magnetite bound iron, possibly a reaction product of bacterial iron reduction (Lovley and Phillips 1988, Fortin and Langley 2005), accounted for 1.9±0.9% of the total iron. Residual iron contributed 5±14% and is expected to be principally organic bound.

Similar to observations for sulfur, most iron was captured in RAPS surface horizons. Sections beneath were comparatively iron depleted (<30 g kg^{-1} dry wt.). Differences of the vertical distribution of iron species might be caused by transformation, remobilisation and iron cycling processes. Whilst HYD-Fe was more abundant in the upper sediment layers in comparison to OX-Fe (HYD-Fe:OX-Fe=2–4.5), this ratio decreased to below one in all cores with depth (HYD-Fe:OX-Fe$_{\text{minimum}}$=0.3 (core 1)).

Decreasing HYD-Fe : OX-Fe ratios suggest that transformation processes occur within the sediment, from labile hydroxides (e.g. schwertmannite, ferrihydrite, Figure 25) into more stable hydroxides (lepidocrocite, goethite) and oxides.

Discussion

The data here presented have shown that, contrary to expectations and observations in other constructed wetlands (Machemer et al. 1993), the removal of iron in the treatment systems is not governed by bacterial sulfate reduction.

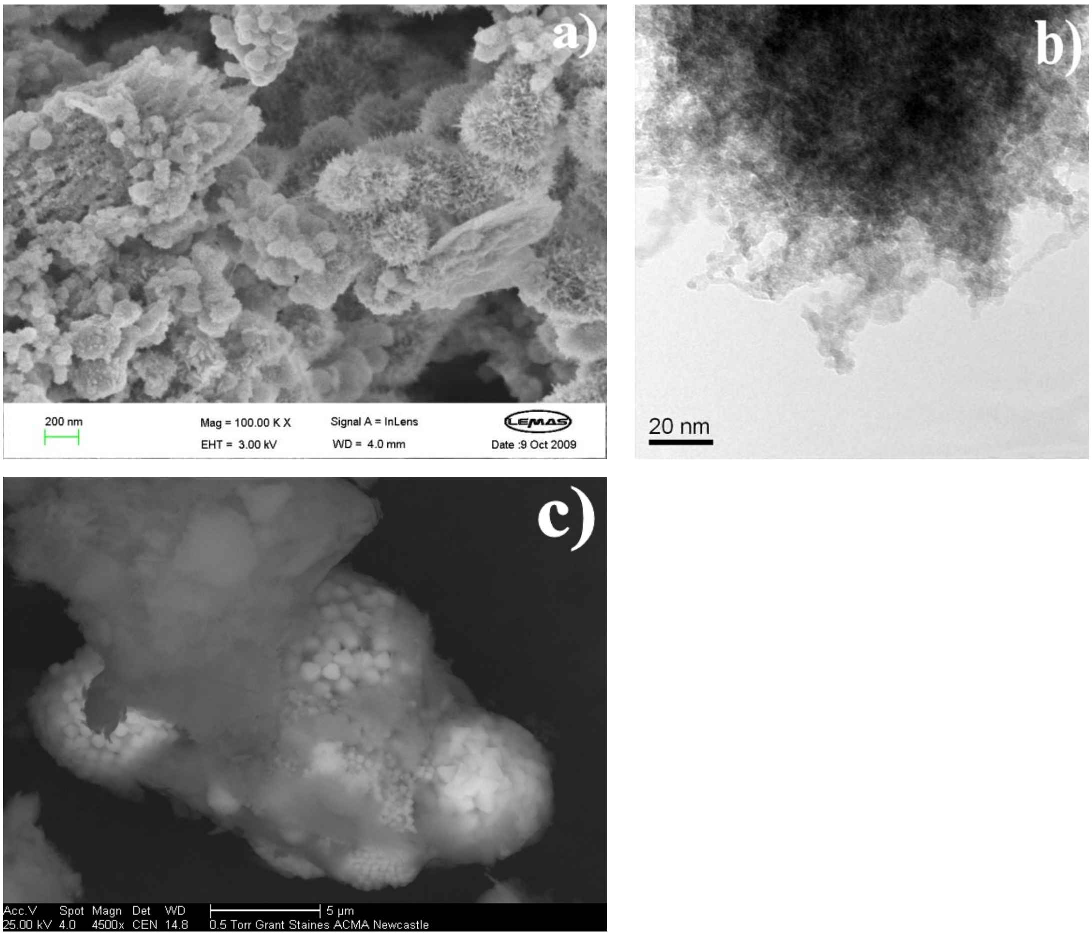

Figure 25 a: Iron and aluminium hydroxides and hydroxysulfates (schwertmannite) in RAPS 2 surface sludge (FEG-SEM), b: schwertmannite (RAPS 2 sediment, 15 cm depth below surface; FEG-TEM), c: clustered pyrite framboids in the surface sludge (1-3 cm below surface) in RAPS 1 (courtesy AM Sarmiento, R Perez-Lopez)

The contribution of pyrite formation to the overall removal of iron is limited to approximately 5%. Rather, the oxidation and hydrolysis of iron, coupled with hydroxide-oxide transformation and carbonate precipitation, is the dominant iron removal pathway.

The formation of pyrite in natural environments is limited by the supply of sulfate, reactive iron, metabolizable organic carbon, or a combination of these (Berner et al. 1985). However, I believe that in the RAPS none of these factors is responsible for the overall low generation of pyrite for the following reasons.

With the exception of the water-sediment interface, total organic carbon concentrations (TOC≥75 g kg^{-1}) were higher than in sediment of marine (4-55 g kg^{-1}, (Böttcher et al. 2000)), euxinic (12-91 g kg^{-1}, (Yücel et al. 2010)) and freshwater origin (0.9-63.1 g kg^{-1}, (Brüchert and

Pratt 1996)) where BSR has been observed. Spearman's correlation coefficient comparing TOC versus AVS-Fe+CRS-Fe indicated no significant link ($p>0.05$), suggesting sulfide formation was not limited by the availability of organic matter. Nonetheless, no information is available on the capacity of TOC to be metabolized. Often a pre-fermentative step is limiting the availability of short chain organic molecules that can be assimilated by sulfate reducing bacteria (Chang et al. 2000, Tsukamoto et al. 2004).

Sulfate was abundant in all waters (effluent 1=242±113 mg L^{-1}, effluent 2=691±284 mg L^{-1}). Harrison (1958) suggested, some SRB might be stressed at sulfate concentrations at or below 57 mg L^{-1}. Whilst interstitial waters of cores 1, 2 (RAPS 2) and 3 (RAPS 1) ranged above this value (142±106 mg L^{-1}), sulfate concentrations in the core close to the effluent of RAPS 1 (core 4) were low (12±20 mg L^{-1}), and close to detection limit at depths below 6 cm, suggesting some sulfate limitation in this part of the treatment system might have occurred.

There was no indication that the easily available iron (bound in (oxy)hydroxides) limits the generation of pyrite. Even though transformation processes to more stable oxides potentially decrease the availability of iron, molar reactive iron to total iron concentrations averaged 0.7 (range: 0.1 = 0.9), and were fairly constant for each core (core 1=0.66±0.03; core 2=0.65±0.21; core 3=0.68±0.08; core 4=0.77±0.06). Hydroxylamine extractable iron (HYD-Fe), assumed to most closely represent the microbial available iron fraction (Lovley and Phillips 1987b) was abundant throughout the cores and always ranged above 13% of TFe.

Degrees of Pyritisation (DOP = CRS-Fe*(CRS-Fe+6N HCl extractable-Fe)$^{-1}$) are indicators for the degree of iron oxide → pyrite conversion. DOP are often reported for natural ancient sediments and, with some caution, for modern sediments (e.g. Berner 1970, Canfield et al. 1992, Raiswell and Canfield 1998, Billon et al. 2001). In the RAPS sediments, DOP were consistently low (0.05.9±0.04), with maxima of 0.12 in subsurface horizons of cores 1 and 3, which is low in comparison to modern natural sediments (0.2-0.4) (Canfield et al. 1992). This confirms that reactive iron is not limiting the formation of pyrite. There was also no significant correlation between CRS-S and HYD-Fe ($p>0.05$) or between CRS-S and (HYD-Fe+OX-Fe) supporting the statement that iron is not limited.

With the data available I cannot completely assess which process is likely to be responsible for the low pyrite concentrations encountered. However, it seems likely that H_2S limitation through reoxidation is the main limiting factor. Hydrogen sulfide can follow four major pathways in the reactive sediment, including exsolution (A) (Cooper et al. 1989). This process should be of minor importance because less than 10% of reduced sulfide should occur as H_2S at circum-neutral to moderate alkaline conditions (Stumm and Morgan 1995) under which HS^- and S^{2-} are the dominant reduced sulfur species. From a similar treatment system less than 1% of the total reduced sulfur was lost via exsolution (Machemer et al. 1993).

(B) Sulfide can be incorporated into organic matter (Canfield et al. 1998, Prietzel et al. 2009) competing with Fe(III)hydroxides (Luther 2005 and citations therein). The latter was not tested as it is unclear whether the organic sulfur derives from the mine water or the original compost material. However, the variability of residual sulfur (1.1-11.0 g kg^{-1}), which is considerably higher than in similar compost or manure (Zagury et al. 2006), suggest that sulfur uptake into the organic matter has occurred to some degree.

(C) The potential complexation of sulfide with organic molecules or metals (Luther 2005) is evidenced by effluent sulfide concentrations largely exceeding the stability products of sulfide minerals in effluents. For the mass balance of sulfur, complexation potentially increases the sulfide mobility but seems here overall not to be significant.

(D) Sulfide can be reoxidised abiotically in the water-sediment interface by oxygen deriving from mine water, dissolved atmospheric oxygen or supplied via radial oxygen loss (Jacob and Otte 2004). Also the reoxidation via ferric iron bound in hydroxides is possible and can also be biotically catalyzed ($2Fe(OH)_3 + HS^- + 5H^+ \rightarrow 2Fe^{2+} + S^0 + 6H_2O$), (Lovley and Phillips 1987a, Lovley and Phillips 1988, Burton et al. 2007). The reoxidation of 80 to 100% of reduced sulfur was observed in natural sediments (Jørgensen 1977, Cornwell and Sampou 1995) and was principally controlled by bioturbation, oxygen diffusion and reaction with iron(III)oxides.

Elevated elemental sulfur concentrations and the SRB-sub-optimal redox potentials (Lyew and Sheppard 1997) in effluents and interstitial waters (effluent 1=70±100 mV, effluent 2=-15±80 mV, interstitial waters=70±70 mV) suggest that indeed reoxidation of hydrogen sulfide is the limiting factor for pyrite formation. The reoxidation could potentially be promoted by physical perturbation, mixing of oxygenated mine water with suboxic sediments and the abundance of reactive Fe(III)minerals. In addition, sulfide oxidizing microorganisms destabilize reduced sulfur and have been observed in similar types of PTS (Johnson and Hallberg 2005), but were not investigated as part of this study. Other energetically more favourable metabolic processes might also outcompete BSR as was shown in some natural wetlands (e.g. Roden and Wetzel 1996) in which the microbial reduction of Fe(III)oxides suppressed the bacterial sulfate reduction.

In summary, because of the low amounts of mineral sulfides (DOP<0.12), elevated concentrations of elemental sulfur and Fe(III)hydroxides, and the occurrence of ferric iron in the interstitial waters, I propose that kinetically rapid reoxidation of H_2S by the presence of electron acceptors limits its availability to react with ferrous iron and consequently hampers the formation of Fe_xS_y.

Summary

- Four sediment cores of RAPS 1 and 2 were analysed to determine inorganic sulfur and iron phases;
- The dominant sulfur phases were: di-sulfides > elemental sulfur > acid soluble sulfate > water soluble sulfate >> acid volatile sulfur;
- The dominant iron phases were bound in: oxides > hydroxides > carbonates >> di-sulfides > acid volatile sulfur ~ water soluble iron ~ ion-exchangeable iron;
- Evidence for bacterial sulfate reduction (BSR) was found in all cores expressed by direct (mono- and di-sulfide minerals) and indirect oxidation (elemental sulfur) products of BSR;
- For the removal of iron, BSR did not play a driving role; iron bound to reduced inorganic sulfur contributed only ~5% of the total iron fraction (range: 0-9% of total iron);
- Overall, removal processes of iron in the anaerobic RAPS seem to compare to those generally attributed to aerobic treatment systems.

4. S, O AND H ISOTOPE RATIOS IN RAPS WATERS AND SEDIMENTS

Sulfate sulfur and sulfate oxygen isotopes have been used widely over the last seven decades to investigate the sulfur cycle in natural sediments (e.g. Harrison and Thode 1958, Nakai and Jensen 1964, Farquhar et al. 2008, Fike and Grotzinger 2008). However, only during the last 20 years have these isotopes found application in tracing sources of pollution, mixing processes and (bio)geochemical processes in relation to mine waters emerging from underground and open pit mines, pit lakes, waste rock dumps and tailings impoundments (Taylor et al. 1984b, Taylor and Wheeler 1994, Wright and Nordstrom 1999, Haubrich and Tichomirowa 2002, Knöller et al. 2004, Dold and Spangenberg 2005, Edraki et al. 2005, Pellicori et al. 2005, Alvaro Gallo and Velasco Roldan 2008, Migaszewski et al. 2008, Hubbard et al. 2009, Tichomirowa and Junghans 2009, Gammons et al. 2010). Still, surprisingly little is known about the sulfur isotope cycles in passive mine water treatment systems (PTS) (Hsu and Maynard 1999, Rees and Bowell 1999, King 2004, Bhattacharya et al. 2008) and the dual isotope approach has apparently not been applied on PTS prior to this study.

In Chapter 3 it has been shown that, contrary to expectations, BSR has only a marginal impact on the removal of iron (~5% of total iron bound in di-sulfide minerals). The bulk of iron is retained as (hydr)oxide, with potentially adverse effects on the longevity of PTS and the long-term stability of scavenged metals.

The significant fractionation induced by BSR makes stable sulfur isotopes a useful tracer for this process. In combination with sulfate oxygen isotope analysis, recycling and re-oxidation processes within the reactive substrate can potentially help to explain the low pyrite generation rates in the substrate and assist in redesigning PTS to enhance removal processes of chalcophilic elements as sulfide minerals and ultimately enhance both PTS longevities and permanent metal retention.

With the help of stable isotopes (S, O, H) the objectives of this study were to identify i) the origin of the mine waters and their principal sulfate source, ii) the principal oxidation pathway of the coal derived mineral sulfides that trigger AMD generation, iii) the occurrence of bacterial sulfate reduction in the RAPS and iv) to explain why only little sulfur is retained as mineral sulfide.

Methods

Between April 2008 and October 2009 monthly surface water monitoring was undertaken to characterize influents (mine waters), effluents (water that has drained through the reactive substrate) and overflows (water that has short-circuited over the reactive substrate) of the two RAPS.

Water Chemistry

During each event, total and filtered (<0.45 µm pore size filter, nitrate cellulose) element concentrations (Ca, Na, Mg, K, Fe, Al, Mn, Zn, Si, S) were sampled following APHA guidelines (Clesceri et al. 1992) and analysed with an Inductively Coupled Plasma-Optical Emission Spectrometer (Vista MPX, Varian). Filtered unpreserved samples (<0.45 µm pore size filter, nitrate cellulose) for the determination of chloride and sulfate concentrations were analysed by Ion Chromatography (IC25 Dionex equipped with an AG16 guard column and an AS17 analytical column). Field measurements included pH, electrical conductivity (EC), redox potentials (Eh), temperature (T, Myron Ultrameter II), dissolved oxygen (DO, YSI 550A dissolved oxygen meter), alkalinity (HACH AL-DT test kit) and flow (Q, bucket and stop watch method). Reduced sulfur and iron were determined after methods of Cline (1969) and Viollier et al. (2000), respectively.

Sulfur Isotopes

Dissolved sulfate was recovered as barium sulfate (n=18) whilst sulfide was precipitated as zinc sulfide (n=14) and later transformed to silver sulfide in a Johnson-Nishita apparatus (Carmody et al. 1998). Sulfur isotopes from sulfate and sulfide were processed after Coleman and Moore (1978) and Robinson and Kusakabe (1975), respectively. The $\delta^{34}S$ were determined with a VG Isogas SIRA II dual inlet mass spectrometer which was calibrated daily against a reference gas and standardized against one internal chalcopyrite CP1 standard ($\delta^{34}S$=-4.6‰) and three external standards: NBS 123 ($\delta^{34}S$=17.1‰), IAEA S 3 ($\delta^{34}S$=-31.5‰) and NBS 127 ($\delta^{34}S$=20.3‰). Based on repeated external and internal standard measurements, the precision for sulfur was ±0.4‰.

Oxygen Isotopes in Sulfate

Sulfate oxygen isotope ratios from barium sulfate samples were determined by graphite reduction method (Halas et al. 2007) and analysed by a VG ISOGAS SIRA II dual inlet mass spectrometer. Reproducibility, based on repeated analyses of the international standard NBS 127 (8.7‰) was ±0.4‰.

Deuterium and Oxygen Isotopes in Water

Water samples (July to October 2009) were filtered (<0.2 µm, Track Etched Filter), stored upside down, in darkness and at 4°C until analysis.

Water hydrogen isotope ratios were determined by chromium reduction (Horita and Kendall 2004, de Groot 2009a) and determined with a calibrated VG Micromass 602D isotope ratio mass spectrometer (internal standards: light water, LT=-93.7‰; seawater, SW=-6.0‰; primary reference material: Greeland Ice Sheet Precipitation (GISP)=-189.7±0.9‰ (Horita and Kendall 2004)). Standard checks were undertaken every ten samples. Due to potential memory effects on the H-line, standards and samples were run in triplicate giving a precision better than, or equal to ±5‰.

Water oxygen isotopes were analysed by equilibration with carbon dioxide (Epstein and Mayeda 1953, Horita and Kendall 2004, de Groot 2009b) and δ^{18}O determined in triplicate with a calibrated Delta V Plus mass spectrometer (internal standards: EKS, East Kilbride Snow=-12.9±0.1‰; DW2, deionised water=-7.4±0.2‰ and DSW, distilled seawater=-0.3±0.1‰). The internal standards were regularly calibrated against international standards (SMOW=-0.1±0.2‰, GISP = -24.9±0.3‰ and SLAP=-55.5±0.2‰) (precision ±0.1‰). Duplicates varied within ±1%.

Hydrogen and oxygen isotopic ratios of meteoric precipitation of two sampling sites in the UK were obtained from the International Atomic Energy Agency (//nds121.iaea.org). Wallingford (51°36’0’’, -1°6’0’’, 48 m a.s.l.) is located 350 km south and Keyworth (52°52’60’’, -1°4’60’’, 60 m a.s.l.) 210 km southeast of the mine water treatment site. Data are available for 1979 to 2005 (n=324, Wallingford) and 1986 to 1996 (n=144, Keyworth).

Sediment

Four sediment cores of the one year old treatment systems (2004) were extracted for their dominant inorganic iron and sulfur phases (Chapter 3). Reduced inorganic sulfur phases (RIS: elemental sulfur (ES), acid volatile sulfur (AVS), chromium reducible sulfur (CRS)) along with acid soluble sulfate (ASS) were recovered from RAPS 1 and transformed to silver sulfide (ES, CRS, AVS) or barium sulfate (ASS) and isotopic ratios analysed. Results of $\delta^{34}S$ are presented here accepting that the time gap between sediment and water analyses only allow for limited comparability.

Isotope ratios are presented in standard delta notation in per mill compared against primary reference materials: Vienna-Standard Mean Ocean Water (δD, $\delta^{18}O$) and Canyon Diablo Troilite ($\delta^{34}S$). Isotope separation (Δ) between two substances was calculated by the difference of the delta notations ($\Delta_{A\text{-}B}=\delta_A- \delta_B$, ‰). Statistical analyses were undertaken with SPSS 17.0. Statistical significance was assumed if $p<0.05$.

Results and Discussion

The complete data set of S, H and O isotope ratios (2008-2009) are presented in Appendix 4.

Water Chemistry

Net-acidic mine waters ($pH_{inf1}=6.02\pm0.76$; $pH_{inf2}=5.11\pm0.66$) were increased by ~1.2 to 1.8 pH units through passive treatment, respectively, in RAPS 1 and 2. During the occasional overflow, pH in overflow 1 was about 1.2 pH units higher than in influent 1, whilst pH in overflow 2 were approximately 0.33 pH units lower compared to influent 2. Over time of monitoring, temperatures ranged between 6.5-12.2°C (influent 1) and 8.0-11.3°C (influent 2, Figure 26). Dissolved oxygen concentrations increased from 7.9±2.4 mg L^{-1} (influent 1) and 7.6±0.82 mg L^{-1} (influent 2) to 9.4±3.3 mg L^{-1} (overflow 1) and 9.1±1.1 mg L^{-1} (overflow 2) and were close to detection limit in both effluents. This was reflected in the redox potentials that were low in effluents compared to the oxidizing conditions measured in influents and overflows ($\Delta Eh_{RAPS\ 1}$=280mV, $\Delta Eh_{RAPS\ 2}$=340mV, $Eh_{effluent\ 1}$=-2±40 mV; $Eh_{effluent2}$=3±30 mV). Flow rates in influent 1 were commonly two to three times lower (30±26 L min^{-1}) compared to influent 2 (69±64 L min^{-1}).

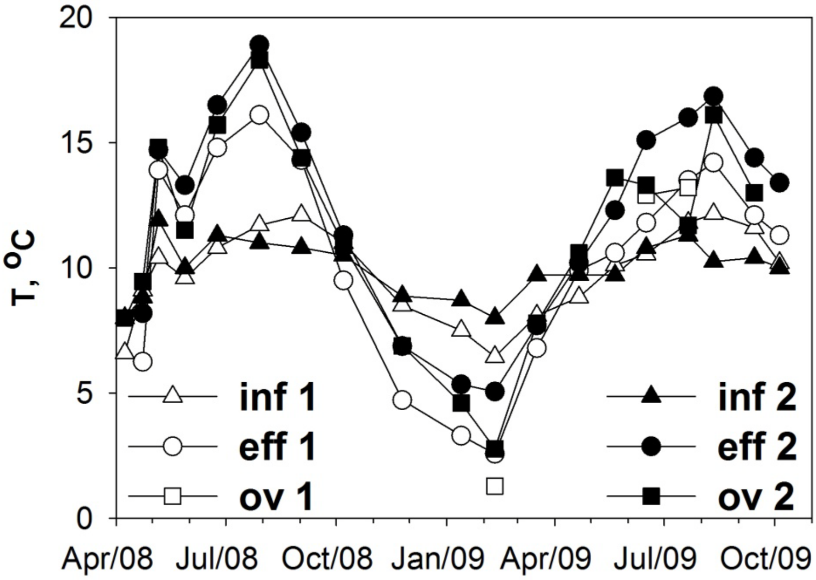

Figure 26 Temperatures in RAPS waters

Sulfate concentrations (influent 1=352±50 mg L^{-1}, influent 2=1212±498 mg L^{-1}) in the mine water decreased substantially in overflows (overflow 1 ΔSO_4=80 mg L^{-1}, overflow 2: ΔSO_4=103 mg L^{-1}) –mainly due to sorption of sulfate and precipitation as oxyhydroxysulfates- and effluents (effluent 1=134 mg L^{-1}, effluent 2=278 mg L^{-1}). On average, nine times higher sulfate loads are discharged into RAPS 2 compared to RAPS 1 (Chapter 1). In addition, reduced sulfur concentrations of up to 0.88 mg L^{-1} and 1.15 mg L^{-1} were recorded in effluent 1 and 2, respectively (Chapter 2). Iron, aluminium, zinc and manganese concentrations in the mine waters reached maxima of 177 mg L^{-1}, 62 mg L^{-1}, 2.2 mg L^{-1} and 13.1 mg L^{-1}, respectively, and were, with exception of manganese, almost quantitatively removed in the waters that have drained through the reactive substrates (Chapter 2).

Water Isotopes

Water isotope data from Bowden Close were compared to the global meteoric water line (Craig 1961) and local meteoric water lines from Wallingford and Keyworth (Figure 27). Typical for young meteoric waters, isotope ratios of all Bowden Close waters were well correlated ($r=0.87$, $p<0.05$). Values ranged between -45‰ and -55‰ (δD) and between -6.9‰ and -8.3‰ ($\delta^{18}O$) and compare well to those reported for the meteoric waters of the British isles (Alley and Cuffey 2001, Aggarwal et al. 2010).

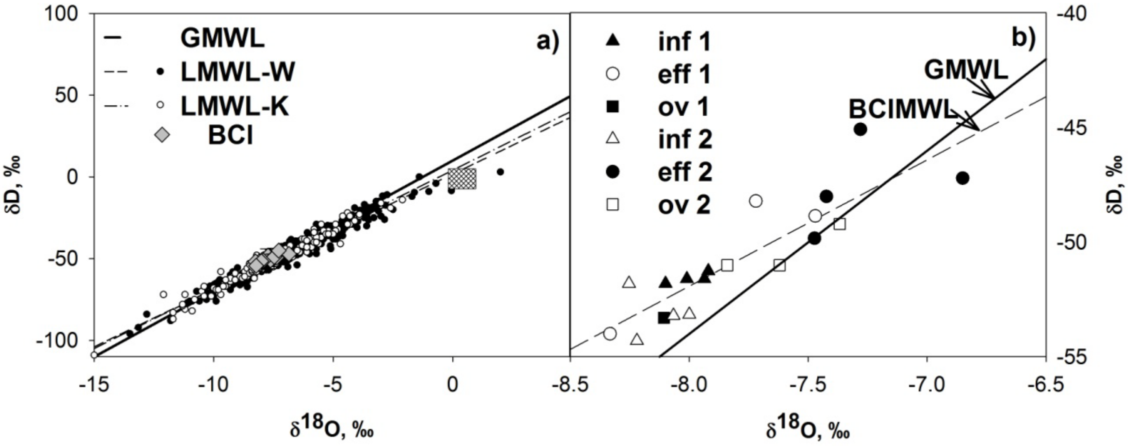

Figure 27 a) Water isotopes in RAPS waters compared to global ($\delta D=8\delta^{18}O + 10$, GMWL, (Craig 1961)) and local meteoric water lines from Wallingford (LMWL-W, $\delta D=7.0\delta^{18}O + 1.7$) and Keyworth (LMWL-K, $\delta D=7.3\delta^{18}O + 4.1$ //nds121.iaea.org); shaded area=modern ocean water; b) water isotope ratios measured in RAPS waters and regression line (i.e. Bowden Close meteoric water line, BClMWL) compared to GMWL

The sample batch was limited to four months, which did not allow for assessing seasonal effects. Despite these limitations, a local meteoric water line was calculated for Bowden Close (BClMWL: $\delta D=5.5\delta^{18}O+7.8$) using least squares regression. The slope is somewhat lower than those of the global meteoric water line (8 to 8.12) (Craig 1961, Rozanski et al. 1993) and the local meteoric water lines from Wallingford and Keyworth (7.0-7.3).

The deuterium excess factor d ($d=\delta D - 8\delta^{18}O$, (Dansgaard 1964)) of the local meteoric water lines were 8.1±4.2‰ (Wallingford) and 9.4±11.0‰ (Keyworth), slightly lower than in the GMWL (10‰). The excess d of BCl (11.6±1.6‰) was slightly higher than in the GMWL, but typical for humid, temperate climates; reflecting a dominance of air masses deriving from the Atlantic Ocean. Characteristic for regions in high latitudes (Alley and Cuffey 2001), excess d were negatively correlated to temperatures ($r_W=-0.3$, $r_K=-0.4$, $r_{BCl}=-0.5$, $p<0.05$). The highest d excess was observed at lowest temperatures similar to observations of Lambert and Aharon (2010) which is possibly caused by reduced isotope fractionation in rain drops during evaporation (Gat 1996).

Comparison of Bowden Close data to LMWL, GMWL and modern seawater (-7-5‰ (δD) and -1.0-0.5‰ ($\delta^{18}O$)) (Epstein and Mayeda 1953) suggest, that both drainages are of meteoric origin. This was not surprising for the waste rock dump drainage (inf 2), but for the underground mine drainage it demonstrates that the bulk of the mine water derives through infiltration of young meteoric water.

Lowest flow conditions are commonly observed during summer months with mean flow rates of $\bar{x}_{inf1}$=9 L min^{-1}, $\bar{x}_{inf2}$=33 L min^{-1} as opposed to $\bar{x}_{inf1}$=45 L min^{-1}, $\bar{x}_{inf2}$=125 L min^{-1} during the remainder of the year (Chapter 1). I therefore expect that any contribution of non-meteoric water should be highest (in per cent) during the summer months in which samples were taken. As I was unable to detect any other non-meteoric water sources during the summer sampling, I am confident to upscale these data to the whole year.

Small isotope fractionations (~±1.2‰) between influents, effluents and overflows indicate that kinetic fractionations induced for instance by evapo(transpi)ration are low.

Sulfur Isotopes in Waters

Sulfate and sulfide sulfur isotope ratios determined in RAPS waters (2008-2009) are presented in Figure 28 and are summarized in Table 6.

Influents

Despite the significant variability of sulfate concentrations in influent 1 (352±50 mg L^{-1}) and 2 (1212±498 mg L^{-1}), isotope ratios of sulfate sulfur are remarkably constant (Table 6, Figure 28). In both influents, $\delta^{34}S_{SO4}$ ranged between 9.4‰-11.6‰ throughout the 18 months of monitoring and are comparable to bulk sulfur isotopic ratios of other coal deposits (Smith and Batts 1974, Krouse 1980, Hackley and Anderson 1986, Pezdic 1998, Baioumy 2010). Differences in sulfate sulfur isotopic ratios in the order of ±0.4‰ are within the margin of error of the analytical technique used.

Studies in aerobic and anaerobic environments, with and without microbial incubation, report minimal sulfur fractionation during mineral sulfide oxidation ($\Delta^{34}S < 0.8‰$) (Taylor et al. 1984b, Heidel et al. 2009). This is valid as long as sulfate is the only reaction product and no sulfur is lost (e.g. $SO_2\uparrow$) (Nordstrom and Alpers 1999a, Brunner et al. 2008, Tichomirowa and Junghans 2009, Thurston et al. 2010). The stable sulfur isotope ratios of sulfate should therefore closely represent $\delta^{34}S$ encountered in the reactant (Atlas and Bartha 1993, Dold and Spangenberg 2005, Balci et al. 2007a).

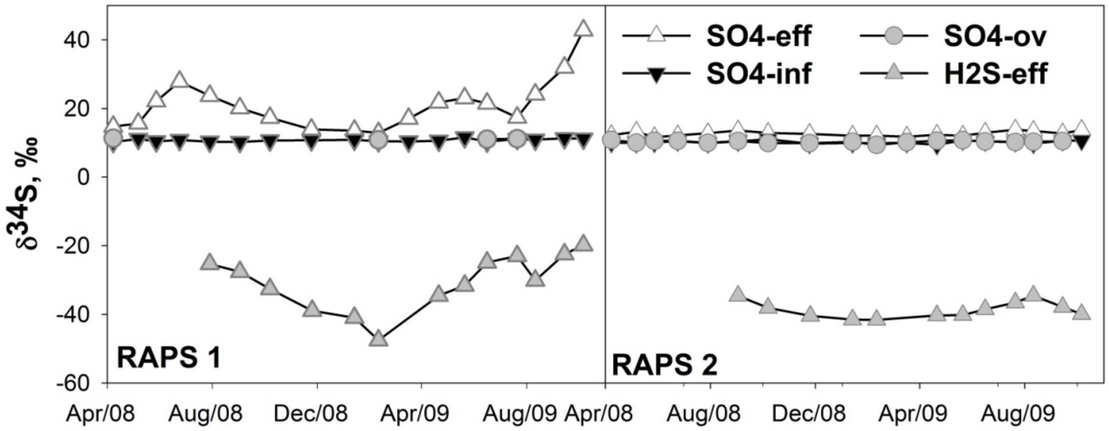

Figure 28 Sulfur isotope ratios of sulfate and hydrogen sulfide in RAPS waters

Table 6 Sulfate sulfur and sulfide sulfur isotope ratios in RAPS waters

	Species	Average	Max, Min	stdev (n)
Influent 1	Sulfate	10.7	11.6, 10.2	0.4 (18)
Overflow 1	Sulfate	11.1	11.3, 10.9	0.2 (4)
Effluent 1	Sulfate	21.2	42.8, 12.9	7.5 (18)
Effluent 1	Sulfide	-30.7	-19.8, -47.6	8.1 (13)
Influent 2	Sulfate	10.2	11.0, 9.4	0.4 (18)
Overflow 2	Sulfate	10.3	10.8, 9.4	0.4 (17)
Effluent 2	Sulfate	12.7	13.8, 11.6	0.7 (18)
Effluent 2	Sulfide	-38.7	-34.6, -41.6	2.4 (12)

Isotope ratios=‰, Max=maximum, Min=minimum, stdev=standard deviation, n=number of samples

My findings suggest that sulfate enrichment in both mine waters derive from the same, single sulfur environment. This is likely to be the oxidation of coal derived mineral sulfides such as pyrite or marcasite. Both minerals are dominant sulfur sinks in high sulfur coals like that from the Durham coalfield (Smith and Batts 1974, Ward 1984, Atlas and Bartha 1993). Traces of sulfur could also be mobilized from pyrrhotite, sphalerite, chalcopyrite and galena, elemental sulfur and sulfate salts (e.g. barite and gypsum) (Smith and Batts 1974). However, since iron concentrations are highly elevated compared to other chalcophilic elements (e.g. Zn) this suggests the likely dominance of iron sulfide as the principal sulfate source.

The differences that were observed in the chemical composition of the two mine waters (Chapter 1) should therefore arise as a result of enhanced weathering occurring in the waste rock dump. Because of the increased reactive surface area of the waste rock dump, reaction rates and hence AMD generation are significantly accelerated compared to underground mine conditions. The variability in seasonal sulfate concentration in both waters seems to be governed purely by dilution through infiltrating meteoric waters (Chapter 1).

Poor correlations between $\delta^{34}S$ and sulfate concentrations (or sulfate loads, $R^2<0.2$) strengthen the theory of a single sulfur source. I expect that contributions from other sulfur sources e.g. of atmospheric origin should be relatively low because of the generally low sulfur concentrations (1.03±1.8 mg L^{-1}) that were measured in precipitation at the Met Office monitoring station in Bannisdale (annual precipitation~650 L m^{-2}, n=635, January 1990-September 2007, 53°56'8.13"N, 1°7'48.81"W, 265 m a.s.l.).

Overflows

Sulfur removal rates in the water covers overlaying the reactive substrate ranged between 0.1-3.7 g d^{-1} m^{-2} (median=0.35 g d^{-1} m^{-2}, n=3). This accounts for approximately one third of the total sulfur removal rates of RAPS 1 (1.13 g d^{-1} m^{-2}). In the water cover of RAPS 2, between -2.56 g d^{-1} m^{-2} and 3.26 g d^{-1} m^{-2} of sulfur were removed (median=0.67 g d^{-1} m^{-2}, n=15) with occasional net-sulfate release, probably due to flood-related flush out, or changes in pH or water chemistry promoting remobilization of sulfate (Chapter 2).

Nonetheless, sulfur isotope ratios of sulfate in overflows were only marginally enriched compared to influent sulfate sulfur ($\Delta^{34}S_{SO4}$ ~1.1‰ (RAPS 1), $\Delta^{34}S_{SO4}$ ~1.2‰ (RAPS 2), Table 6).

During the precipitation of sulfate as (oxyhydroxy)sulfate mineral (e.g. gypsum, alunite, jarosite, anglesite, brochantite, basaluminite) under ambient, oxic conditions, only minor sulfur isotope fractionation is observed (<±1.72‰) (Gavelin et al. 1960, Thode and Monster 1965, Field and Gustafson 1976, Dowuona et al. 1992, Taylor and Wheeler 1994, Seal and Wandless 1997, Prietzel and Mayer 2005, Alvaro Gallo and Velasco Roldan 2008, Alvaro and Velasco 2009). Highest fractionations occur during slow precipitation rates. The least fractionation is observed for schwertmannite (<0.1‰) (Alvaro Gallo and Velasco Roldan 2008, Alvaro and Velasco 2009) and no fractionation is observed during sulfate sorption (van Stempvoort et al. 1990). The dominant form of sulfate removal in the water covers of the RAPS has been shown to be oxyhydroxysulfate (Chapter 3).

Effluents

Compared to mine water $\delta^{34}S$-SO_4, hydrogen sulfide sulfur isotope ratios were significantly different (Table 6, Figure 28). These disequilibria between sulfate and sulfide are a result of slow isotopic exchange between the substances ($H_2{}^{34}S + {}^{32}SO_4 \leftrightarrow H_2{}^{32}S + {}^{34}SO_4$) and commonly observed at ambient temperatures (Sakai 1968, Rye et al. 1981, Seal et al. 2000).

In effluent 1, sulfate was enriched in ^{34}S by on average 10.5‰ and hydrogen sulfide was depleted by 41.4‰ compared to influent sulfate. In effluent 2 the sulfate $\delta^{34}S$ was enriched by about 2.5‰ whilst hydrogen sulfide was depleted on average by 48.9‰. Clear seasonal trends were observed in $\delta^{34}S$ with highest isotope differences during summer months (RAPS 1). Little or no seasonality of $\delta^{34}S_{SO4}$ was observed in RAPS 2.

These isotopic differences ($\Delta^{34}S_{SO4\text{-}H2S}$) observed compare to ranges reported from some natural freshwater and marine sediments (10-60‰) and passive mine water treatment systems (23-33‰) (Goldhaber and Kaplan 1975, Tuttle et al. 1989, Böttcher and Lepland 2000, Wortmann et al. 2001, King 2004).

The only process responsible for effecting sulfur isotope fractionation on the scale observed here is bacterial sulfate reduction (BSR). The reaction model described by Rees (1973) proposes maximum isotope fractionation between the initial sulfate and hydrogen sulfide of 47‰. The Rees model has been revised in recent years by Brunner and Bernasconi (2005) and Donahue et al. (2008) who raised the maximum sulfur isotope fractionation to ~70‰ and ~53‰, respectively. The modified Rees model can therefore theoretically explain the maximum fractionation of $\Delta^{34}S_{SO4\text{-}H2S}$ ~58.0‰ here observed. Canfield (2001b) suggested that this significant ^{34}S depletion in hydrogen sulfide should be indicative of metabolically slow reduction rates and exchange equilibrium conditions between internal and external sulfur pools.

Nonetheless, additional sulfur fractionation by: i) disproportionation of intermediate oxidation products (e.g. elemental sulfur, thiosulfate, sulfite) (Jørgensen 1990, Canfield and Thamdrup 1994, Böttcher and Thamdrup 2001), ii) oxidation of hydrogen sulfide (or intermediates) (e.g. by iron(III)hydroxides) or iii) sulfur assimilation (Atlas and Bartha 1993) might have influenced the sulfur cycle in the wetlands. This is as yet unexplored in the RAPS.

The degree of sulfur isotope fractionation caused by BSR depends on a variety of internal and external factors including temperature, pH, Eh, DO, the strains of sulfate reducing bacteria (SRB) and their metabolic pathways, specific sulfate reduction rates (SRR), availability and type of organic matter and sulfate concentrations (Harrison and Thode 1958, Berner 1970, Boudreau and Westrich 1984, Roden and Wetzel 1996, Habicht and Canfield 1997, Detmers et al. 2001, Praharaj and Fortin 2008). My data cannot discriminate which of these factors likely has influenced the sulfur isotope fractionation in Bowden Close. However, I do note the similarities in physico-chemical parameters in both RAPS and the exactly similar reactive substrate (horse manure, straw compost, limestone gravel), and speculate that neither Eh, DO, SRB or the type of organic matter are likely to explain the isotopic differences observed between the systems.

Seasonal temperature differences (Δ~17°C, Figure 26) could have influenced SRR. Coastal sediments showed distinct SRR with changes of up to three orders of magnitude (Ingvorsen et al. 1981, Spratt et al. 1987, Kostka et al. 1999, Brüchert et al. 2001, Wadham et al. 2004). At increasing sulfate reduction rates, smaller isotope fractionation was observed (Harrison and Thode 1958, Kaplan and Rittenberg 1964, Böttcher et al. 1997). My results from RAPS 1 however showed positive correlations (r=0.5) between T and $\Delta^{34}S_{SO4-H2S}$ and in RAPS 2 no correlations was observable ($p>0.05$). This suggests that factors other than temperature may be responsible for the fractionation.

Despite the large seasonal variations in sulfate concentration (RAPS 2), there is a consistency of $\delta^{34}S_{H2S}$ and of influent and effluent sulfate $\delta^{34}S$ (Figure 28). Given this consistency, and the gravitational downward flow of the mine water through the substrate, it appears that the flux of sulfate largely exceeded its microbial reduction in RAPS 2. This scheme thus behaves as open system (Tuttle et al. 1989, Habicht and Canfield 1997) or as a semi-closed through-flow system (Gat 1996) with largely unlimited sulfate supply. Consequently, sulfate isotope ratios in the effluent are essentially stable and similar to those in the influent. $\delta^{34}S$ of hydrogen sulfide is consistently depleted throughout the time of monitoring without perceivable variations.

As a consequence, Rayleigh fractionation (RF, equation (6),(7)) that assumes closed system conditions and constant sulfate reduction rates (Hartman and Nielsen 1969) does not apply in RAPS 2, as in many natural sediments (Canfield 2001a). This was confirmed by uncorrelated sulfate sulfur fractionation compared to sulfate removal (F, $p>0.05$).

Furthermore, non-BSR related sulfate removal processes such as the removal of sulfate (oxyhydroxysulfates) form a significant process of sulfate retention in the reactive substrate (Chapter 3). If unaccounted for, this leads to an underestimation of fractionation factors ($\alpha_{RAPS2,SO4-SO4}=1.0095$) (Aharon and Fu 2003).

(6)

$$\alpha = ((\delta^{34}S_{SO4}-\delta^{34}S_{SO40})(\ln F)^{-1}1000^{-1})+1$$

α=fractionation factor, $\delta^{34}S_{SO4}$=sulfate sulfur isotope ratio of the effluent, $\delta^{34}S_{SO40}$=sulfate sulfur isotope ration of the influent, F=fraction of sulfate remaining after treatment (Mizutani and Rafter 1973)

(7)

$$\delta^{34}S_{H2S} = \delta^{34}S_{SO40} - \varepsilon\ (F\ln F)(1-F)^{-1}$$

$\delta^{34}S_{H2S}$=sulfide sulfur isotope ratio of the effluent, enrichment factor ε~1000(α-1)

Based on sulfur removal and observed sulfate sulfur isotope fractionation in RAPS 2, I suggest that even though BSR is taking place, it has little impact on the overall sulfur geochemistry in the system. Otherwise, we would see what can be observed in RAPS 1, i.e. an impact on $\delta^{34}S$ of unconsumed sulfate. Rather, processes must be dominating sulfate removal that have little impact on sulfur isotope fractionation (Chapter 3, e.g. sulfate removal through sorption and precipitation). Further, the dominance of these processes seems to mask any isotopic effects by BSR on the unconsumed sulfate.

If one assumes open system conditions in RAPS 2 in which sulfate is unlimited (i.e. F~1, equation (8)), isotope fractionation for all sampling events range in between 1.0439-1.0509 ($\bar{x}_{\alpha}$=1.0484±0.0024). This is substantially higher than what was suggested through the Rayleigh approach (~1.0095) and lies within the measured $\Delta^{34}S_{SO4-H2S}$ ~ 48.9±7.0‰, supporting the appropriateness of the “open system approach”.

Distinct positive correlations between sulfate sulfur and sulfide sulfur isotope ratios in effluent 1, particularly during the summer low flow conditions, were observed. Sulfate sulfur isotope fractionation exceeded 30‰ during this time suggesting at least semi-closed conditions (Figure 29). The increased sulfate limitation indicates that conditionally the application of the Rayleigh equation would be applicable, at least during the months of low flow.

Brüchert et al. (1996) suggested that sulfate isotope enrichments of $\Delta^{34}S$>7‰ are a product of diffusion limitation with sulfate reduction rates exceeding sulfate supply. Nonetheless, sulfate concentrations observed in effluent 1 generally exceeded the proposed limit of sulfate reduction (<1 mM, ~96 mg L^{-1}) (Canfield 2001b). The formation of preferential flow paths is a common observation in PTS (Maier et al. 2009). It is therefore likely, that despite the apparently sufficient sulfate concentrations in the effluent, niches of sulfate limitation may have formed within the substrate, in which sulfate was limited which led to the observed fractionation. Goldhaber and Kaplan (1982) suggested that sulfate reduction occurred independently of sulfate concentration (i.e. of zero order) at sulfate concentrations >10 mM (~961 mg L^{-1}).

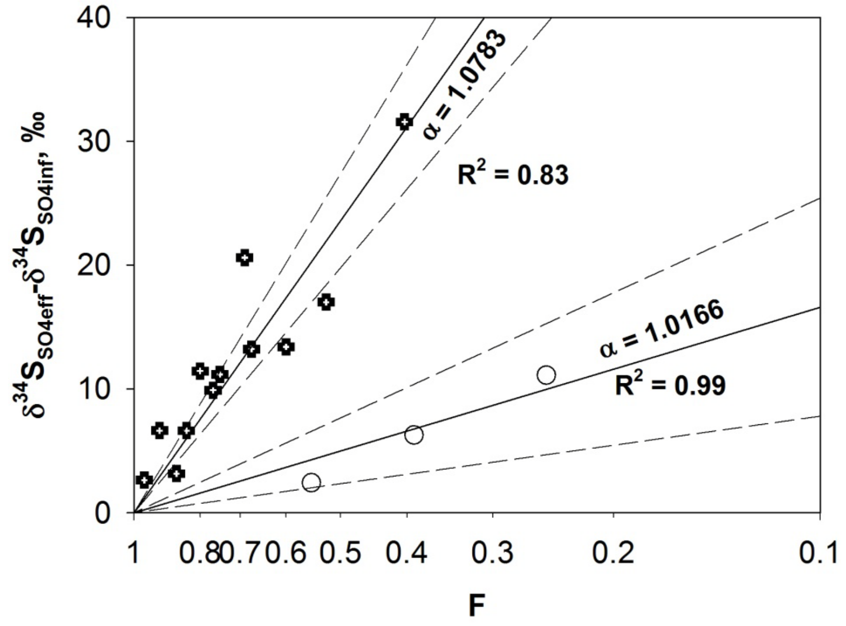

Figure 29 Sulfate sulfur fractionation in RAPS 1 influent and effluent versus unconsumed sulfate (F); the three samples plotting on the α=1.0166 regression line were obtained in February, June and July 2009; solid lines = regression lines; dashed lines = 95% confidence intervals

The Rayleigh plot in Figure 29 shows a significant positive relationship between the degree of fractionation and sulfate consumption with a fractionation factor (α_{RAPS1}) in the order of 1.0783. The significantly lower fractionation (α~1.0166) of three samples is not yet fully understood.

In order to assess the appropriateness of using Rayleigh fractionation, $\delta^{34}S$ of hydrogen sulfide were calculated (equation (7)) using isotope fractionation factors calculated with equation (6) (Figure 29). Measured and calculated $\delta^{34}S_{H2S}$ varied by 13.4±20.1‰ (n=13) in RAPS 1. This indicates that this RAPS can equally not be considered as fully closed and sulfur removal through processes other than BSR are likely to occur which was confirmed in Chapter 3.

(8)

$$\alpha \sim (\delta^{34}S_{H2S} - \delta^{34}S_{SO4})(1000+\delta^{34}S_{SO4})^{-1} + 1)$$

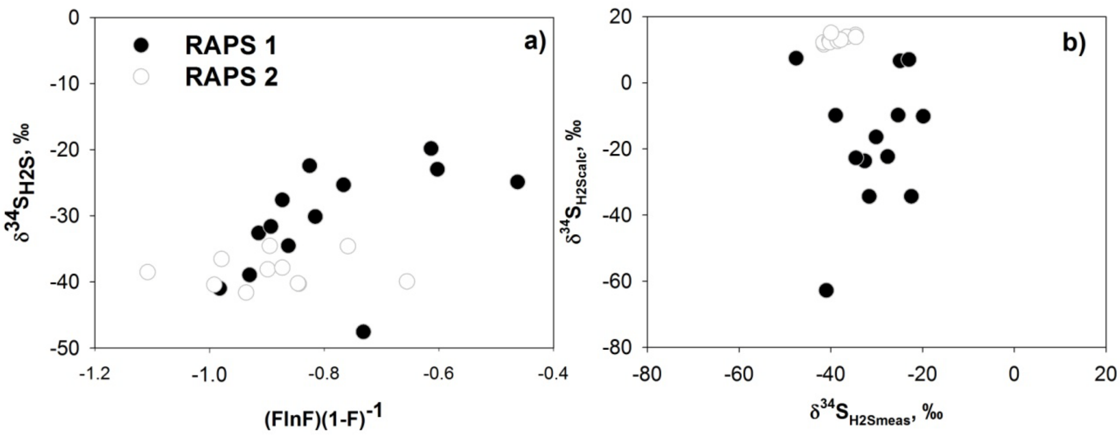

Figure 30 a) Sulfide sulfur fractionation in the RAPS versus unconsumed sulfate ($F(\ln F)(1-F)^{-1}$), b) measured and calculated sulfide sulfur isotope ratios in RAPS 1 and 2, calculations based on closed system conditions

Sulfur Mass Balance

Based on sulfur loads in the waters and their respective sulfur isotope ratios, sulfur mass balances were calculated to determine the overall sulfur removal rates and bulk sediment sulfur isotopic ratios (equation (9), (10), Figure 31)). Effluent hydrogen sulfide concentrations were very low compared to those of sulfate. I therefore excluded them from this simplified approach.

(9)

$$L_{sed} = L_{inf} - L_{eff} - L_{ov}$$

(10)

$$\delta^{34}S_{sed} = (x_1 d^{34}S_{inf} - x_2 d^{34}S_{eff} - x_3 d^{34}S_{ov})x_4^{-1}$$

L=sulfate load in g min^{-1}, δ^{34}S=sulfur isotopic ratio in ‰, sed=sediment, inf=influent, ov=overflow, eff=effluent, x=percentage amounts of respective sulfur phases compared to total sulfur concentration

Results showed distinct differences between the treatment systems. RAPS 1 is characterized by low sulfur removal rates (average=1 g min^{-1}, range: 0.1-5.8 g min^{-1}). From these data and the sulfate sulfur isotope ratios, bulk sediment δ^{34}S were calculated. Bulk sediment sulfur isotope ratios in RAPS 1 ranged between 6‰ to -63‰ (average=-21‰) with a clear inverse relation to sulfate retention rates (Figure 31).

Bulk sediment sulfur ratios in RAPS 2 ranged between 11 and -23‰ (average=4.5‰), an offset of 5-7‰ compared to the $\delta^{34}S$ of the original mine water sulfur. These calculations strongly support the claim that sulfate isotope fractionation is governed by the "masking effect" of the open (or semi-closed) conditions.

In order to calculate the amount of pyrite generated in the system I assumed, in a highly simplified approach, that sulfate is retained in two principal phases: i) pyrite: i.e. $\delta^{34}S_{CRS}$~$\delta^{34}S_{H2S}$ and ii) sulfate: (oxyhydroxysulfate) i.e. $\delta^{34}S_{ASS}$~$\delta^{34}S_{SO4}$ (equation (11)). From the bulk sediment sulfur isotope ratios calculated above and the sulfate (in the mine water) and hydrogen sulfide isotope ratios (in the effluent) the percentage amount of sulfate and sulfide retained in the sediment was estimated.

(11)

$$\delta^{34}S_{sed} = x\delta^{34}S_{SO4} + (1-x)\delta^{34}S_{H2S}$$

$\delta^{34}S_{SO4} \sim 10.2‰$, $\delta^{34}S_{H2S} \sim -38.7‰$

For those events, in which sulfate effluent loads were smaller than sulfate influent loads, on average 12±18% (median=4%, -2-68%, n=14) of the overall sulfate removal in RAPS 2 occurred as pyrite. Consequently, more than >88% of all sulfate is retained in form of sulfate. The same approach applied on RAPS 1, led to a hydrogen sulfide contribution ranging between 13-142% (average~70%, median~68%). Overall, the predicted pyrite retention rates largely exceeded those observed in the sediment (Chapter 3), suggesting a substantial amount of pyrite (or H_2S) has been reoxidised.

Sulfate Oxygen Isotopes

Sulfate oxygen isotope ratios in influents were stable during July to October 2009 and showed an offset of 7.6±0.3‰ compared to $\delta^{18}O_{H2O}$ (Figure 32, Table 7). Similar differences were observed by Heidel et al. (2009) (2.9-8.1) and Taylor et al. (1984b) (4.1-12.1‰). There was also little variability of $\delta^{18}O_{SO4}$ (Figure 32). In effluent 1 and 2, sulfate oxygen isotope ratios were significantly enriched by up to 26.3‰ and 11.2‰, respectively, compared to influent sulfate oxygen.

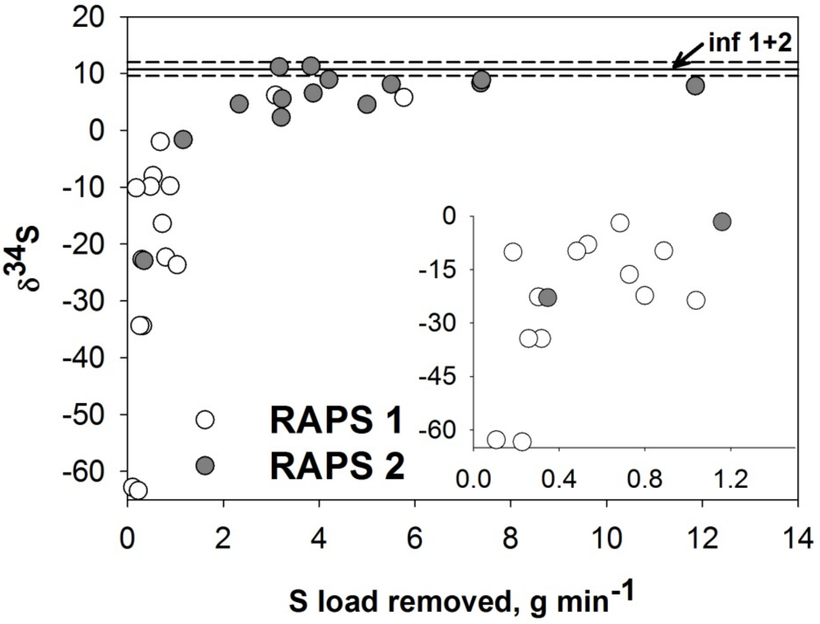

Figure 31 Sulfate removal rates in the RAPS versus bulk sediment sulfur isotope ratios calculated from influent and effluent sulfate sulfur isotope ratios and sulfur load removal rates; inf 1, 2=mine water sulfate sulfur isotope ratios, small graph shows a detailed view at sulfur load removals between 0 and 1.2 g min^{-1}

Long equilibration times between water and sulfate oxygen under ambient conditions ($S^{16}O_4 + H_2{}^{18}O \leftrightarrow S^{18}O^{16}O_3 + H_2{}^{16}O$) (Lloyd 1967, Zak et al. 1980, Chiba and Sakai 1985) lead to isotopic disequilibria. The combined results of $\delta^{18}O_{H2O}$ and $\delta^{18}O_{SO4}$ can therefore elucidate the principal sulfide oxidation processes, in which either atmospheric oxygen, water oxygen or both are incorporated into sulfate (equations (12) and (13)). Fractionation of atmospheric O_2 (~23.5‰, (Kroopnick and Craig 1972)) upon dissolution is low (ε~0.7‰) (Benson and Krause 1984) so that we can use atmospheric oxygen isotopic values accepting only minor sources of error during the dissolution process ($O_{2(g)} \leftrightarrow O_{2(diss)}$).

Pyrite oxidation in aerobic environment is assumed to be governed by atmospheric oxygen (equation (12)) (Seal et al. 2000). In this case, only minor amounts (~12.5%) of water derived oxygen is incorporated into sulfate. On the other hand, pyrite oxidation with ferric iron as main oxidizing agent leads to a 100% water O contribution to sulfate oxygen (equation (13)) and consequently no atmospheric oxygen is incorporated into the sulfate molecule.

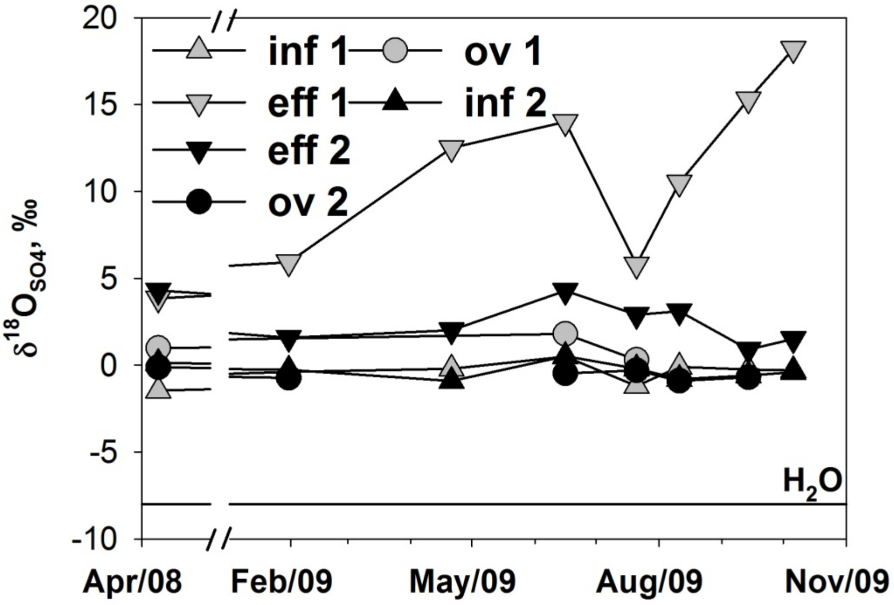

Figure 32 Variations of sulfate oxygen isotope ratios in RAPS waters; H_2O=water oxygen isotope ratios (July-October 2009)

Table 7 Sulfate oxygen isotope ratios in RAPS surface waters

Site	Average	Max, Min	Stdev (n)
Influent 1	-0.4	0.5, -1.5	0.6 (8)
Overflow 1	1.0	1.8, 0.3	0.8 (3)
Effluent 1	10.8	18.2, 3.8	5.1 (8)
Influent 2	-0.3	0.5, -0.9	0.5 (8)
Overflow 2	-0.5	-0.1, -0.9	0.3 (7)
Effluent 2	2.6	4.3, 0.9	1.3 (8)

Isotope ratios=‰, Max=maximum, Min=minimum, stdev=Standard deviation, n=number of samples

(12)

$$FeS_2 + 3.5O_2 + H_2O \rightarrow 2SO_4^{2-} + 2Fe^{2+} + 2H^+$$

(13)

$$FeS_2 + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+$$

Based on these equations a mass balance (equation (14)) was proposed to estimate the principal oxidation pathway of pyrite (Lloyd 1967).

(14)

$$\delta^{18}O_{SO4} = X(\delta^{18}O_{H2O} + \varepsilon H_2O) + (1-X)(0.875(\delta^{18}O_{O2} + \varepsilon O_2) + 0.125(\delta^{18}O_{H2O} + \varepsilon H_2O))$$

Isotope enrichment factors (ε_{H2O}, ε_{O2}) reported by a variety of studies for aerobic and anaerobic environments (with or without microbial catalization) are summarized in Table 8.

Table 8 Literature isotope enrichment factors for water and atmospheric oxygen during sulfide oxidation and incorporation into sulfate

ε_{H2O}, ‰	ε_{O2}, ‰	Reference
0	-8.7	Lloyd (1967)
4.1	-11.2	Taylor et al. (1984a)
0	-4.3	Taylor et al. (1994)
2.9-3.6	-9.8	Balci et al. (2007b)

The influent sulfate data fall within the proposed range of sulfate generated by sulfide oxidation (Figure 33) (van Stempvoort and Krouse 1994). Using the enrichment factors reported by Balci (2007b), Taylor and Wheeler (1994) and Taylor et al. (1984a), about 73-79%, 71-75% and 76-83%, respectively, of all sulfate oxygen is derived from water.

This suggests that despite the elevated dissolved oxygen (~7.6-9.4 mg L^{-1}) and moderate acidic pH (~5.11-6.02), in underground mine and waste rock dump similar - mostly anaerobic - pyrite oxidation processes prevail (equation (13)). Partial incorporation of dissolved oxygen up to around 30% agree with observations of Heidel et al. (2009) who showed, that because of the intermediate sulfite oxidation product during pyrite oxidation, a limited amount of atmospheric oxygen is incorporated into the sulfate even at advanced oxidation states. Microbial catalysis of the oxidation process was not distinguishable by $\delta^{18}O_{SO4}$ (Toran and Harris 1989, Balci et al. 2007b).

Influent and overflow sulfate oxygen isotopic ratios are similar and fairly constant suggesting i) no fractionation occurred during sulfate removal as oxyhydroxysulfate and ii) insignificant hydrogen sulfide has diffused to the upper parts of the sediment or into the water/sediment interface where it would be reoxidised to sulfate and consequently lead to shifts in $\delta^{18}O_{SO4}$ and $\delta^{34}S_{SO4}$.

Oxygen isotope fractionation of sulfate in the effluents is closely linked to the fractionation of sulfur (Figure 34). ΔS:ΔO ($\Delta S_{SO4}=\delta^{34}S_{SO4eff}-\delta^{34}S_{SO4inf}$, $\Delta O_{SO4}=\delta^{18}O_{SO4eff}-\delta^{18}O_{SO4inf}$) ranged between 0.5-1.5 (Figure 35) in both RAPS. The lowest ratios were determined during winter months with increasing ratios reaching maxima in October 2009 (Figure 34).

The strong relationship between oxygen and sulfur fractionation in sulfate reducing systems has been observed previously (Mizutani and Rafter 1973, Aharon and Fu 2000, Aharon and Fu 2003, Mandernack et al. 2003, Knöller et al. 2004). Rarely, however, have fractionation ratios as low as ~0.5 been observed before (Strebel et al. 1990, Böttcher et al. 1998a).

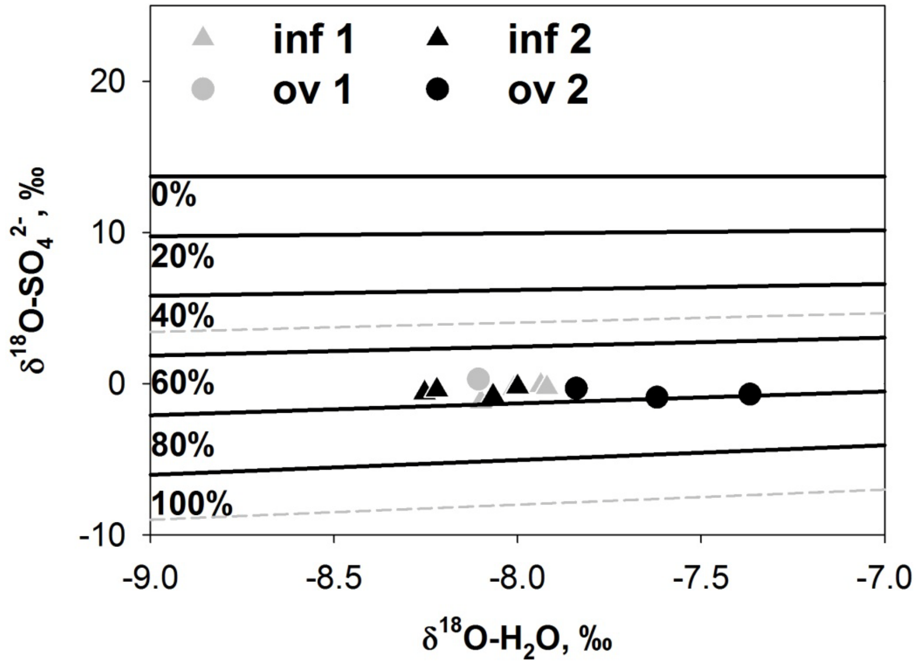

Figure 33 Water and sulfate oxygen isotope ratios in waters (July-October 2009); percentage contribution of O-H_2O calculated after Balci et al. (2007b) (ε_{H2O}=2.9‰, ε_{O2}=-9.8‰.); dotted grey lines=sulfate generated by sulfide oxidation after van Stempvoort and Krouse (1994), (lower limit: $\varepsilon_{H2O}=0$, $\varepsilon_{O2}=0$; upper limit: $\delta^{18}O_{SO4}=0.62\delta^{18}O_{H2O}+9$)

Mizutani and Rafter (1973) proposed ΔS:ΔO around 4, reflecting the stoichiometric ratio of S and O in sulfate. Similar fractionation ratios were reported by Mandernack et al. (2003) (ΔS:ΔO~4.4). Aharon and Fu (2000) reported ratios varying between 3.5 and 1.4 and in a later study ratios of 2.4 (Aharon and Fu 2003). Knöller et al. (2004) reported 3.1, whilst Böttcher et al. (1998a) and Strebel et al. (1990) reported ratios between 0.66-2 and 0.71, respectively.

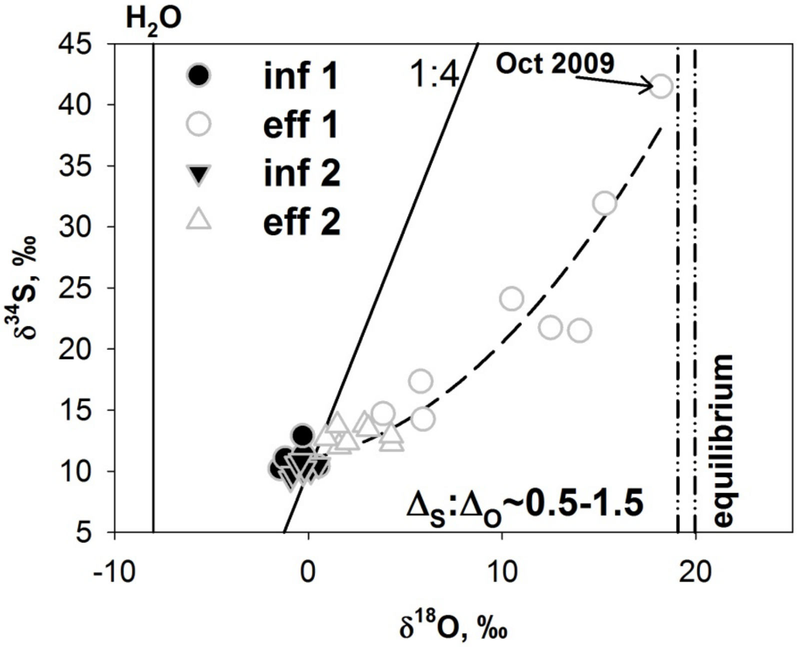

Figure 34 Sulfate oxygen and sulfate sulfur isotopic ratios in RAPS influents and effluents; the 1:4 ratio line=kinetic fractionation ratios as proposed by Mizutani and Rafter (1973); H_2O=water oxygen isotope ratios measured between July and October 2009, equilibrium=temperature dependent water oxygen – sulfate oxygen equilibration suggested by Fritz et al. (1989), (~27-28‰ at T=11-17°C)

In contrast to sulfur, the Rayleigh plot of $\delta^{18}O_{SO4}$ did not lead to any additional information because no correlation was detected for either of the treatment systems (Figure 36, p>0.05).

About the cause of the sulfate oxygen fractionation the literature is in disagreement. Kinetic processes influenced by sulfate reduction rates and temperature were proposed to drive the oxygen fractionation by some researchers (e.g. Chambers and Trudinger 1979, Aharon and Fu 2000, Mandernack et al. 2003). Others suggested that fractionation is caused by equilibration reactions with (cytoplasmic) water (Fritz et al. 1989, Brunner et al. 2005, Turchyn et al. 2010).

For the latter to take place, intermediate sulfur oxidation products are required. These can be generated intracellular (i.e. exchange with sulfite or adenosine 5’phosphosulfate, (Mizutani and Rafter 1973, Brunner et al. 2005, Turchyn et al. 2010) or extracellular (sulfite or thiosulfate (van Stempvoort and Krouse 1994, Böttcher et al. 2001)) during sulfide oxidation (Cline and Richards 1969, Chen and Morris 1972, Jørgensen 1988, Kelly 1988) or bacterial sulfate reduction (Rees

1973, Turchyn et al. 2010). The intermediate sulfur oxidation products are, in contrast to sulfate, highly reactive towards water and quickly exchange oxygen isotopes.

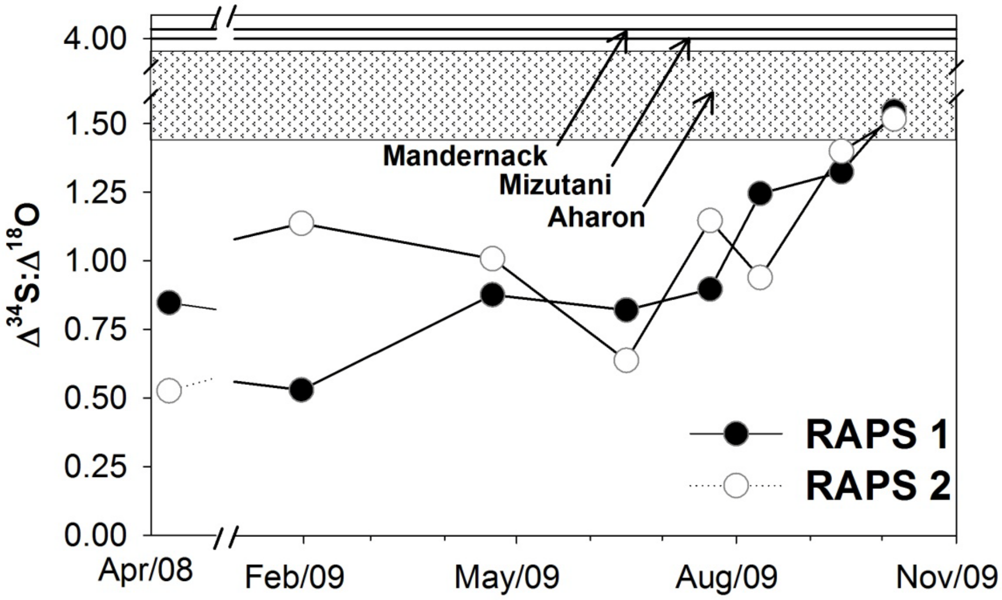

Figure 35 Sulfate sulfur versus sulfate oxygen isotope fractionation in RAPS influents versus effluents; vertical lines and shaded area represent S:O ratios reported in Mandernack et al. (2003), Mizutani and Rafter (1973) and Aharon and Fu (2000)

Fritz et al. (1989), Brunner et al. (2005) and Böttcher et al. (1999) reported positive, non-linear relationships between sulfate sulfur and sulfate oxygen isotopes similar to my data: $\delta^{34}S_{SO4}=11.43+0.065\delta^{18}O_{SO4}+0.05(\delta^{18}O_{SO4})^2$. Whilst the fractionation of sulfur appeared to be unlimited over time of measurement, the fractionation of oxygen approached equilibrium.

Temperature dependent fractionation ratios between water and sulfate oxygen (Fritz et al. (1989): ~25‰ at T=30°C, ~27‰ at T=17°C and 29‰ at T=5°C; 24-29‰ at 0-20°C, (Zeebe 2010)) would here (T=11.3-16°C between June-October 2009) lead to equilibration values between ~27-28‰. Figure 34 shows that indeed October 2009 data nearly matched these fractionations (~26‰) suggesting oxygen isotope fractionation reached equilibrium during this event. Brunner et al. (2005) also supported the "equilibration theory" and argued that conditions here observed ($\Delta^{18}O \geq \Delta^{34}S$) are indicative for slow specific sulfate reduction rates.

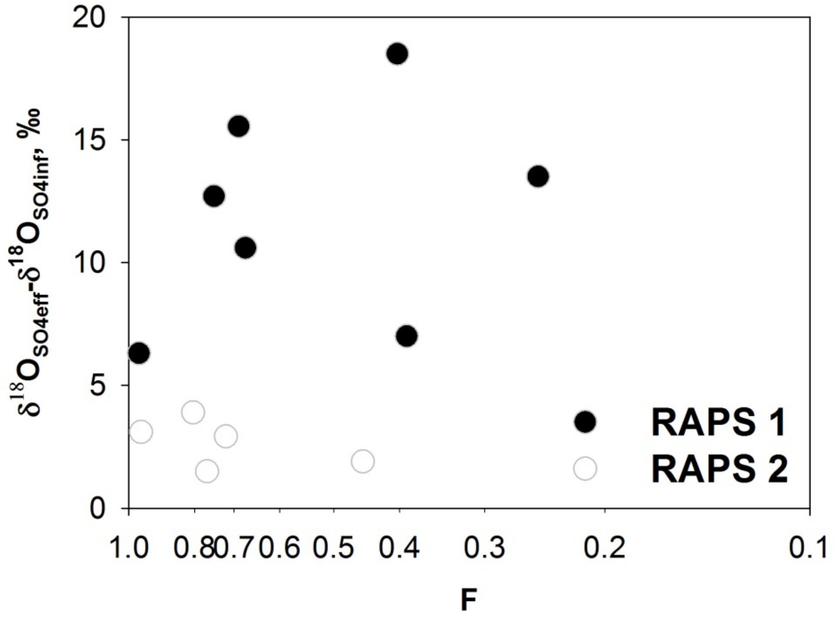

Figure 36 Sulfate oxygen fractionation in the RAPS versus unconsumed sulfate (F)

Sediment Sulfur

The principal inorganic sulfur sinks in the reactive substrate of RAPS 1 and 2 are chromium reducible sulfur (CRS, e.g. (mostly framboidal) pyrite=20.5±11% of total sulfur (TS)) > elemental sulfur (ES=14.7±7% of TS) > acid soluble sulfates (ASS=10.3±7% of TS, e.g. iron and aluminium hydroxysulfates) > water soluble sulfates (WSS=9.0±5% of TS, sorbed or occluded sulfate) and trace amounts of acid volatile sulfur (AVS, e.g. mackinawite and partially greigite, Chapter 3). The largest sulfur sink was organic sulfur (OS=43.6±14% of TS).

Isotope ratios of the principal inorganic sulfur species (ISS) are presented in Figure 37.

The isotope ratios of ISS showed (with exceptions) decreasing depletion: $\delta^{34}S_{CRS}<\delta^{34}S_{AVS}\sim\delta^{34}S_{ES}<\delta^{34}S_{ASS}$. The $\delta^{34}S_{ASS}$ ranged between 1.9-12.6‰ (average=7.0±3.3‰, n=12). Reduced inorganic sulfur species AVS and CRS ranged between -12.4-5.9‰ (average=-5.0±5.1‰, n=10) and -29.3-6.9‰ (average=-19.6±5.3‰, n=22), respectively. Elemental sulfur isotope ratios ranged between -25.9-8.7‰ (average=-5.8±9.6‰, n=21).

Distinct differences in sulfur isotopic ratios were observed between pyrite and iron monosulfides (Figure 37). Similar to observations of Butler et al. (2004), dissolved sulfide had the lowest $\delta^{34}S$ whilst AVS was enriched in ^{34}S compared to pyrite and dissolved sulfide. $\delta^{34}S_{CRS}$ plot in the area of hydrogen sulfide isotopic ratios (2008/2009). The generation of pyrite via the H_2S-pathway (equation (15)) (Boulegue et al. 1982) is therefore proposed. This pathway was found to dominate over the alternative polysulfide pathway (equation (16)) at circum-neutral conditions (Wilkin and Barnes 1996).

(15)

$$FeS_{(aq)} + H_2S_{(aq)} \rightarrow FeS_{2(s)} + H_{2(g)}$$

(16)

$$FeS_{(aq)} + S_n^{2-} \rightarrow FeS_{2(s)} + S_{n-1}^{2-}$$

Price et al. (1979) suggested that during pyrite formation from hydrogen sulfide little (<1‰) sulfur fractionation occurred and therefore pyrite sulfur isotope ratios would closely match the sulfide source. Similarly, Böttcher et al. (1998b) reported small fractionations during the reaction of iron with sulfide. The significant difference to $\delta^{34}S_{AVS}$ was also found in natural sediments close to water-sediment interfaces and during bioturbation (Lein et al. 2002). AVS to pyrite transformation, long believed to be a requirement of pyrite formation, can with the here presented data not be supported. Davison et al. (1985) suggested that this diagenetic conversion is not a dominant process in freshwater systems.

The kinetic isotope effect observed by Fry et al. (1988) during oxidation of hydrogen sulfide by oxygen in the order of 5‰ can clearly not explain the fractionation observed between elemental sulfur and pyrite. It therefore appears, that ES is a product of oxidation of acid volatile sulfide potentially induced by Fe(III)hydroxides or dissolved oxygen from mine water or radial oxygen loss from wetland species (Roden and Wetzel 1996). Highest ^{34}S depletion in ASS in the upper sediment horizons of RAPS 1 could indicate a re-oxidation of ^{34}S depleted hydrogen sulfide to sulfate which consequently lowers the bulk $\delta^{34}S$ of ASS.

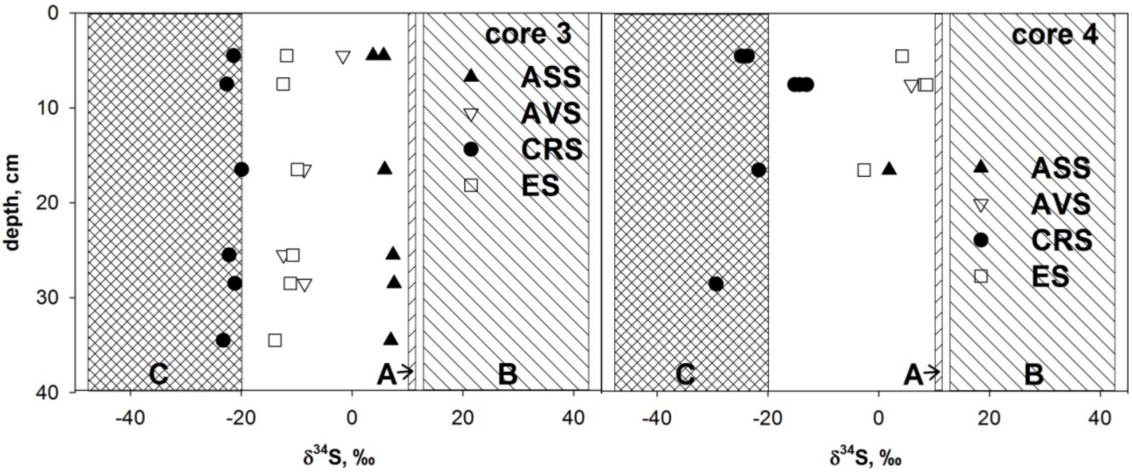

Figure 37 Sulfur isotope ratios of acid soluble sulfate (ASS), acid volatile sulfur (AVS), chromium reducible sulfur (CRS) and elemental sulfur (ES) in sediment cores 3 and 4 (RAPS 1, core 3=close to the influent, core 4=close to the effluent); shaded areas indicate ranges of sulfur isotopic ratios of A: mine water sulfate sulfur, B: effluent sulfate sulfur and C: effluent sulfide sulfur (2008-2009)

Summary

- Over 18 months, influents and effluents of the RAPS were monitored in monthly intervals to measure sulfate ($\delta^{34}S$, $\delta^{18}O$), sulfide ($\delta^{34}S$) isotopes and (in four occasions) water isotopes (δD, $\delta^{18}O$);
- Sulfur isotopes of the inorganic sulfur phases that were presented in Chapter 3 are presented alongside;
- Both mine waters are of meteoric origin and have one single sulfur source;
- More than 70% of the sulfate oxygen in the mine waters derived from water oxygen;
- Sulfide oxidation in the coal mine and the waste rock dump were dominated by anaerobic oxidation with ferric iron as the main oxidizing agent;
- Sulfate oxygen isotopic ratios in the mine waters showed an offset of ~7.6‰ compared to $\delta^{18}O_{H2O}$ over four months of measurement;
- Seasonal changes of sulfate concentrations in the mine waters are a product of dilution effects with infiltrating meteoric waters;
- The substantial sulfate removal in the water-sediment interface of the RAPS only lead to marginal sulfate sulfur isotope fractionation (~1.2‰);
- The mine water that had percolated through the reactive substrate (effluent) showed depletion of sulfate and dissolved oxygen and trace amounts of hydrogen sulfide (≤1.15 mg L^{-1});
- The occurrence of bacterial sulfate reduction was confirmed by highly ^{34}S depleted hydrogen sulfide compared to mine water sulfates ($\Delta^{34}S_{H2S\text{-}SO4}$~ 45.0±7.0‰);

- RAPS 2 is characterised by open system conditions with largely unlimited sulfate concentrations;
- RAPS 1 is characterised by semi-closed conditions reflected in significant $\delta^{34}S$ values of up to 31.6‰ in unconsumed sulfate compared to ~10.3‰ in the mine waters;
- Solid phase sulfate sulfur showed $\delta^{34}S$ close to mine water sulfate, whilst reduced inorganic sulfur species were depleted in ^{34}S: $\delta^{34}S_{ES} > \delta^{34}S_{AVS} > \delta^{34}S_{CRS}$;
- The formation of pyrite seems to occur through direct reaction of iron and sulfide species without an intermediate solid AVS phase which is reflected in the similar $\delta^{34}S$ of both dissolved and solid phases;
- Elemental sulfur appears to be a direct oxidation product of acid volatile sulfur with marginal sulfur isotope fractionation;
- Non-linear positive relations were observed between isotope ratios of sulfate sulfur and sulfate oxygen that were subjected to bacterial sulfate reduction;
- Sulfate sulfur and sulfate oxygen isotope fractionation between influents and effluents ($\Delta^{34}S$:$\Delta^{18}O$) varied between 0.5-1.5;
- Sulfate oxygen in effluent 1 approached equilibrium conditions of $\Delta^{18}O_{SO4}$~26 ‰ compared to $\delta^{18}O_{H2O}$ (~-8‰, T=11.3-16.9°C).

CONCLUSIONS AND RECOMMENDATIONS

In the final section of this thesis, the main outcomes are summarized. In the first four sections, the conclusions of Chapters one to four are presented. Recommendations that might lead to future work are suggested in the final section.

Chapter 1 - Treatment Performance

More than five years of passive treatment data for two net-acidic coal mine discharges from northeast England have been assessed. The treatment system performed well for the removal of iron, aluminium and acidity, and constantly increased pH and alkalinity. Manganese, zinc and sulfate were partially removed in the system, but occasionally remobilized. Removal ratios of iron and sulfate indicated that in addition to sulfide minerals, other Fe, S sinks exist. Manganese removal as a carbonate is to be confirmed and so are the reasons for its seasonal remobilisation.

Trend analysis indicated that removal rates of the main contaminants, though seasonal, were constant over the five and a half years of monitoring. This is encouraging in that, despite the increase in surface ochre sludge and significant overflow through the RAPS, the treatment system still performs well. However, a decrease in calcium and bicarbonate mobilization, possibly caused by the armouring of limestone, suggests that regeneration of the system may be required in the near future.

To increase the life time of the PTS it is important to remove the surface sludge covering the RAPS. Also controlled flushing of secondary precipitates (Kepler and Mc Cleary 1997, Watzlaf et al. 2002) have been shown to increase the void space. However, this will be of limited use to remove surface precipitates from the apparently armoured limestone. It appears unavoidable therefore, that the reactive substrate will have to be replaced as soon as pH are no longer sufficiently buffered in order to avoid dissolution of mineral precipitates which could lead to the remobilisation of the target elements. Replacement of PTS substrate is a major undertaking, particularly with respect to disposal of the spent substrate, which can be very costly, especially if the only disposal route is to landfill. Therefore, investigations of the type discussed here provide valuable insight into both the longevity of such PTS and the overall costs and benefits of PTS for remediation of pervasive waste streams such as mine water pollution.

Chapter 2 - Geochemistry of RAPS Waters

Iron, aluminium and zinc were quantitatively removed from the water that has passed through the reactive RAPS substrate. Manganese was only partially removed in RAPS 2 and even remobilized from the reactive substrate of RAPS 1. The latter was potentially caused by reductive dissolution of compost derived manganese oxides. Zinc and manganese concentrations in the water that short-circuited over the reactive substrate remained unaffected, whilst iron and aluminium were substantially removed in the water-sediment interface.

Geochemical modelling suggested that dominant sinks of zinc and manganese were carbonates and to a limited extent sulfides. Removal via sorption onto hydroxides and organic matter is also likely. The principal removal processes of iron and aluminium: oxidation (Fe), hydrolysis and precipitation, caused an increase in proton acidities in the sediment-water interface followed by substantial remobilization of aluminium when pH dropped below 5.

The preferential retention of iron and aluminium as meta-stable oxyhydroxy(sulfates) (e.g. schwertmannite, ferrihydrite and (hydro)basaluminite) potentially jeopardizes the long-term performance of the treatment system because of the decrease in substrate permeability (clogging), armouring of the limestone and decrease of the available freeboard.

Alkalinity and pH were significantly increased through the passive treatment leading to a partial retention of iron and manganese as carbonates. Carbon isotopes of total dissolved inorganic carbon suggested that both limestone dissolution and anaerobic microbial respiration processes contributed to the alkalinity generated by the RAPS. The percentage contribution of the dominant alkalinity source was assessed via two mass balances:

i) Based on iron, aluminium and proton consumption and bicarbonate generation and

ii) Based on carbon isotope ratios of total dissolved inorganic carbon, limestone and organic matter and concentration changes of alkalinities.

Both models indicated that the oxidation of organic matter is the dominant bicarbonate source. In RAPS 1, 79% and 74% of the generated alkalinity derived from organic matter, after mass balance (i) and (ii), respectively. Substantial differences, however, were observed in RAPS 2. Between 85% and 52% of total alkalinity generation after models (i) and (ii), respectively, were accounted to the oxidation of organic matter.

Overall, it became clear that what seemed to be established in the research literature on mine water treatment systems can be source of substantial error: a) Calcium mobilization cannot fully account for limestone dissolution due to the oversaturation of carbonates in the effluents. b) Sulfate retention cannot by readily used to measure BSR due to the substantial sorption of sulfate and precipitation as oxyhydroxysulfate in the substrate. c) Carbon isotopes of TDIC alone are unable to predict the alkalinity source with confidence.

Chapter 3 - Iron and Sulfur Speciation in RAPS Sediments

As shown in Chapters one to three, the Bowden Close treatment system has been working effectively in removing iron and increasing pH and alkalinity over the last 6 years of operation. However, I have demonstrated also that the dominant iron removal processes do not match expectations for these RAPS. Rather, the dominant metal removal processes are in fact comparable to those observed in aerobic mine water treatment systems (i.e. oxidation and hydrolysis). As a consequence, the accumulation of iron in the highly mobile (hydr)oxide bound fraction suggests an elevated remobilization potential upon changes in redox conditions or increases in acidity. In addition, iron hydroxides effectively scavenge trace elements (Fischer et al. 2009) that would at least partially be remobilized upon transformation and dissolution of the iron hydroxides. The hydrolysis of iron and aluminium further generates proton acidity that consumes the generated bicarbonate alkalinity and enhances remobilization of aluminium from the ochre sludge.

The high abundance of hydroxide precipitation and their low densities may cause: i) clogging of the sediment pores, ii) armouring of the limestone, iii) decrease in the system freeboard, iv) decrease in substrate permeability and ultimately v) jeopardise the long-term performance of the system. These problems are currently exacerbated by accumulation of iron-rich surface sludge, the result of which is that there is now only a partial water cover over the RAPS. This may increase potential for oxygen diffusion into the substrate, promoting an increase in redox potential and conceivably reoxidation of redox sensitive metal species within the substrate.

This study has shown that only 10-42% of the total sulfur occurred as inorganic reduced sulfur. In other studies of similar anaerobic treatment systems, BSR was assumed to be the dominant sulfate removal process (Barton and Karathanasis 1999, Riefler et al. 2008). My results suggest that the potential for sulfide mineral formation and microbially generated bicarbonate by BSR may in fact be overestimated. This could have potentially significant effects on predictions of longevity and system performance.

Thus, neither sulfate removal rates, nor mineral sulfide concentrations within the substrate, give a clear indication of the activity of sulfate reducing bacteria and their potential to generate alkalinity.

Results obtained during this study suggest that pyrite formation in the RAPS is hampered by limited reaction times. However, tracer tests suggested that retention times ranged between 4-8 d and 4-6 d in RAPS 1 and 2 (Wolkersdorfer et al. 2005), respectively, and are therefore far greater than the recommended 14 hours (Younger et al. 2002). Considering the SRB sub-optimal redox potentials, only an increase in the RAPS footprint or a diversion of a fraction of the mine water around the RAPS could enhance anaerobic microbial respiration within the system. Thereby, metal sulfide formation could be promoted and might decrease reoxidation and recycling processes within the substrate.

Chapter 4 - S, O and H Isotope Ratios in RAPS Waters and Sediments

The sulfate in both influents is a product of coal derived iron sulfide oxidation with identical sulfur isotope ratios in both influents: 10.7±0.4‰ (inf 1) and 10.2±0.4‰ (inf 2). The process by which the oxidation takes place is similar in both systems and is dominated by anaerobic oxidation, deriving around 70-80% of sulfate oxygen from water.

Despite the significant sulfate retention in the water-sediment interface of treatment systems, the sulfur and oxygen isotope fractionation of sulfate were negligible suggesting sulfate retention occurred by sorption or precipitation (e.g. oxyhydroxysulfates).

Results confirmed BSR in both RAPS. However, it was of little importance for the overall sulfur cycle and for the removal of iron as was shown in Chapter 3.

Distinct characteristics in surface waters in terms of sulfate concentrations and also in their sulfur and oxygen isotope ratios were observed. RAPS 2 is relatively stable in its behaviour in terms of isotope fractionation – showing no seasonal variation. However, BSR, whilst recognized, does not appear to be a major control on the sulfur cycle in this system. It is suggested that amounts of sulfide produced are small and masked by the abundance of sulfate concentrations (open system conditions). It is clear that measuring sulfate sulfur isotope ratios of the surface waters alone (Rees and Bowell 1999, Bhattacharya et al. 2008) will only indicate the occurrence of BSR under closed system conditions in which sulfate is highly depleted.

RAPS 1 is distinct. Its sulfate influent loads are lower than RAPS 2 by about nine times. There is clear evidence that seasonally (semi-)closed system behaviour has taken place, with positive correlations on Rayleigh plots. The formation of preferential flow paths through the passive treatment system must be called upon, for the creation of niche environments where closed system behaviours are encouraged at these sulfate concentrations. This behaviour is well correlated to summer periods, in which sulfate loads and flow through are reduced.

Effluent sulfate sulfur and sulfate oxygen isotope fractionation are positively, non-linearly correlated in both RAPS. Sulfate sulfur fractionation between influents and effluents compared to sulfate oxygen fractionation between these sampling points showed ratios in the order of 0.5-1.5 for both treatment systems. This suggests that similar processes occur –though on a different magnitude. Whilst sulfur fractionation is commonly thought to occur through BSR induced kinetic fractionation, it is suggested that oxygen fractionation are caused by equilibrium fractionation of sulfur intermediate oxidation products and (cytoplasmic) water. The extreme oxygen fractionation compared to sulfur fractionation may indicate slow and bi-directional sulfate reduction.

Due to difficulties faced during sediment sampling, only 50% of the sediment cores could be recovered. The potential of increased pyrite accumulation in the lower sediment part that was not sampled is likely and will have to be confirmed.

The time lag between sediment sampling (2004) and surface water sampling (2008-2009) allowed only limited comparison of both data sets. Nonetheless, I can draw some conclusions from the data.

Pyrite formation seems to be generated from H_2S (i.e. H_2S-pathway) showing similar sulfur isotopic ratios. However, a limitation has been observed that ultimately will apply to all natural sediment sulfur studies. The pyrite sulfur isotope ratios only reflect a bulk $\delta^{34}S$ whilst it has been shown from surface water data that the isotopic ratios of H_2S can seasonally vary to significant extend. It is therefore clear, that measuring purely sediment sulfur and neglecting interstitial waters and their seasonal variability would have missed a lot of additional information about the overall sulfur cycle. Further, if we assume that fractionation rates were unchanged throughout the six years of treatment, we observe that pyrite $\delta^{34}S$ plot on the heavier side of the $\delta^{34}S$ measured in hydrogen sulfide. The heaviest $\delta^{34}S_{H2S}$ were observed during summer to early autumn which could indicate that most pyrite is generated during this season and any pyrite generated during the reminder of the year is comparatively less important.

Elemental sulfur isotope ratios appear to be a product of AVS oxidation. Both phases showed similar $\delta^{34}S$ which are significantly enriched in ^{34}S compared to pyrite. Acid soluble sulfate mostly represent mine water sulfate isotope ratios with a small offset (~4.2‰). It therefore appears that if hydrogen sulfide is completely reoxidised to sulfate within the system, its overall contribution to ASS is small and had little impact on bulk δ^{34}S of ASS.

Bulk sediment sulfur isotope ratios calculated from surface water mass balances indicated distinct differences between RAPS 1 (average=-21‰) and RAPS 2 (average=4.5‰) stressing that BSR in RAPS 1 substrate was significantly more important on the geochemistry of sulfur than in RAPS 2.

Significance

The water and sediment data obtained from the RAPS of the Bowden Close treatment scheme have shown that the bacterial reduction of sulfate is not a driver for the retention of chalcophilic elements (here: Fe). Upscaling these results to other treatment systems is difficult and potentially affected by a multitude of factors: influent loads, retention times, climatic conditions being some of them. However, the data have highlighted the fact that no assumptions can be made about the principal biogeochemical reactions occurring within these systems by solely measuring influent and effluent water qualities. In consequence this should be borne in mind when considering results reported for anaerobic treatment systems in which BSR was assumed -but not confirmed, (e.g. Barton and Karathanasis 1999, Riefler et al. 2008). The potential for sulfide mineral formation and microbially generated bicarbonate reported from these systems may well have been overestimated. It is therefore of great importance to analyse inorganic (and organic) sinks of the pollutants in these systems to clarify the importance of reaction processes.

In addition, the potential recycling and remobilization of the contaminants driven by redox processes is a critical point to investigate further. Iron is preferentially retained as Fe(III)hydroxide in the upper sediment horizon, partially transported by gravitational flow in lower sediment horizons where it is then potentially released through abiotic or biotic reduction processes. These processes lead to a remobilization not only of iron but also of other elements formerly sorbed onto the hydroxides. Further, the highly reactive Fe(III)hydroxides are effective scavengers of H_2S formed by BSR that ultimately prevent the formation of $FeS_{(aq)}$ and pyrite. Similar limitations are likely to occur in other PTS and we therefore should rethink the design criteria of RAPS, e.g by constructing aerobic wetlands or settling ponds before the RAPS to decrease the iron loads to the RAPS. This, in combination with an increased retention time of at least a fraction of the mine water to be treated could potentially enhance microbial reactivity and the retention of iron as di-sulfide mineral. However, before thinking about the modification of the design criteria we need more studies on this or similar systems to assess which metabolic processes are indeed taking place and enhance (or compromise) the treatment process.

Similar iron and sulfur recycling processes observed in the RAPS have been reported also from natural wetlands and sediments. Particularly tidal marshes and coastal acid sulfate soils (Ivarson et al. 1982, van Breemen 1982, Burton et al. 2006a, Mac Donald et al. 2007) show strong similarities to the artificial systems, be it the highly saline waters, the vertical flow conditions or the sulfur and iron redox reactions. However, two main characteristics of the way RAPS are constructed hamper the direct comparison to the natural systems: a) the extreme organic carbon concentrations, that should significantly enhance microbial activities in RAPS as opposed to natural sediments and b) the permanent water cover that restricts the diffusion of oxygen and reoxidation potentials. Nonetheless, it appears that much is still to be learnt from natural environments to enhance understanding over the functioning of our constructed wetlands.

Recommendations

The individual chapters have highlighted a number of questions and limitations that might lead to future research studies.

- The study has shown that iron (hydr)oxides are the dominant iron sinks in the RAPS. These minerals, however, seem to buffer most of the hydrogen sulfide generated by BSR through reoxidation to intermediate sulfur oxidation species or sulfate. Future designs need to focus on limiting reoxidation of hydrogen sulfide by promoting anaerobic conditions within the substrate, therefore maximizing rates of BSR and pyrite formation.
- The discrimination of the main alkalinity sources by the application of stable carbon isotope ratios on total dissolved organic carbon highlighted significant limitations. One source of error was identified in the insufficient knowledge about carbon isotope fractionation processes in relation to the oxidation of organic matter. A more detailed study should therefore assess the fractionation of $\delta^{13}C$ in TDIC depending on environmental parameters (e.g. T, pH, Eh), the principal organic substrate, the microorganisms and their metabolic pathway.
- Sulfate oxygen isotope analyses indicated intermediate sulfur compounds could play an important role in the cycling of sulfur. It is vital, therefore, to analyse intermediate sulfur species in interstitial waters as well as in influents and effluents. Getting a clearer picture of sulfur intermediates (both organic and inorganic) in the surface and pore waters would potentially enhance understanding of this highly complex (bio)geochemical sulfur cycle in the RAPS.
- Sulfur isotopes suggested that elemental sulfur in wetland and PTS forms from the oxidation of meta-stable acid volatile sulfides. Future assessments have to include a detailed study on the reoxidation of AVS to be able to discriminate whether the trace amounts of AVS in the substrate are indeed through rapid reoxidation processes in the sediment or whether this phenomenon is an artefact of sampling, storage and analysis. Further, the formation processes of pyrite and AVS in the RAPS need closer attention.

- The research has also stressed that more attention should be given to the microbial ecology in future studies surrounding passive treatment systems. Microorganisms form an integrated part of the treatment process through i) generating alkalinity and ii) enhancing metal removal. It is clear also that these studies should not only focus on sulfate reducers. Sulfide oxidizers, methanogens, metal reducers and metal oxidizers potentially can outcompete SRB for organic substrate or jeopardize the treatment process by sulfide oxidation and metal remobilization. In addition, fermenting bacteria and the assessment of the degradability of the organic substrate in the PTS is essential to understanding potentially (SRB) limiting processes.

References

Åberg, G., Satake, K., 2009. Sources of dissolved mine drainage and atmospheric transported lead: A comparative case study in Japan and Sweden. *Science of The Total Environment*, **408**(1): 117-121.

Aggarwal, P.K., Araguas-Araguas, L.J., Groening, M., Kulkarni, K.M., Kurttas, T., Newman, B.D., Vitvar, T., 2010. Global hydrological isotope data and data networks. *In:* West, J.B., Bowen, G.J., Dawson, T.E., Tu, K.P. (eds.), *Isoscapes: Understanding movement, pattern, and process on Earth through isotope mapping*. Springer, London.

Agricola, G., 1556. *De Re Metallica libri XII*. *In:* translated by Hoover H. C. and Hoover L. C. (Editor). Dover, New York, 638.

Aharon, P., Fu, B., 2000. Microbial sulfate reduction rates and sulfur and oxygen isotope fractionation at oil and gas seeps in deepwater Gulf of Mexico. *Geochimica et Cosmochimica Acta*, **54**(2): 233-246.

Aharon, P., Fu, B., 2003. Sulfur and oxygen isotopes of coeval sulfate-sulfide in pore fluids of cold seep sediments with sharp redox gradients. *Chemical Geology*, **195**: 201-218.

Alley, R.B., Cuffey, K.M., 2001. Oxygen- and hydrogen-isotopic ratios of water in precipitation: Beyond paleothermometry. *In:* Valley, J.W., Cole, C.V. (eds.), *Stable isotope geochemistry*. Reviews in mineralogy and geochemistry. Mineralogical Society of America and Geochemical Society, Washington, USA.

Alvaro, A., Velasco, F., 2009. *Stable isotope composition of acid mine drainage minerals from San Miguel massive sulphide mine wastes (Iberian Pyrite Belt, Spain)*, ICARD 2009: Proceedings from the 8th International Conference on Acid Rock Drainage, Skelleftea, Sweden.

Alvaro Gallo, A., Velasco Roldan, F., 2008. Isotopic fractionation of sulphur during precipitation of iron sulphate minerals from Acid Mine Drainage (San Miguel Mine, IPB). *MACLA*, **10**: 105-106.

Amos, P.W., Younger, P.L., 2003. Substrate characterisation for a subsurface reactive barrier to treat colliery spoil leachate. *Water Research*, **37**: 108-120.

Anderson, B., Scalan, R.S., Behrens, E.W., Parker, P.L., 1992. Stable carbon isotope variations in sediment from Baffin Bay, Texas, USA: Evidence for cyclic changes in organic matter source. *Chemical Geology*, **101**: 223-233.

Asta, M.P., Ayora, C., Román-Ross, G., Cama, J., Acero, P., Gault, A.G., Charnock, J.M., Bardelli, F., 2010. Natural attenuation of arsenic in the Tinto Santa Rosa acid stream (Iberian Pyritic Belt, SW Spain): The role of iron precipitates. *Chemical Geology*, **271**(1-2): 1-12.

Atekwana, E.A., Krishnamurthy, R.V., 2004. Extraction of dissolved inorganic carbon (DIC) in natural waters for isotopic analyses. *In:* de Groot, P.A. (ed.), *Handbook of stable isotope analytical techniques*. Elsevier, London.

Atlas, R.M., Bartha, R., 1993. Biogeochemical cycling: Nitrogen, sulfur, phosphorus, iron, and other elements. *In:* Atlas, R.M., Bartha, R. (eds.), *Microbial ecology: Fundamentals and applications*. Benjamin Cummings Publishing, Redwood City.

Ávila, P.F., Ferreira da Silva, E., Salgueiro, A.R., Farinha, J.A., 2008. Geochemistry and mineralogy of mill tailings impoundments from the Panasqueira Mine (Portugal):

Implications for the surrounding environment. *Mine Water and the Environment*, **27**(4): 210-224.

Baioumy, H., 2010. Sulfur geochemistry of Jurassic high-sulfur coals from Egypt. *Chemie der Erde*, **70**(1): 61-67.

Baker, J.P., Schofield, C.L., 1982. Aluminium toxicity to fish in acidic waters. *Water Air and Soil Pollution*, **18**: 289-309.

Balci, N., Mandernack, K.W., Shanks, W.C., III, 2007a. *Effect of sulfide mineralogy on isotopic composition of sulfate: Implications for acid mine drainage (AMD) formation*. *In:* Loredo Lopez, J. (ed.), 23rd International Applied Geochemistry Symposium (IAGS). Departamento de Explotacíon y Prospección de Minas, University of Oviedo, Oviedo.

Balci, N., Shanks , W.C., III, Mayer, B., Mandernack, K.W., 2007b. Oxygen and sulfur isotope systematics of sulfate produced by bacterial and abiotic oxidation of pyrite. *Geochimica et Cosmochimica Acta*, **71**: 3796-3811.

Banks, S.B., 2002. *The Coal Authority mine water treatment programme: An update on performance of operational schemes*. *In:* Nuttall, C.A. (ed.), Mine Water Treatment: A Decade of Progress, Newcastle, United Kingdom, 79-83.

Barnes, A., Sapsford, D.J., Dey, M., Williams, K.P., 2009. Heterogeneous Fe(II) oxidation and zeta potential. *Journal of Geochemical Exploration*, **100**(2-3): 192-198.

Barnhisel, R.I., Powell, J.L., Akin, G.W., Ebelhar, M.W., 1982. *Characteristics and reclamation of acid sulphate mine spoils*. *In:* Kittrick, J.A., Fanning, D.S., Hossner, L.R. (eds.), Acid Sulfate Weathering. Soil Science Society of America, Fort Collins, Colorado, 225-234.

Barton, C.D., Karathanasis, A.D., 1999. Renovation of a failed constructed wetland treating acid mine drainage. *Environmental Geology*, **39**(1): 39-50.

Batty, L., Hooley, D., Younger, P., 2008. Iron and manganese removal in wetland treatment systems: Rates, processes and implications for management. *Science of The Total Environment*, **394**(1): 1-8.

Becaria, A., Lahiri, D.K., Bondy, S., Chen, D., Hamadeh, A., Li, H., Taylor, R., Campbell, A., 2006. Aluminium and copper in drinking water enhance inflammatory or oxidative events specially in the brain. *Journal of Neuroimmunology*, **176**: 16-23.

Benson, B., Krause, D., 1984. The concentration and isotopic fractionation of oxygen dissolved in freshwater and seawater in equilibrium with the atmosphere. *Limnology and Oceanography*, **29**(3): 620-632.

Berner, R.A., 1970. Sedimentary pyrite formation. *American Journal of Science*, **268**: 1-23.

Berner, R.A., Leeuw, J.W.D., Spiro, B., Murchison, D.G., Eglinton, G., 1985. Sulphate reduction, organic matter decomposition and pyrite formation [and Discussion]. *Philosophical Transactions of the Royal Society of London. Series A, Mathematical and Physical Sciences (1934-1990)*, **315**(1531): 25-38.

Bhattacharya, J., Ji, S., Lee, H., Cheong, Y., Yim, G., Min, J., Choi, Y., 2008. Treatment of acidic coal mine drainage: Design and operational challenges of Successive Alkalinity Producing Systems. *Mine Water and the Environment*, **27**(1): 12-19.

Bigham, J.M., Schwertmann, U., Carlson, L., Murad, E., 1990. A poorly crystallized oxyhydroxysulfate of iron formed by bacterial oxidation of Fe(II) in acid mine waters. *Geochimica et Cosmochimica Acta*, **54**: 2743-2758.

Bigham, J.M., Schwertmann, U., Pfab, G., 1996a. Influence of pH on mineral speciation in a bioreactor simulating acid mine drainage. *Applied Geochemistry*, **11**(6): 845-849.

Bigham, J.M., Schwertmann, U., Traina, S.J., Winland, R.L., Wolf, M., 1996b. Schwertmannite and the chemical modeling of iron in acid sulfate waters. *Geochimica et Cosmochimica Acta*, **60**(12): 2111-2121.

Bigham, J.M., Nordstrom, D.K., 2000. Iron and aluminium hydroxysulfates from acid sulfate waters. *In:* Alpers, C.N., Jambor, J.L., Nordstrom, D.K. (eds.), *Sulfate minerals: Crystallography, geochemistry, and environmental significance*. Reviews in mineralogy and geochemistry. Mineralogical Society of America, Geochemical Society, Washington.

Billon, G., Ouddane, B., Laureyns, J., Boughriet, A., 2001. Chemistry of metal sulfides in anoxic sediments. *Physical Chemistry Chemical Physics*, **3**: 3586-3592.

Billon, G., Ouddane, B., Recourt, P., Boughriet, A., 2002. Depth variability and some geochemical characteristics of Fe, Mn, Ca, Mg, Sr, S, P, Cd and Zn in anoxic sediments from Authie Bay (Northern France). *Estuarine, Coastal and Shelf Science*, **55**(2): 167-181.

Bird, G., Brewer, P.A., Macklin, M.G., Nikolova, M., Kotsev, T., Mollov, M., Swain, C., 2010. Dispersal of contaminant metals in the mining-affected Danube and Maritsa drainage basins, Bulgaria, Eastern Europe. *Water Air and Soil Pollution*, **206**(1-4): 105-127.

Blowes, D.W., Jambor, J.L., 1990. The pore-water geochemistry and the mineralogy of the vadose zone of sulfide tailings, Waite Amulet, Quebec, Canada. *Applied Geochemistry*, **5**(3): 327-346.

Bologo, V., Maree, J.P., Zvinowanda, C.M., 2009. Treatment of acid mine drainage using magnesium hydroxide, International Mine Water Conference 2009, Pretoria, South Africa.

Bonneville, S., Behrends, T., van Cappellen, P., 2009. Solubility and dissimilatory reduction kinetics of iron(III) oxyhydroxides: A linear free energy relationship. *Geochimica et Cosmochimica Acta*, **73**(18): 5273-5282.

Botha, M., Bester, L., Hardwick, E., 2009. *Removal of uranium from mine water using ion exchange at Driefontein mine*, International Mine Water Conference, Pretoria, South Africa.

Böttcher, M.E., Rusch, A., Höpner, T., Brumsack, H.-J., 1997. Stable sulfur isotope effects related to local intense sulfate reduction in a tidal sandflat (southern North Sea): Results from loading experiments. *Isotopes Environmental Health Studies*, **33**: 109-129.

Böttcher, M.E., H.-J, B., de Lange, G.J., 1998a. *Sulfate reduction and related stable isotope (^{34}S, ^{18}O) variations in interstitial waters from the eastern Mediterranean. In:* Robertson, A.H.F., Emeis, K.-C., Richter, C., Camerle, A. (eds.), Ocean Drilling Program, Scientific Results College Station, TX, USA, 365-373.

Böttcher, M.E., Smock, A.M., Cypionka, H., 1998b. Sulfur isotope fractionation during experimental precipitation of iron(II) and manganese(II) at room temperature. *Chemical Geology*, **146**: 127-134.

Böttcher, M.E., Bernasconi, S.M., Brumsack, H.-J., 1999. *Carbon, sulfur, and oxygen isotope geochemistry of interstitial waters from the western Mediterranean. In:* Zahn, R., Comas, M.C., Klaus, A. (eds.), Ocean Drilling Program, Scientific Results College Station, TX, USA, 413–421.

Böttcher, M.E., Hespenheide, B., Llobet-Brossa, E., Beardsley, C., Larsen, O., Schramm, A., Wieland, A., Böttcher, G., Berninger, U.-G., Amann, R., 2000. The biogeochemistry, stable isotope geochemistry, and microbial community structure of a temperate intertidal mudflat: An integrated study. *Continental Shelf Research*, **20**(12-13): 1749-1769.

Böttcher, M.E., Lepland, A., 2000. Biogeochemistry of sulfur in a sediment core from the west-central Baltic Sea: Evidence from stable isotopes and pyrite textures. *Journal of Marine Systems*, **25**: 299-312.

Böttcher, M.E., Thamdrup, B., 2001. Anaerobic sulfide oxidation and stable isotope fractionation associated with bacterial sulfur disproportionation in the presence of MnO_2. *Geochimica et Cosmochimica Acta*, **65**(10): 1573-1581.

Böttcher, M.E., Thamdrup, B., Vennemann, T.W., 2001. Oxygen and sulfur isotope fractionation during anaerobic bacterial disproportionation of elemental sulfur. *Geochimica et Cosmochimica Acta*, **65**(10): 1601-1609.

Boudreau, B.P., Westrich, J.T., 1984. The dependence of bacterial sulfate reduction on sulfate concentration in marine sediments. *Geochimica et Cosmochimica Acta*, **48**(12): 2503-2516.

Boulegue, J., Lord, C.J., Church, T.M., 1982. Sulfur speciation and associated trace metals (Fe, Cu) in the pore waters of Great Marsh, Delaware. *Geochimica et Cosmochimica Acta*, **46**(3): 453-464.

Bourrié, G., Trolard, F., Genin, J.-M.R., Jafrezic, A., Maitre, V., Adbdelmoula, M., 1999. Iron control by equilibria between hydroxy-green rust and solutions in hydromorphic soils. *Geochimica et Cosmochimica Acta*, **63**(19-20): 3417-3427.

Bowell, R.J., 2004. *A review of sulfate removal options for mine waters*. *In:* Jarvis, A.P., Dudgeon, B.A., Younger, P.L. (eds.), Mine Water 2004: Process, Policy and Progress, Newcastle, United Kingdom, 75-91.

Brodie, G.A., Hammer, D.A., Tomljanovich, D.A., 1989. Treatment of acid drainage with a constructed wetland at the Tennessee Valley Authority 950 coal mine. *In:* Hammer, D.A. (ed.), *Constructed wetlands for wastewater treatment: Municipal, industrial and agricultural*. Lewis Publishers, Chelsea.

Brown, M., Barley, B., Wood, H., 2002. *Minewater treatment technology, application and policy*. IWA, Dorchester.

Brown, M.M.E., Atkinson, K., Wilkins, C., Norton, P.J., 1994. *Contaminated mine water amelioration: Study of a long established natural wetland*. *In:* Reddish, D.J. (ed.), 5th International Mine Water Association Congress. International Mine Water Association, Nottingham, UK, 499-519.

Brüchert, V., Pratt, L.M., 1996. Contemporaneous early diagenetic formation of organic and inorganic sulfur in estuarine sediments from St. Andrew Bay, Florida, USA. *Geochimica et Cosmochimica Acta*, **60**(13): 2325-2332.

Brüchert, V., Knoblauch, C., Jørgensen, B.B., 2001. Controls on stable sulfur isotope fractionation during bacterial sulfate reducing in Arctic sediments. *Geochimica et Cosmochimica Acta*, **65**(5): 763-776.

Brunner, B., Bernasconi, S., 2005. A revised isotope fractionation model for dissimilatory sulfate reduction in sulfate reducing bacteria. *Geochimica et Cosmochimica Acta*, **69**(20): 4759-4771.

Brunner, B., Bernasconi, S.M., Kleikemper, J., Schroth, M.H., 2005. A model for oxygen and sulfur isotope fractionation in sulfate during bacterial sulfate reduction processes. *Geochimica et Cosmochimica Acta*, **69**(20): 4773-4785.

Brunner, B., Yu, J.-Y., Mielke, R.E., MacAskill, J.A., Madzunkov, S., McGenity, T.J., Coleman, M., 2008. Different isotope and chemical patterns of pyrite oxidation related to lag and exponential growth phases of *Acidithiobacillus ferrooxidans* reveal a microbial growth strategy. *Earth and Planetary Science Letters,* **270**(1-2): 63-72.

Bryan, C.G., Hallberg, K.B., Johnson, D.B., 2004. *Microbial populations in surface spoil at the abandoned Mynydd Parys copper mines. In:* Jarvis, A.P., Dudgeon, B.A., Younger, P.L. (eds.), Mine Water 2004: Process, Policy and Progress, Newcastle, United Kingdom, 107-112.

BS 7755-3.8, 1995. *Soil quality: Chemical methods: Determination of organic and total carbon after dry combustion (elementary analysis). In:* British Standards (Editor). Soil Quality: Chemical Methods.

Buil, B., Gomez, P., Gaffafon, A., Turmero, M.J., 2007. *Factors controlling mobility of heavy metals and rare earth elements in a stream affected by mine drainages (NW Spain). In:* Loredo Lopez, J. (ed.), 23rd International Applied Geochemistry Symposium (IAGS). Departamento de Explotacion y Prospeccion de Minas, University of Oviedo, Oviedo, Spain.

Burton, E.D., Bush, R.T., Sullivan, L.A., 2006a. Sedimentary iron geochemistry in acidic waterways associated with coastal lowland acid sulfate soils. *Geochimica et Cosmochimica Acta*, **70**(22): 5455-5468.

Burton, E.D., Bush, R.T., Sullivan, L.A., 2006b. Acid-volatile sulfide oxidation in coastal flood plain drains: Iron-sulfur cycling and effects on water quality. *Environmental Science and Technology,* **40**: 1217-1222.

Burton, E.D., Bush, R.T., Sullivan, L.A., Mitchell, D.R.G., 2007. Reductive transformation of iron and sulfur in schwertmannite-rich accumulations associated with acidified coastal lowlands. *Geochimica et Cosmochimica Acta*, **71**(18): 4456-4473.

Burton, E.D., Bush, R.T., Sullivan, L.A., Hocking, R.K., Mitchell, D.R.G., Johnston, S.G., Fitzpatrick, R.W., Raven, M., Mc Clure, S., Jang, L.Y., 2009. Iron-monosulfide oxidation in natural sediments: Resolving microbially mediated S transformations using XANES, electron microscopy, and selective extractions. *Environmental Science and Technology,* **43**(9): 3128-3134.

Butler, I.B., Böttcher, M.E., Rickard, D., Oldroyd, A., 2004. Sulfur isotope partitioning during experimental formation of pyrite via the polysulfide and hydrogen sulfide pathways: Implications for the interpretation of sedimentary and hydrothermal pyrite isotope records. *Earth and Planetary Science Letters*, **228**: 495-509.

Campbell, A., Hannai, D., Bondy, S.C., 2001. Differential toxicity of aluminium salts in human cell lines of neural origin: Implications for neurodegeneration. *Neurotoxicology,* **22**: 63-71.

Canfield, D., Thamdrup, B., 1993. The production of ^{34}S-depleted sulfide during bacterial disproportionation of elemental sulfur *Science*, **266**: 1973-1975.

Canfield, D.E., Raiswell, R., Bottrell, S.H., 1992. The reactivity of sedimentary iron minerals toward sulfide. *American Journal of Science,* **292**: 659-683.

Canfield, D.E., Thamdrup, B., 1994. The production of ^{34}S-depleted sulfide during bacterial disproportionation of elemental sulfur. *Science*, **266**: 1973-1975.

Canfield, D.E., Boudreau, B.P., Mucci, A., Gundersen, J.K., 1998. The early diagenetic formation of organic sulfur in the sediments of Mangrove Lake, Bermuda. *Geochimica et Cosmochimica Acta*, **62**(5): 767-781.

Canfield, D.E., 2001a. Biogeochemistry of sulfur isotopes. *In:* Valley, J.W., Cole, C.V. (eds.), *Stable isotope geochemistry*. Reviews in mineralogy and geochemistry. Mineralogical Society of America and Geochemical Society, Washington, USA.

Canfield, D.E., 2001b. Isotope fractionation by natural populations of sulfate-reducing bacteria. *Geochimica et Cosmochimica Acta*, **65**(7): 1117-1124.

Canovas, C.R., Olias, M., Nieto, J.M., Galvan, L., 2007. *Hydrgeochemistry variations along the Tinto river course (SW Spain). In:* Loredo Lopez, J. (ed.), 23rd International Applied Geochemistry Symposium (IAGS). Departamento de Explotacíon y Prospección de Minas, University of Oviedo, Oviedo.

Carmody, R.W., Plummer, L.N., Busenberg, E., Coplen, T.B., 1998. *Methods for collection of dissolved sulfate and sulfide and analysis of their sulfur isotopic composition*, U.S. Geological Survey, Reston, Virginia.

Casiot, C., Egal, M., Elbaz-Poulichet, F., Bruneel, O., Bancon-Montigny, C., Cordier, M.-A., Gomez, E., Aliaume, C., 2009. Hydrological and geochemical control of metals and arsenic in a Mediterranean river contaminated by acid mine drainage (the Amous River, France); Preliminary assessment of impacts on fish (*Leuciscus cephalus*). *Applied Geochemistry*, **24**(5): 787-799.

Chambers, L.A., Trudinger, P.A., 1979. Microbiological fractionation of stable sulphur isotopes: A review and critique. *Geomicrobiology Journal*, **1**: 249-293.

Chang, I.S., Shin, P.K., Kim, B.H., 2000. Biological treatment of acid mine drainage under sulphate-reducing conditions with solid waste materials as substrate. *Water Research*, **34**(4): 1269-1277.

Chen, K.Y., Morris, J.C., 1972. Kinetics of oxidation of aqueous sulfide by oxygen. *Environmental Science and Technology*, **6**(6): 529-537.

Chiba, H., Sakai, H., 1985. Oxygen isotope exchange rate between dissolved sulfate and water at hydrothermal temperatures. *Geochimica et Cosmochimica Acta*, **49**: 993-1000.

Clark, I., Fritz, P., 1997. *Environmental isotopes in hydrogeology*. Lewis, New York.

Clesceri, L.S., Greenberg, A.E., Rhodes Trussell, R. (eds.), 1992. *Metodos normalizados: Para el analisis de aguas potables y residuales*. Diaz de Santos S.A., Madrid.

Cline, J.D., 1969. Spectrophotometric determination of hydrogen sulfide in natural waters. *Limnology and Oceanography*, **14**(3): 454-458.

Cline, J.D., Richards, F.A., 1969. Oxygenation of hydrogen sulfide in seawater at constant salinity, temperature and pH. *Environmental Science and Technology*, **3**(9): 838-843.

Cocos, I.A., Zagury, G.J., Clement, B., Samson, R., 2002. Multiple factor design for reactive mixture selection for use in reactive walls in mine drainage treatment. *Water Research*, **36**(1): 167-177.

Coleman, M.L., Moore, M.P., 1978. Direct reduction of sulfates to sulfur dioxide for isotopic analysis. *Analytical Chemistry*, **50**(11): 1594-1595.

Cooper, D.J., Cooper, W.J., de Mello, W.Z., Saltzman, E.S., Zika, R.G., 1989. *Variability in biogenic sulfur emissions from Florida wetlands. In:* Saltzman, E.S., Cooper, W.J. (eds.), Biogenic sulfur in the environment: ACS symposium series. American Chemical Society, Washington, DC, 31-43.

Cornell, R.M., Schwertmann, U., 2003. *The iron oxides: Structure, properties, reactions, occurrences and uses*. Wiley-VCH, Weinheim.

Cornwell, J.C., Morse, J.W., 1987. The characterization of iron sulfide minerals in anoxic marine sediments. *Marine Chemistry*, **22**(2-4): 193-206.

Cornwell, J.C., Sampou, P.A., 1995. Environmental controls on iron sulfide mineral formation in a coastal plain estuary. *In:* Vairavamurthy, M.A., Schoonen, M.A.A. (eds.), *Geochemical transformations of sedimentary sulfur*. American Chemical Society, Washington, D.C.

Craig, H., 1961. Isotopic variations in meteoric waters. *Science*, **133**: 1702-1703.

Cravotta , C.A., 2008a. Dissolved metals and associated constituents in abandoned coal-mine discharges, Pennsylvania, USA. Part 1: Constituent quantities and correlations. *Applied Geochemistry*, **23**(2): 166-202.

Cravotta , C.A., 2008b. Dissolved metals and associated constituents in abandoned coal-mine discharges, Pennsylvania, USA. Part 2: Geochemical controls on constituent concentrations. *Applied Geochemistry*, **23**(2): 203-226.

Cruz Viggi, C., Pagnanelli, F., Cibati, A., Uccelletti, D., Palleschi, C., Toro, L., 2010. Biotreatment and bioassessment of heavy metal removal by sulphate reducing bacteria in fixed bed reactors. *Water Research*, **44**(1): 151-158.

Danehy, T.P., Hilton, T., Watzlaf, G.R., Johnson, F., Busler, S.L., Denholm, C.F., Dunn, M.H., 2001. *Advancement in vertical flow-hybrid passive treatment systems*, West Virginia Surface Mine Drainage Task Force Symposium, Morgantown, USA.

Dansgaard, W., 1964. Stables isotopes in precipitation. *Tellus*, **16**: 436-468.

Das, A., Krishnaswami, S., Bhattacharya, S.K., 2005. Carbon isotope ratio of dissolved inorganic carbon (DIC) in rivers draining the Deccan Traps, India: Sources of DIC and their magnitudes. *Earth and Planetary Science Letters*, **236**(1-2): 419-429.

Davison, W., Lishman, J.P., Hilton, J., 1985. Formation of pyrite in freshwater sediments: Implications for C/S ratios. *Geochimica et Cosmochimica Acta*, **49**(7): 1615-1620.

de Groot, P.A., 2009a. Hydrogen. *In:* de Groot, P.A. (ed.), *Handbook of stable isotope analytical techniques*. Elsevier, London.

de Groot, P.A., 2009b. Oxygen. *In:* de Groot, P.A. (ed.), *Handbook of stable isotope analytical techniques*. Elsevier, London.

de Lange, H.J., van Griethuysen, C., Koelmans, A.A., 2008. Sampling method, storage and pretreatment of sediment affect AVS concentrations with consequences for bioassay responses. *Environmental Pollution*, **151**(1): 243-251.

de Vos, W., Tarvainen, T., 2006. *Geochemical atlas of Europe. Part 2: Interpretation of geochemical maps, additional tables, figures, maps, and related publications*. Espoo: Geological Survey of Finland.

Demchak, J., Morrow, T., Skousen, J., 2001. Treatment of acid mine drainage by four vertical flow wetlands in Pennsylvania. *Geochemistry: Exploration, Environment and Analysis*, **1**(1): 71-80.

Dent, D.L., Pons, L.J., 1995. A world perspective on acid sulphate soils. *Geoderma*, **67**: 263-276.

Desborough, G.A., Smith, K.S., Lowers, H.A., Swayze, G.A., Hammarstrom, J.M., Diehl, S.F., Leinz, R.W., Driscoll, R.L., 2010. Mineralogical and chemical characteristics of some natural jarosites. *Geochimica et Cosmochimica Acta*, **74**(3): 1041-1056.

Detmers, J., Brüchert, V., Habicht, K.S., Kuever, J., 2001. Diversity of sulfur isotope fractionations by sulfate-reducing prokaryotes. *Applied and Environmental Microbiology*, **67**(2): 888-894.

Deuser, W.G., Degens, E.T., 1967. Carbon isotope fractionation in the system $CO_{2(gas)}$-$CO_{2(aqueous)}$-$HCO_3^-{}_{(aqueous)}$. *Nature*, **215**(5105): 1033-1035.

Diaz, M.A., Monhemius, A.J., Narayanan, A., 1997. *Consecutive hydroxide-sulphide precipitation treatment of acid rock drainage*, 4th International Conference on Acid Rock Drainage, Vancouver, Canada, 1179-1193.

Doctor, D.H., Kendall, C., Sebestyen, S.D., Shanley, J.B., Ohte, N., Boyer, E.W., 2008. Carbon isotope fractionation of dissolved inorganic carbon (DIC) due to outgassing of carbon dioxide from a headwater stream. *Hydrological Processes*, **22**(14): 2410-2423.

Dold, B., Spangenberg, J.E., 2005. Sulfur speciation and stable isotope trends of water-soluble sulfates in mine tailings profiles. *Environmental Science and Technology*, **39**(15): 5650-5656.

Donahue, M.A., Werne, J.P., Meile, C., Lyons, T.W., 2008. Modeling sulfur isotope fractionation and differential diffusion during sulfate reduction in sediments of the Cariaco Basin. *Geochimica et Cosmochimica Acta*, **72**(9): 2287-2297.

Dowuona, G.N., Mermut, A.R., Krouse, H.R., 1992. Stable isotopes in some acid sulfate soils in North America. *Soil Science Society of America Journal*, **56**: 1646-1653.

Duan, W.-M., Coleman, M.L., Pye, K., 1997. Determination of reduced sulphur species in sediments: An evaluation and modified technique. *Chemical Geology*, **141**(3-4): 185-194.

Dutrizac, J.E., Jambor, J.L., 2000. Jarosites and their application in hydrometallurgy. *In:* Alpers, C.N., Jambor, J.L., Nordstrom, D.K. (eds.), *Sulfate minerals: Crystallography, geochemistry, and environmental significance*. Reviews in mineralogy and geochemistry. Mineralogical Society of America, Geochemical Society, Washington.

Edraki, M., Golding, S.D., Baublys, K.A., Lawrence, M.G., 2005. Hydrochemistry, mineralogy and sulfur isotope geochemistry of acid mine drainage at the Mt. Morgan mine environment, Queensland, Australia. *Applied Geochemistry*, **20**(4): 789-805.

Edwards, P.J., Bolton, C.P., Ranson, C., Smith, A.C., 1997. *The river Pelenna minewater treatment project*, Abandoned Mines: Problems and Solutions. Environment Agency, Sheffield, UK, 18-24.

Eger, P., Melchert, D., Antonson, D., Wagner, J., 1993. The use of wetland treatment to remove trace metals from mine drainage. *In:* Moshiri, G.A. (ed.), *Constructed wetlands for water quality improvements*. CRC Press, Boca Raton.

Ehrlich, H.L., 1996. Biogenesis and biodegradation of sulfide minerals on the Earth's surface, *Geomicrobiology*. Marcel Dekker, New York.

Eppinger, R.G., Fuge, R., 2009. Natural low-pH environments unaffected by human activity. *Applied Geochemistry*, **24**(2): 189-190.

Epstein, S., Mayeda, T., 1953. Variation of O^{18} content of waters from natural sources. *Geochimica et Cosmochimica Acta*, **4**: 213-224.

Fabian, D., Aplin, A.C., Younger, P.L., 2005. *Geochemical performance of a Reducing and Alkalinity-Producing System (RAPS) for the passive treatment of acidic mine drainage at Bowden Close, United Kingdom. In:* Loredo, J., Pendas, F. (eds.), Mine Water: Mine Closure, Oviedo, Spain, 383-387.

Fabian, D., Jarvis, A.P., Younger, P.L., Harries, N.D., 2006a. *Contaminated land: Applications in real environments (CL:AIRE)*, London, 38.

Fabian, D., Pérez-López, R., Miguel Sarmiento, A., Aplin, A.C., 2006b. *Geochemical and mineralogical insights into processes governing passive treatment of acidic mine drainage*, 4th Mine Water Interdisciplinary Network of Europe Workshop on Hardpan Formation and Waste Rock Geochemistry and Hydrology, Kjeoy, Norway, 5.

Farquhar, G.D., Ehleringer, J.R., Hubick, K.T., 1989. Carbon isotope discrimination and photosynthesis. *Annual Review of Plant Physiology and Plant Molecular Biology,* **74**: 503-537.

Farquhar, J., Canfield, D.E., Masterson, A., Bao, H., Johnston, D., 2008. Sulfur and oxygen isotope study of sulfate reduction in experiments with natural populations from Faellestrand, Denmark. *Geochimica et Cosmochimica Acta,* **72**(12): 2805-2821.

Field, C.W., Gustafson, L.B., 1976. Sulfur isotopes in the porphyry copper deposit at El Salvador, Chile. *Economic Geology,* **71**: 1533-1548.

Fike, D.A., Grotzinger, J.P., 2008. A paired sulfate-pyrite $\delta^{34}S$ approach to understanding the evolution of the Ediacaran-Cambrian sulfur cycle. *Geochimica et Cosmochimica Acta,* **72**(11): 2636-2648.

Fischer, C., Karius, V., Lüttge, A., 2009. Correlation between sub-micron surface roughness of iron oxide encrustations and trace element concentrations. *Science of The Total Environment*, **407**(16): 4703-4710

Forsberg, B.R., Araujo-Lima, C.A.R.M., Martinelli, L.A., Victoria, R.L., Bonassi, J.A., 1993. Autotrophic carbon sources for fish of the central Amazon. *Ecology,* **74**(3): 644-652.

Fortin, D., Langley, S., 2005. Formation and occurrence of biogenic iron-rich minerals. *Earth-Science Reviews,* **72**(1-2): 1-19.

Fritz, P., Basharmal, G.M., Drimmie, R.J., Ibsen, J., Qureshi, R.M., 1989. Oxygen isotope exchange between sulphate and water during bacterial reduction of sulphate. *Chemical Geology*, **79**: 99-105.

Frostman, T.M., 1993. A peat / wetland treatment approach to acidic mine drainage abatement. *In:* Moshiri, G.A. (ed.), *Constructed wetlands for water quality improvements*. CRC Press, Boca Raton.

Fry, B., Ruf, W., Gest, H., Hayes, J.M., 1988. Sulfur isotope effects associated with oxidation of sulfide by O_2 in aqueous solution. *Chemical Geology,* **73**: 205-210.

Gammons, C.H., Frandsen, A.K., 2001. *Fate and transport of metals in H_2S-rich waters at a treatment wetland*, Geochemical Transactions, 15.

Gammons, C.H., Duaime, T.E., Parker, S.R., Poulson, S.R., Kennelly, P., 2010. Geochemistry and stable isotope investigation of acid mine drainage associated with abandoned coal mines in central Montana, USA. *Chemical Geology*, **269**(1-2): 100-112.

Gat, J.R., 1996. Oxygen and hydrogen isotopes in the hydrologic cycle. *Annual Review of Earth and Planetary Sciences,* **24**(1): 225-262.

Gavelin, S., Parvel, A., Ryhage, R., 1960. Sulfur isotope fractionation in sulfide mineralization. *Economic Geology*, **55**: 510-530.

Giraldi, D., de'Michieli Vitturi, M., Zaramella, M., Marion, A., Iannelli, R., 2009. Hydrodynamics of vertical subsurface flow constructed wetlands: Tracer tests with rhodamine WT and numerical modelling. *Ecological Engineering*, **35**(2): 265-273.

Glocker, E.F., 1853. Über den Eisensinter von Obergund bei Zuckmantel. *Poggendorff's Annalen Physik Chemie,* **89**: 189-220.

Goevert, D., Conrad, R., 2008. Carbon isotope fractionation by sulfate-reducing bacteria using different pathways for the oxidation of acetate. *Environmental Science and Technology*, **42**(21): 7813-7817.

Goevert, D., Conrad, R., 2010. Stable carbon isotope fractionation by acetotrophic sulfur-reducing bacteria. *FEMS Microbiology Ecology*, **71**(2): 218-225.

Goldhaber, M.B., Kaplan, I.R., 1975. Apparent dissociation constants of hydrogen sulfide in chloride solutions. *Marine Chemistry*, **3**(2): 83-104.

Goldhaber, M.B., Kaplan, I.R., 1982. *Controls and consequences of sulfate reduction rates in recent marine sediments*. *In:* Kittrick, J.A., Fanning, D.S., Hossner, L.R. (eds.), Acid Sulfate Weathering. Soil Science Society of America, Fort Collins, Colorado, 19-36.

Guo, M., Chorover, J., Rosario, R., Fox, R.H., 2001. Leachate chemistry of field-weathered spent mushroom substrate. *Journal of Environmental Quality*, **30**: 1699-1709.

Habicht, K.S., Canfield, D.E., 1997. Sulfur isotope fractionation during bacterial sulfate reduction in organic-rich sediments. *Geochimica et Cosmochimica Acta*, **61**(24): 5351-5361.

Hackley, K.C., Anderson, T.F., 1986. Sulfur isotopic variations in low-sulfur coals from the Rocky Mountain region. *Geochimica et Cosmochimica Acta*, **50**: 1703-1713.

Halas, S., Szaran, J., Czarnacki, M., Tanweer, A., 2007. Refinements in $BaSO_4$ to CO_2 preparation and $\delta^{18}O$ calibration of the sulfate reference materials NBS-127, IAEA SO-5 and IAEA SO-6. *Geostandards and Geoanalytical Research*, **31**(1): 61-68.

Hammack, R.W., Hedin, R.S., 1989. *Microbial sulfate reduction for the treatment of acid mine drainage: A laboratory study*, 9th Annual West Virginia Surface Mine Drainage Task Force Symposium, Morgantown, USA.

Hammer, D.A., Bastian, R.K., 1989. Wetlands ecosystems: Natural water purifiers ? *In:* Hammer, D.A. (ed.), *Constructed wetlands for wastewater treatment: Municipal, industrial and agricultural*. Lewis Publishers, Chelsea.

Hancock, S., 2005. *Quantifying ochre arisings: Output from the UK Coal Authority's mine water treatment sites*. *In:* Loredo, J., Pendás, F. (eds.), Mine Water 2005: Mine Closure, Oviedo, Spain, 395-402.

Harrison, A.G., Thode, H.G., 1958. Mechanisms of the bacterial reduction of sulphate from isotope fractionation studies. *Transactions of the Faraday Society*, **54**: 84-92.

Hartman, M., Nielsen, H., 1969. δ^{34}-Werte in rezenten Meeressedimenten und ihre Deutung am Beispiel einiger Sedimentprofile aus der westlichen Ostsee. *Geologische Rundschau*, **58**: 621-655.

Haubrich, F., Tichomirowa, M., 2002. Sulfur and oxygen isotope geochemistry of acid mine drainage: The polymetallic sulfide desposit "Himmelfahrt Fundgrube" in Freiberg (Germany). *Isotopes Environmental Health Studies*, **38**(2): 121-138.

Havas, M., Likens, G.E., 1985. *Changes in Na influx and outflux in Daphnia magna as a function of elevated Al concentrations in soft water at low pH*, Proceedings of the National Academy of Science, 7345-7349.

Havens, K.E., Heath, R.T., 1989. Acid and aluminum effects on freshwater zooplankton: An in situ Mesocosm study. *Environmental Pollution*, **62**(2-3): 195-211.

Havens, K.E., Heath, R.T., 1990. Phytoplankton succession during acidification with and without increasing aluminum levels. *Environmental Pollution*, **68**(1-2): 129-145.

Hedin, R.S., Nairn, R.W., Kleinmann, R.L.P., 1994. *Passive treatment of coal mine drainage*. IC9389, Bureau of Mines US Department of the Interior, Washington, DC, 35.

Heidel, C., Tichomirowa, M., Junghans, M., 2009. The influence of pyrite grain size on the final oxygen isotope difference between sulphate and water in aerobic pyrite oxidation experiments. *Isotopes Environmental Health Studies*, **45**(4): 321-342.

Hem, J.D., 1985. *Study and interpretation of the chemical characteristics of natural water*. U.S. Geological Survey.

Henrot, J., Wieder, R.K., 1990. Processes of iron and manganese retention in laboratory peat microcosms subjected to acid mine drainage. *Journal of Environmental Quality*, **19**: 312-320.

Herbert, R.B., Benner, S.G., Blowes, D.W., 2000. Solid phase iron-sulfur geochemistry of a reactive barrier for treatment of mine drainage. *Applied Geochemistry*, **15**: 1331-1343.

Hinman, N.W., Kotler, J.M., Yan, B., Tenesch, A., Morris, R.V., Tveter, A., Stoner, D.L., Scott, J.R., 2009. Controls on chemistry and diagenesis of naturally occurring iron-oxide phases. *Applied Geochemistry*, **24**(7): 1185-1197.

Hoefs, J., 2004. *Stable isotope geochemistry*. Springer, London.

Horita, J., Kendall, C., 2004. Stable isotope analysis of water and aqueous solutions by conventional dual-inlet mass spectrometry. *In:* de Groot, P.A. (ed.), *Handbook of stable isotope analytical techniques*. Elsevier, London.

Howard, D., Grobler, C., Robinson, R.E.G., Cole, P.M., 2009. Sustainable purification of mine water using ion exchange technology, International Mine Water Conference 2009, Pretoria, South Africa.

Howard, E.A., Emerick, J.C., Wildeman, T.R., 1989. Design and construction of a research site for passive mine drainage treatment in Idaho Springs, Colorado. *In:* Hammer, D.A. (ed.), *Constructed wetlands for wastewater treatment: Municipal, industrial and agricultural*. Lewis Publishers, Chelsea.

Hsu, J.H., Lo, S.-L., 2001. Effect of composting on characterization and leaching of copper, manganese, and zinc from swine manure. *Environmental Pollution*, **114**: 119-127.

Hsu, S.C., Maynard, J.B., 1999. The use of sulfur isotopes to monitor the effectiveness of constructed wetlands in controlling acid mine drainage. *Environmental Engineering and Policy*, **1**: 223-233.

Hubbard, C.G., Black, S., Coleman, M.L., 2009. Aqueous geochemistry and oxygen isotope compositions of acid mine drainage from the Río Tinto, SW Spain, highlight inconsistencies in current models. *Chemical Geology*, **265**(3-4): 321-334.

Huminicki, D.M.C., Rimstidt, J.D., 2008. Neutralization of sulfuric acid solutions by calcite dissolution and the application to anoxic limestone drain design. *Applied Geochemistry*, **23**(2): 148-165.

Huntsman, B.E., Brehm Laboratory, 1986. *Sphagnum dominated man-made wetlands used for acid mine drainage abatement: Preliminary performance evaluation*, 7th Annual West Virginia Surface Mine Drainage Task Force Symposium, Morgantown, USA.

Ingvorsen, K., Zeikus, J.G., Brock, T.D., 1981. Dynamics of bacterial sulfate reduction in a eutrophic lake. *Applied and Environmental Microbiology*, **42**(6): 1029-1036.

Ivarson, K.C., Ross, G.J., Miles, N.M., 1982. *Microbiological transformation of iron and sulfur and their applications to acid sulfate soils and tidal marshes*. *In:* Kittrick, J.A., Fanning, D.S., Hossner, L.R. (eds.), Acid Sulfate Weathering. Soil Science Society of America, Fort Collins, Colorado, 57-75.

Jacob, D.L., Otte, M.L., 2004. Influence of *Typha latifolia* and fertilization on metal mobility in two different Pb-Zn mine tailings types. *Science of The Total Environment*, **333**(1-3): 9-24.

Jacobs, L., Emerson, S., Skei, J., 1985. Partitioning and transport of metals across the O_2/H_2S interface in a permanently anoxic basin: Framvaren Fjord, Norway. *Geochimica et Cosmochimica Acta*, **49**(6): 1433-1444.

Janson, E., Gzyl, G., Banks, D., 2009. The occurrence and quality of mine water in the Upper Silesian coal basin, Poland. *Mine Water and the Environment*, **28**: 232-244.

Jarvis, A., England, A., 2002. *Operational and treatment performance of a unique Reducing and Alkalinity Producing System (RAPS) for acidic leachate remediation in Lancashire, UK. In:* Merkel, B.J., Planer-Friedrich, B., Wolkersdorfer, C. (eds.), Uranium in the Aquatic Environment. Springer, Freiberg, Germany, 1019-1026.

Jarvis, A.P., Younger, P.L., 1997. Dominating chemical factors in mine water induced impoverishment of the invertebrate fauna of two streams in the Durham Coalfield, UK. *Chemistry and Ecology*, **13**: 249-270.

Jarvis, A.P., Younger, P.L., 2000. *Passive treatment of net-acidic mine waters: Field experiences in the UK*, 7th International Mine Water Association Congress. International Mine Water Association, Ustron, Poland, 398-405.

Jena, V.K., Jaiswal, N.K., Patel, K.S., 2007. *Arsenic and other toxic elements in coal leachates of Korba: A review of central India*. *In:* Loredo Lopez, J. (ed.), 23rd International Applied Geochemistry Symposium (IAGS). Departamento de Explotacíon y Prospección de Minas, University of Oviedo, Oviedo.

Ji, S., Kim, S., Ko, J., 2008. The status of the passive treatment systems for acid mine drainage in South Korea. *Environmental Geology*, **55**(6): 1181-1194.

Ji, S.W., Kim, S.J., 2008. Lab-scale study on the application of In-Adit-Sulfate-Reducing System for AMD control. *Journal of Hazardous Materials*, **160**(2-3): 441-447.

Johnson, D.B., Hallberg, K.B., 2002. Pitfalls of passive mine water treatment. *Reviews in Environmental Science and Biotechnology*, **1**: 335-343.

Johnson, D.B., Rowe, O., Kimura, S., Hallberg, K.B., 2004. *Development of an integrated microbiological approach for remediation of acid mine drainage and recovery of heavy metals*. *In:* Jarvis, A.P., Dudgeon, B.A., Younger, P.L. (eds.), Mine Water 2004: Process, Policy and Progress, Newcastle, United Kingdom, 151-157.

Johnson, D.B., Hallberg, K.B., 2005. Biogeochemistry of the compost bioreactor components of a composite acid mine drainage passive remediation system. *Science of The Total Environment*, **338**(1-2): 81-93.

Jönsson, J., Persson, P., Sjoberg, S., Lovgren, L., 2005. Schwertmannite precipitated from acid mine drainage: Phase transformation, sulphate release and surface properties. *Applied Geochemistry*, **20**(1): 179-191.

Jørgensen, B.B., 1977. The sulfur cycle of a coastal marine sediment (Limfjorden, Denmark). *Limnology and Oceanography*, **22**(5): 814-832.

Jørgensen, B.B., 1988. *Ecology of the sulphur cycle: Oxidative pathways in sediments*. *In:* Cole, J.A., Ferguson, S.J. (eds.), The nitrogen and sulphur cycles: 42nd Symposium of the

Society for General Microbiology. Society for General Microbiology, Southampton, 31-63.

Jørgensen, B.B., 1990. A thiosulfate shunt in the sulfur cycle of marine sediments. *Science*, **249**: 152-154.

Kadlec, R.H., 2000. The inadequacy of first-order treatment wetland models. *Ecological Engineering*, **15**: 105-119.

Kaksonen, A.H., Puhakka, J.A., 2007. Sulfate reduction based bioprocesses for the treatment of acid mine drainage and the recovery of metals. *Engineering in Life Sciences*, **7**(6): 541-564.

Kalin, M., 2001. Biogeochemical and ecological considerations in designing wetland treatment systems in post-mining landscapes. *Waste Management*, **21**: 191-196.

Kalin, M., Fyson, A., Wheeler, W.N., 2006. The chemistry of conventional and alternative treatment systems for the neutralization of acid mine drainage. *Science of The Total Environment*, **366**(2-3): 395-408.

Kaplan, I.R., Rittenberg, S.C., 1964. Microbiological fractionation of sulphur isotopes. *Journal of General Microbiology*, **34**: 195-212.

Kazadi, T.K., Petersen, J., 2008. Kinetic measurement of biological oxidation of ferrous iron at low ferric to ferrous ratios in a controlled potential batch reactor. *Hydrometallurgy*, **94**(1-4): 48-53.

Kelly, D.P., 1988. *Oxidation of sulphur compounds*. *In:* Cole, J.A., Ferguson, S.J. (eds.), The nitrogen and sulphur cycles: 42nd Symposium of the Society for General Microbiology. Society for General Microbiology, Southampton, 65-98.

Kelm, U., Helle, S., Matthies, R., Morales, A., 2009. Distribution of trace elements in soils surrounding the El Teniente porphyry copper deposit, Chile: The influence of smelter emissions and a tailings deposit. *Environmental Geology*, **57**(2): 365-376.

Kepler, D.A., Mc Cleary, E.C., 1994. Successive Alkalinity-Producing Systems (SAPS) for the treatment of acidic mine drainage, International Land Reclamation and Mine Drainage Conference and the 3rd International Conference on the Abatement of Acidic Drainage, Pittsburgh, USA.

Kepler, D.A., Mc Cleary, E.C., 1995. *Successive Alkalinity-Producing Systems (SAPS)*, 16th Annual West Virginia Surface Mine Drainage Task Force Symposium, Morgantown, USA.

Kepler, D.A., Mc Cleary, E.C., 1997. *Passive aluminium treatment successes*, 18th Annual West Virginia Surface Mine Drainage Task Force Symposium, Morgantown, USA.

Kim, Y.T., Yoon, H.O., Yoon, C., Woo, N.C., 2009. Arsenic species in ecosystems affected by arsenic-rich spring water near an abandoned mine in Korea. *Environmental Pollution*, **157**(12): 3495-3501.

King, E.L., 2004. *Constructed wetlands for acid mine drainage treatment: Internal processes and their sustainability*, Leeds University, Leeds, 282.

Kinniburg, D.G., Jackson, M.L., Syers, J.K., 1976. Adsorption of alkaline earth, transition and heavy metal cations by hydrous oxide gels of iron and aluminium. *Soil Science Society of America Journal*, **40**: 796-799.

Kirby, C.S., Cravotta, C.A., III, 2005a. Net alkalinity and net acidity 1: Theoretical considerations. *Applied Geochemistry*, **20**(10): 1920-1940.

Kirby, C.S., Cravotta, C.A., III, 2005b. Net alkalinity and net acidity 2: Practical considerations. *Applied Geochemistry*, **20**(10): 1941-1964.

Klusman, R.W., Machemer, S.D., 1991. Natural processes of acidity reduction and metal removal from acid mine drainage. *In:* Peters, D.C. (ed.), *Geology in coal resource utilization*. Tech Books, Fairfax.

Knöller, K., Fauville, A., Mayer, B., Strauch, G., Friese, K., Veizer, J., 2004. Sulphur cycling in an acid mining lake and its vicinity in Lusatia, Germany. *Chemical Geology*, **204**: 303-323.

Kostka, J.E., Thamdrup, B., Nohr Glud, R., Canfield, D.E., 1999. Rates and pathways of carbon oxidation in permanently cold Arctic sediments *Marine Ecology Progress Series*, **180**: 7-21.

Kroopnick, P., Craig, H., 1972. Atmospheric oxygen: Isotopic composition and solubility fractionation. *Science*, **175**: 54-55.

Kröpfelová, L., Vymazal, J., Svehla, J., Stíchová, J., 2009. Removal of trace elements in three horizontal sub-surface flow constructed wetlands in the Czech Republic. *Environmental Pollution*, **157**(4): 1186-1194.

Krouse, H.R., 1980. Sulphur isotopes in our environment. *In:* Fritz, P., Fontes, J.-C. (eds.), *Handbook of environment isotope geochemistry: I The terrestrial environment*. Elsevier, Amsterdam.

Kuyucak, N., 1999. *Acid mine drainage prevention and control options*, International Mine Water Conference, Seville, Spain.

Kwong, Y.T.J., Whitley, G., Roach, P., 2009. Natural acid rock drainage associated with black shale in the Yukon Territory, Canada. *Applied Geochemistry*, **24**(2): 221-231

Lambert, J.W., Aharon, P., 2010. Oxygen and hydrogen isotopes of rainfall and dripwater at DeSoto Caverns (Alabama, USA): Key to understanding past variability of moisture transport from the Gulf of Mexico. *Geochimica et Cosmochimica Acta*, **74**(3): 846-861.

Lavergren, U., Aström, M.E., Falk, H., Bergbäck, B., 2009. Metal dispersion in groundwater in an area with natural and processed black shale - Nationwide perspective and comparison with acid sulfate soils. *Applied Geochemistry*, **24**(3): 359-369.

Lein, A., Pimenov, N., Guillou, C., Martin, J.M., Lancelot, C., Rusanov, I., Yusupov, S., Miller, Y., Ivanov, M., 2002. Seasonal dynamics of the sulphate reduction rate on the North-western Black Sea shelf. *Estuarine, Coastal and Shelf Science*, **54**(3): 385-401.

Lenter, C.M., Mc Donald, L.M., Skousen, J.G., Ziemkiewicz, P.F., 2002. The effects of sulfate on the physical and chemical properties of actively treated acid mine drainage floc. *Mine Water and the Environment*, **21**(3): 114-120.

Li, Y.-T., Becquer, T., Dai, J., Quantin, C., Benedetti, M.F., 2009. Ion activity and distribution of heavy metals in acid mine drainage polluted subtropical soils. *Environmental Pollution*, **157**(4): 1249-1257.

Liu, C.-p., Luo, C.-l., Gao, Y., Li, F.-b., Lin, L.-w., Wu, C.-a., Li, X.-d., 2010. Arsenic contamination and potential health risk implications at an abandoned tungsten mine, southern China. *Environmental Pollution*, **158**(3): 820-826.

Lloyd, R.M., 1967. Oxygen-18 composition of oceanic sulfate. *Science*, **156**(3779): 1228-1231.

Londry, K.L., des Marais, D.J., 2003. Stable carbon isotope fractionation by sulfate-reducing bacteria. *Applied and Environmental Microbiology*, **69**(5): 2942-2949.

Lovley, D.R., Phillips, E.J.P., 1987a. Competitive mechanisms for inhibition of sulfate reduction and methane production in the zone of ferric iron reduction in sediments. *Applied and Environmental Microbiology*, **53**(11): 2636-2641.

Lovley, D.R., Phillips, E.J.P., 1987b. Rapid assay for microbially reducible ferric iron in aquatic sediments. *Applied and Environmental Microbiology*, **53**(7): 1536-1540.

Lovley, D.R., Phillips, E.J.P., 1988. Novel mode of microbial energy metabolism: Organic carbon oxidation coupled to dissimilatory reduction of iron or manganese. *Applied and Environmental Microbiology*, **54**(6): 1472-1480.

Luther, G.W., III, 2005. Acid volatile sulfide: A comment. *Marine Chemistry*, **97**(3-4): 198-205.

Lyew, D., Sheppard, D., 1997. Effects of physical parameters of a gravel bed on the activity of sulphate-reducing bacteria in the presence of acid mine drainage. *Journal of Chemical Technology and Biotechnology*, **70**: 223-230.

Mac Causland, A., Mc Tammany, M.E., 2007. The impact of episodic coal mine drainage pollution on benthic macroinvertebrates in streams in the Anthracite region of Pennsylvania. *Environmental Pollution*, **149**(2): 216-226.

Mac Donald, B.C.T., White, I., Astrom, M.E., Keene, A.F., Melville, M.D., Reynolds, J.K., 2007. Discharge of weathering products from acid sulfate soils after a rainfall event, Tweed River, eastern Australia. *Applied Geochemistry*, **22**(12): 2695-2705.

Machemer, S.D., Wildeman, T.R., 1992. Adsorption compared with sulfide precipitation as metal removal processes from acid mine drainage in a constructed wetland. *Journal of Contaminant Hydrology*, **9**: 115-131.

Machemer, S.D., Reynolds, J.S., Laudon, L.S., Wildeman, T.R., 1993. Balance of S in a constructed wetland built to treat acid mine drainage, Idaho Springs, Colorado, USA. *Applied Geochemistry*, **8**(6): 587-603.

Maier, U., de Biase, C., Baeder-Bederski, O., Bayer, P., 2009. Calibration of hydraulic parameters for large-scale vertical flow constructed wetlands. *Journal of Hydrology*, **369**(3-4): 260-273.

Majzlan, J., Navrotsky, A., Schwertmann, U., 2004. Thermodynamics of iron oxides: Part III. Enthalpies of formation and stability of ferrihydrite ($\sim Fe(OH)_3$), schwertmannite ($\sim FeO(OH)_{3/4}(SO_4)_{1/8}$), and e-$Fe_2O_3$. *Geochimica et Cosmochimica Acta*, **68**(5): 1049-1059.

Mäkinen, J., Lerssi, J., 2007. Characteristics and seasonal variation of sediments in Lake Junttiselkä, Pyhäsalmi, Finland. *Mine Water and the Environment*, **26**(4): 217-228.

Mandernack, K.W., Krouse, H.R., Skei, J.M., 2003. A stable sulfur and oxygen isotopic investigation of sulfur cycling in an anoxic marine basin, Framvaren Fjord, Norway. *Chemical Geology*, **195**(1-4): 181-200.

Mason, B., Moore, B.C., 1985. *Grundzüge der Geochemie*. Ferdinand Enke, Stuttgart, Germany.

Mataix Gonzalez, C., 1999. *Acid mine drainages treatment by passive systems: An experience in Limeisa Coal Mine (La Coruña, Spain)*, International Mine Water Conference, Seville, Spain.

Matthies, R., Aplin, A.C., Boyce, A.J., Jarvis, A.P., 2009a. *Is bacterial sulfate reduction a dominant process for the removal of iron in Reducing and Alkalinity Producing Systems?*, ICARD: Proceedings from the 8th International Conference on Acid Rock Drainage, Skelleftea, Sweden.

Matthies, R., Jarvis, A.P., Aplin, A.C., 2009b. *Performance evaluation of two RAPS in Northeast England after 4 years of monitoring*, International Mine Water Conference, Pretoria, South Africa.

Matthies, R., Aplin, A.C., Boyce, A.J., Jarvis, A.P., 2010a. *Tracking dominant alkalinity sources in a passive mine water treatment system with stable carbon isotopes*, International Mine Water Conference, Sydney, Canada.

Matthies, R., Aplin, A.C., Boyce, A.J., Jarvis, A.P., 2010b. *Stable sulfur, oxygen and carbon isotopes unravel bacterial sulfate reduction in passive mine water treatment systems* European Geosciences Union 2010, Vienna, Austria.

Matthies, R., Aplin, A.C., Jarvis, A.P., in press. Performance of a passive treatment system for net-acidic coal mine drainage over five years of operation. *Science of The Total Environment*.

Mayer, B., Krouse, H.R., 2004. Procedures for sulfur isotope abundance studies. *In:* de Groot, P.A. (ed.), *Handbook of stable isotope analytical techniques*. Elsevier, London.

Mayes, W.M., Potter, H.A.B., Jarvis, A.P., 2009. Novel approach to zinc removal from circum-neutral mine waters using pelletised recovered hydrous ferric oxide. *Journal of Hazardous Materials*, **162**(1): 512-520.

Mayes, W.M., Potter, H.A.B., Jarvis, A.P., 2010. Inventory of aquatic contaminant flux arising from historical metal mining in England and Wales. *Science of The Total Environment*, **408**(17): 3576-3583.

Mc Allan, J., Banks, D., Beyer, N., Watson, I., 2009. Alkalinity, temporary (CO_2) and permanent acidity: An empirical assessment of the significance of field and laboratory determinations on mine waters. *Geochemistry: Exploration, Environment, Analysis*, **9**(4): 299-312.

Migaszewski, Z.M., Galuszka, A., Halas, S., Dolegowska, S., Dabek, J., Starnawska, E., 2008. Geochemistry and stable sulfur and oxygen isotope ratios of the Podwisniówka pit pond water generated by acid mine drainage (Holy Cross Mountains, south-central Poland). *Applied Geochemistry*, **23**(12): 3620-3634.

Mihaljevic, Z., Ternjej, I., Stankovic, I., Kerovec, M., Kopjar, N., 2009. Application of the comet assay and detection of DNA damage in haemocytes of medicinal leech affected by aluminium pollution: A case study. *Environmental Pollution*, **157**(5): 1565-1572.

Mingee, T.J., Crites, R.W., 1989. Constructed wetlands for secondary treatment. *In:* Hammer, D.A. (ed.), *Constructed wetlands for wastewater treatment: Municipal, industrial and agricultural*. Lewis Publishers, Chelsea.

Mizutani, Y., Rafter, T.A., 1973. Isotopic behaviour of sulphate oxygen in the bacterial reduction of sulphate. *Geochemical Journal*, **6**: 183-191.

Morrison, M., Aplin, A., 2009. Redox geochemistry in organic-rich sediments of a constructed wetland treating colliery spoil leachate. *Applied Geochemistry*, **24**(1): 44-51.

Mucci, A., 2004. The behavior of mixed Ca–Mn carbonates in water and seawater: Controls of manganese concentrations in marine porewaters *Aquatic Geochemistry*, **10**(1-2): 139-169

Nairn, R., Mercer, M., 2000. Alkalinity generation and metals retention in a Successive Alkalinity Producing System. *Mine Water and the Environment*, **19**(2): 124-133.

Nakai, N., Jensen, M.L., 1964. The kinetic isotope effect in the bacterial reduction and oxidation of sulfur. *Geochimica et Cosmochimica Acta*, **28**: 1893-1912.

Neculita, C.-M., Zagury, G.J., Bussière, B., 2008. Effectiveness of sulfate-reducing passive bioreactors for treating highly contaminated acid mine drainage: II. Metal removal mechanisms and potential mobility. *Applied Geochemistry*, **23**(12): 3545-3560.

Nordstrom, D.K., 1982a. *Aqueous pyrite oxidation and the consequent formation of secondary iron minerals*. *In:* Kittrick, J.A., Fanning, D.S., Hossner, L.R. (eds.), Acid Sulfate Weathering. Soil Science Society of America, Fort Collins, Colorado, 37-56.

Nordstrom, D.K., 1982b. The effect of sulfate on aluminum concentrations in natural waters: Some stability relations in the system Al_2O_3-SO_3-H_2O at 298 K. *Geochimica et Cosmochimica Acta*, **46**(4): 681-692.

Nordstrom, D.K., 1985. *The rate of ferrous iron oxidation in a stream receiving acid mine effluent*, US Geological Survey Water-Supply, 113-119.

Nordstrom, D.K., Ball, J.W., 1986. The geochemical behaviour of aluminium in acidified surface waters. *Science*, **232**(54-56).

Nordstrom, D.K., Southam, G., 1997. Geomicrobiology of sulfide mineral oxidation. *In:* Banfield, J.F., Nealson, K.H. (eds.), *Reviews in Mineralogy*. The Mineralogical Society of America, Washington.

Nordstrom, D.K., Alpers, C.N., 1999a. Geochemistry of acid mine waters. *In:* Plumlee, G.S., Logsdon, M.J. (eds.), *The Environmental Geochemistry of Mineral Deposits, Part A: Processes, Techniques, and Health Issues*. Reviews in Economic Geology, Littleton, USA.

Nordstrom, D.K., Alpers, C.N., 1999b. *Negative pH, efflorescent mineralogy, and consequences for environmental restoration at the Iron Mountain Superfund site, California*, (NAS Colloquium) Geology, Mineralogy, and Human Welfare. National Academy of Sciences, 3455-3462.

Norton, P.J., Norton, C.J., Tyrrell, W., 1998. *The design, construction and cost of an engineered wetland for treatment of acid drainage from sulphide mineral-rich strata*. *In:* Nel, P. (ed.), Symposium on Mine Water and Environmental Impacts. International Mine Water Association, Johannesburg, South Africa, 425-432.

Parker, K., 2002. *Mine water management on a national scale: Experiences from the Coal Authority*. *In:* Nuttall, C.A. (ed.), Mine Water Treatment: A Decade of Progress, Newcastle, United Kingdom, 102-113.

Parkhurst, D.L., 1997. Geochemical mole-balance modelling with uncertain data. *Water Resources Research*, **33**(8): 1957-1970.

Pellicori, D.A., Gammons, C.H., Poulson, S.R., 2005. Geochemistry and stable isotope composition of the Berkeley pit lake and surrounding mine waters, Butte, Montana. *Applied Geochemistry*, **20**(11): 2116-2137.

Peltier, E.F., Dahl, A.L., Gaillard, J.-F., 2005. Metal speciation in anoxic sediments: When sulfides can be construed as oxides. *Environmental Science and Technology*, **39**: 311-316.

Peplow, D., Edmonds, R., 2006. Cell pathology and developmental effects of mine waste contamination on invertebrates and fish in the Methow river, Okanogan Country, Washington (USA). *Mine Water and the Environment*, **25**(4): 190-203.

Peretyazhko, T., Zachara, J.M., Boily, J.F., Xia, Y., Gassman, P.L., Arey, B.W., Burgos, W.D., 2009. Mineralogical transformations controlling acid mine drainage chemistry. *Chemical Geology*, **262**(3-4): 169-178.

Pezdic, J., 1998. *Simulation of solubility and equilibration rate of relevant coal seam: A stable isotope and chemical study*. *In:* Nel, P. (ed.), Symposium on Mine Water and Environmental Impacts. International Mine Water Association, Johannesburg, South Africa, 43-49.

Pham, A.N., Waite, T.D., 2008. Oxygenation of Fe(II) in natural waters revisited: Kinetic modeling approaches, rate constant estimation and the importance of various reaction pathways. *Geochimica et Cosmochimica Acta*, **72**: 3616-3630.

PIRAMID Consortium, 2003. *Engineering guidelines for the passive remediation of acidic and/or metalliferous mine drainage and similar wastewaters*, University of Newcastle, Newcastle, 166.

Poulton, S.W., Canfield, D.E., 2005. Development of a sequential extraction procedure for iron: Implications for iron partitioning in continentally derived particulates. *Chemical Geology*, **214**(3-4): 209-221.

Praharaj, T., Fortin, D., 2008. Seasonal variations of microbial sulfate and iron reduction in alkaline Pb-Zn mine tailings (Ontario, Canada). *Applied Geochemistry*, **23**: 3728-3740.

Price, F.T., Shieh, Y.N., 1979. Fractionation of sulfur isotopes during laboratory synthesis of pyrite at low temperatures. *Chemical Geology,* **27**: 245-253.

Prieto, G., Mery Duitama, L., 1999. *Environmental impacts and acid drainage of coal mining in Cundinamarca Department, Colombia*, International Mine Water Conference, Seville, Spain.

Prietzel, J., Mayer, B., 2005. Isotopic fractionation of sulfur during formation of basaluminite, alunite, and natroalunite. *Chemical Geology,* **215**: 525-535.

Prietzel, J., Tyufekchieva, N., Eusterhues, K., Kögel-Knabner, I., Thieme, J., Paterson, D., Mc Nulty, I., de Jonge, M., Eichert, D., Salomé, M., 2009. Anoxic versus oxic sample pretreatment: Effects on the speciation of sulfur and iron in well-aerated and wetland soils as assessed by X-ray absorption near-edge spectroscopy (XANES). *Geoderma,* **153**(3-4): 318-330.

Raiswell, R., Canfield, D.E., 1998. Sources of iron for pyrite formation in marine sediments. *American Journal of Science*, **298**: 219-245.

Rees, C.E., 1973. A steady-state model for sulphur isotope fractionation in bacterial reduction processes. *Geochimica et Cosmochimica Acta*, **37**: 1141-1162.

Rees, S.B., Bowell, R.J., 1999. *Stable isotopic modelling of the longevity of treatment processes operating in a constructed wetland for the amelioration of acid mine drainage*, Mine, Water and the Environment, Seville, Spain, 585-589.

Regenspurg, S., Brand, A., Peiffer, S., 2004. Formation and stability of schwertmannite in acidic mining lakes. *Geochimica et Cosmochimica Acta,* **68**(6): 1185-1197.

Reimann, C., de Caritat, P., 1998. *Chemical elements in the environment: Factsheets for the geochemist and environmental scientist*. Springer, London.

Riefler, R.G., Krohn, J., Stuart, B., Socotch, C., 2008. Role of sulfur-reducing bacteria in a wetland system treating acid mine drainage. *Science of The Total Environment,* **394**(2-3): 222-229.

Robertson, W.D., Murphy, A.M., Cherry, J.A., 1995. Low-cost on-site treatment of landfill leachate using infiltration beds: Preliminary field trial. *Ground Water Monitoring and Remediation,* **15**(1): 107-115.

Robinson, B.W., Kusakabe, M., 1975. Quantitative preparation of sulfur dioxide, for $^{34}S/^{32}S$ analyses, from sulfides by combustion with cuprous oxide. *Analytical Chemistry*, **47**(7): 1179-1181.

Roden, E.E., Wetzel, R.G., 1996. Organic carbon oxidation and suppression of methane production by microbial Fe(III) oxide reduction in vegetated and unvegetated freshwater wetland sediments. *Limnology and Oceanography*, **41**(8): 1733-1748.

Rondeau, V., Commenges, D., Jaqmin-Gadda, H., Dartigues, J.-F., 2000. Relation between aluminium concentrations in drinking water and Alzheimer's disease: An 8-year follow-up study. *American Journal of Epidemiology*, **152**(1): 59-66.

Rozanski, K., Araguas-Araguas, L., Gonfiantini, R., 1993. Isotopic patters in the modern global precipitation. *In:* Swart, P.K., Lohmann, K.C., McKenzie, J.A., Savin, S. (eds.), *Geophysical Monographs*.

Rüde, T.R., 2004. *Natures acid drainage laboratory: Lessons from the Rötlbach (Zillertaler Alps/ Austria)*. *In:* Jarvis, A.P., Dudgeon, B.A., Younger, P.L. (eds.), Mine Water 2004: Process, Policy and Progress, Newcastle, United Kingdom, 219-224.

Rye, R.O., Back, W., Hanshaw, B.B., Rightmire, C.T., Pearson, F.J., 1981. The origin and isotopic composition of dissolved sulfide in groundwater from carbonate aquifers in Florida and Texas. *Geochimica et Cosmochimica Acta*, **45**: 1941-1950.

Sakai, H., 1968. Isotope fractionation of sulfur compounds in hydrothermal processes. *Geochemical Journal*, **2**: 29-49.

Salminen, R., 2005. *Geochemical atlas of Europe. Part 1: Background information, methodology and maps*. Espoo: Geological Survey of Finland.

Sanchez España, J., Lopez Pamo, E., Santofimia, E., Aduvire, O., Reyes, J., Barettino, D., 2005. Acid mine drainage in the Iberian pyrite belt (Odiel river watershed, Huelva, SW Spain): Geochemistry, mineralogy and environmental implications. *Applied Geochemistry*, **20**: 1320-1356.

Sanchez España, J., Lopes Pamo, E., Santofimia Pastor, E., Reyes Andres, J., Martin Rubi, J.A., 2006. The removal of dissolved metals by hydroxysulphate precipitates during oxidation and neutralization of acid mine waters, Iberian Pyrite Belt. *Aquatic Geochemistry*, **12**: 269-298.

Saunders, J.R., Knopper, L.D., Koch, I., Reimer, K.J., 2010. Arsenic transformations and biomarkers in meadow voles (*Microtus pennsylvanicus*) living on an abandoned gold mine site in Montague, Nova Scotia, Canada. *Science of The Total Environment*, **408**(4): 829-835.

Scheffer, F., Schachtschabel, P., 2002. *Lehrbuch der Bodenkunde*. Spektrum, Heidelberg.

Seal, R.R., II, Wandless, G.A., 1997. *Stable isotope characteristics of waters draining massive sulfide deposits in the eastern United States*. *In:* Wanty, R.B., Marsh, S.P., Gough, L.P. (eds.), 4th International Symposium of Environmental Geochemistry.

Seal, R.R., II, Alpers, C.N., Rye, R.O., 2000. Stable isotope systematics of sulfate minerals. *In:* Alpers, C.N., Jambor, J.L., Nordstrom, D.K. (eds.), *Sulfate minerals: Crystallography, geochemistry, and environmental significance*. Reviews in mineralogy and geochemistry. Mineralogical Society of America, Geochemical Society, Washington.

Silver, M., 1989. Control of acid mine drainage including coal pile and ash pond seepage: Biology and chemistry of generation, prevention and abatement of acid mine drainage. *In:* Hammer, D.A. (ed.), *Constructed wetlands for wastewater treatment: Municipal, industrial and agricultural*. Lewis Publishers, Chelsea.

Silverman, M.P., 1967. Mechanism of bacterial pyrite oxidation. *Journal of Bacteriology*, **94**(4): 1046-1051.

Singer, P.C., Stumm, W., 1970. Acid mine drainage: The rate-determining step. *Science*, **167**: 1121-1123.

Skidmore, M., Sharp, M., Tranter, M., 2004. Kinetic isotopic fractionation during carbonate dissolution in laboratory experiments: Implications for detection of microbial CO_2 signatures using δ^{13}C-DIC. *Geochimica et Cosmochimica Acta*, **68**(21): 4309-4317.

Smith, B.N., Epstein, S., 1971a. Two categories of $^{13}C/^{12}C$ ratios for higher plants. *Plant Physiology*, **47**(3): 380-384.

Smith, B.N., Epstein, S., 1971b. Categories of C-13/C-12 ratios for higher plants. *Plant Physiology*, **47**: 380-410.

Smith, J.W., Batts, B.D., 1974. The distribution and isotopic composition of sulfur in coal. *Geochimica et Cosmochimica Acta*, **38**(1): 121-133.

Spratt, H.G., Morgan, M.D., Good, R.E., 1987. Sulfate reduction in peat from a New Jersey pinelands cedar swamp *Applied and Environmental Microbiology*, **53**: 1406-1411.

Stern, J., Wang, Y., Gu, B., Newman, J., 2007. Distribution and turnover of carbon in natural and constructed wetlands in the Florida Everglades. *Applied Geochemistry*, **22**(9): 1936-1948.

Stewart, D.P.C., Cameron, K.C., Cornforth, I.S., Main, B.E., 1998. Release of sulphate, potassium, calcium and magnesium from spent mushroom compost under laboratory conditions. *Biology and Fertility of Soils*, **26**: 146-151.

Stewart, D.P.C., Cameron, K.C., Cornforth, I.S., Main, B.E., 2000. Release of sulphate-sulphur, potassium, calcium and magnesium from spent mushroom compost under field conditions. *Biology and Fertility of Soils*, **31**: 128-133.

Strebel, O., Böttcher, J., Fritz, P., 1990. Use of isotope fractionation of sulfate-sulfur and sulfate-oxygen to assess bacterial desulfurication in sandy aquifer. *Journal of Hydrology*, **121**: 155-172.

Stumm, W., Morgan, J.J., 1995. *Aquatic chemistry: Chemical equilibria and rates in natural waters*. Environmental Science and Technology. Wiley, New York.

Tan, G.-L., Shu, W.-S., Zhou, W.-H., Li, X.-L., Lan, C.-Y., Huang, L.-N., 2009. Seasonal and spatial variations in microbial community structure and diversity in the acid stream draining across an ongoing surface mining site. *FEMS Microbiology Ecology*, **70**(2): 277-285.

Taylor, B.E., Wheeler, M.C., Nordstrom, D.K., 1984a. Stable isotope geochemistry of acid mine drainage: Experimental oxidation of pyrite. *Geochimica et Cosmochimica Acta*, **48**(12): 2669-2678.

Taylor, B.E., Wheeler, M.C., Nordstrom, K.D., 1984b. Isotope composition of sulphate in acid mine drainage as measure of bacterial oxidation. *Nature*, **308**(538-541).

Taylor, B.E., Wheeler, M.C., 1994. *Sulfur- and oxygen isotope geochemistry of acid mine drainage in the western United States*. *In:* Alpers, C.N., Blowes, D.W. (eds.), Environmental geochemistry of sulfide oxidation. American Chemical Society, 481-514.

Thode, H.G., Monster, J., 1965. *Sulfur-isotope geochemistry of petroleum, evaporites, and ancient seas*. *In:* American Association of Petroleum Geologists (Editor), Fluids in Subsurface Environments, 367-377.

Thurston, R.S., Mandernack, K.W., Shanks III, W.C., 2010. Laboratory chalcopyrite oxidation by Acidithiobacillus ferrooxidans: Oxygen and sulfur isotope fractionation. *Chemical Geology*, **269**(3-4): 252-261.

Tichomirowa, M., Junghans, M., 2009. Oxygen isotope evidence for sorption of molecular oxygen to pyrite surface sites and incorporation into sulfate in oxidation experiments. *Applied Geochemistry*, **24**(11): 2072-2092.

Toran, L., Harris, R.F., 1989. Interpretation of sulfur and oxygen isotopes in biological and abiological sulfide oxidation. *Geochimica et Cosmochimica Acta*, **53**: 2341-2348.

Tsukamoto, T.K., Killion, H.A., Miller, G.C., 2004. Column experiments for microbiological treatment of acid mine drainage: Low-temperature, low-pH and matrix investigations. *Water Research*, **38**(6): 1405-1418.

Turchyn, A.V., Brüchert, V., Lyons, T.W., Engel, G.S., Balci, N., Schrag, D.P., Brunner, B., 2010. Kinetic oxygen isotope effects during dissimilatory sulfate reduction: A combined theoretical and experimental approach. *Geochimica et Cosmochimica Acta*, **74**(7): 2011-2024.

Tuttle, J.H., Dugan, P.R., Macmillan, C.B., Randles, C.I., 1969a. Microbial dissimilatory sulfur cycle in acid mine water. *Journal of Bacteriology*, **97**(2): 594-602.

Tuttle, J.H., Dugan, P.R., Randles, C.I., 1969b. Microbial sulfate reduction and its potential utility as an acid mine water pollution abatement procedure. *Applied Microbiology*, **17**(2): 297-302.

Tuttle, M.L., Rice, C.A., Goldhaber, M.B., 1989. *Geochemistry of organic and inorganic sulfur in ancient and modern lacustrine environments*. *In:* Orr, W.L., White, C.M. (eds.), Geochemistry of sulfur in fossil fuels. American Chemical Society, Washington, DC, 114-148.

US EPA 3050B, 1996. *Acid digestion of sediments, sludges, and soils*. US EPA, 12.

van Breemen, N., 1982. *Genesis, morphology, and classification of acid sulfate soils in coastal plains*. *In:* Kittrick, J.A., Fanning, D.S., Hossner, L.R. (eds.), Acid Sulfate Weathering. Soil Science Society of America, Fort Collins, Colorado, 95-108.

van Damme, P.A., Hamel, Ayala, A.C., Bervoets, L., 2008. Macroinvertebrate community response to acid mine drainage in rivers of the High Andes (Bolivia). *Environmental Pollution*, **156**: 1061–1068.

van der Watt, H.v.H., Sumner, M.E., Cabrera, M.L., 1994. Heavy metals in the environment: Bioavailability of copper, manganese, and zinc in poultry litter *Journal of Environmental Quality*, **23**: 43-49.

van Hille, R., Foster, T., Storey, A., Duncan, J., Lewis, A., 2004. *Heavy metal precipitation by sulphide and bicarbonate: Evaluation methods to predict anaerobic digester overflow performance*. *In:* Jarvis, A.P., Dudgeon, B.A., Younger, P.L. (eds.), Mine Water 2004: Process, Policy and Progress, Newcastle, United Kingdom, 141-150.

van Stempvoort, D.R., Reardon, E.J., Fritz, P., 1990. Fractionation of sulfur and oxygen isotopes in sulfate soil sorption. *Geochimica et Cosmochimica Acta*, **54**: 2817-2826.

van Stempvoort, D.R., Krouse, H.R., 1994. *Controls of* $\delta^{18}O$ *in sulfate*. *In:* Alpers, C.N., Blowes, D.W. (eds.), Environmental geochemistry of sulfide oxidation. American Chemical Society, 446-480.

Verplanck, P.L., Nordstrom, D.K., Bove, D.J., Plumlee, G.S., Runkel, R.L., 2009. Naturally acidic surface and ground waters draining porphyry-related mineralized areas of the

Southern Rocky Mountains, Colorado and New Mexico. *Applied Geochemistry*, **24**(2): 255-267.

Viollier, E., Inglett, P.W., Hunter, K., Roychoudhury, A.N., van Cappellen, P., 2000. The ferrozine method revisited: Fe(II)/Fe(III) determination in natural waters. *Applied Geochemistry*, **15**(6): 785-790.

Wadham, J.L., Bottrell, S., Tranter, M., Raiswell, R., 2004. Stable isotope evidence for microbial sulphate reduction at the bed of a polythermal high Arctic glacier. *Earth and Planetary Science Letters*, **219**(3-4): 341-355.

Wagner, D.P., Fanning, D.S., Foss, J.E., Patterson, M.S., Snow, P.A., 1982. *Morphological and mineralogical features related to sulfide oxidation under natural and disturbed land surfaces in Maryland*. *In:* Kittrick, J.A., Fanning, D.S., Hossner, L.R. (eds.), Acid Sulfate Weathering. Soil Science Society of America, Fort Collins, Colorado, 109-125.

Ward, C.R. (ed.), 1984. *Coal geology and coal technology*. Blackwell Scientific Publications, Oxford.

Watson, I.A., Taylor, K., Sapsford, D.J., Banks, D., 2009. *Tracer testing to investigate hydraulic performance of a RAPS treating mine water in South Wales*, ICARD: Proceedings from the 8th International Conference on Acid Rock Drainage, Skelleftea, Sweden.

Watson, J.T., Danzig, A.J., 1993. Pilot-scale nitrification studies using vertical-flow and shallow horizontal-flow constructed wetland cells. *In:* Moshiri, G.A. (ed.), *Constructed wetlands for water quality improvements*. CRC Press, Boca Raton.

Watzlaf, G.R., Kairies, C.L., Schroeder, K.T., Danehy, T., Beam, R., 2002. *Quantitative results from the flushing of four reducing and alkalinity-producing systems*, West Virginia Surface Mine Drainage Task Force Symposium, Morgantown, USA.

WHO, 2003a. *Manganese in drinking-water: Background document for preparation of WHO Guidelines for drinking-water quality*, Geneva.

WHO, 2003b. *Aluminium in drinking-water: Background document for preparation of WHO Guidelines for drinking-water quality*, Geneva.

Wieder, R.K., Lang, G.E., 1984. Influence of wetlands and coal mining on stream water chemistry. *Water, Air and Soil Pollution*, **23**: 381-396.

Wieder, R.K., Lang, G.E., 1986. Fe, Al, Mn, and S chemistry of *Sphagnum* peat in four peatlands with different metal and sulfur input. *Water, Air and Soil Pollution*, **29**: 309-320.

Wieder, R.K., 1993. Ion input/output budgets for five wetlands constructed for acid coal mine drainage. *Water, Air and Soil Pollution*, **71**(3-4): 231-270.

Wilkin, R.T., Barnes, H.L., 1996. Pyrite formation by reactions of iron monosulfides with dissolved inorganic and organic sulfur species. *Geochimica et Cosmochimica Acta*, **60**(21): 4167-4179.

Wilkin, R.T., Barnes, H.L., Brantley, S.L., 1996. The size distribution of framboidal pyrite in modern sediments: An indicator of redox conditions. *Geochimica et Cosmochimica Acta*, **60**(20): 3897-3912.

Williams, D.J., Bigham, J.M., Cravotta, C.A., III, Traina, S.J., Anderson, J.E., Lyon, J.G., 2002. Assessing mine drainage pH from the color and spectral reflectance of chemical precipitates. *Applied Geochemistry*, **17**(10): 1273-1286.

Witthar, S.R., 1993. Wetland water treatment system. *In:* Moshiri, G.A. (ed.), *Constructed wetlands for water quality improvements*. CRC Press, Boca Raton.

Wolkersdorfer, C., Hasche, A., Göbel, J., Younger, P.L., 2005. Tracer test in the Bowden Close passive treatment system (UK): Preliminary results, 56. Berg- und Hüttenmännischer Tag: Behandlungstechnologien für bergbaubeeinflusste Wässer, Freiberg.

Wortmann, U.G., Bernasconi, S.M., Böttcher, M.E., 2001. Hypersulfidic deep biosphere indicates extreme sulfur isotope fractionation during single-step microbial sulfate reduction. *Geology*, **29**: 647-650.

Woulds, C., Ngwenya, B.T., 2004. Geochemical processes governing the performance of a constructed wetland treating acid mine drainage, Central Scotland. *Applied Geochemistry*, **19**: 1773-1783.

Wright, W.G.A., Nordstrom, D.K., 1999. Oxygen isotopes of dissolved sulfate as a tool to distinguish natural and mining-related dissolved constituents, 6th International Conference on Tailings and Mine Waste, Fort Collins, Colorado.

Wu, P., Tang, C., Liu, C., Zhu, L., Pei, T., Feng, L., 2009. Geochemical distribution and removal of As, Fe, Mn and Al in a surface water system affected by acid mine drainage at a coalfield in Southwestern China. *Environmental Geology*, **57**(7): 1457-1467.

Xiong, H., Liao, Y., Zhou, L., 2008. Influence of chloride and sulfate on formation of akaganeite and schwertmannite through ferrous biooxidation by *Acidithiobacillus ferrooxidans* cells. *Environmental Science and Technology*, **42**(23): 8681-8686.

Yanes, Y., Delgado, A., Castillo, C., Alonso, M.R., Ibanez, M., De la Nuez, J., Kowalewski, M., 2008. Stable isotope δ^{18}O, δ^{13}C, and δD signatures of recent terrestrial communities from a low-latitude, oceanic setting: Endemic land snails, plants, rain, and carbonate sediments from the eastern Canary Islands. *Chemical Geology*, **249**(3-4): 377-392.

Younger, P.L., 1997. The longevity of minewater pollution: A basis for decision-making. *Science of The Total Environment*, **194-195**: 457-466.

Younger, P.L., 1998a. *Design, construction and initial operation of full-scale compost-based passive systems for treatment of coal mine drainage and spoil leachate in the UK. In:* Nel, P. (ed.), Symposium on Mine Water and Environmental Impacts. International Mine Water Association, Johannesburg, South Africa, 413-424.

Younger, P.L., 1998b. Coalfield abandonment: Geochemical processes and hydrochemical products. *In:* Nicholson, K. (ed.), *Energy and the environment: Geochemistry of fossil, nuclear and renewable resources*. Environmental geochemistry series, vol. 1 Mac Gregor Science, Insch.

Younger, P.L., Banwart, S.A., Hedin, R.S., 2002. *Mine water: Hydrology, pollution, remediation*. Environmental Pollution, **5**. Kluwer, London.

Younger, P.L., Jayaweera, A., Elliot, A., Wood, R., Amos, P., Daugherty, A., Martin, A., Bowden, L., Aplin, A.C., Johnson, D.B., 2003. Passive treatment of acidic mine waters in subsurface-flow systems: Exploring RAPS and permeable reactive barriers. *Land Contamination and Reclamation*, **11**(2): 127-135.

Younger, P.L., Jayaweera, A., Wood, R., 2004. A full-scale Reducing and Alkalinity-Producing System (RAPS) for the passive treatment of acidic, aluminium-rich mine site drainage at Bowden Close, County Durham, CL:AIRE Annual Project Conference. University College, London.

Yu, J.-Y., Heo, B., 2001. Dilution and removal of dissolved metals from acid mine drainage along Imgok Creek, Korea. *Applied Geochemistry*, **16**(9-10): 1041-1053.

Yücel, M., Konovalov, S.K., Moore, T.S., Janzen, C.P., Luther III, G.W., 2010. Sulfur speciation in the upper Black Sea sediments. *Chemical Geology*, **269**(3-4): 364-375.

Zagury, G.J., Kulnieksa, V.I., Neculita, C.M., 2006. Characterization and reactivity assessment of organic substrates for sulphate-reducing bacteria in acid mine drainage treatment. *Chemosphere*, **64**(6): 944-954.

Zak, I., Sakai, H., Kaplan, I.R., 1980. Factors controlling the $^{18}O/^{16}O$ and $^{34}S/^{32}S$ isotope ratios of ocean sulfates, evaporites and interstital sulfates from modern deep sea sediments. *In:* Institute of Geophysics and Planetary Physics (ed.), *Isotope marine chemistry*. University of California Los Angeles.

Zeebe, R.E., 2010. A new value for the stable oxygen isotope fractionation between dissolved sulfate ion and water. *Geochimica et Cosmochimica Acta*, **74**(3): 818-828.

Zeng, G., Liang, J., Guo, S., Shi, L., Xiang, L., Li, X., Du, C., 2009. Spatial analysis of human health risk associated with ingesting manganese in Huangxing Town, Middle China. *Chemosphere*, **77**(3): 368-375.

Zhang, J., Quay, P.D., Wilbour, D.O., 1995. Carbon isotope fractionation during gas-water exchange and dissolution of CO_2. *Geochimica et Cosmochimica Acta*, **59**: 107-114.

Ziemkiewicz, P.F., Skousen, J.G., Simmons, J., 2003. Long-term performance of passive acid mine drainage treatment systems. *Mine Water and the Environment*, **22**(3): 118-129.

Zinder, S.H., Brock, T.D., 1978. *Microbial transformations of sulfur in the environment*. *In:* Nriagu, J.O. (ed.), Sulfur in the environment: Ecological impacts. Wiley, 441-466.

APPENDIX 1 – IMAGES OF THE BOWDEN CLOSE MINE WATER TREATMENT SCHEME

Figure 1 Images, taken in October 2007 and January 2008, show the Reducing and Alkalinity Producing System 1 (RAPS 1) with seasonally dependent inflow rates (A, B). The water is characterized by high turbidity and reddish colour. The water is backed up around the influent chamber rather than distributed equally throughout the RAPS. *Typha* and other wetland species have established on the system through natural succession and contribute to the accumulation of organic matter (C-F).

Figure 2 During January 2008 reddish (A) and greyish-white (B) froth was observable on the water surface of RAPS 1 near the inlet. Figure C shows the manhole chamber which collects RAPS 1 effluent water before discharge via a 58 m long subsurface drainage pipe into the polishing wetland. The effluent pipe is adjustable in order to control the height of the water cover overlying the reactive substrate (free board). In cases of high flow, a fraction of the water from the free board is discharged into the wetland via a subsurface overflow pipe (D), i.e. without having previously been in contact with the reactive substrate.

Figure 3 Contrary to RAPS 1, limited plant growth is observed on the RAPS 2 (Oct. 2007, A). Reddish and white staining are is noted in the influent (B, C, D) and on the sediment surface. The increased precipitation of ochre sludge, especially around the inlet, causes a reduction of the free boards. At ~0.5 cm below surface (E) the colour of the sediment changes to black. Overflow pipe in RAPS 2 (F).

Figure 4 The wetland is overgrown by *Typha latifolia* and *Juncus effusus* (A) and receives mine water from overflows and effluents of the RAPS (B). In addition, agricultural runoff is collected in a channel surrounding the treatment site and in seasons of high precipitation discharges additional water into the wetland (C). The wetland (D) and the outlet chamber of the wetland (E) are covered by reddish precipitates. Some staining was also observed at the final discharge point into Willington Burn (F).

APPENDIX 2 – METHODOLOGY

Preliminary Investigations

Preliminary investigations undertaken on the Bowden Close treatment scheme before October 2007 are outlined in Johnson (2007), (Figure 1). Monthly monitoring of Bowden Close surface water was conducted since December 2003 (Figure 2). Furthermore, four sediment cores were extracted from RAPS 1 and 2 in November 2004.

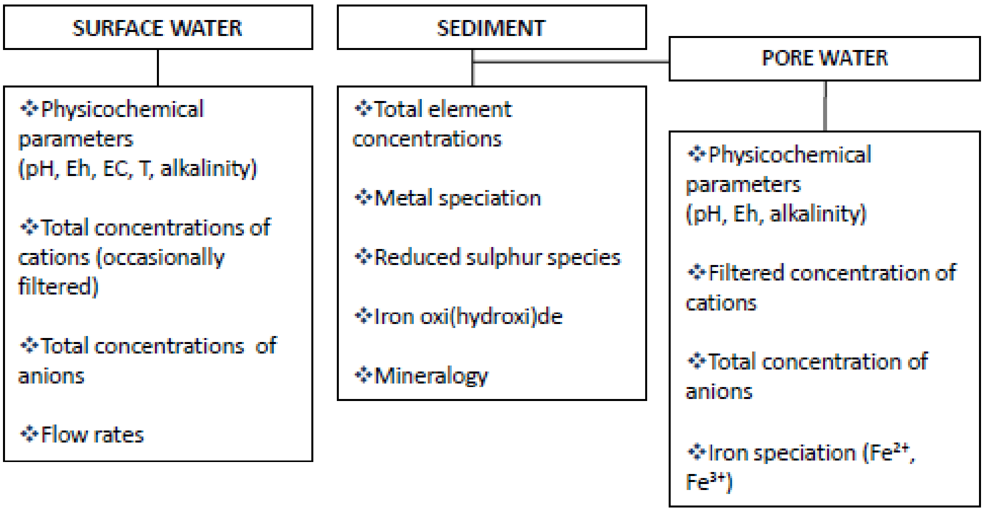

Figure 1 Preliminary work undertaken on surface water and sediment samples of the Bowden Close mine water treatment scheme; (Eh = redox potential, EC = electrical conductivity, T = temperature, cations: Ca, Mg, K, Na, Fe, Al, Zn, Mn, S, Si; anions: SO_4^{2-},Cl^-)

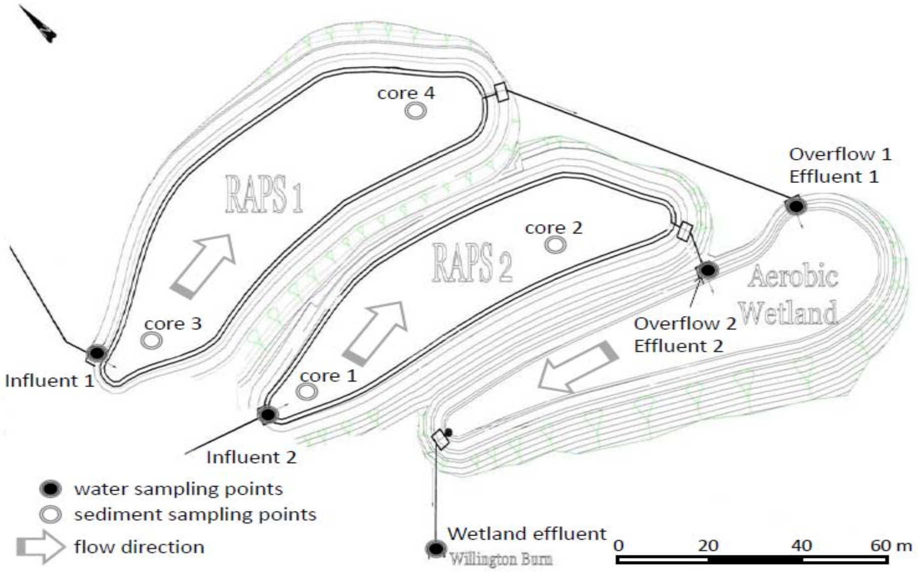

Figure 2 Sampling points of surface water and sediment cores at Bowden Close

Surface Water

As part of this study, surface water and sediments were analysed (Figure 3).

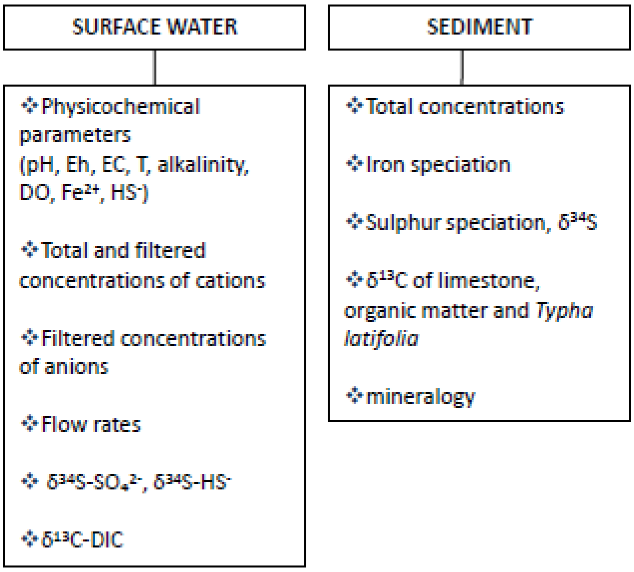

Figure 3 Methods applied on surface water and sediment samples of the Bowden Close mine water treatment scheme

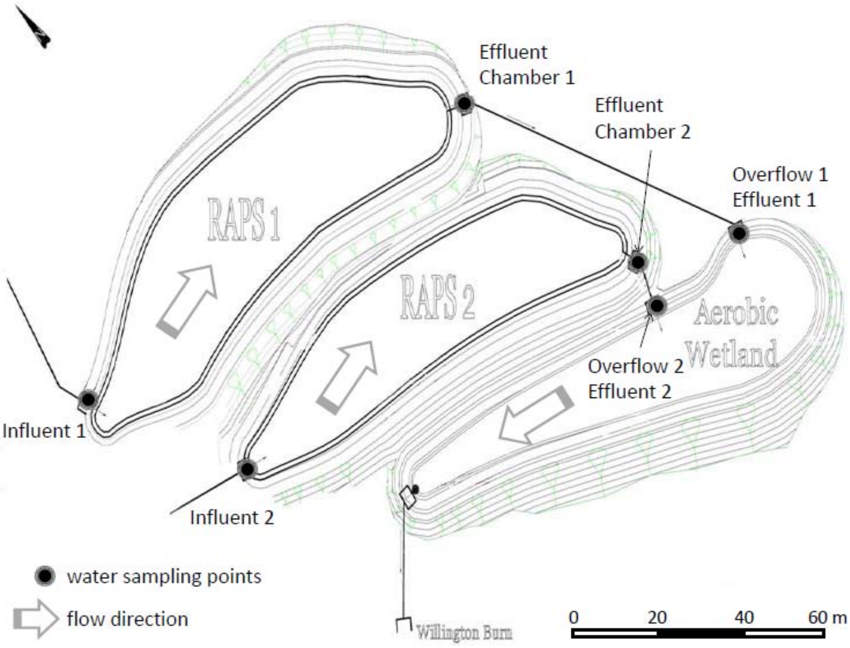

Figure 4 Water sampling during this study focused on influents, overflows and effluents of the RAPS

Between April 2008 and October 2009 a monthly surface water monitoring programme was undertaken. The sampling interval was later raised to five weeks. The main focus of the water sampling was on the treatment performance and biogeochemical processes occurring in the Reducing and Alkalinity-Producing Systems (RAPS 1 and 2). The wetland was not part of the monitoring.

The outlets of the RAPS into the aerobic wetland consist of i) an underground flow pipe, that discharges water which has passed through the compost/limestone substrate (effluent) and ii) an overflow pipe that discharges untreated free-board water in high flow events via subsurface pipes in the aerobic wetland.

On each sampling event, influents (inf) and effluents (eff) from both RAPS were monitored (Figure 4). Due to the significant short-circuiting of water over the reactive substrate it was important to include these waters in the monitoring to allow the assessment of element mass balances. Chemical characteristics of the overflow water had not been previously analysed. Overflows were sampled at their point of discharge into the aerobic wetland after partial aeration during the passage through the underground pipes. Effluents were sampled from the effluent chamber directly after leaving the underdrain. In the monitoring undertaking before, RAPS effluents had been sampled at the influent point into the aerobic wetland (Figure 2), i.e. after reaeration.

On five occasions (April -July 2008), effluents were taken in parallel from the chambers and the discharge points into the wetland to assess any water chemical differences that might have been caused through the contact with air and to enable the comparison of results obtained during the preliminary and the actual water monitoring.

Differences in water composition ranged below ±1% for most parameters, except manganese (total and filtered fraction: ±4.8%), potassium (filtered fraction: ±2.5%) and iron (filtered fraction: ±16.3%). Zinc and aluminium were mostly undetectable during the five sampling events so that comparison was limited. Reduced iron concentrations were up to 19.4% higher before partial aeration. Significant increases in dissolved oxygen (~49%) and redox potentials (~26%) possibly caused a reoxidation of ferrous iron and hydrolysis. Consequently, the particulate iron fraction (>0.45 µm) increased at the expense of the dissolved and colloidal fraction, whilst total iron concentrations (<0.45 µm) remained constant. With this in mind, the sampling of effluent water at the discharge points in the wetland was ceased. It has to be considered in future water chemical assessments that redox potentials and filtered iron concentrations obtained during the preliminary monitoring programme might differ considerably from the original state of the treated water.

Field Analysis

During each sampling event, pH, electrical conductivity (EC), temperature (T), alkalinity (Alk), dissolved oxygen (DO) and flow rates (Q) were determined. A Myron Ultrameter II was calibrated prior to each sampling (pH 4, 7 and 10, EC 1214 µS cm^{-1} standard solution). The Ultrameter measures with an accuracy of ±0.01 for pH (range: 0-14), ±1 mV for the redox potential (range ±999 mV), ±1% for the electrical conductivity (range: 0-9999 µS cm^{-1}, and 10-200 mS cm^{-1}) and ±0.1°C for the temperature (range: 0-71°C). The electrodes were cleaned with deionised water and rinsed three times with the mine water prior to each measurement. Dissolved oxygen was measured with an YSI 550A dissolved oxygen meter which was calibrated against atmospheric oxygen. Redox potentials were corrected to the standard hydrogen electrode and converted to pE (Nernst equation).

Alkalinity was determined in 0.45 µm filtered water samples by colorimetric titration with 1.6 N sulfuric acid until colour change of the bromocresol green-methyl red indicator at pH 4.5 (detection range: 10-4000 mg L^{-1} $CaCO_3$ eq, HACH AL-DT). Turbidity in influent waters made the filtration necessary, as otherwise the visual detection of the colour change would have affected end results. Alkalinities, expressed in mg L^{-1} $CaCO_3$ equivalent, were transformed into milligram per litre of the pH dependent predominant inorganic carbon species (Hounslow 1995). Physicochemical parameters were measured repeatedly to control precision. The coefficient of variance ($V = \sigma * \bar{x}^{-1} * 100\%$, relative standard deviation) for all field parameters lay within ±6%, except for alkalinity (±30%). The increased error rate for alkalinities was due to errors induced at alkalinities <10 mg L^{-1} $CaCO_3$ eq, i.e. below or close to detection limit.

Flow rates were determined in triplicate by bucket and stop watch. Since 2007, water started to back up near the influent of RAPS 1 and covered at first partially, later fully (since 2009) the inflow pipe. Therefore, flow rates of RAPS 1 influent had to be estimated by the combined flow rates of overflow 1 and effluent 1 assuming losses from evapo(transpi)ration and additions from precipitation being negligible.

Sample Collection, Preservation and Storage

Polyethylene bottles were acid washed (10% HNO_3) for 24 hours and thereafter rinsed three times with tap water and deionised water. The latter was purified with a MilliQ purification system (Elga Purelab Ultra, Ultra Scientific).

Sample bottles were filled completely to minimise oxidation reactions and maintained at 4°C and in absence of light. Any filtration was undertaken in situ and with a 0.45 µm pore size nitrate cellulose filter.

Despite the commonly applied preservation of samples for cation analysis with nitric acid (Clesceri *et al.* 1992) the application of hydrochloric acid was considered in order to allow simultaneous determination of dissolved ferrous iron. The formation of iron-chloride complexes hamper the oxidation of Fe^{2+} (Wallmann *et al.* 1993). Samples for the determination of reduced iron in the filtered fraction were preserved with hydrochloric acid (1% v/v) and determined within 4 hours.

Preservation methods using hydrochloric and nitric acids were compared to justify pooling historical and actual data. Results differed within ±6%. Outliers for aluminium (26.9%) and iron (41.7%) were identified when concentrations of both elements ranged close to detection limit (Grubb's test: $Z = |X-Y|/\sigma$; X = average, Y = value, σ = standard deviation).

Water samples for the determination of reduced sulfur concentrations in the filtered fraction were preserved with 0.5 M sodium hydroxide solution (Clesceri *et al.* 1992) to stabilize dissolved sulfur as HS^- and prevent exsolution of $H_2S_{(g)}$.

Samples for sulfate and chloride determination were filtered (<0.45 µm) and analysed within two weeks. Samples for the determination of cations (Mg, Ca, Na, K, Fe, Al, Mn, Zn, Si, and S) were preserved with reagent grade hydrochloric acid (1% v/v) and analysed within three months.

Laboratory Analyses

Reduced Iron

Ferrous iron concentrations were determined by ferrozine method (Viollier *et al.* 2000) (Genesys 6, Thermo Electron Corporation, λ=562 nm). If concentrations exceeded detection maxima, samples (and blank) were diluted 20 times, reanalysed and outputs compared to a calibration curve of diluted standards.

The spectrophotometer was calibrated with iron (II) sulfate-7-hydrate solution (250 µM, 100 µM, 50 µM, 25 µM, 5 µM, 1 µM). Ferric iron concentrations were calculated by difference between total iron of the filtered fraction and ferrous iron concentration. During each sampling event, at least one field duplicate was sampled (variance of ~±2%).

Reduced Sulfur

Reduced sulfur (including H_2S, HS^-, S^{2-}, FeS, ZnS, terminal polysulfides: S_nS^{2-}) was determined by methylene blue method (Fischer 1883, Cline 1969) (Genesys 6, λ=670 nm, iodine titration). Dissolved organic matter has not been determined as part of this study, but could potentially have caused overestimation of reduced sulfur concentrations in the effluents (Mylon and Benoit 2001).

Despite preservation and analysis no longer than 4 hours after sampling, the oxidation rate of reduced sulfur, possibly enhanced by catalytic reactions (Nriagu and Hem 1978), inhibited the detection of any reduced sulfur during the first sampling events (April-November 2008). For this reason colorimetric test kits (Microquant, range: 0.02-0.25 mg L^{-1}; Aquaquant, range: 0.1-5 mg L^{-1}; Merck KGaA, Germany) were used alongside. Results were temperature adjusted as to manufacturer's guidelines.

Aquaquant and Microquant test kit results were occasionally contradictory. Microquant indicated values above detection limit (>0.25 mg L^{-1}), Aquaquant, however, indicated values at around 0.1 mg L^{-1}. Clearly, the test kits can only give a rough indication about the range of sulfide concentrations.

During January and February 2009, a trial was undertaken to quantify dissolved sulfide in effluent waters based on different preservation techniques. Triplicates (in January) or duplicates (in February) of samples were taken and either left unpreserved or preserved with a) 1 M zinc acetate (1% v/v, (modified after Clesceri *et al.* 1992)); b) concentrated hydrochloric acid (1% v/v) or c) 0.5 M sodium hydroxide (1% v/v, only in February, (Clesceri *et al.* 1992)).

Zinc acetate (ZnAc) fixes dissolved sulfide as zinc sulfide and hampers its oxidation. Hydrochloric acid decreased the pH of the sample. The predominant sulfide specie under acid conditions, H_2S, is characterized by lower oxidation kinetics compared to pH neutral or alkaline reduced sulfur species (HS^-, S_2^-). Sodium hydroxide was used as a matter of comparison to sampling events undertaken before January 2009. All samples were filtered (<0.45 µm) and preserved in situ. Matrix matched blanks were prepared.

Results from HCl- and ZnAc- preserved samples were not significantly different but differed compared to unpreserved samples (Table 1). In sodium hydroxide preserved and unpreserved samples, sulfide concentrations were 26-64% and 66-80% lower, respectively, in comparison to ZnAc and HCl preserved samples. Possibly the catalytic oxidation of sulfide in unpreserved and sodium hydroxide preserved samples affected the outcome. Since March 2009, samples were zinc acetate preserved. Duplicates varied within ±4%.

Table 1 Sulfide concentrations in Bowden Close effluent waters using different preservation techniques

Sample	c, ZnAc	c, HCl	c, NaOH	c, unpres.
RAPS 1, Jan 09	8.62±0.43	8.71±0.12	na	2.75±0.37
RAPS 1, Feb 09	6.66±0.55	6.06±0.89	4.51±0.80	2.12±0.21
RAPS 2, Jan 09	16.37±0.39	15.93±0.52	na	3.33±0.12
RAPS 2, Feb 09	12.72±2.03	13.69±0.59	4.90±0.76	3.52±1.86

c = concentration mean in µmol L^{-1} ± standard deviation; ZnAc = preserved with 1 M zinc acetate solution (1%, v/v); HCl = preserved with concentrated hydrochloric acid (1%, v/v); NaOH = preserved with 0.5 M sodium hydroxide (1%, v/v), unpres.= unpreserved sample, na = not analysed

Cations and Anions

Anion concentrations were determined with an ion chromatograph (IC, type IC25 Dionex equipped with an AG16 guard column and an AS17 analytical column). The IC was one-point calibrated (10 mg L^{-1} Cl^-, 20 mg L^{-1} SO_4^{2-} standard solution). Duplicates, replicates and blanks were analysed after ten samples and standard checks made every three samples. If analytical results of standard checks exceeded ±5%, the IC was recalibrated (detection limits: ~0.1 mg Cl^- L^{-1}, ~0.5 mg SO_4^{2-} L^{-1}). Samples from RAPS 1 and 2 had to be diluted 50 and 100 times, respectively, to prevent overload of the IC column. Dilutions were prepared using deionised water in standardized volumetric flasks.

Cation concentrations were analysed with an Inductively Coupled Plasma – Optical Emission Spectrometer (Vista MPX, CCP Simultaneous ICP-OES, Varian). Samples were diluted 10-200 times using standardized volumetric flasks and deionised water. Blanks, standard checks, replicates and reference materials (Thames river water: LGC6019, landfill leachate: LGC6175 and riverrine water SLRS-3: National Research Council, Canada) were run every 15 samples. Detection limits were 0.01 mg L^{-1} except for aluminium (0.1 mg L^{-1}) and potassium (1 mg L^{-1}). The ICP-OES was recalibrated when the standard check differed by more than ±5%.

The ICP-OES was calibrated with standards prepared from 1000 mg L^{-1} and 10 000 mg L^{-1} (S) stock solutions. Standards and blanks were set up in a matrix of 1% hydrochloric acid (v/v). In addition, three matrix matched low sulfur standards (5, 10 and 15 mg L^{-1}) were prepared from a 1000 mg L^{-1} sulfur stock solution. The acceptance criteria for the linear calibration curve were set to ±5%. The upper limit of the linear calibration curve was set to +5% above the upper standard concentration.

Table 2 Standards used for the calibration of the ICP-OES

Element	Standards	Elements	Standards
Calcium	10 / 20 / 50	Aluminium	1 / 5 / 10
Magnesium	1 / 5 / 10	Zinc	1 / 2 / 5
Sodium	1 / 5 / 10	Silicon	1 / 10 / 20
Iron	1 / 5 / 10	Sulfur	100 / 200 / 300
Manganese	1 / 2 / 5	Potassium	5 / 25 / 50

standard 1 / 2 / 3 in mg L^{-1}

Ion balances (IA, IA=100(c-a)$(c+a)^{-1}$; c = cation and a = anion concentration in meq L^{-1}) ranged within 5±7.5%. Duplicates varied within ±7%. More than 90% of blanks analysed by ICP-OES were undetectable for all elements except sulfur (56%). For the latter, maxima of 3.2 mg L^{-1} were recorded.

Maxima of chloride and sulfate in the blank ranged at 0.54 mg L^{-1} and 1.92 mg L^{-1}, respectively. Sulfur concentrations determined by ICP-OES and IC varied within ±4%. Replicates of standard reference material varied within ±10% except for iron in SLRS3. The latter possibly was due to the low iron concentrations close to detection limit in the standard. Analysed reference concentrations compared well to original values (±10%), except for iron (SLRS3, LGC6019, RSD = 18%), potassium (LGC6019, RSD = 85%) and aluminium (LGC6019, RSD = 17%). Whilst inconsistencies for iron and aluminium were due to the generally low concentrations, the error observed for potassium is unexplained but might me due to reduced precision of the ICP-OES for this element (pers. comm. J.Davis).

Stable Isotope Analysis

Samples for sulfate sulfur ($\delta^{34}S-SO_4^{2-}$), sulfate oxygen ($\delta^{18}O-SO_4^{2-}$) and dissolved inorganic carbon stable isotope analyses ($\delta^{13}C$-TDIC) in the surface water were taken on each sampling event since April 2008. In four monitoring events during 2009, water samples were taken for $\delta D-H_2O$ and $\delta^{18}O-H_2O$. The recovery of sulfide sulfur for the isotopic determination of $\delta^{34}S-H_2S$ (includes H_2S, HS^-, S_2^-) was commenced in September 2008. Isotope analyses were undertaken at the Scottish Universities Environment Research Centre (SUERC, East Kilbride, Scotland).

Sulfur

Surface water was preserved following two approaches:

- **A:** applied between April and September 2008,
- **B:** applied since September 2008.

One litre unfiltered sample was stored in 500 mL previously acid washed (10% HNO_3 v/v) and deionised water rinsed polyethylene bottles and either kept unpreserved (A) or was preserved with 1-2 mL zinc acetate (1 M, B) to precipitate any sulfide as zinc sulfide ($ZnAcetate + HS- \rightarrow ZnS + H^+ + 2Acetate$).

Samples were stored in absence of light and at 4°C. Within 24 hours of collection, the samples were filtered (0.45 µm, cellulose nitrate filter). After acidification with concentrated hydrochloric acid (to pH <3) and heating to 50°C in a water bath to evolve CO_2, 20-40 mL $BaCl_2$ (0.25 M) were added to precipitate SO_4^{2-} as barium sulfate ($BaCl_2 + SO_4^{2-} \rightarrow BaSO_4\downarrow + 2Cl^-$). After thoroughly shaking, samples were kept in the water bath to cool down to ambient temperatures until the next day. The barium sulfate precipitate was continuously filtered on pre-weighed 0.45 µm pore size filters and washed with deionised water to remove unreacted barium chloride. Filters were reweighed after air drying and the barium sulfate homogenized, scraped into micro tubes and stored in a silica gel desiccator.

As to the low concentrations of inorganic reduced sulfur in the filtered phase (molar sulfate:sulfide ratios exceeded 270:1 and 970:1 in effluents 1 and 2, respectively), it is unlikely that a reoxidation of reduced sulfur to sulfate has significantly affected $\delta^{34}S\text{-}SO_4^{2-}$, which likely occurred in approach A. This was confirmed by the results of both methods applied in September 2008 (differences within ±0.6‰). Results of both methods were pooled.

Sulfide sulfur was recovered from the effluents. No sulfide was determined in influents or overflows. About 10 L of water was preserved with excess zinc acetate (~1 M) to fix reduced sulfide as zinc sulfide. Bottles were filled, sealed with parafilm, stored in absence of light and at ambient temperatures. Samples were filtered without delay but at most within 72 hours through 0.45 µm pore size filter paper. The precipitate was air dried. In a nitrogen flushed Johnson-Nishita reduction-distillation apparatus the zinc sulfide was dissolved in 10 mL hydrochloric acid (50%) and 16 mL chromous chloride (2 M in 10% hydrochloric acid). The evolving hydrogen sulfide was trapped in silver nitrate ($H_2S\uparrow + 2AgNO_3 \rightarrow Ag_2S\downarrow + 2H^+ + 2NO_3^-$) (e.g. Tuttle *et al.* 1986, de Groot 2009a).

Barium sulfate and silver sulfide samples were processed after Coleman and Moore (1978) and Robinson and Kusakabe (1975) and oxidized to sulfur dioxide on a vacuum S-line. Sulfur dioxide was analysed on an Isotope Ratio Mass Spectrometer (IRMS, VG Isogas SIRA II).

The IRMS was calibrated against internal chalcopyrite CP1 (δ^{34}S -4.56‰) and two external standards: sphalerite NBS 123 (δ^{34}S=17.1‰, δ= ±0.308‰) and silver sulfide IAEA S 3 (δ^{34}S= -31.5‰, δ= ±0.2‰). The accuracy was checked daily against an internal SO_2 gas. Duplicate samples were run regularly (5-10% of total sample number) together with one of the standards above or NBS 127 $BaSO_4$ (δ^{34}S= 20.3‰). In the case of differences of more than ±10% between duplicates or differences of the standard to its original value, samples were rerun. Isotope results for yields above 70% were converted to δ-notation in per mill compared to the V-CDT standard ($\delta = (R_{sample}/R_{standard} - 1)*1000‰$). Sulfur isotopic ratios are reported within an error of ±0.4‰.

Oxygen and Hydrogen

Oxygen and hydrogen in Bowden Close surface water samples were taken in 12 mL glass exetainers. To minimize microbial activity, samples were filtered (0.2 µm, Track Etched Filter) and stored upside down, in darkness and at 4°C. Bottles were filled completely without head space and wrapped in parafilm to reduced exchange with atmospheric water vapour. Despite occasionally elevated salt concentrations, water was not pretreated because of the often significant isotope fractionation induced during distillation (Horita and Kendall 2004).

The δD and δ^{18}O isotopic ratios were determined by chromium reduction and O-H_2O equilibration with CO_2 (Horita and Kendall 2004, de Groot 2009b). The latter method is based on procedures developed by Cohn and Urey (1938), Mills and Urey (1939) and Mills and Urey (1940). The method is also known as Epstein-Mayeda method (Epstein and Mayeda 1953) which was later modified by Roether (1970) and Kishima and Sakai (1980). The reduction using chromium was first reported by Gehre et al. (1996).

Hydrogen isotope ratios were determined by a V.G. Micromass 602 isotope ratio mass spectrometer (Winsford, England) previously calibrated with two internal standards (light water, LT: -93.7‰; seawater, SW: -6.0‰) and one primary reference material (Greeland Ice Sheet Precipitation (GISP): -189.73±0.87‰ (Horita and Kendall 2004)). Commonly after 10 samples, one of these standards were analysed as standard checks. Due to potential memory effects, samples were run in triplicate. The precision was ±5‰.

Oxygen isotope ratios were determined in triplicate with a Delta V Plus mass spectrometer (Thermo Scientific) calibrated against three internal standards (EKS = East Kilbride Snow: -12.93±0.1‰; DW2

= deionised water: -7.44±0.16‰ and DSW = distilled seawater: -0.26±0.06‰). The internal standards were regularly calibrated against international standards (SMOW = -0.09±0.19‰, GISP = -24.87±0.28‰ and SLAP = -55.49±0.17‰). The precision was ±0.1‰. Duplicates varied within 1%.

The δD and $\delta^{18}O$ in atmospheric precipitation derived from two sampling sites in the UK (http://nds121.iaea.org), Wallingford (51.6 latitude, -1.1 longitude, 48 m a.s.l.; 348 km south of Bowden Close) and Keyworth (52.9 latitude, -1.1 longitude, 60 m a.s.l.; 212 km southeast of Bowden Close) which were monitored by the IAEA between 1979-2005 (n = 324) and 1986-1996 (n = 144), respectively.

Sulfate oxygen from barium sulfate was determined by graphite reduction method which is based on publications of Longinelli and Craig (1967), Sakai (1977) and Claypool et al. (1980) and was more recently modified by Halas et al. (2007). Carbon monoxide was oxidized to CO_2 by high voltage platinum electrodes (Mizutani 1971). The carbon dioxide $\delta^{18}O$ was analysed by the V.G. Micromass 602. Regularly standards (NBS 127: 8.7‰) were run alongside.

Carbon

Stable carbon isotope ratios of total dissolved inorganic carbon (TDIC) were initially determined by the standard procedure that includes precipitation with strontium chloride ($SrCl_2 + HCO_3^- \rightarrow SrCO_3\downarrow + 2Cl^- + H^+$) (e.g. Atekwana and Krishnamurthy 2004). Parallel to that, a modified approach after Atekwana and Krishnamurthy (2004) was applied.

Due to potential isotope fractionations (Bishop 1990), the method was later abandoned. Potential isotopic fractionation might have been introduced by the type of filter used for filtration, contact with atmospheric carbon dioxide (e.g. evolution of CO_2 from highly alkaline samples and adsorption of CO_{2atm} into low alkaline samples) during filtration, drying and storage; type of material used for the sample bottles, the length of storage time of the carbonate precipitates until analysis and elevated ionic strengths (particularly excess sulfate concentrations) (Bishop 1990).

The carbon stable isotope ratios of strontium carbonate were analysed on an Analytical Precision AP 2003 mass spectrometer (AP-MS). The samples were reacted with phosphoric acid for three days at 70°C.

In addition, several specimens of limestone grains from the reactive sediments were phosphoric acid digested to determine carbon isotope ratios.

The mass spectrometer was conditioned prior to each analysis with seven internal marble standards (MARB, medium marble 85/160, $\delta^{13}C$=2.48‰) and calibrated with four MARB, sodium bicarbonate ($\delta^{13}C$=-4.67‰) and calcium carbonate ($\delta^{13}C$=-24.23‰). For each of them, 16 samples were prepared in a range of 0.04-1.8 mg to cover the alkalinity observed in Bowden Close surface waters. After 40 samples the AP-MS was recalibrated. Each sample was analysed at least twice. If the concentrations of duplicates differed more than ±5%, a third sample was analysed. In addition, blanks and additional marble standards were run to assess precision and accuracy. The international standards IAEA CO-1 (calcite, $\delta^{13}C$=2.48‰, σ=0.025‰), and NBS 18 (calcite, $\delta^{13}C$=-5.029‰, σ=0.049‰), IAEA CO-8 ($\delta^{13}C$=-5.749‰, σ=0.063‰) and IAEA CO-9 (barium carbonate, $\delta^{13}C$=-47.119‰, σ=0.149‰) were used to calibrate the mass spectrometer and check for accuracy on a monthly basis. Results were converted to per mill compared to V-Pee Dee Belemnite.

The modified approach of Atekwana and Krishnamurthy (2004) was followed to determine stable carbon isotopic ratios in TDIC. Several modifications on the original methodology had to be undertaken to minimize exposure of the sample to atmospheric carbon dioxide. Initially, nitric acid (10% v/v) washed 12 mL exetainers were flushed for several minutes with nitrogen via needle fittings through the rubber septum. Following an injection of 180 µL concentrated, deoxygenated (one hour heating) concentrated phosphoric acid on site, 10 mL sample was introduced via the septum with a needle and 20 mL syringes under the water surface. Due to the increasing pressure inside the glass vials, during the filling, excess gas had to be released. It can be expected that in addition to nitrogen, carbon dioxide produced by reaction of bicarbonate with phosphoric acid ($HCO_3^- + H_3PO_4 \rightarrow CO_2\uparrow + PO_4^{3-} + 2H^+ + H_2O$) has been released potentially causing carbon isotope fractionation.

For this reason, the phosphoric acid was added to the closed exetainers after the sample injection. Due to the different head spaces in each exetainer, isotope ratios were difficult to measure. In the third modification, samples were preserved with 240 µL formaldehyde to reduce microbial activity. Exetainers were filled to the top, sealed with parafilm and stored until analysis upside down in absence of light at 4°C. For each sampling site (and event) three 12 mL vials were sampled. Trials using 0.2 µm filtered samples did not show significant differences compared to unfiltered samples.

To determine the carbon isotope ratios in the water samples, 6 mL water was transferred via syringe fittings into helium-purged exetainers, avoiding any contact with air. Thereafter, about 200 µL hot, previously deaerated concentrated phosphoric acid was added and vortexed. After reaction and equilibration over two days, $\delta^{13}C$ was analysed by a Prism3, Fisons Instruments. The instrument was calibrated as explained for the AP system. To guarantee equal head spaces, about 6 mL hot, deaerated phosphoric acid (10%) was injected into the helium purged bottles with the standards. Standard deviation of replicates and duplicates ranged within ±5‰.

Carbon isotope ratios of atmospheric carbon dioxide were obtained from Mace Head monitoring station (Galway, Ireland; 53.3260°N, 9.899°W, 25 m a.s.l.) of the Earth System Research Laboratory, Global Monitoring Division (NOAA, www.cmdl.noaa.gov). Isotopic ratios were monitored between June 1991and November 1992 (n=126).

Sediment

Four sediment cores were taken in November 2004, two in each RAPS. In each case one core was taken relatively close to the influent and the other close to the effluent. The sediments were maintained frozen until analysis (-32°C), which was found to be the best preservation method to prevent (bio)geochemical changes of the sediment (de Lange *et al.* 2008).

All samples were freeze dried to stable weight prior to the analysis. Limestone grains exceeding 1 mm diameter and bigger leaf and root material were separated. The remaining sediment was ground in an agate mortar.

Sequential Extraction of Sulfur

A sequential extraction procedure for the sulfur species in sediment was developed based on Duan et al. (1997) and Mayer et al. (2004). The main focus in this extraction procedure was on six inorganic sulfur species: water soluble sulfate (I, WSS); elemental sulfur (II, ES); acid-volatile sulfur (III, AVS), acid soluble sulfate (IV, ASS), chromium reducible sulfur (V, CRS) and adsorbed sulfate (VI, AS).

Because recoveries of the AVS sulfur fraction were found to be very low, the initial sample size of 2.5 g was increased to 12 g (if available), divided into subsamples of approximately 2.5 g dry weight. This was to extract sufficient material for the determination of stable sulfur isotope ratios of AVS.

I: Water Soluble Sulfate (WSS)

About 2.5 g of freeze dried, agate-mortar grinded sample was mixed in a 60 mL screw cap PTFE centrifugable flask with 30 mL of deoxygenated, deionised water. The sample was agitated (200 rpm) for six hours. The sample was centrifuged (10000 rpm, 10 min) and the aliquot pipetted into 50 mL volumetric flasks. The sediment residue was washed twice with 10 mL deionised water and after resuspension by vortexing centrifuged as above. The aliquots were pooled into volumetric flasks, acidified (hydrochloric acid (1% v/v) and made up to 50 mL with deionised water. Duplicates and standard checks were not significantly different. Sulfur concentrations in blanks occasionally reached 1.85 mg L^{-1}. Duplicates varied within ±5%. Analysis of standard checks were not significantly different from the hypothesized population mean.

II: Elemental Sulfur (ES)

Distilled dichloromethane (DCM, 30 mL) was added to the residue of extraction step I to dissolve elemental sulfur. The sample was shaken for 16 hours (200 rpm). After sedimentation, the aliquot was pipetted into 100 mL-borosilicate flasks. The remaining sediment sample was washed with 20 mL DCM and pooled with the former aliquot. DCM was evaporated under a steady nitrogen flux to prevent oxidation of elemental sulfur. The three-neck flask was then introduced into a Johnson-Nishita reduction-distillation apparatus and after 10 minutes of flushing under a nitrogen stream, 16 mL of chromous chloride (2 M) and 10 mL of 50% hydrochloric acid were injected. Elemental sulfur was reduced to hydrogen sulfide at boiling temperatures over one hour ($2H^+ + Cr^{2+} + S^o \rightarrow H_2S\uparrow + Cr^{3+}$) and trapped into silver nitrate (1 M) solution as silver sulfide.

The chromous chloride solution was prepared in advance in a Jones reactor by reducing chromium(III)chloride by mercury(II)nitrate and nitric acid-activated zinc pebbles in 10% hydrochloric acid under nitrogen atmosphere. A colour change from green to dark blue indicated the complete reduction of chromium after approximately 10 hours reaction time. The solution was stored in sealed 60 mL syringes under absence of light at 4°C.

III: Acid-Volatile Sulfur (AVS)

The sediment residue from step II was introduced into a clean three-neck flask and fitted into the Johnson-Nishita apparatus. After 10 minutes flushing with nitrogen, 20 mL hydrochloric acid (6 M) was added via a side neck. The sample was boiled for one hour to exsolve hydrogen sulfide from meta-stable mineral sulfides (e.g. mackinawite, $2HCl + FeS \rightarrow H_2S\uparrow + Fe^{2+} + 2Cl^-$). This procedure was applied on sediment from cores three and four (RAPS 1). For sediments of RAPS 2 (i.e. core 1 and 2), about 5 g of stannous chloride was added to the sediment residue of step II. After establishing a reducing environment with nitrogen, 20 mL HCl (6 M) was added and AVS digested for one hour under ambient temperatures. The evolving hydrogen sulfide was trapped in silver nitrate. Silver sulfide samples of subsamples were pooled to gain sufficient material for later determination of stable sulfur isotope ratios.

This reaction step likely mobilizes non-extracted pore water sulfide, dissolved iron complexes as well as iron mono-sulfides (e.g. mackinawite) (Morse and Rickard 2004) and partially mobilizes greigite (Fossing and Jørgensen 1989) and pyrite (Morse and Rickard 2004).

The purpose of the addition of stannous chloride was to reduce any ferric iron to ferrous iron and therewith to inhibit the oxidation of hydrogen sulfide by Fe^{3+} (Pruden and Bloomfield 1968, Berner 1974, Cornwell and Morse 1987, Fossing and Jørgensen 1989). Because of the potential dissolution of di-sulfide minerals under boiling conditions (Cornwell and Morse 1987, Rice et al. 1993), the extraction was undertaken at room temperature. Nonetheless, some studies suggest that due to the low solubility of stannous chloride, Sn(II) was not liberated sufficiently, affecting the recovery of AVS. No significant differences in AVS concentrations were observed whether $SnCl_2$ was applied or not.

IV: Acid Soluble Sulfate (ASS)

This fraction represents sulfur bound in oxyhydroxysulfates, gypsum, surface complexes, acid soluble low molecular weight organic sulfur compounds (Herbert *et al.* 2000). The sediment residue from the previous step was filtered (<0.45 µm) and washed with abundant deionised water. The filtered aliquots were transferred into 100 mL volumetric flasks and added up with deionised water. Sulfate was precipitated with barium chloride (0.25 M) solution on ashless filter paper (n^o 42). After drying at ambient temperatures, the filter paper was burned off at 850°C. The remaining solid (i.e. barium sulfate) was recovered into micro tubes. Subsamples were pooled.

V: Chromium Reducible Sulfur (CRS)

Pyrite was extracted by hot chromous chloride solution. The mobilization of organic sulfur by this reaction step is unclear and the literature disagrees on that (e.g. Fossing and Jørgensen 1989).

The residue from step IV was transferred into a three neck flask with small amounts of hydrochloric acid (6 M) and fitted into the Johnson-Nishita apparatus. After nitrogen flushing for about 10 minutes, a volume of 16 mL chromous chloride solution (2 M in 10% HCl) and 10 mL 50% HCl was added and the sample boiled for one hour. Thereby, pyrite is dissolved and any hydrogen sulfide ($4H^+ + 2Cr^{2+} + FeS_2 \rightarrow 2H_2S\uparrow + 2Cr^{3+} + Fe^{2+}$) is precipitated in silver nitrate. Additional silver nitrate was injected into the trap when turbidities increased. Canfield et al. (1998) and Francois (1987) observed some mobilization of organic sulfur (e.g. organic polysulfides) upon treatment with boiling chromous chloride. A potential release of hydrogen sulfide from these sources could both affect results of pyrite concentrations and isotope ratios.

Silver sulfide was filtered on 0.2 µm track etched filters, washed with deionised water, air dried and reweighed to determine sulfur concentrations gravimetrically. The agate-mortar homogenized precipitates were transferred in micro tubes, wrapped in aluminium foil to prevent photolytic oxidation and stored in a desiccator until analysis of $\delta^{34}S$-Ag_2S.

Standard deviations (and standard errors) ranged between 0.04-0.70 g kg^{-1} (0.32-0.02) and 0.07-1.33 g kg^{-1} (0.04-0.59) for sulfur concentrations in elemental sulfur and chromium reducible sulfur subsamples, respectively. Standard deviations for isotope ratios were in average ±1.86‰ for ES and ±1.37‰ for CRS. Results obtained for the reference material (CP1 and NBS 123) were not statistically different from the original values.

VI: Adsorbed Sulfate (AS)

This reaction step aims to mobilizing any remaining sorbed inorganic sulfate. However, also organic sulfur fractions could potentially be mobilized (Watwood and Fitzgerald 1988). The residue of sulfur from step V was washed into 60 mL centrifugable polypropylene flasks and 30 mL of dipotassium hydrophosphate solution (0.08M) added to desorb remaining sulfate. The sample was shaken for 16 hours at 200 rpm, centrifuged (3000 rpm, 15 min) and washed twice with 10 mL deionised water, resuspending the sediment in between by vortexing. After centrifugation, the supernatants were pooled into 50 mL volumetric flasks and acidified with concentrated hydrochloric acid (1% v/v) to pH < 2. Duplicates were not significantly different from each other ($p>0.59$, Mann Whitney rank sum test). Occasionally, sulfur concentrations exceeded 0.08 mg L^{-1} in the blanks. The one sample t-test, which was compared to the hypothesised population mean (5 mg L^{-1}), showed no significant difference for sulfur concentrations determined in the standard checks (95%: 4.97-5.13 mg L^{-1}).

The residual sulfur not mobilised by the sequential extraction is expected to represent organic bound sulfur (OrgS).

Sulfur concentrations in the supernatants of extraction steps I, IV and VI were analysed by ICP-OES (Vista MPX, CCP Simultaneous ICP-OES, Varian) previously calibrated with matrix matched sulfur standards and blanks (1, 5, 10 mg L^{-1}). For each sample, aliquots of two subsamples were analysed. Every 15 samples one blank, one standard check and one replicate were analysed. Duplicates of sulfur analysis in inorganic sulfur extracted sediments with Leco Carbon Sulfur Analyzer showed no significant difference.

Iron Sequential Extraction

A sequential extraction for eight iron phases in Bowden Close sediments was undertaken on freeze dried and agate mortar ground sediments (Poulton and Canfield 2005).

- Step I consists largely of water soluble iron,
- Step II consists of adsorbed ion-exchangable iron that was determined as a difference between the magnesium chloride extracted iron and the water extracted iron,

- Step III recovers carbonate bound iron,
- Easily reducible oxides, such as ferrihydroxide and lepidocrocite, are mobilized in step IV,
- Extraction step V mobilizes reducible oxides like goethite, hematite and akaganeite,
- Step VI mobilizes magnetite bound iron and
- Iron bound to iron mono- and di-sulfides (VII and VIII) was determined from the silver sulfide recovered during the sulfur sequential extraction.

Each sample was run in duplicate. Duplicates were not significantly different.

The leachates were analysed on an ICP-OES (Vista MPX, CCP Simultaneous ICP-OES, Varian). For each extraction step three matrix matched standards and one blank were prepared. The standards contained 1 mg L^{-1}, 3 mg L^{-1} and 5 mg L^{-1} iron except for extraction step VI were standards of 0.5 mg L^{-1}, 1.5 mg L^{-1} and 3 mg L^{-1} were prepared. For oxalate extracted samples (VI) a short torch in combination with a Sturmann Masters Spray Chamber fitted with a v-grove nebulizer was used to avoid clogging of the nebulizer due to the high ionic strength. This measure reduced the sensitivity of the ICP-OES about four-fold. Every 15 samples, replicates, blanks and standard checks were analysed alongside.

Total Concentrations

A multi-acid digestion adapted after Hossner (2005) and the US EPA method 3052 (1996) was applied for the total extraction of sediment samples. Element concentrations were determined on an ICP-OES. Duplicates were not significantly different. Potassium ($\bar{x}$: 0.34 mg L^{-1}), sodium ($\bar{x}$: 0.03 mg L^{-1}), and sulfur ($\bar{x}$: 1.03 mg L^{-1}) were occasionally determined in matrix matched blanks. Significant differences between standard checks were detected.

Limestone grains (1-2 cm diameter) of the sediment were surface leached with concentrated hydrochloric acid to dissolve secondary mineral precipitates. After washing with deionised water and air drying, the grains were ground in an agate mortar and continuously acid digested.

A Carbon-Sulfur Leco analyser (type CS-244) was used to determine total carbon (TC) and total sulfur (TS) concentrations in the freeze dried and agate mortar ground sediments. Total organic carbon (TOC) was determined by British standard method (BS 7755-3.8 1995) and total inorganic carbon (TIC) calculated as the difference of TC and TOC. Tungsten and iron accelerators (SL 266, AR 077; Leco) were added to each sample, blank and reference material to guarantee complete ignition. Five carbon-sulfur steel rings (C: 0.80-1.00%, S: 0.005-0.03%) were used for calibration. Every three samples, a duplicate was included in the carbon and sulfur measurements and every ten samples a standard and one blank. Carbon was not detectable in blanks, but sulfur concentrations of 0.105% ($\bar{x}$, σ: ±0.159%) were measured. Duplicates were not significantly different ($p>0.55$, Mann Whitney rank sum test).

Carbon Stable Isotopes in Compost and Plant Species

Bulk $\delta^{13}C$ ratios of the organic matter in the sediment were analysed. Eleven inorganic sulfur extracted samples (i.e. the remaining sediment after step V of the sulfur sequential extraction) were analysed for this purpose. Three duplicates and one blank were analysed alongside. Standard deviation averaged ±0.4‰ (isotope ratios) and ±0.8% (carbon concentrations). Concentrations and isotope ratios were undetectable in the blanks.

The samples were air dried, homogenized and about 1 mg weighed into tin capsules (5×3.5 mm, D1002) with a Mettler Toledo MX5 high precision scale. During the sulfur sequential extraction, organic matter ought to be only negligibly affected. $\delta^{13}C$ in the residual should therefore range close to original compost carbon isotope ratios.

In addition, one sample of the most abundant plant species populating RAPS 1, *Typha latifolia*, was determined for $\delta^{13}C$. After thoroughly washing the plant with tap water followed by deionised water, the plant was cut, dried (40°C) and ground (MM301 Retsch, 2 minutes, 24 rps). Two subsamples of root and leaf material were analysed. Standard deviations for carbon stable isotope ratios averaged ±0.2‰ and for the carbon concentrations ±0.1%.

The isotope ratios and carbon concentrations were analysed on a Thermo Finnigan-Delta plus XP coupled to a Costech Elemental Combustion System. The apparatus was calibrated daily against 14N Alanine (-10.65‰, stdv: ±0.03‰), 15N Alanine, (-23.25‰, stdv: ±0.03‰), Gelatine, (-20.17‰, stdv: ±0.03‰) and Tryptophans (-10.51‰ (stdv: ±0.04‰)) and once per month against international standards (IAEA N1: 0.3‰ (stdv: ±0.02‰); IAEA N2: 20.4‰ (stdv: ±0.19‰), USGS 25: -30.2‰ (stdv: ±0.08‰), USGS 24: -15.91 (stdv: ±0.03‰), IAEA PEF CH 7: -31.85 (stdv: ±0.04‰), IAEA Surcose CH6: -10.49‰ (stdv: ±0.05‰)).

Microscopy

Selected samples from the surface sludge and from 15 cm depth (RAPS 2) were analysed by Field Emission Gun- Scanning Electron Microscopy (FEG-SEM, LEO 1530) and Field Emission Gun - Transmission Electron Microscopy (FEG-TEM, Philips CM200). Elemental analyses on mineral species were undertaken by Energy Dispersive X-Ray Spectroscopy (EDS, Oxford Instruments INCA

350 and UTW ISIS). Analyses were undertaken at Leeds University (Institute for Material Science, Leeds Electron Microscopy and Spectroscopy Centre).

Samples for microscopic analysis were taken in October 2009 and remained frozen until analysis. Samples for FEG-SEM were dried within five minutes onto an aluminium plate and Pt/Pd coated (5 nm) with an Agar high resolution sputter coater (80 mA, 0.04 mbar). The samples were analysed under high vacuum ($2.0*10^{-5}$ mbar). The sample for FEG-TEM was dispersed in methanol (10 min ultra-sonified) and dried onto carbon plates.

References

Atekwana, E.A., Krishnamurthy, R.V., 2004. Extraction of dissolved inorganic carbon (DIC) in natural waters for isotopic analyses. *In:* de Groot, P.A. (ed.), *Handbook of stable isotope analytical techniques*. Elsevier, London.

Berner, R.A., 1974. Iron sulfides in Pleistocen deep Black Sea sediments and their paleo-oceanographic significance. *In:* Degens, E.T., Ross, D.A. (eds.), *The Black Sea: Geology, chemistry, and biology*. The American Association of Petroleum Geologists, Tusla.

Bishop, P.K., 1990. Precipitation of dissolved carbonate species from natural waters for $\delta^{13}C$ analysis: A critical appraisal. *Chemical Geology*, **80**: 251-259.

BS 7755-3.8, 1995. *Soil quality: Chemical methods: Determination of organic and total carbon after dry combustion (elementary analysis). In:* British Standards (Editor). Soil Quality: Chemical Methods.

Canfield, D.E., Boudreau, B.P., Mucci, A., Gundersen, J.K., 1998. The early diagenetic formation of organic sulfur in the sediments of Mangrove Lake, Bermuda. *Geochimica et Cosmochimica Acta*, **62**(5): 767-781.

Claypool, G.E., Holser, W.T., Kaplan, I.R., Sakai, H., Zak, I., 1980. The age curves of sulfur and oxygen isotopes in marine sulfate and their mutual interpretation. *Chemical Geology*, **28**: 199-260.

Clesceri, L.S., Greenberg, A.E., Rhodes Trussell, R. (eds.), 1992. *Metodos normalizados: Para el analisis de aguas potables y residuales*. Diaz de Santos S.A., Madrid.

Cline, J.D., 1969. Spectrophotometric determination of hydrogen sulfide in natural waters. *Limnology and Oceanography*, **14**(3): 454-458.

Cohn, M., Urey, H.C., 1938. Oxygen exchange reactions of organic compounds and water. *Journal of the American Chemical Society*, **60**: 679-682.

Coleman, M.L., Moore, M.P., 1978. Direct reduction of sulfates to sulfur dioxide for isotopic analysis. *Analytical Chemistry*, **50**(11): 1594-1595.

Cornwell, J.C., Morse, J.W., 1987. The characterization of iron sulfide minerals in anoxic marine sediments. *Marine Chemistry*, **22**(2-4): 193-206.

de Groot, P.A., 2009a. Sulfur. *In:* de Groot, P.A. (ed.), *Handbook of stable isotope analytical techniques*. Elsevier, London.

de Groot, P.A., 2009b. Oxygen. *In:* de Groot, P.A. (ed.), *Handbook of stable isotope analytical techniques*. Elsevier, London.

de Lange, H.J., van Griethuysen, C., Koelmans, A.A., 2008. Sampling method, storage and pretreatment of sediment affect AVS concentrations with consequences for bioassay responses. *Environmental Pollution*, **151**(1): 243-251.

Duan, W.-M., Coleman, M.L., Pye, K., 1997. Determination of reduced sulphur species in sediments: An evaluation and modified technique. *Chemical Geology*, **141**(3-4): 185-194.

Epstein, S., Mayeda, T., 1953. Variation of O^{18} content of waters from natural sources. *Geochimica et Cosmochimica Acta*, **4**: 213-224.

Fischer, E., 1883. Bildung von Methylenblau als Reaktion auf Schwefelwasserstoff. *Berichte der deutschen chemischen Gesellschaft*, **16**(2): 2234-2236.

Fossing, H., Jørgensen, B.B., 1989. Measurement of bacterial sulfate reduction in sediments: Evaluation of a single-step chromium reduction method. *Biogeochemistry*, **8**: 205-222.

Francois, R., 1987. A study of sulphur enrichment in the humic fraction of marine sediments during early diagenesis. *Geochimica et Cosmochimica Acta*, **51**(1): 17-27.

Gehre, M., Hoefling, R., Kowski, P., Strauch, G., 1996. Sample preparation device for quantitative hydrogen isotope analysis using chromium metal. *Analytical Chemistry*, **68**: 4414-4417.

Halas, S., Szaran, J., Czarnacki, M., Tanweer, A., 2007. Refinements in $BaSO_4$ to CO_2 preparation and $\delta^{18}O$ calibration of the sulfate reference materials NBS-127, IAEA SO-5 and IAEA SO-6. *Geostandards and Geoanalytical Research*, **31**(1): 61-68.

Herbert, R.B., Benner, S.G., Blowes, D.W., 2000. Solid phase iron-sulfur geochemistry of a reactive barrier for treatment of mine drainage. *Applied Geochemistry*, **15**: 1331-1343.

Horita, J., Kendall, C., 2004. Stable isotope analysis of water and aqueous solutions by conventional dual-inlet mass spectrometry. *In:* de Groot, P.A. (ed.), *Handbook of stable isotope analytical techniques*. Elsevier, London.

Hossner, L.R., 2005. Dissolution for total elemental analysis. *In:* Sparks, D.L., Page, A.L., Helmke, P.A., Loeppert, R.H., Soltanpour, P.N., Tabatabai, M.A., Johnston, C.T., Sumner, M.E. (eds.), *Methods of soil analysis: Chemical methods*. Soil Science Society of America, Madison, Wisconsin, USA.

Hounslow, A.W., 1995. *Water quality data: Analysis and interpretation*. Lewis Publishers, London.

Johnson, K.E., 2007. *A geochemical assessment of passive mine water treatment through a Reducing and Alkalinity Producing System (RAPS) at Bowden Close, County Durham*, University of Newcastle upon Tyne, Newcastle, 134.

Kishima, N., Sakai, H., 1980. Oxygen-18 and deuterium determination on a single water sample of a few milligrams. *Analytical Chemistry*, **52**: 356-358.

Longinelli, A., Craig, H., 1967. Oxygen-18 variations in sulfate ions in seawater and saline lakes. *Science*, **156**(3771): 56-59.

Mayer, B., Krouse, H.R., 2004. Procedures for sulfur isotope abundance studies. *In:* de Groot, P.A. (ed.), *Handbook of stable isotope analytical techniques*. Elsevier, London.

Mills, A., Urey, H.C., 1940. The kinetics of isotopic exchange between carbon dioxide, bicarbonte ion, carbonate ion, and water. *Journal of the American Chemical Society*, **62**: 1019-1026.

Mills, G.A., Urey, H.C., 1939. Oxygen exchange between carbon dioxide, bicarbonate ion, carbonate ion and water. *Journal of the American Chemical Society*, **61**: 534.

Mizutani, Y., 1971. An improvement in the carbon reduction method for the oxygen isotopic analysis of sulfates. *Geochemical Journal*, **5**: 69-77.

Morse, J.W., Rickard, D., 2004. Chemical dynamics of sedimentary acid volatile sulfide. *Environmental Science and Technology*, **38**: 132A-136A.

Mylon, S.E., Benoit, G., 2001. Subnanomolar detection of acid-labile sulfides by the classical methylene blue method coupled to HPLC. *Environmental Science and Technology*, **35**(22): 4544-4548.

Nriagu, J.O., Hem, J.D., 1978. *Chemistry of pollutant sulfur in natural waters*. *In:* Nriagu, J.O. (ed.), Sulfur in the environment: Ecological impacts. Wiley, 211-270.

Poulton, S.W., Canfield, D.E., 2005. Development of a sequential extraction procedure for iron: Implications for iron partitioning in continentally derived particulates. *Chemical Geology*, **214**(3-4): 209-221.

Pruden, G., Bloomfield, C., 1968. The determination of iron(II)sulphide in soil in the presence of iron(III)oxide. *The Analyst*, **93**: 532-534.

Rice, C.A., Tuttle, M.L., Reynolds, R.L., 1993. The analysis of forms of sulfur in ancient sediments and sedimentary rocks: Comments and cautions. *Chemical Geology*, **107**(1-2): 83-95.

Robinson, B.W., Kusakabe, M., 1975. Quantitative preparation of sulfur dioxide, for $^{34}S/^{32}S$ analyses, from sulfides by combustion with cuprous oxide. *Analytical Chemistry*, **47**(7): 1179-1181.

Roether, W., 1970. Water-CO_2 exchange set-up for the routine oxygen18 assay of natural waters. *International Journal of Applied Radiation Isotopes*, **21**: 379-387.

Sakai, H., 1977. Sulfate-water isotope thermometry applied to geothermal systems. *Geothermics*, **5**(1-4): 67-74.

Sharp, Z., 2007. *Principles of stable isotope geochemistry*. Pearson, Prentice Hall, New Jersey.

Tuttle, M.L., Goldhaber, M.B., Williamson, D.L., 1986. An analytical scheme for determining forms of sulphur in oil shales and associated rocks. *Talanta*, **33**(12): 953-961.

US EPA 3052, 1996. *Microwave assisted acid digestion of siliceous and organically based matrices*. US EPA, 20.

Viollier, E., Inglett, P.W., Hunter, K., Roychoudhury, A.N., van Cappellen, P., 2000. The ferrozine method revisited: Fe(II)/Fe(III) determination in natural waters. *Applied Geochemistry*, **15**(6): 785-790.

Wallmann, K., Hennies, K., König, I., Petersen, W., Knauth, H.-D., 1993. New procedure for determining reactive Fe(III) and Fe(II) minerals in sediments. *Limnology and Oceanography*, **38**(8): 1803-1812.

Watwood, M.E., Fitzgerald, J.W., 1988. Sulfur transformation in forest litter and soil: Results of laboratory and field incubations. *Soil Science Society of America Journal*, **52**: 1478-1483.

LEGEND
SURFACE WATER

Parameter	Abbreviation	Unit
adl	above detection limit	
Al	aluminium	mg L^{-1}
Alk	alkalinity	mg eq $CaCO_3$
bdl	below detection limit	
Ca	calcium	mg L^{-1}
Cl	chloride	mg L^{-1}
EC	electrical conductivity	µS cm^{-1}
Eh	redox potential (uncorrected)	mV
Fe	iron	mg L^{-1}
Fe (II)	ferrous iron	mg L^{-1}
K	potassium	mg L^{-1}
Mg	magnesium	mg L^{-1}
Mn	manganese	mg L^{-1}
Na	sodium	mg L^{-1}
NA	not available	
nd	not determined	
Q	flow	L min^{-1}
Qov	flow of overflow	L min^{-1}
Si	silicium	mg L^{-1}
SO4	sulfate	mg L^{-1}
T	temperature	°C
Zn	zinc	mg L^{-1}
IA	ion balance	%

RAW DATA OF SURFACE WATER MONITORING OF THE BOWDEN CLOSE TREATMENT SCHEME (DECEMBER 2003 - MAY 2009)

RAPS 1 INFLUENT	T	pH	EC	Eh	Alk	Q	Cl	SO4	Ca	Mg	Na	K	Fe	Mn	Al	Zn	Si
Nov-03	8.9	8.45	1122	374	25	nd	172	276	104.0	17.0	95.5	19.0	0.7	0.5	1.3	0.1	nd
Dec-03	7.8	6.46	980	353	37	nd	53	433	113.0	37.4	27.6	7.5	5.9	1.4	4.9	0.3	nd
Jan-04	7.1	6.02	911	373	20	nd	51	432	118.0	32.2	24.0	6.5	7.6	1.2	5.6	0.3	nd
Feb-04	7.5	4.30	963	529	bdl	41	39	510	110.0	32.7	20.3	5.6	19.5	1.9	9.6	0.4	nd
Mar-04	6.5	3.90	1011	548	bdl	29	87	579	110.0	34.2	35.1	6.4	19.9	1.6	9.6	0.4	nd
Apr-04	7.6	3.93	871	526	bdl	27	42	396	84.6	24.1	22.1	4.9	24.5	1.5	9.2	0.4	nd
May-04	9.1	5.82	801	361	10	41	60	346	91.4	24.3	34.4	5.1	16.3	1.0	5.2	0.3	nd
Jun-04	11.5	6.30	830	300	10	6	44	484	118.0	26.8	21.2	6.2	16.2	1.8	6.3	0.3	nd
Jul-04	12.7	5.05	1041	428	bdl	2	34	459	128.0	31.2	24.1	6.3	15.8	2.3	9.5	0.4	nd
Aug-04	11.3	5.85	893	356	10	14	51	419	113.0	27.8	28.6	6.1	15.9	1.6	6.1	0.3	nd
Sep-04	11.7	5.33	867	316	17	31	51	385	112.0	29.7	23.0	5.6	15.1	1.3	6.1	0.3	nd
Oct-04	11.6	5.60	865	281	27	10	52	352	106.0	26.8	24.4	6.0	14.7	1.3	4.9	0.2	nd
Nov-04	10.9	5.54	801	391	3	83	33	330	97.3	24.7	19.8	5.3	17.6	1.6	5.7	0.3	nd
Dec-04	8.6	6.54	791	236	18	35	32	287	94.4	23.5	19.5	6.2	16.2	1.0	3.8	0.2	nd
Jan-05	7.5	5.08	784	390	1	47	37	364	92.7	23.5	19.4	5.7	19.5	1.1	5.1	0.3	nd
Feb-05	9.9	4.97	763	382	17	38	51	382	94.4	24.1	18.4	6.2	23.4	1.2	4.6	0.2	nd
Mar-05	5.3	4.14	844	588	bdl	100	142	189	60.3	19.8	56.5	4.7	10.5	0.6	2.6	0.1	nd
Apr-05	7.7	5.41	550	316	21	120	102	136	38.7	12.3	38.5	2.8	6.6	0.4	1.5	0.1	nd
May-05	9.6	6.01	775	277	17	32	43	295	94.6	23.2	22.5	5.9	21.9	1.2	3.9	0.2	nd
Jun-05	11.9	6.41	823	198	55	6	49	293	107.0	23.6	21.5	6.7	18.0	1.1	3.1	0.2	nd
Jul-05	13.1	6.57	816	237	71	3	53	305	109.0	21.9	27.1	6.3	7.1	1.1	4.0	0.2	10.0
Aug-05	13.5	6.35	847	318	76	2	71	253	112.0	24.5	29.3	6.3	2.2	0.9	3.8	0.1	9.1
Sep-05	14.1	6.82	800	290	85	4	83	201	102.0	26.8	29.3	5.6	1.0	0.6	2.9	0.1	8.3
Oct-05	11.4	6.86	854	222	76	17	65	229	99.8	27.6	30.4	7.6	2.9	0.5	1.2	0.1	8.7
Nov-05	8.2	6.60	816	312	31	57	39	313	96.9	25.6	19.5	6.3	12.6	0.9	3.5	0.2	9.4
Dec-05	8.3	6.41	795	334	22	56	33	312	98.3	24.8	20.8	6.2	12.7	1.1	4.0	0.2	11.9
Jan-06	7.1	6.27	778	297	25	51	51	338	89.3	23.3	26.3	5.9	13.8	0.9	3.5	0.2	10.3
Feb-06	8.6	6.31	726	299	12	44	50	291	91.3	24.1	21.7	5.9	18.0	0.9	3.5	0.2	10.5
Mar-06	6.7	4.47	901	583	bdl	66	74	396	98.7	24.6	39.3	7.0	21.6	1.2	6.6	0.3	18.0
Apr-06	10.4	6.27	795	252	20	38	33	340	95.6	24.8	19.2	6.4	23.2	1.0	4.5	0.3	10.9
May-06	9.5	6.24	749	272	20	47	30	317	96.4	23.1	20.6	5.9	15.0	0.9	3.1	0.2	10.4

RAW DATA OF SURFACE WATER MONITORING OF THE BOWDEN CLOSE TREATMENT SCHEME (DECEMBER 2003 - MAY 2009)

RAPS 1 INFLUENT	T	pH	EC	Eh	Alk	Q	Cl	SO4	Ca	Mg	Na	K	Fe	Mn	Al	Zn	Si
Jun-06	10.5	6.79	778	152	31	25	37	319	95.9	24.2	20.6	7.2	18.9	0.9	2.9	0.2	10.8
Jul-06	11.5	6.64	819	335	48	12	33	327	100.0	23.5	19.9	7.2	19.9	0.9	2.8	0.2	11.1
Aug-06	13.3	6.54	1016	159	29	1	100	323	122.0	27.5	42.9	6.5	6.0	1.0	5.0	0.2	11.5
Sep-06	13.8	6.56	1022	338	54	1	79	355	133.0	26.6	36.1	6.2	1.6	1.2	5.3	0.2	15.5
Oct-06	12.2	6.43	984	371	56	4	58	387	133.0	28.7	32.8	7.7	3.1	1.1	2.7	0.2	10.7
Nov-06	11.1	6.16	957	335	25	11	30	427	133.0	32.9	26.5	8.5	12.3	1.3	4.0	0.3	12.5
Dec-06	8.8	3.23	1033	638	bdl	56	25	748	98.2	25.1	14.3	4.4	24.0	1.4	7.9	0.4	15.5
Jan-07	5.8	6.29	380	279	20	132	23	122	37.5	10.9	10.2	3.3	4.6	0.2	2.0	0.1	5.9
Feb-07	7.8	3.82	879	630	bdl	41	20	599	92.1	23.7	13.2	4.2	23.1	1.4	6.6	0.3	14.4
Mar-07	8.1	4.40	1261	450	bdl	66	20	421	93.0	24.1	14.1	4.8	26.7	1.4	6.6	0.4	12.4
Apr-07	8.8	5.97	844	234	19	25	23	451	106.0	26.6	17.6	7.1	29.9	1.1	4.6	0.3	11.8
May-07	9.7	6.03	899	232	24	6	23	509	115.0	28.3	18.7	7.3	36.4	1.4	5.8	0.3	13.2
Jun-07	11.1	5.27	655	338	10	33	30	427	95.1	18.3	19.6	4.9	35.0	0.8	13.3	0.2	12.0
Jul-07	11.1	5.51	744	267	23	35	17	326	94.0	24.9	16.7	5.5	12.2	1.0	3.6	0.2	12.4
Aug-07	11.8	5.90	829	302	35	12	20	360	104.0	27.5	22.0	7.1	21.9	1.1	3.9	0.2	12.6
Sep-07	14.0	5.71	914	248	20	7	39	420	127.0	30.3	28.1	7.1	25.2	1.2	6.4	0.3	13.4
Oct-07	9.7	4.63	1036	390	bdl	1	31	495	142.0	31.2	24.0	6.9	17.5	1.8	9.6	0.3	15.8
Nov-07	9.3	6.79	875	240	65	12	30	315	127.0	31.5	20.8	7.6	3.6	0.8	1.8	0.1	9.7
Dec-07	7.8	5.02	857	378	10	39	37	355	117.0	31.2	16.5	6.6	13.7	1.0	4.5	0.2	12.0
Jan-08	7.7	3.48	994	603	bdl	78	22	599	118.0	28.9	13.0	4.9	30.1	1.5	9.2	0.4	15.1
Feb-08	7.1	5.90	837	152	7	27	31	392	106.0	27.2	17.8	5.8	25.2	1.0	6.8	0.3	11.7
Mar-08	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Apr-08	6.6	5.50	751	315	5	40	29	382	94.3	24.1	16.0	4.8	21.0	1.1	5.1	0.2	12.2
May-08	9.3	4.38	758	193	bdl	20	23	347	94.3	24.4	14.3	5.6	23.2	1.2	5.4	0.3	12.7
Jun-08	10.2	6.38	853	135	50	10	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Jul-08	11.7	6.30	828	265	67	18	22	354	108.9	29.0	19.7	6.7	29.1	1.2	6.9	0.2	13.7
Aug-08	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Sep-08	12.1	6.73	769	202	32	30	24	334	99.0	26.4	16.9	6.3	25.9	1.1	5.3	0.2	13.6
Oct-08	11.0	6.23	757	242	40	57	26	324	88.1	24.6	17.1	6.9	18.9	1.0	5.2	0.2	13.0
Nov-08	8.5	6.18	779	332	64	31	26	344	94.9	25.5	16.7	6.1	21.9	1.1	5.4	0.2	13.2
Dec-08	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Jan-09	7.5	6.50	763	301	16	28	30	357	81.1	23.1	18.9	5.8	22.2	1.0	5.1	0.2	12.2

RAW DATA OF SURFACE WATER MONITORING OF THE BOWDEN CLOSE TREATMENT SCHEME (DECEMBER 2003 - MAY 2009)

RAPS 1 INFLUENT	T	pH	EC	Eh	Alk	Q	Cl	SO4	Ca	Mg	Na	K	Fe	Mn	Al	Zn	Si
Feb-09	6.5	4.93	829	351	8	43	27	488	103.7	26.9	21.8	5.4	31.5	1.3	10.1	0.4	14.7
Mar-09	8.1	5.93	752	300	16	24	26	382	86.6	24.3	18.0	6.0	27.9	1.1	5.7	0.2	12.4
Apr-09	8.8	6.47	774	208	35	10	29	360	132.8	27.5	29.2	7.2	177.0	0.8	62.0	0.3	31.6
May-09	10.1	6.54	719	229	46	15	56	316	86.4	23.5	19.7	7.4	16.1	0.9	3.5	0.5	12.2

RAPS 2 INFLUENT	T	pH	EC	Eh	Alk	Q	Cl	SO4	Ca	Mg	Na	K	Fe	Mn	Al	Zn	Si
Nov-03	9.8	4.62	2332	427	bdl	nd	32	2097	166.0	151.0	32.3	10.6	95.8	20.5	85.0	2.8	nd
Dec-03	8.7	5.17	1258	308	10	63	40	730	118.0	58.7	22.6	7.2	37.8	5.3	21.6	0.7	nd
Jan-04	6.9	6.18	641	284	50	adl	35	212	62.3	27.8	13.2	4.7	12.1	1.2	5.9	0.2	nd
Feb-04	7.9	6.05	847	253	35	adl	23	400	95.0	40.0	16.2	5.5	20.5	2.2	10.8	0.4	nd
Mar-04	7.7	5.15	1170	377	10	120	28	779	117.0	55.9	17.3	6.1	39.0	4.5	21.3	0.8	nd
Apr-04	8.5	5.07	1212	360	bdl	105	29	720	112.0	51.4	17.0	6.4	45.4	4.1	21.5	0.8	nd
May-04	9.0	5.04	1386	355	bdl	74	21	816	148.0	68.0	19.5	7.1	48.0	5.9	26.3	1.1	nd
Jun-04	9.9	4.52	2216	373	bdl	24	45	1746	181.0	124.0	27.4	9.7	77.8	14.3	54.5	2.2	nd
Jul-04	10.3	5.06	2400	383	bdl	18	26	1686	187.0	124.0	26.7	8.8	99.0	14.1	66.0	2.4	nd
Aug-04	9.9	4.82	1947	366	bdl	36	31	1408	180.0	109.0	24.6	8.6	71.9	11.6	47.5	1.8	nd
Sep-04	10.0	4.42	1655	380	bdl	50	18	1053	164.0	79.5	19.8	6.4	54.2	7.2	37.3	1.2	nd
Oct-04	10.0	4.52	1927	438	bdl	30	21	1314	159.0	102.0	22.5	7.8	85.9	9.2	41.3	1.7	nd
Nov-04	10.0	4.97	1214	380	bdl	128	21	651	119.0	48.5	15.3	5.3	42.8	4.6	19.5	0.7	nd
Dec-04	9.6	4.97	1483	300	4	62	17	945	153.0	70.3	17.5	8.7	61.8	6.2	22.2	1.0	nd
Jan-05	8.8	4.91	1187	281	1	100	31	692	126.0	55.7	19.3	7.4	44.6	4.2	17.5	0.7	nd
Feb-05	6.6	5.26	1236	323	12	97	22	646	123.0	53.4	13.0	7.5	44.4	4.1	16.0	0.7	nd
Mar-05	7.0	5.76	860	300	16	adl	22	381	96.8	39.7	14.8	6.9	24.7	2.3	9.9	0.4	nd
Apr-05	8.0	6.02	761	179	72	adl	23	324	83.8	34.1	16.1	6.5	14.6	1.5	6.4	0.2	nd
May-05	9.6	4.44	1681	440	bdl	59	24	1159	185.0	86.8	20.1	9.0	77.5	7.4	34.9	1.2	nd
Jun-05	18.5	4.59	2279	490	bdl	18	25	1846	259.0	130.0	25.5	12.2	112.0	12.4	53.2	1.9	nd
Jul-05	10.2	4.17	2509	496	bdl	17	24	2055	275.0	148.0	29.7	14.7	115.0	14.3	63.4	2.2	20.7
Aug-05	10.5	4.39	2446	482	bdl	16	141	2117	271.0	150.0	31.0	15.6	116.0	14.6	63.3	2.2	20.0
Sep-05	11.4	4.49	2467	484	bdl	15	25	2124	278.0	158.0	34.6	16.6	117.0	15.6	63.7	2.3	24.0
Oct-05	10.0	4.47	2344	476	bdl	19	28	1806	244.0	131.0	32.3	15.8	107.0	13.1	52.0	1.9	20.7
Nov-05	9.4	4.93	1367	319	1	97	21	815	148.0	63.4	15.4	8.6	50.6	4.8	23.6	0.8	7.6
Dec-05	8.7	5.54	900	385	14	adl	19	451	98.1	39.3	14.3	6.9	25.5	2.5	12.2	0.4	10.7

RAW DATA OF SURFACE WATER MONITORING OF THE BOWDEN CLOSE TREATMENT SCHEME (DECEMBER 2003 - MAY 2009)

RAPS 2 INFLUENT	T	pH	EC	Eh	Alk	Q	Cl	SO4	Ca	Mg	Na	K	Fe	Mn	Al	Zn	Si
Jan-06	8.6	5.08	1095	357	27	131	24	618	117.0	51.4	14.0	6.9	40.7	3.7	16.6	0.6	11.5
Feb-06	6.6	4.87	1497	391	2	63	22	916	158.0	70.6	15.6	8.4	57.5	5.6	24.2	1.0	13.7
Mar-06	6.4	5.58	1070	312	16	135	31	504	122.0	47.5	18.0	7.6	35.3	3.1	13.0	0.5	13.0
Apr-06	9.5	4.68	1704	432	2	69	24	1128	195.0	88.2	22.0	10.4	79.2	7.1	33.1	1.2	15.2
May-06	9.5	5.61	950	272	30	175	18	454	108.0	44.6	16.7	6.5	29.9	2.8	11.6	0.5	10.6
Jun-06	10.1	4.52	2009	441	bdl	44	23	1342	224.0	107.0	27.9	10.9	94.7	9.6	42.9	1.6	17.3
Jul-06	10.2	4.33	2278	418	bdl	29	21	1651	256.0	124.0	23.5	11.3	108.0	11.6	48.2	2.0	18.7
Aug-06	10.2	4.27	2327	457	bdl	19	25	1860	252.0	137.0	28.4	11.5	97.2	12.7	57.9	2.0	18.6
Sep-06	10.4	4.40	2526	459	bdl	18	26	2010	278.0	149.0	28.3	13.6	122.0	15.0	62.4	2.0	28.3
Oct-06	10.2	4.62	2287	382	bdl	21	27	1756	241.0	133.0	31.8	12.3	97.7	12.3	51.6	1.8	18.8
Nov-06	9.8	4.85	1736	342	4	35	25	1217	186.0	89.8	25.4	11.2	72.8	7.8	34.0	1.3	16.0
Dec-06	9.1	5.54	835	429	40	adl	27	363	88.6	32.3	12.6	5.9	18.7	1.8	9.3	0.3	9.5
Jan-07	6.8	5.96	622	254	75	adl	19	202	66.4	26.2	10.1	5.1	13.9	1.1	1.1	0.2	7.7
Feb-07	8.4	5.27	1094	412	12	175	21	579	115.0	49.9	14.6	6.2	35.6	3.4	16.4	0.6	11.3
Mar-07	9.0	4.78	968	397	6	102	19	1068	176.0	77.5	18.6	8.5	64.1	5.5	28.9	1.1	14.1
Apr-07	9.7	4.43	2040	430	bdl	42	22	1556	226.0	106.0	23.2	11.0	92.6	9.4	42.6	1.5	16.5
May-07	9.7	4.30	2176	441	bdl	31	19	1632	248.0	120.0	25.1	11.5	104.0	11.0	49.3	1.8	17.9
Jun-07	10.2	5.50	803	266	10	adl	17	374	111.0	40.3	15.4	7.9	nd	3.9	40.8	0.8	19.0
Jul-07	10.2	4.52	1604	419	bdl	adl	15	1470	190.0	82.2	20.8	8.8	66.5	6.6	30.2	1.1	14.8
Aug-07	10.6	4.38	2004	421	bdl	40	25	1294	219.0	107.0	22.6	10.6	93.2	9.7	44.6	1.6	17.3
Sep-07	10.3	4.17	2373	477	bdl	22	21	1605	260.0	133.0	26.5	12.1	114.0	12.5	55.4	2.0	19.5
Oct-07	9.9	4.20	2599	417	bdl	17	30	1733	286.0	151.0	30.5	13.9	130.0	14.7	65.9	2.3	20.9
Nov-07	9.6	4.80	1557	270	9	41	26	835	183.0	84.5	21.9	9.9	64.9	7.0	28.7	1.0	14.0
Dec-07	8.8	5.31	1057	322	32	97	44	460	123.0	49.7	15.6	7.1	32.7	3.0	12.3	0.5	10.2
Jan-08	8.6	5.06	1325	273	17	136	23	695	158.0	66.7	20.6	8.2	39.8	4.2	23.8	0.8	11.9
Feb-08	9.1	4.57	1901	189	bdl	59	20	1477	219.0	100.1	24.5	9.8	83.8	7.9	39.7	1.3	16.2
Mar-08	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Apr-08	8.0	6.33	952	260	68	180	23	415	111.0	45.2	16.0	6.3	25.7	2.4	10.6	0.4	10.0
May-08	10.2	4.96	1507	180	15	72	20	879	186.0	80.0	24.7	10.5	57.4	5.1	nd	0.9	14.0
Jun-08	10.4	4.42	2256	267	bdl	23	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Jul-08	10.4	4.45	1960	248	bdl	31	22	1202	228.0	107.0	30.7	11.8	87.4	8.8	38.5	1.4	17.3
Aug-08	11.0	5.95	1618	311	15	adl	22	890	200.0	87.4	28.4	11.3	62.8	6.4	27.0	1.0	15.4

RAW DATA OF SURFACE WATER MONITORING OF THE BOWDEN CLOSE TREATMENT SCHEME (DECEMBER 2003 - MAY 2009)

RAPS 2 INFLUENT	T	pH	EC	Eh	Alk	Q	Cl	SO4	Ca	Mg	Na	K	Fe	Mn	Al	Zn	Si
Sep-08	11.3	5.93	1724	338	8	76	24	1092	200.0	93.0	31.0	10.8	66.9	7.4	32.7	1.2	15.7
Oct-08	9.5	5.41	1805	377	4	adl	28	1118	205.0	96.7	28.4	11.5	80.1	8.1	34.7	1.3	16.1
Nov-08	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Dec-08	8.9	6.71	1110	249	65	177	32	534	135.0	54.5	22.6	8.5	33.1	2.7	12.1	0.5	11.1
Jan-09	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Feb-09	7.8	6.20	1070	273	60	adl	24	490	127.0	50.5	18.9	7.9	32.2	2.7	11.0	0.4	10.6
Mar-09	9.6	4.49	2012	223	bdl	55	23	1250	231.0	107.0	28.8	12.6	96.6	8.5	36.5	1.4	16.6
Apr-09	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
May-09	9.9	4.85	1678	403	5	55	38	986	196.0	90.2	26.2	10.8	67.9	7.2	28.2	1.1	14.6

EFFLUENT	T	pH	EC	Eh	Alk	Q	Cl	SO4	Ca	Mg	Na	K	Fe	Mn	Al	Zn	Si
Nov-03	8.9	6.41	2663	408	220	nd	67	1780	632.0	187.0	45.9	124.0	4.1	20.2	0.5	0.2	nd
Dec-03	2.5	7.03	1219	205	70	nd	88	421	132.0	51.5	27.0	59.2	10.9	2.8	2.0	0.3	nd
Jan-04	5.3	7.02	717	281	71	adl	46	176	82.5	26.4	14.1	15.0	3.9	1.0	0.7	0.1	nd
Feb-04	8.1	7.18	787	234	52	adl	29	311	105.0	31.9	14.9	11.5	9.6	1.8	0.8	0.2	nd
Mar-04	4.7	6.61	1122	357	67	190	38	472	148.0	49.9	19.4	15.8	12.2	3.4	5.9	0.3	nd
Apr-04	9.3	6.90	1175	324	100	150	28	491	157.0	44.3	19.4	17.8	6.6	3.6	1.7	0.1	nd
May-04	13.5	7.49	1266	254	160	117	42	469	166.0	50.3	27.0	22.5	3.0	4.9	0.7	0.1	nd
Jun-04	23.6	6.98	1851	214	320	29	43	821	305.0	92.5	30.1	27.8	6.5	14.1	2.1	0.1	nd
Jul-04	18.0	7.87	2088	327	322	19	30	867	299.0	115.0	30.3	28.5	1.0	6.1	0.5	0.1	nd
Aug-04	17.9	7.51	1709	290	254	49	40	730	253.0	84.0	28.8	26.6	2.8	5.1	0.8	0.1	nd
Sep-04	12.4	6.71	1334	197	71	66	27	698	224.0	63.1	21.3	11.7	0.5	5.4	0.8	0.3	nd
Oct-04	11.3	7.10	1716	188	228	45	31	852	280.0	72.1	24.8	18.8	0.4	6.3	0.5	0.1	nd
Nov-04	9.4	6.10	1047	322	32	adl	17	475	135.0	42.1	16.2	9.6	0.7	3.8	0.6	0.4	nd
Dec-04	6.5	7.22	1362	144	146	93	27	576	199.0	54.6	19.8	20.0	0.6	5.3	0.5	0.1	nd
Jan-05	4.0	6.47	1069	157	50	194	31	517	147.0	45.5	21.6	15.9	4.9	3.5	1.2	0.2	nd
Feb-05	2.0	6.21	965	282	52	adl	34	390	130.0	38.1	13.9	12.3	6.1	2.7	1.2	0.1	nd
Mar-05	6.0	6.61	784	250	40	adl	64	238	87.9	28.7	27.8	8.3	4.0	1.5	0.5	0.2	nd
Apr-05	8.2	6.98	579	101	62	adl	41	164	60.7	20.2	22.9	5.5	3.8	0.9	0.7	0.1	nd
May-05	11.5	7.11	1482	250	146	82	33	678	246.0	67.0	20.9	13.8	0.1	4.1	0.5	0.1	nd
Jun-05	16.2	6.99	2190	186	195	23	35	1161	387.0	116.0	27.4	29.5	7.2	5.1	4.3	0.1	nd
Jul-05	13.6	7.49	2359	190	250	17	32	1280	411.0	128.0	33.0	34.7	0.2	5.0	0.5	0.1	8.8

RAW DATA OF SURFACE WATER MONITORING OF THE BOWDEN CLOSE TREATMENT SCHEME (DECEMBER 2003 - MAY 2009)

EFFLUENT	T	pH	EC	Eh	Alk	Q	Cl	SO4	Ca	Mg	Na	K	Fe	Mn	Al	Zn	Si
Aug-05	13.6	7.63	2293	269	262	17	31	1189	394.0	124.0	32.9	34.9	0.3	4.0	0.5	0.1	8.5
Sep-05	16.6	7.29	2412	232	256	13	33	1332	426.0	136.0	35.6	41.2	0.5	4.0	0.5	0.1	8.9
Oct-05	10.8	7.23	1636	225	168	30	47	668	232.0	74.9	30.5	36.6	0.1	2.4	0.5	0.1	8.3
Nov-05	1.7	5.73	1172	334	12	125	29	584	153.0	52.8	18.7	13.2	9.1	4.2	6.0	0.5	10.6
Dec-05	5.3	6.92	802	363	58	adl	21	312	99.4	32.4	14.2	8.7	4.1	2.0	0.5	0.2	7.9
Jan-06	2.8	6.74	1016	209	62	adl	40	387	129.0	41.7	18.7	10.4	7.0	3.1	0.8	0.2	8.0
Feb-06	2.4	6.56	1160	232	63	100	35	529	167.0	50.0	21.3	13.5	11.0	3.8	3.5	0.2	8.9
Mar-06	4.0	6.53	910	281	35	200	29	391	122.0	37.5	16.8	9.9	14.0	2.8	2.7	0.3	11.2
Apr-06	13.6	6.83	1433	203	48	75	25	717	230.0	68.7	20.1	12.5	7.7	4.7	4.1	0.3	9.5
May-06	16.0	6.85	968	191	45	200	18	411	132.0	43.4	17.6	7.8	20.0	2.9	8.2	0.3	9.3
Jun-06	18.6	7.14	1734	175	144	60	24	852	280.0	83.6	26.7	15.1	1.1	7.7	0.5	0.1	8.2
Jul-06	17.5	6.90	2152	364	156	31	28	1125	361.0	106.0	24.6	17.6	0.8	8.7	0.5	0.1	7.4
Aug-06	14.0	7.30	2299	163	186	24	31	1225	392.0	122.0	29.4	22.8	1.3	8.9	0.6	0.1	6.8
Sep-06	15.6	7.49	2421	161	150	26	29	1328	418.0	126.0	25.7	19.2	0.7	7.2	0.5	0.1	8.9
Oct-06	12.4	7.40	1966	200	166	24	31	983	302.0	100.0	37.7	27.5	0.6	6.7	0.5	0.1	7.8
Nov-06	6.8	7.01	1361	220	103	50	25	636	203.0	62.4	23.6	19.5	2.5	4.9	1.3	0.1	8.3
Dec-06	6.7	7.02	772	181	51	adl	29	290	91.1	27.6	11.9	7.6	6.5	1.6	1.6	0.2	8.3
Jan-07	4.9	6.66	606	204	46	adl	19	229	71.6	23.2	10.4	6.6	10.2	1.3	3.8	0.2	9.6
Feb-07	7.3	6.56	959	214	45	adl	22	404	119.0	39.5	13.2	7.4	11.7	2.7	2.4	0.3	9.2
Mar-07	7.7	5.91	1440	283	20	adl	20	582	173.0	54.8	16.6	9.5	10.5	4.0	5.4	0.5	9.9
Apr-07	13.9	6.83	1846	195	113	49	33	903	281.0	87.6	26.4	40.5	1.7	6.2	0.5	0.2	7.4
May-07	11.2	7.06	1982	181	174	30	24	941	338.0	99.3	26.0	34.8	1.4	6.0	0.5	0.1	5.5
Jun-07	11.2	7.21	1585	177	176	16	25	639	247.0	70.6	24.0	44.5	3.4	5.1	0.9	0.1	5.3
Jul-07	16.2	6.50	1157	182	113	84	16	487	172.0	48.6	17.5	15.5	1.6	3.0	0.5	0.1	7.1
Aug-07	13.6	7.18	1653	165	120	69	20	820	260.0	80.9	21.2	19.1	1.2	4.6	0.5	0.1	8.2
Sep-07	11.6	7.08	1803	157	230	37	24	831	292.0	86.7	22.1	25.6	2.2	3.6	0.5	0.1	7.3
Oct-07	7.9	7.06	2382	194	208	23	19	1301	419.0	126.0	27.7	23.6	10.4	3.5	1.4	0.1	8.5
Nov-07	5.4	6.71	1530	177	127	57	38	661	238.0	74.0	22.3	25.4	4.4	4.2	0.5	0.1	8.0
Dec-07	2.9	6.92	990	124	82	157	38	357	136.0	42.3	15.3	13.3	5.0	2.3	0.5	0.2	7.2
Jan-08	7.6	8.63	1114	176	55	adl	22	546	158.0	51.4	17.2	9.6	6.3	2.8	0.5	0.4	9.0
Feb-08	5.6	6.00	1381	123	30	95	24	728	211.0	65.2	21.0	12.1	21.0	4.8	17.9	0.5	12.1
Mar-08	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd

RAW DATA OF SURFACE WATER MONITORING OF THE BOWDEN CLOSE TREATMENT SCHEME (DECEMBER 2003 - MAY 2009)

EFFLUENT	T	pH	EC	Eh	Alk	Q	Cl	SO4	Ca	Mg	Na	K	Fe	Mn	Al	Zn	Si
Apr-08	7.1	6.67	840	231	60	adl	24	336	111.0	36.7	14.7	7.4	14.3	2.1	3.1	0.2	8.1
May-08	18.5	6.40	1177	169	60	58	20	563	169.0	53.9	20.0	11.0	4.7	2.9	0.4	0.2	8.2
Jun-08	13.0	7.12	1780	199	148	44	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Jul-08	16.5	6.92	1439	194	166	54	17	621	233.0	63.1	24.3	11.6	1.8	3.8	0.5	0.1	8.1
Aug-08	16.9	6.65	1281	113	36	adl	18	639	188.0	65.6	23.8	10.8	19.6	4.3	4.0	0.4	12.2
Sep-08	11.2	6.98	1247	217	75	113	18	622	181.0	59.6	23.6	9.6	5.2	3.5	0.8	0.3	9.9
Oct-08	4.7	7.10	1329	221	62	70	22	651	196.0	65.0	24.3	12.2	3.1	3.9	1.3	0.2	9.4
Nov-08	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Dec-08	7.0	6.65	932	224	65	adl	20	391	125.0	43.4	19.1	8.8	10.6	2.0	1.5	0.2	9.6
Jan-09	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Feb-09	2.5	6.56	876	139	65	adl	22	369	109.0	37.4	15.0	7.5	13.4	1.9	1.2	0.2	8.4
Mar-09	7.9	5.73	1440	165	9	72	24	770	204.0	70.3	23.7	12.8	20.9	5.2	5.2	10.0	12.3
Apr-09	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
May-09	11.5	6.66	1333	243	70	63	25	637	193.0	63.5	22.2	15.5	4.7	4.1	1.3	0.2	8.6

LEGEND
PORE WATER

Parameter	Abbreviation	Unit
Al	aluminium	mg L^{-1}
Alk	alkalinity	mg eq $CaCO_3$
As	arsenic	mg L^{-1}
Ba	barium	mg L^{-1}
bdl	below detection limit	
Ca	calcium	mg L^{-1}
Cd	cadmium	mg L^{-1}
Cl	chloride	mg L^{-1}
Co	cobalt	mg L^{-1}
Cr	chromium	mg L^{-1}
Cu	copper	mg L^{-1}
depth	average depth below surface	cm
Eh	redox potential (uncorrected)	mV
Fe	iron	mg L^{-1}
Fe (II)	ferrous iron in filtered fraction	mg L^{-1}
Fe (III)	ferric iron in filtered fraction	mg L^{-1}
Hg	mercury	mg L^{-1}
K	potassium	mg L^{-1}
Li	lithium	mg L^{-1}
Mg	magnesium	mg L^{-1}
Mn	manganese	mg L^{-1}
Mo	molybdenum	mg L^{-1}
Na	sodium	mg L^{-1}
nd	not determined	
Ni	nickel	mg L^{-1}
Pb	lead	mg L^{-1}
pH		
S	sulfur	mg L^{-1}
Sb	antimony	mg L^{-1}
Se	selenium	mg L^{-1}
Si	silicium	mg L^{-1}
SO4	sulfate	mg L^{-1}
Sr	strontium	mg L^{-1}
Tl	thallium	mg L^{-1}
Zn	zinc	mg L^{-1}

PORE WATER

RAPS 1

Core	Depth	pH	Eh	Alk	Cl	SO4
3	2	nd	nd	nd	21.6	126
3	4.5	nd	nd	nd	32.4	210
3	7.5	8.7	84	115	nd	nd
3	10.5	nd	nd	nd	40.5	249
3	13.5	8.4	181	240	nd	nd
3	19.5	8.7	153	180	nd	nd
3	22.5	nd	nd	nd	36.3	229
4	2	nd	nd	nd	49.1	279
4	4.5	nd	nd	nd	115	44.3
4	7.5	9.2	89	1000	nd	nd
4	10.5	nd	nd	nd	502	4
4	13.5	9.4	6	2095	nd	nd
4	19.5	9.5	35	2495	nd	nd
4	22.5	nd	nd	nd	802	3

RAPS 2

Core	Depth	pH	Eh	Alk	Cl	SO4
1	2	nd	nd	nd	13.6	598
1	4.5	6.1	28	30	23.8	1284
1	7.5	nd	nd	nd	12.5	664
1	10.5	6.2	-21	35	29.7	1354
1	13.5	nd	nd	nd	27.1	538
1	19.5	8.7	-8	740	nd	nd
1	22.5	nd	nd	nd	42.2	82
2	2	nd	nd	nd	10.3	347
2	4.5	6.2	-1	40	38.4	953
2	7.5	nd	nd	nd	48.7	491
2	10.5	8.8	162	395	135	582
2	13.5	nd	nd	nd	162	285
2	19.5	9.4	83	1340	nd	nd
2	22.5	nd	nd	nd	391	171

PORE WATER

RAPS 1

Core	Depth	Al	As	Ba	Ca	Cd	Co	Cr	Cu	Fe	Hg	K	Li	Mg	Mn	Mo	Na	Ni	Pb	S	Sb	Se	Si	Sr	Tl	Zn
3	2	bdl	0.01	0.08	52.36	bdl	bdl	bdl	bdl	bdl	bdl	8.21	0.09	17.33	1.20	bdl	12.0	bdl	0.03	46.7	bdl	bdl	2.73	0.18	0.07	bdl
3	4.5	bdl	bdl	0.09	88.32	bdl	bdl	bdl	bdl	bdl	bdl	9.55	0.13	26.04	1.02	bdl	19.7	bdl	0.03	84.4	bdl	bdl	6.43	0.31	0.12	bdl
3	7.5	bdl	bdl	0.18	81.78	bdl	bdl	bdl	bdl	0.14	0.02	12.42	0.13	30.22	0.82	bdl	21.2	bdl	0.03	82.6	bdl	bdl	3.89	0.32	0.10	bdl
3	10.5	bdl	bdl	0.12	91.49	bdl	bdl	bdl	bdl	bdl	bdl	11.67	0.14	30.11	0.60	bdl	20.8	bdl	0.03	85.0	bdl	bdl	8.37	0.34	0.01	bdl
3	13.5	bdl	bdl	0.16	81.56	bdl	bdl	bdl	bdl	bdl	0.00	16.51	0.13	30.54	0.72	bdl	22.4	bdl	0.03	71.4	bdl	bdl	4.20	0.32	0.06	bdl
3	19.5	bdl	bdl	0.16	68.33	bdl	bdl	bdl	bdl	bdl	0.01	12.42	0.11	26.19	0.83	bdl	19.0	bdl	0.02	70.2	bdl	bdl	2.60	0.28	0.12	bdl
3	22.5	bdl	bdl	0.14	87.94	bdl	bdl	bdl	bdl	bdl	bdl	13.17	0.14	29.17	0.58	bdl	20.6	bdl	0.04	81.3	bdl	bdl	8.48	0.32	0.05	bdl
4	2	bdl	bdl	0.08	77.82	bdl	bdl	bdl	bdl	bdl	bdl	29.41	0.11	28.71	1.14	bdl	22.5	bdl	0.04	51.6	bdl	bdl	8.00	0.30	0.13	bdl
4	4.5	bdl	bdl	0.11	60.12	bdl	bdl	bdl	bdl	3.72	bdl	129	0.11	52.34	0.82	bdl	49.3	bdl	0.05	15.3	bdl	bdl	10.2	0.28	0.05	bdl
4	7.5	bdl	bdl	0.06	39.13	bdl	bdl	bdl	bdl	2.46	bdl	337	0.07	84.20	0.17	bdl	106.1	bdl	0.02	bdl	bdl	bdl	2.14	0.19	0.09	bdl
4	10.5	bdl	bdl	0.03	46.61	bdl	bdl	bdl	bdl	bdl	0.01	615	0.08	146	bdl	bdl	179.2	bdl	0.04	4.1	bdl	bdl	8.01	0.31	0.06	bdl
4	13.5	0.05	0.001	0.39	119	bdl	bdl	bdl	bdl	18.9	bdl	672	0.07	132	4.77	bdl	195.4	bdl	0.04	bdl	bdl	bdl	3.58	0.50	0.08	bdl
4	19.5	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
4	22.5	bdl	bdl	0.01	36.47	bdl	bdl	bdl	bdl	0.38	bdl	916	0.07	160	bdl	bdl	247.3	bdl	0.04	5.6	bdl	bdl	3.23	0.21	0.12	bdl

PORE WATER

RAPS 2

Core	Depth	Al	As	Ba	Ca	Cd	Co	Cr	Cu	Fe	Hg	K	Li	Mg	Mn	Mo	Na	Ni	Pb	S	Sb	Se	Si	Sr	Tl	Zn
1	2	bdl	bdl	bdl	111.2	bdl	bdl	bdl	bdl	114	0.02	9.02	0.26	51.80	4.75	bdl	15.9	bdl	0.03	239	bdl	bdl	0.93	0.26	0.13	bdl
1	4.5	0.60	bdl	0.07	156.1	bdl	bdl	bdl	bdl	230	bdl	15.07	0.40	72.40	8.76	bdl	24.4	0.003	0.03	379	bdl	bdl	4.42	0.42	0.06	bdl
1	7.5	bdl	bdl	bdl	116.8	bdl	bdl	bdl	bdl	85.9	bdl	6.94	0.21	36.78	4.04	bdl	11.8	bdl	0.03	206	bdl	bdl	1.30	0.27	0.05	bdl
1	10.5	0.21	bdl	0.04	142.8	bdl	bdl	bdl	bdl	233	0.07	17.83	0.39	77.45	8.46	bdl	25.7	bdl	0.04	375	bdl	bdl	2.88	0.31	0.13	bdl
1	13.5	bdl	bdl	bdl	168.1	bdl	bdl	bdl	bdl	7.19	bdl	36.40	0.49	114	5.96	bdl	35.0	bdl	0.03	248	bdl	bdl	1.72	0.46	0.10	bdl
1	19.5	4.10	bdl	0.82	234.3	bdl	bdl	bdl	bdl	66	0.003	77.07	0.60	119	14.6	bdl	47.5	bdl	0.11	53.7	bdl	bdl	7.54	1.24	0.14	0.11
1	22.5	bdl	bdl	bdl	43.97	bdl	bdl	bdl	bdl	0.18	bdl	77.86	0.58	134	bdl	bdl	45.7	bdl	0.03	28.5	bdl	bdl	3.88	0.26	0.12	bdl
2	2	bdl	bdl	bdl	87.18	bdl	bdl	bdl	bdl	43.8	0.004	5.55	0.20	29.51	2.42	bdl	9.5	bdl	0.04	140	bdl	bdl	1.70	0.20	0.03	bdl
2	4.5	bdl	bdl	0.05	132.3	bdl	bdl	bdl	bdl	87.1	0.003	40.58	0.43	67.22	6.37	bdl	27.6	bdl	0.03	269	bdl	bdl	3.26	0.34	0.13	bdl
2	7.5	bdl	bdl	bdl	145.2	bdl	bdl	bdl	bdl	2.09	bdl	77.62	0.41	71.66	4.90	bdl	34.4	bdl	0.04	212	bdl	bdl	2.02	0.40	0.02	bdl
2	10.5	bdl	bdl	0.03	50.61	bdl	bdl	bdl	bdl	bdl	bdl	82.37	0.20	52.36	1.13	bdl	28.2	bdl	0.02	71.4	bdl	bdl	1.67	0.18	0.06	bdl
2	13.5	bdl	0.001	bdl	43.42	bdl	bdl	bdl	bdl	bdl	bdl	274	0.36	113	bdl	bdl	81.6	bdl	0.04	96.3	bdl	bdl	12.2	0.24	0.12	bdl
2	19.5	bdl	bdl	0.02	65.93	bdl	bdl	bdl	bdl	0.28	0.01	387	0.19	105	0.70	bdl	109	bdl	0.02	84.0	bdl	bdl	0.97	0.22	0.13	bdl
2	22.5	bdl	bdl	0.12	65.59	bdl	bdl	bdl	bdl	5.22	0.01	616	0.11	135	0.57	bdl	166	bdl	0.04	62.3	bdl	bdl	10.3	0.28	0.02	bdl

PORE WATER

RAPS 1

Core	Depth	Fe	Fe (II)	Fe (III)
3	2	bdl	nd	nd
3	4.5	0.14	0.05	0.09
3	7.5	bdl	nd	nd
3	10.5	bdl	0.05	bdl
3	13.5	bdl	nd	nd
3	19.5	bdl	0.05	bdl
3	22.5	bdl	nd	nd
4	2	bdl	nd	nd
4	4.5	2.79	nd	nd
4	7.5	2.46	0.05	2.41
4	10.5	bdl	nd	nd
4	13.5	18.87	0.21	18.67
4	19.5	nd	nd	nd
4	22.5	0.29	nd	nd

RAPS 2

Core	Depth	Fe	Fe (II)	Fe (III)
1	2	85.29	nd	nd
1	4.5	230	119	111
1	7.5	64.41	nd	nd
1	10.5	233	186	47.34
1	13.5	5.39	nd	nd
1	19.5	66.41	5.14	61.26
1	22.5	0.13	nd	nd
2	2	32.89	nd	nd
2	4.5	87.09	31.28	55.80
2	7.5	1.57	nd	nd
2	10.5	bdl	26.97	bdl
2	13.5	bdl	nd	nd
2	19.5	0.28	5.14	bdl
2	22.5	3.91	nd	nd

LEGEND
SEDIMENT

Parameter	Abbreviation	Unit
Al	aluminium	g kg^{-1}
As	arsenic	g kg^{-1}
AVS	acid-volatile sulfur (dry wt)	mg kg^{-1}
Ba	barium	g kg^{-1}
bdl	below detection limit	
Ca	calcium	g kg^{-1}
Cd	cadmium	g kg^{-1}
Co	cobalt	g kg^{-1}
Cr	chromium	g kg^{-1}
CRS	chromium reducible sulfur (dry wt)	mg kg^{-1}
Cu	copper	g kg^{-1}
ES	elemental sulfur (dry wt)	mg kg^{-1}
Fe	iron	g kg^{-1}
Hg	mercury	g kg^{-1}
HydFe	hydroxide bound iron	mg kg^{-1}
K	potassium	g kg^{-1}
Li	lithium	g kg^{-1}
Mg	magnesium	g kg^{-1}
Mn	manganese	g kg^{-1}
Mo	molybdenum	g kg^{-1}
Na	sodium	g kg^{-1}
Ni	nickel	g kg^{-1}
Pb	lead	g kg^{-1}
S	sulfur	g kg^{-1}
Sb	antimony	g kg^{-1}
Se	selenium	g kg^{-1}
Si	silicium	g kg^{-1}
Sr	strontium	g kg^{-1}
TAD	total acid digests	g kg^{-1}
Tl	thallium	g kg^{-1}
water content	(weight wet-weight dry)/(weight wet)*100%	%
Zn	zinc	g kg^{-1}

WATER CONTENT, REDUCED INORGANIC SULFUR AND HYDROXIDE BOUND IRON

RAPS 1

Core	Depth	Water Content	ES	AVS	CRS	HydFe
3	2	73.8	82	122	3838	620
3	4.5	61.6	332	66	565	267
3	10.5	67.4	402	402	1912	85
3	22.5	50.6	319	160	213	460
4	2	51.4	338	1072	1185	553
4	4.5	43.5	229	413	734	356
4	10.5	40.4	bdl	125	375	585
4	22.5	39.6	bdl	bdl	28	614

RAPS 2

Core	Depth	Water Content	ES	AVS	CRS	HydFe
1	2	77.8	bdl	1813	906	1153
1	7.5	83.9	bdl	2421	1210	2296
1	13.5	54.0	bdl	128	384	296
1	22.5	41.5	bdl	61	162	527
2	2	74.8	bdl	2098	4982	124
2	7.5	82.5	5275	2743	316	2764
2	13.5	81.3	2023	1180	1854	1779
2	22.5	56.8	450	bdl	193	506

TOTAL ACID DIGESTION

RAPS 1

Core	Depth	Ba	Sb	Hg	Si	S	Li	Al	As	Ca	Co	Cr	Cu	Fe	K	Mg	Mn	Mo	Na	Ni	Pb	Se	Sr	Tl	Zn
3	2	0.13	0.001	0.001	2.54	3.37	0.01	7.99	0.01	52.24	0.04	0.01	0.08	29.24	1.25	3.70	3.23	0.002	0.28	0.07	0.06	0.006	0.32	0.001	0.35
3	4.5	0.16	bdl	0.001	1.23	3.00	0.01	6.67	0.01	36.26	0.01	0.02	0.03	20.88	1.20	2.52	0.66	0.001	0.23	0.01	0.05	0.003	0.18	0.001	0.14
3	10.5	0.07	bdl	0.002	1.39	5.83	0.00	2.99	bdl	67.40	0.01	0.01	0.03	12.83	1.08	3.81	0.45	0.001	0.29	0.03	0.03	0.002	0.31	0.001	0.22
3	22.5	0.11	0.001	0.001	1.84	5.33	0.01	5.59	0.01	76.05	0.01	0.01	0.02	17.67	1.53	5.22	0.45	0.002	0.29	0.01	0.05	0.003	0.51	0.003	0.17
4	2	0.08	bdl	0.002	0.54	3.25	0.01	4.51	0.01	127.84	bdl	0.02	0.03	13.74	1.67	4.75	0.43	0.002	0.29	bdl	0.04	0.003	0.87	0.003	0.05
4	4.5	0.15	bdl	0.002	0.56	3.30	0.01	5.35	0.02	88.38	bdl	0.01	0.03	17.58	2.39	5.60	0.62	0.002	0.32	bdl	0.06	0.004	0.45	0.002	0.07
4	10.5	0.31	bdl	0.001	0.68	2.39	0.01	4.11	0.02	76.19	bdl	0.01	0.04	16.91	3.48	4.02	0.57	0.002	0.41	bdl	0.06	0.004	0.39	0.002	0.07
4	22.5	0.14	bdl	0.001	0.75	2.12	0.01	4.25	0.01	78.12	bdl	0.02	0.02	17.82	4.48	4.89	0.62	0.002	0.51	bdl	0.06	0.004	0.40	0.002	0.05

RAPS 2

Core	Depth	Ba	Sb	Hg	Si	S	Li	Al	As	Ca	Co	Cr	Cu	Fe	K	Mg	Mn	Mo	Na	Ni	Pb	Se	Sr	Tl	Zn
1	2	0.04	0.001	0.002	7.85	15.07	0.01	91.89	0.02	6.65	bdl	0.02	0.12	86.77	0.50	0.78	0.12	0.003	0.20	0.01	0.17	0.006	0.03	0.001	0.31
1	7.5	0.04	0.001	0.001	5.81	17.55	0.01	65.63	0.02	15.73	0.01	0.02	0.09	179	0.72	1.29	0.17	0.003	0.25	0.00	0.22	0.006	0.10	0.001	0.24
1	13.5	0.10	bdl	0.001	1.92	4.77	0.02	24.28	0.01	65.86	0.01	0.01	0.04	28.70	1.05	4.08	0.40	0.002	0.23	0.00	0.10	0.003	0.30	0.001	0.18
1	22.5	0.10	bdl	0.002	0.59	3.03	0.01	6.03	0.01	95.73	0.01	0.01	0.03	15.59	1.52	5.15	0.70	0.002	0.25	0.00	0.06	0.003	0.56	0.003	0.13
2	2	0.07	0.001	0.002	7.15	14.59	0.01	60.78	0.02	9.82	0.01	0.02	0.08	167	0.63	1.22	0.16	0.003	0.24	0.02	0.16	0.004	0.05	0.000	0.58
2	7.5	0.07	0.001	0.003	1.66	7.36	0.01	7.00	0.01	46.51	0.01	0.01	0.05	22.41	1.55	2.55	0.53	0.001	0.31	0.01	0.03	0.002	0.17	0.001	0.17
2	13.5	0.12	bdl	0.002	1.43	5.45	0.01	5.11	0.01	35.23	bdl	0.01	0.04	15.38	3.63	3.35	0.79	0.001	0.54	bdl	0.03	0.003	0.17	0.000	0.09
2	22.5	0.19	0.001	0.001	1.45	1.98	0.01	8.23	0.01	23.96	0.01	0.02	0.04	24.78	3.69	3.92	0.82	0.001	0.40	bdl	0.04	0.003	0.12	0.001	0.08

SEQUENTIAL EXTRACTION

RAPS 1

Core	Depth	Step	Ba	Si	S	Li	Al	Ca	Co	Cu	Fe	K	Mg	Mn	Na	Ni	Pb	Sr	Zn
3	2	1	0.03	0.47	0.62	nd	0.05	22.3	0.012	bdl	bdl	0.54	1.52	1.73	0.13	0.020	bdl	0.175	0.11
3	2	2	0.08	1.27	0.07	nd	3.77	17.1	0.025	0.018	10.41	0.24	1.35	1.39	0.04	0.046	0.035	0.080	0.19
3	2	3	0.01	0.78	2.60	nd	1.36	10.1	0.005	0.051	4.35	0.13	0.35	0.05	0.05	0.005	0.008	0.055	0.03
3	2	4	0.01	0.01	0.09	nd	2.81	2.8	0.001	0.007	14.48	0.35	0.50	0.05	0.06	bdl	0.015	0.014	0.02
3	4.5	1	0.04	0.19	0.55	nd	0.03	14.9	0.007	bdl	0.35	0.43	1.18	0.42	0.10	bdl	bdl	0.077	0.05
3	4.5	2	0.07	0.45	0.04	nd	1.47	14.2	0.005	0.006	4.34	0.21	0.44	0.16	0.02	0.011	0.027	0.065	0.06
3	4.5	3	0.02	0.58	2.18	nd	0.89	6.9	0.002	0.021	2.74	0.10	0.26	0.02	0.05	bdl	0.005	0.029	0.01
3	4.5	4	0.03	0.01	0.23	nd	4.27	0.3	0.001	0.006	13.46	0.46	0.63	0.06	0.06	bdl	0.014	0.007	0.02
3	10.5	1	0.02	0.17	1.12	nd	0.03	21.2	0.006	bdl	0.50	0.51	1.65	0.30	0.13	0.009	bdl	0.136	0.09
3	10.5	2	0.04	0.32	0.07	nd	0.85	21.5	0.004	0.003	5.01	0.20	1.04	0.09	0.03	0.023	0.021	0.082	0.11
3	10.5	3	0.01	0.89	3.88	nd	0.80	20.1	0.002	0.027	2.98	0.15	0.70	0.06	0.06	0.001	0.005	0.074	0.01
3	10.5	4	bdl	0.01	0.75	nd	1.32	4.5	0.000	0.001	4.33	0.23	0.42	0.00	0.07	bdl	bdl	0.023	0.00
3	22.5	1	0.02	0.11	0.86	nd	0.02	25.2	0.004	bdl	0.25	0.47	1.33	0.27	0.11	0.001	bdl	0.268	0.03
3	22.5	2	0.04	0.28	0.05	nd	0.64	30.7	0.003	bdl	3.47	0.23	2.05	0.10	0.05	0.011	0.022	0.147	0.10
3	22.5	3	0.01	0.35	3.36	nd	0.38	15.5	0.002	0.022	3.55	0.11	1.19	0.03	0.06	0.001	0.009	0.076	0.02
3	22.5	4	0.04	1.10	1.06	nd	4.54	4.7	0.001	0.002	10.39	0.72	0.65	0.04	0.09	bdl	0.017	0.018	0.01
4	2	1	0.02	0.07	0.43	nd	0.02	22.8	0.001	bdl	bdl	0.33	0.59	0.95	0.27	0.080	bdl	0.174	0.01
4	2	2	0.03	0.17	0.03	nd	0.44	30.6	0.002	bdl	bdl	2.26	0.18	1.07	0.09	0.037	0.016	0.156	0.02
4	2	3	0.01	0.22	2.56	nd	0.21	47.2	bdl	0.002	0.01	1.68	0.14	1.59	0.04	0.081	0.003	0.356	0.01
4	2	4	0.02	0.09	0.23	nd	3.84	27.3	0.005	0.014	0.02	9.46	0.75	1.14	0.03	0.091	0.023	0.182	0.01
4	4.5	1	0.02	0.09	0.32	nd	0.02	21.7	0.002	bdl	bdl	0.25	1.38	1.09	0.34	0.134	bdl	0.152	0.01
4	4.5	2	0.07	0.22	0.03	nd	0.54	26.7	0.003	bdl	bdl	3.20	0.26	1.17	0.14	0.034	0.027	0.121	0.03
4	4.5	3	0.02	0.22	2.68	nd	0.34	33.1	0.003	0.003	0.02	2.40	0.15	2.06	0.07	0.065	bdl	0.160	0.01
4	4.5	4	0.04	0.03	0.27	nd	4.44	6.9	0.011	0.010	0.01	11.73	0.60	1.28	0.06	0.082	0.030	0.019	0.03

SEQUENTIAL EXTRACTION

RAPS 1 (continued)

Core	Depth	Step	Ba	Si	S	Li	Al	Ca	Co	Cu	Fe	K	Mg	Mn	Na	Ni	Pb	Sr	Zn
4	10.5	1	0.02	0.11	0.15	nd	0.02	21.0	0.002	bdl	0.00	0.18	2.55	1.18	0.32	0.242	bdl	0.138	0.01
4	10.5	2	0.09	0.28	0.03	nd	0.65	27.7	0.003	bdl	0.01	2.79	0.39	1.15	0.16	0.039	0.028	0.123	0.03
4	10.5	3	0.03	0.28	2.01	nd	0.44	23.8	0.002	0.003	0.03	2.00	0.14	1.20	0.04	0.060	0.005	0.113	0.01
4	10.5	4	0.17	0.01	0.20	nd	3.01	3.8	0.011	0.009	0.01	11.94	0.40	0.48	0.05	0.070	0.029	0.014	0.02
4	22.5	1	0.02	0.11	0.10	nd	0.01	21.6	0.001	bdl	0.00	0.25	3.50	1.21	0.28	0.351	bdl	0.143	0.00
4	22.5	2	0.06	0.27	0.01	nd	0.53	26.4	0.001	bdl	0.00	2.60	0.41	1.48	0.21	0.032	0.025	0.119	0.02
4	22.5	3	0.02	0.30	1.94	nd	0.26	26.0	0.001	0.002	0.01	1.94	0.12	1.56	0.07	0.058	0.004	0.126	0.01
4	22.5	4	0.04	0.07	0.08	nd	3.45	4.1	0.006	0.018	0.01	13.03	0.46	0.64	0.06	0.073	0.028	0.008	0.02

RAPS 2

Core	Depth	Step	Ba	Si	S	Li	Al	Ca	Co	Cu	Fe	K	Mg	Mn	Na	Ni	Pb	Sr	Zn
1	2	1	0.02	0.95	0.62	0.004	8.44	5.1	bdl	bdl	0.01	0.66	0.14	0.49	0.08	0.084	0.000	0.021	0.11
1	2	2	0.02	1.72	3.04	0.003	23.18	0.9	0.001	0.001	0.01	7.54	0.04	0.09	0.02	0.008	0.041	0.007	0.10
1	2	3	0.01	4.67	7.68	0.000	46.87	0.4	0.003	0.006	0.08	18.37	0.08	0.03	bdl	0.052	0.059	0.005	0.07
1	2	4	bdl	0.51	3.73	0.005	13.40	0.2	0.015	0.012	0.03	60.20	0.24	0.16	bdl	0.057	0.071	0.001	0.02
1	8.5	1	0.02	0.67	1.11	0.001	4.30	13.9	bdl	bdl	bdl	0.35	0.21	0.75	0.11	0.127	0.000	0.079	0.05
1	8.5	2	0.02	1.70	2.58	0.003	22.29	1.6	0.002	0.001	0.00	9.98	0.05	0.27	0.03	0.009	0.037	0.011	0.10
1	8.5	3	0.01	3.40	6.49	bdl	22.67	0.1	bdl	0.006	0.06	18.42	0.09	0.03	bdl	0.053	0.045	0.003	0.05
1	8.5	4	bdl	0.04	7.37	0.009	16.37	0.2	0.022	0.013	0.03	150	0.37	0.25	0.02	0.066	0.138	0.001	0.04
1	13.5	1	0.01	0.13	0.66	bdl	0.35	18.2	bdl	bdl	bdl	0.32	0.32	1.09	0.18	0.085	0.000	0.104	0.04
1	13.5	2	0.04	0.87	0.55	0.004	8.21	22.4	0.001	bdl	bdl	4.64	0.12	1.37	0.11	0.023	0.033	0.098	0.07
1	13.5	3	0.01	0.89	2.99	bdl	8.32	24.5	bdl	0.002	0.02	1.92	0.11	0.98	0.04	0.057	0.016	0.096	0.02
1	13.5	4	0.03	0.02	0.58	0.011	7.40	0.7	0.011	0.007	0.01	21.83	0.49	0.64	0.07	0.064	0.053	0.006	0.05
1	22.5	1	0.02	0.06	0.27	bdl	0.02	22.8	0.001	bdl	bdl	0.43	0.56	1.09	0.35	0.091	0.000	0.197	0.03
1	22.5	2	0.04	0.20	0.04	0.001	0.67	33.1	0.001	bdl	bdl	2.80	0.17	1.93	0.22	0.031	0.019	0.169	0.06
1	22.5	3	0.01	0.23	2.58	bdl	0.42	34.1	0.001	0.002	0.02	2.13	0.11	1.57	0.08	0.062	0.002	0.183	0.01
1	22.5	4	0.03	0.11	0.14	0.007	4.92	5.8	0.006	0.010	0.01	10.24	0.68	0.55	0.05	0.070	0.036	0.013	0.02

SEQUENTIAL EXTRACTION

RAPS 2 (continued)

Core	Depth	Step	Ba	Si	S	Li	Al	Ca	Co	Cu	Fe	K	Mg	Mn	Na	Ni	Pb	Sr	Zn
2	2	1	0.02	0.59	0.63	0.003	1.90	8.65	bdl	8.65	bdl	0.88	0.23	0.85	0.13	0.122	bdl	0.040	0.21
2	2	2	0.04	2.06	1.62	0.002	16.71	0.84	0.001	0.84	bdl	14.52	0.06	0.09	0.02	0.010	0.026	0.006	0.27
2	2	3	0.01	4.37	5.74	bdl	26.87	0.16	0.001	0.16	0.07	21.63	0.08	0.02	bdl	0.048	0.031	0.002	0.07
2	2	4	bdl	0.12	6.60	0.006	15.31	0.16	0.017	0.16	0.02	130	0.26	0.25	0.01	0.056	0.106	0.001	0.03
2	7.5	1	0.02	0.18	1.66	0.001	0.14	15.99	bdl	15.99	bdl	1.69	1.09	1.59	0.41	0.185	bdl	0.072	0.06
2	7.5	2	0.04	0.64	0.47	0.001	4.32	11.55	0.002	11.55	0.01	11.01	0.17	0.41	0.10	0.018	0.023	0.044	0.10
2	7.5	3	0.01	0.82	4.61	bdl	1.47	18.14	0.002	18.14	0.05	5.41	0.13	0.32	0.02	0.053	0.008	0.056	0.01
2	7.5	4	bdl	0.02	0.61	0.004	1.07	0.83	0.001	0.83	bdl	4.30	0.17	0.22	bdl	0.057	bdl	0.002	bdl
2	13.5	1	0.04	0.22	1.26	bdl	0.04	17.93	0.001	17.93	bdl	0.67	2.89	2.41	0.59	0.404	bdl	0.092	0.03
2	13.5	2	0.07	0.36	0.15	0.001	2.11	13.16	0.002	13.16	0.01	6.96	0.31	0.49	0.18	0.025	0.020	0.058	0.06
2	13.5	3	0.01	0.80	3.62	bdl	0.96	3.93	0.001	3.93	0.03	4.41	0.10	0.23	0.02	0.047	0.006	0.019	0.01
2	13.5	4	bdl	0.04	0.42	0.005	2.00	0.22	0.001	0.22	bdl	3.34	0.32	0.22	bdl	0.065	bdl	0.002	bdl
2	22.5	1	0.03	0.20	0.37	bdl	0.03	14.65	0.001	14.65	bdl	0.36	2.60	1.90	0.40	0.258	bdl	0.065	0.02
2	22.5	2	0.10	0.48	0.05	0.001	1.64	7.71	0.002	7.71	0.01	5.67	0.32	1.04	0.31	0.018	0.027	0.039	0.04
2	22.5	3	0.02	0.74	1.46	bdl	1.03	1.31	0.001	1.31	0.02	3.37	0.11	0.33	0.03	0.044	0.005	0.012	0.01
2	22.5	4	0.04	0.03	0.10	0.008	5.53	0.28	0.003	0.28	0.01	15.38	0.66	0.66	0.07	0.078	0.011	0.004	0.02

LEGEND
SURFACE WATER

Parameter	Abbreviation	Unit
adl	above detection limit	
Al	aluminium	mg L^{-1}
Alk	alkalinity	mg eq $CaCO_3$
bdl	below detection limit	
Ca	calcium	mg L^{-1}
Cl	chloride	mg L^{-1}
DO	dissolved oxygen	%, mg L^{-1}
EC	electrical conductivity	µS cm^{-1}
Eh	redox potential (uncorrected)	mV
Fe	iron	mg L^{-1}
Fe (II)	ferrous iron	mg L^{-1}
K	potassium	mg L^{-1}
Mg	magnesium	mg L^{-1}
Mn	manganese	mg L^{-1}
Na	sodium	mg L^{-1}
NA	not available	
nd	not determined	
nf	no flow	
nm	not measured	
Q	flow	L min^{-1}
Qov	flow of overflow	L min^{-1}
Si	silicium	mg L^{-1}
SO4	sulfate	mg L^{-1}
S(II)	sulfide	mg L^{-1}
T	temperature	°C
Zn	zinc	mg L^{-1}
IA	ion balance	%

SURFACE WATER

Date	Sample	T	pH	EC	Eh	Alk	DO, %	DO, mg/L	S(II)	Fe(II)	Q	Cl	SO4	Ca T	Mg T	Na T	K T	Fe T	Mn T
Apr-08	influent 1	6.6	5.50	751	315	5	91	10.9	nm	13.35	40	29	382	94.3	24.1	16.0	4.8	21.0	1.1
Apr-08	influent 1	9.1	4.44	785	418	12	54	6.1	nm	14.53	nf	nm	nm	nm	nm	nm	nm	nm	nm
May-08	influent 1	10.4	4.63	767	411	7	75	8.2	nm	17.30	nm	28	356	94.2	24.4	15.9	5.7	54.9	1.2
May-08	influent 1	9.6	6.40	836	217	34	83	9.4	nm	18.66	nm	29	347	106.2	27.7	20.0	7.0	29.0	1.0
Jun-08	influent 1	10.8	6.28	869	220	54	77	8.9	nm	23.62	8	30	380	105.0	26.9	19.7	7.8	34.8	1.2
Jul-08	influent 1	11.7	6.30	828	265	61	86	9.2	nm	18.78	18	22	354	108.9	29.0	19.7	6.7	29.1	1.2
Sep-08	influent 1	12.1	6.73	769	202	32	77	8.3	nm	14.67	30	24	334	99.0	26.4	16.9	6.3	25.9	1.1
Oct-08	influent 1	11.0	6.23	757	242	40	79	8.9	nm	16.83	57	26	324	88.1	24.6	17.1	6.9	18.9	1.0
Nov-08	influent 1	8.5	6.18	779	332	43	48	5.9	nm	18.13	31	26	344	94.9	25.5	16.7	6.1	21.9	1.1
Jan-09	influent 1	7.5	6.50	763	301	16	80	8.9	nm	17.80	28	30	357	81.1	23.1	18.9	5.8	22.2	1.0
Feb-09	influent 1	6.5	4.93	829	351	8	55	6.4	nm	19.96	43	27	488	103.7	26.9	21.8	5.4	31.5	1.3
Mar-09	influent 1	8.1	5.93	752	300	16	90	11.0	bdl	23.38	24	26	382	86.6	24.3	18.0	6.0	27.9	1.1
Apr-09	influent 1	8.8	6.47	774	208	35	82	9.5	0.011	19.55	10	29	360	132.8	27.5	29.2	7.2	177.0	0.8
May-09	influent 1	10.1	6.54	719	229	46	86	9.9	bdl	12.99	15	56	316	86.4	23.5	19.7	7.4	16.1	0.9
Jun-09	influent 1	10.6	6.44	668	260	62	80	7.1	bdl	6.33	104	26	248	86.1	22.0	19.7	6.2	10.5	0.6
Jul-09	influent 1	11.8	4.20	726	482	bdl	nm	nm	0.002	9.51	52	20	368	86.1	24.1	14.0	4.8	16.0	1.3
Aug-09	influent 1	12.2	6.49	795	237	13	nm	nm	0.002	15.18	19	21	356	97.6	28.4	17.1	6.8	21.4	1.1
Sep-09	influent 1	11.6	6.57	721	234	41	73	8.1	bdl	7.51	8	29	297	90.9	25.7	19.1	8.0	12.9	0.8
Oct-09	influent 1	10.2	5.72	804	279	8	8	0.9	bdl	10.98	2	23	371	99.0	26.3	18.3	7.7	18.4	1.2

SURFACE WATER

Date	Sample	T	pH	EC	Eh	Alk	DO, %	DO, mg/L	S(II)	Fe(II)	Q	Cl	SO4	Ca T	Mg T	Na T	K T	Fe T	Mn T
Apr-08	effluent 1	nm	nm	nm	nm	nm	1	0.1	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm
Apr-08	effluent 1	6.3	7.15	887	26	109	1	0.1	nm	1.91	nm	nm	nm	nm	nm	nm	nm	nm	nm
May-08	effluent 1	13.9	7.35	830	7	113	1	0.1	nm	1.22	nm	25	271	127.5	24.2	16.0	13.0	1.6	1.1
May-08	effluent 1	12.1	7.11	963	37	251	1	0.1	nm	2.01	20	26	232	155.2	31.1	20.4	19.4	1.8	1.7
Jun-08	effluent 1	14.8	7.08	994	-13	316	1	0.2	nm	2.14	8	20	189	150.4	31.3	22.1	31.4	0.4	2.4
Jul-08	effluent 1	16.1	7.51	903	-67	238	1	0.1	nm	2.09	18	18	213	148.3	28.8	18.7	14.1	2.0	2.7
Sep-08	effluent 1	14.3	7.56	862	-57	184	1	0.1	nm	2.21	30	24	243	133.9	25.5	16.2	10.9	2.0	2.3
Oct-08	effluent 1	9.5	6.99	887	49	169	1	0.1	nm	2.02	57	35	257	133.1	25.9	17.1	12.0	2.0	2.1
Nov-08	effluent 1	4.7	7.29	852	10	139	1	0.1	nm	1.76	31	nm	nm	131.6	25.3	13.1	12.2	1.5	1.4
Jan-09	effluent 1	3.3	7.56	901	66	92	1	0.1	0.276	1.86	28	27	337	131.8	25.6	18.1	10.9	1.5	1.3
Feb-09	effluent 1	2.6	7.41	850	-25	107	2	0.3	0.214	1.58	28	29	341	141.2	26.4	20.2	10.3	1.5	1.2
Mar-09	effluent 1	6.8	7.22	880	13	132	1	0.2	0.344	1.32	24	28	293	146.6	27.1	19.9	12.3	1.3	1.0
Apr-09	effluent 1	9.9	7.28	970	-9	227	2	0.2	0.496	1.10	10	32	248	148.1	28.8	24.4	23.6	1.1	1.1
May-09	effluent 1	10.6	7.17	903	4	220	2	0.2	0.599	1.25	15	28	218	135.2	26.7	16.2	22.5	1.1	1.3
Jun-09	effluent 1	11.8	7.00	776	-6	263	2	0.2	0.741	1.13	48	21	129	118.5	23.9	15.6	20.7	1.4	1.1
Jul-09	effluent 1	13.5	7.15	624	16	148	nm	nm	0.882	0.79	43	12	40	90.6	17.2	10.8	13.5	0.7	1.3
Aug-09	effluent 1	14.2	7.07	878	-14	207	nm	nm	0.808	1.11	19	20	201	141.5	26.9	17.4	11.3	0.9	2.2
Sep-09	effluent 1	12.1	7.07	987	12	265	nm	nm	0.630	1.09	8	27	184	156.2	30.7	19.4	20.1	0.9	2.3
Oct-09	effluent 1	11.3	6.94	1046	-81	369	nm	nm	0.517	1.68	2	26	145	162.5	32.6	21.9	26.2	1.5	2.5

SURFACE WATER

Date	Sample	T	pH	EC	Eh	Alk	DO, %	DO, mg/L	S(II)	Fe(II)	Q	Cl	SO4	Ca T	Mg T	Na T	K T	Fe T	Mn T
Apr-08	overflow 1	8.0	6.27	684	241	5	85	9.3	nm	2.08	18	29	293	90.5	21.9	15.4	5.1	2.0	1.0
Apr-08	overflow 1	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf
May-08	overflow 1	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf
May-08	overflow 1	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf
Jun-08	overflow 1	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf
Jul-08	overflow 1	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf
Sep-08	overflow 1	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf
Oct-08	overflow 1	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf
Nov-08	overflow 1	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf
Jan-09	overflow 1	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf
Feb-09	overflow 1	1.3	5.70	754	277	1	83	11.7	nm	0.20	15	69	594	107.9	26.4	19.4	6.4	0.0	1.4
Mar-09	overflow 1	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf
Apr-09	overflow 1	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf
May-09	overflow 1	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf
Jun-09	overflow 1	12.9	6.89	278	309	49	65	7.0	0.054	0.38	56	16	66	30.8	7.7	7.2	11.0	5.2	0.1
Jul-09	overflow 1	13.2	7.15	547	233	40	nm	nm	0.004	24.39	8	14	216	68.6	18.3	10.4	6.7	1.2	1.2
Aug-09	overflow 1	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf
Sep-09	overflow 1	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf
Oct-09	overflow 1	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf

SURFACE WATER

Date	Sample	T	pH	EC	Eh	Alk	DO, %	DO, mg/L	S(II)	Fe(II)	Q	Cl	SO4	Ca T	Mg T	Na T	K T	Fe T	Mn T
Apr-08	influent 2	8.0	6.33	952	260	68	57	6.7	nm	24.09	180	23	415	111.0	45.2	16.0	6.3	25.7	2.4
Apr-08	influent 2	8.8	5.89	1412	303	27	63	7.3	nm	44.41	nm	nm	nm	nm	nm	nm	nm	nm	nm
May-08	influent 2	11.9	5.51	1363	354	37	70	8.0	nm	43.82	nm	22	746	170.9	74.2	28.9	10.0	50.3	4.4
May-08	influent 2	10.0	4.70	2077	350	25	69	7.8	nm	77.42	39	23	1435	241.2	116.8	29.5	12.0	99.9	9.7
Jun-08	influent 2	11.3	4.66	2110	409	17	72	8.1	nm	77.53	29	24	1807	241.2	119.0	28.5	11.6	100.4	10.7
Jul-08	influent 2	11.0	4.95	1966	359	8	77	8.7	nm	69.27	51	9	625	233.5	114.2	32.0	11.9	92.1	9.1
Sep-08	influent 2	10.8	5.21	1784	307	15	71	7.9	nm	67.35	49	23	1149	204.8	96.1	28.7	11.5	72.8	7.4
Oct-08	influent 2	10.5	4.74	1753	339	bdl	63	7.2	nm	66.20	59	18	1117	201.5	97.3	23.5	11.7	73.9	7.1
Nov-08	influent 2	8.9	6.10	1264	263	43	62	7.1	nm	38.06	90	23	701	150.1	68.1	19.4	9.1	43.2	4.4
Jan-09	influent 2	8.7	5.40	1537	376	10	60	6.9	nm	56.63	65	21	1087	166.3	78.3	21.1	8.8	58.8	5.4
Feb-09	influent 2	8.0	5.47	1471	314	27	63	7.4	nm	46.18	93	27	855	189.0	81.4	27.0	10.1	56.2	4.8
Mar-09	influent 2	9.7	4.38	1979	396	7	70	nm	bdl	72.81	55	22	1554	236.3	110.5	34.3	11.6	96.4	8.7
Apr-09	influent 2	9.7	4.90	2146	343	6	77	8.8	0.004	74.32	36	23	1885	248.5	121.2	32.7	12.0	107.2	10.5
May-09	influent 2	9.7	4.84	1872	378	10	75	8.5	0.038	68.94	38	40	1442	211.1	102.3	22.9	11.4	82.4	8.2
Jun-09	influent 2	10.8	6.30	747	256	88	50	5.7	bdl	15.06	274	17	288	83.6	34.1	13.5	5.6	22.1	1.7
Jul-09	influent 2	11.3	6.13	1222	289	125	nm	nm	0.004	5.99	153	21	553	155.8	67.2	24.5	9.5	28.3	2.7
Aug-09	influent 2	10.3	4.61	1956	401	9	nm	nm	0.002	70.98	39	21	1419	224.2	111.1	27.6	10.7	95.5	9.3
Sep-09	influent 2	10.4	4.33	2155	379	bdl	63	7.1	bdl	75.41	22	33	1593	245.9	129.8	29.2	12.4	119.8	10.9
Oct-09	influent 2	10.0	4.28	2420	379	bdl	69	7.8	bdl	76.65	19	23	1887	266.3	144.5	30.3	13.5	116.3	13.1

SURFACE WATER

Date	Sample	T	pH	EC	Eh	Alk	DO, %	DO, mg/L	S(II)	Fe(II)	Q	Cl	SO4	Ca T	Mg T	Na T	K T	Fe T	Mn T
Apr-08	effluent 2	nm	nm	nm	nm	nm	1	0.1	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm
Apr-08	effluent 2	8.2	6.91	1485	25	169	1	0.1	nm	1.53	nm	nm	nm	nm	nm	nm	nm	nm	nm
May-08	effluent 2	14.7	7.12	1466	32	176	1	0.0	nm	1.38	nm	19	631	245.9	65.3	21.8	10.8	1.9	4.6
May-08	effluent 2	13.3	7.04	1976	45	178	1	0.1	nm	2.37	20	22	1031	342.7	101.2	30.4	13.0	2.1	6.8
Jun-08	effluent 2	16.5	6.84	2230	4	204	1	0.1	nm	4.32	21	22	1266	382.7	116.3	29.4	15.0	3.8	9.0
Jul-08	effluent 2	18.9	7.30	1782	-47	187	1	0.1	nm	3.84	27	11	411	313.9	85.5	27.9	12.1	3.6	6.4
Sep-08	effluent 2	15.4	7.23	1623	-75	220	1	0.1	nm	3.60	18	20	715	264.7	70.4	25.6	10.7	3.6	5.3
Oct-08	effluent 2	11.3	6.43	1790	29	166	1	0.1	nm	4.57	19	28	910	300.8	88.1	29.4	12.2	4.2	5.3
Nov-08	effluent 2	6.9	7.27	1523	0	189	1	0.1	nm	3.17	13	20	642	246.1	73.0	20.7	10.0	2.9	5.1
Jan-09	effluent 2	5.4	7.21	1691	54	144	1	0.2	0.525	3.07	12	22	826	289.9	83.7	24.6	10.1	2.6	5.5
Feb-09	effluent 2	5.1	6.44	1414	-11	149	1	0.2	0.407	3.40	12	32	700	261.8	71.8	26.7	9.5	2.3	4.7
Mar-09	effluent 2	7.7	6.70	1759	28	181	3	0.3	0.492	2.44	12	24	863	302.6	88.0	31.2	10.8	2.2	5.3
Apr-09	effluent 2	10.2	7.12	2099	3	174	2	0.2	0.544	5.07	14	22	1160	350.1	111.3	26.7	13.7	5.1	8.1
May-09	effluent 2	12.3	6.85	1929	10	185	1	0.1	0.634	4.83	16	47	1047	322.8	99.2	23.0	12.0	4.3	7.1
Jun-09	effluent 2	15.1	6.84	2061	-10	253	1	0.2	0.893	5.40	18	32	1088	358.2	112.3	27.5	12.3	4.9	8.2
Jul-09	effluent 2	16.0	6.86	1892	4	185	nm	nm	1.149	6.06	15	20	954	322.6	99.8	26.3	11.5	5.5	6.9
Aug-09	effluent 2	16.9	6.90	1878	-19	195	nm	nm	1.016	5.50	17	26	946	327.8	95.1	25.9	11.3	5.0	6.6
Sep-09	effluent 2	14.4	6.79	2135	16	157	1	0.1	0.425	7.69	20	26	1043	372.5	118.7	27.5	12.9	6.7	9.2
Oct-09	effluent 2	13.4	6.83	2430	2	206	nm	nm	0.450	9.41	13	23	1346	369.3	118.0	29.5	13.3	6.8	9.4

SURFACE WATER

Date	Sample	T	pH	EC	Eh	Alk	DO, %	DO, mg/L	S(II)	Fe(II)	Q	Cl	SO4	Ca T	Mg T	Na T	K T	Fe T	Mn T
Apr-08	overflow 2	8.0	6.31	854	204	44	64	7.0	nm	14.64	adl	22	374	99.2	39.6	14.1	6.0	17.7	2.1
Apr-08	overflow 2	9.5	5.83	1315	321	69	78	8.8	nm	30.71	nm	nm	nm	nm	nm	nm	nm	nm	nm
May-08	overflow 2	14.8	5.80	1301	322	23	74	7.6	nm	29.70	nm	20	702	163.9	70.3	28.9	10.1	36.4	4.1
May-08	overflow 2	11.5	4.55	2080	444	bdl	75	8.1	nm	38.32	18	22	1437	243.2	116.4	30.6	13.3	46.3	9.6
Jun-08	overflow 2	15.7	3.61	2036	632	bdl	82	8.1	nm	4.91	3	22	1703	227.0	101.7	30.9	13.1	13.0	9.8
Jul-08	overflow 2	18.3	3.99	1856	615	bdl	85	7.9	nm	0.73	5	10	551	216.4	102.3	30.9	12.0	9.2	7.8
Sep-08	overflow 2	14.4	4.09	1701	550	bdl	85	8.7	nm	11.57	20	27	1087	194.7	89.6	29.6	10.7	16.5	6.6
Oct-08	overflow 2	10.9	4.55	1663	403	7	77	8.6	nm	35.90	34	23	1079	190.7	92.4	22.0	11.9	40.4	6.6
Nov-08	overflow 2	6.9	7.27	1523	0	25	83	11.5	nm	35.78	69	23	753	157.5	71.9	25.0	9.9	39.1	4.8
Jan-09	overflow 2	4.6	5.40	1515	407	4	74	9.6	nm	50.72	83	22	950	183.0	84.0	22.4	9.7	55.1	5.6
Feb-09	overflow 2	2.8	6.05	1393	332	18	79	10.8	nm	40.57	79	24	805	162.1	72.3	28.1	9.5	43.2	4.4
Mar-09	overflow 2	7.8	4.37	1952	431	6	86	10.3	bdl	70.15	33	23	1397	234.2	109.6	29.1	11.6	80.9	8.4
Apr-09	overflow 2	10.6	4.23	2224	465	bdl	84	9.4	0.004	42.58	16	24	1791	246.9	119.6	34.3	12.1	49.2	10.2
May-09	overflow 2	13.6	3.88	1797	565	bdl	83	8.6	0.002	24.51	15	42	1382	196.2	94.6	21.7	10.5	27.8	7.4
Jun-09	overflow 2	13.3	6.37	743	239	99	61	7.9	bdl	11.51	276	20	276	85.0	35.0	12.1	6.1	13.1	1.6
Jul-09	overflow 2	11.7	6.56	1140	229	123	nm	nm	0.002	14.35	137	19	486	146.3	63.0	19.5	9.2	18.2	2.3
Aug-09	overflow 2	16.1	3.34	2038	674	bdl	nm	nm	0.002	1.62	20	20	1426	223.3	111.0	28.7	11.6	12.1	9.0
Sep-09	overflow 2	13.0	3.05	2203	664	bdl	83	8.7	bdl	1.19	2	25	1516	235.7	122.5	27.1	13.0	12.1	10.3
Oct-09	overflow 2	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf

SURFACE WATER

Date	Sample	Al T	Zn T	Si T	S T	Ca	Mg	Na	K	Fe	Mn	Al	Zn	Si	S
Apr-08	influent 1	5.1	0.2	12.2	115.0	95.6	24.3	18.7	5.0	17.3	1.1	3.48	0.25	12.2	121.3
Apr-08	influent 1	nm	nm	nm	nm	104.1	27.5	17.6	5.7	16.6	1.3	3.25	0.25	13.0	129.7
May-08	influent 1	16.3	0.2	14.9	122.7	93.9	24.6	17.4	5.6	10.4	1.2	4.85	0.25	13.3	126.4
May-08	influent 1	5.5	0.2	12.3	126.7	110.1	28.0	21.4	6.9	20.6	0.9	bdl	0.11	10.8	124.7
Jun-08	influent 1	7.9	0.2	14.2	133.2	107.3	27.5	20.1	7.5	26.0	1.1	bdl	0.15	11.2	123.8
Jul-08	influent 1	6.9	0.2	13.7	123.7	104.6	28.1	19.0	6.8	27.7	1.2	5.48	0.18	13.7	125.2
Sep-08	influent 1	5.3	0.2	13.6	112.9	94.9	25.7	16.8	6.4	16.4	1.1	bdl	0.17	12.4	116.5
Oct-08	influent 1	5.2	0.2	13.0	112.5	89.0	24.6	14.6	6.8	16.9	1.0	0.50	0.16	11.8	108.5
Nov-08	influent 1	5.4	0.2	13.2	117.4	94.5	25.4	13.3	6.2	18.1	1.1	0.08	0.18	12.6	120.9
Jan-09	influent 1	5.1	0.2	12.2	108.6	82.6	23.5	13.5	6.3	19.5	1.1	0.11	0.21	12.2	117.2
Feb-09	influent 1	10.1	0.4	14.7	132.5	103.8	27.2	19.4	5.4	23.7	1.3	2.75	0.26	13.8	129.5
Mar-09	influent 1	5.7	0.2	12.4	113.1	92.1	24.9	14.9	5.8	26.7	1.0	2.88	0.22	11.5	108.9
Apr-09	influent 1	62.0	0.3	31.6	119.2	93.2	24.3	21.1	7.1	20.5	1.0	0.05	0.15	11.1	114.1
May-09	influent 1	3.5	0.5	12.2	108.0	93.3	25.4	16.2	7.0	14.3	0.8	0.00	0.36	11.0	100.5
Jun-09	influent 1	2.9	0.1	10.8	88.7	83.6	21.6	19.2	5.9	6.2	0.6	0.16	0.05	9.2	83.0
Jul-09	influent 1	5.5	0.2	15.3	118.4	85.8	24.1	14.9	4.8	10.8	1.3	4.29	0.47	15.4	120.0
Aug-09	influent 1	4.5	0.2	13.2	118.2	98.7	28.6	20.8	6.7	17.7	1.1	2.27	0.14	12.8	120.0
Sep-09	influent 1	3.2	0.1	12.4	100.8	91.5	25.1	19.3	8.2	7.3	0.9	bdl	0.07	11.5	106.9
Oct-09	influent 1	4.7	0.1	13.7	124.4	98.6	26.3	18.9	7.8	10.9	1.2	0.29	0.15	12.2	126.3

SURFACE WATER

Date	Sample	Al T	Zn T	Si T	S T	Ca	Mg	Na	K	Fe	Mn	Al	Zn	Si	S
Apr-08	effluent 1	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm
Apr-08	effluent 1	nm	nm	nm	nm	136.1	26.7	17.4	14.2	0.0	1.2	bdl	bdl	11.1	112.9
May-08	effluent 1	bdl	bdl	11.3	99.8	124.6	24.4	14.6	13.2	0.0	1.1	bdl	bdl	11.8	103.9
May-08	effluent 1	bdl	bdl	12.2	87.3	152.3	30.7	20.2	19.3	1.8	1.7	bdl	bdl	12.4	87.7
Jun-08	effluent 1	bdl	bdl	13.9	69.9	143.1	30.1	18.5	29.9	1.7	2.2	bdl	bdl	12.5	64.8
Jul-08	effluent 1	bdl	bdl	11.6	74.2	140.3	27.3	17.8	13.3	2.0	2.6	bdl	bdl	11.2	71.6
Sep-08	effluent 1	bdl	bdl	12.0	86.6	137.6	26.2	16.6	10.8	2.0	2.3	bdl	bdl	11.9	86.1
Oct-08	effluent 1	bdl	bdl	11.3	94.3	132.0	25.6	13.8	11.7	1.8	2.1	bdl	0.09	10.9	91.6
Nov-08	effluent 1	bdl	bdl	10.7	101.7	132.4	25.5	16.1	12.1	1.7	1.4	bdl	bdl	10.7	102.1
Jan-09	effluent 1	bdl	bdl	10.8	104.9	128.3	24.9	17.7	11.4	1.6	1.4	bdl	bdl	11.1	110.0
Feb-09	effluent 1	bdl	bdl	11.2	112.6	139.7	26.3	20.0	10.2	1.4	1.2	bdl	bdl	11.1	111.5
Mar-09	effluent 1	bdl	bdl	11.3	103.8	141.3	26.2	16.4	11.6	1.1	1.0	bdl	0.68	10.4	95.5
Apr-09	effluent 1	bdl	bdl	11.5	89.3	153.5	29.9	24.6	24.1	1.4	1.1	bdl	bdl	11.7	85.9
May-09	effluent 1	bdl	bdl	10.5	86.5	145.9	28.3	19.0	22.9	1.0	1.2	bdl	bdl	10.5	80.3
Jun-09	effluent 1	0.4	bdl	10.3	48.2	115.3	22.7	19.1	19.9	1.0	1.1	bdl	bdl	9.0	46.1
Jul-09	effluent 1	bdl	bdl	8.6	55.3	89.4	17.5	10.9	13.5	0.7	1.3	bdl	bdl	8.6	54.5
Aug-09	effluent 1	bdl	bdl	10.5	79.6	141.4	27.0	17.6	11.5	1.0	2.3	bdl	bdl	10.6	81.4
Sep-09	effluent 1	bdl	bdl	11.4	69.5	153.3	29.8	19.5	20.6	1.0	2.4	bdl	bdl	11.8	71.5
Oct-09	effluent 1	bdl	bdl	12.4	50.1	164.4	33.2	22.2	26.1	1.3	2.5	bdl	bdl	12.4	49.7

SURFACE WATER

Date	Sample	Al T	Zn T	Si T	S T	Ca	Mg	Na	K	Fe	Mn	Al	Zn	Si	S
Apr-08	overflow 1	0.5	0.2		100.0	90.5	22.4	18.2	5.3	1.8	1.1	0.40	0.20		103.0
Apr-08	overflow 1	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf
May-08	overflow 1	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf
May-08	overflow 1	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf
Jun-08	overflow 1	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf
Jul-08	overflow 1	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf
Sep-08	overflow 1	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf
Oct-08	overflow 1	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf
Nov-08	overflow 1	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf
Jan-09	overflow 1	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf
Feb-09	overflow 1	1.5	0.2	13.0	124.3	102.7	25.5	15.3	6.1	0.2	1.3	1.44	0.22	12.3	116.8
Mar-09	overflow 1	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf
Apr-09	overflow 1	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf
May-09	overflow 1	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf
Jun-09	overflow 1	8.2	bdl	15.0	20.0	31.7	7.6	7.8	9.9	2.8	0.1	3.24	0.05	7.5	21.7
Jul-09	overflow 1	0.1	bdl	9.4	74.7	66.6	17.9	13.2	6.7	0.8	1.2	bdl	bdl	9.3	73.3
Aug-09	overflow 1	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf
Sep-09	overflow 1	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf
Oct-09	overflow 1	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf

SURFACE WATER

Date	Sample	Al T	Zn T	Si T	S T	Ca	Mg	Na	K	Fe	Mn	Al	Zn	Si	S
Apr-08	influent 2	10.6	0.4	10.0	145.0	nm	46.2	17.8	6.4	26.1	2.5	1.96	0.42	9.7	150.1
Apr-08	influent 2	nm	nm	nm	nm	172.3	75.8	29.3	10.1	49.9	4.7	5.47	0.80	12.6	270.2
May-08	influent 2	20.3	0.7	13.2	260.4	163.3	70.7	28.5	9.8	44.3	4.3	2.58	0.70	11.5	245.3
May-08	influent 2	43.7	1.6	17.7	477.6	238.8	114.7	29.6	12.1	95.8	9.6	38.98	1.64	18.1	473.7
Jun-08	influent 2	47.3	1.7	17.2	490.5	230.2	124.4	27.5	12.4	93.1	10.2	41.14	1.75	18.1	467.4
Jul-08	influent 2	39.2	1.4	17.7	433.3	231.1	114.3	30.4	11.7	87.9	9.1	28.76	1.44	17.2	423.6
Sep-08	influent 2	33.7	1.2	16.8	363.9	211.0	99.6	31.0	11.2	72.5	7.7	22.54	1.22	15.9	380.1
Oct-08	influent 2	32.6	1.2	16.6	344.4	200.6	96.4	26.3	11.6	73.8	7.0	20.26	1.20	15.7	327.1
Nov-08	influent 2	17.2	0.7	12.7	233.9	151.6	68.5	19.8	9.1	41.6	4.4	2.66	0.69	11.7	229.6
Jan-09	influent 2	23.3	0.9	13.4	282.1	163.3	77.5	21.4	9.2	56.0	4.5	10.00	0.92	13.2	284.2
Feb-09	influent 2	22.2	0.8	14.1	278.7	186.3	80.9	28.4	11.4	54.3	4.7	5.82	0.77	13.0	272.4
Mar-09	influent 2	38.1	1.3	16.7	461.6	232.4	108.9	28.1	11.3	92.9	8.5	32.87	1.33	16.4	444.2
Apr-09	influent 2	46.1	1.7	19.3	496.7	229.3	111.9	30.1	11.6	95.3	9.6	41.24	1.69	17.8	445.9
May-09	influent 2	34.8	1.5	17.4	393.0	229.2	110.2	27.8	11.3	86.4	9.2	33.22	1.54	17.8	437.7
Jun-09	influent 2	6.3	0.2	10.0	92.0	84.3	34.7	12.5	5.4	16.4	1.7	0.34	0.19	9.2	94.5
Jul-09	influent 2	10.2	0.3	12.1	183.6	160.9	68.5	25.6	9.6	27.4	2.7	0.72	2.47	11.3	182.2
Aug-09	influent 2	45.2	1.5	17.5	415.7	223.0	111.0	27.3	10.9	91.8	9.3	39.19	1.55	17.2	408.9
Sep-09	influent 2	49.7	1.7	19.1	454.1	243.9	129.3	27.5	12.7	111.6	10.8	46.19	2.70	19.6	449.2
Oct-09	influent 2	57.3	2.2	20.7	524.8	266.2	144.4	30.7	13.2	114.9	13.2	55.88	2.04	20.2	528.4

SURFACE WATER

Date	Sample	Al T	Zn T	Si T	S T	Ca	Mg	Na	K	Fe	Mn	Al	Zn	Si	S
Apr-08	effluent 2	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm
Apr-08	effluent 2	nm	nm	nm	nm	245.2	66.3	21.1	9.9	0.0	4.8	bdl	bdl	7.2	236.9
May-08	effluent 2	bdl	bdl	7.4	239.9	224.0	59.1	29.4	9.3	0.0	4.1	bdl	bdl	6.4	205.6
May-08	effluent 2	0.7	bdl	7.7	369.2	347.5	102.5	31.3	12.2	1.9	6.9	bdl	bdl	7.5	372.2
Jun-08	effluent 2	1.0	bdl	10.5	417.0	380.6	119.3	29.8	14.5	3.6	9.1	bdl	bdl	10.1	426.1
Jul-08	effluent 2	0.1	bdl	7.9	309.8	298.1	81.5	28.0	11.3	3.5	6.0	bdl	bdl	7.5	296.5
Sep-08	effluent 2	bdl	bdl	8.1	255.3	267.3	71.2	25.8	9.7	3.1	4.8	bdl	bdl	7.2	230.3
Oct-08	effluent 2	0.3	bdl	6.7	315.7	297.1	86.9	24.1	11.5	4.0	5.2	0.07	bdl	6.3	293.5
Nov-08	effluent 2	bdl	bdl	8.0	245.7	246.1	73.0	24.6	10.0	2.9	5.1	0.10	bdl	8.0	244.2
Jan-09	effluent 2	0.1	bdl	7.3	270.2	260.8	76.3	26.5	10.6	2.6	4.5	bdl	bdl	7.4	276.1
Feb-09	effluent 2	0.4	bdl	7.6	225.5	257.0	72.4	25.3	9.5	1.9	4.7	bdl	0.67	7.7	230.3
Mar-09	effluent 2	0.3	bdl	7.1	282.5	301.3	87.7	27.5	10.5	2.0	5.2	bdl	bdl	6.9	277.6
Apr-09	effluent 2	0.9	bdl	10.7	372.8	355.8	112.2	37.3	14.1	5.8	8.1	0.11	bdl	10.6	390.4
May-09	effluent 2	0.5	0.1	9.6	340.1	342.4	104.7	27.2	12.2	4.4	7.9	bdl	bdl	10.1	367.7
Jun-09	effluent 2	1.4	bdl	10.5	352.7	358.9	112.4	30.6	12.5	4.8	8.0	0.06	1.04	10.7	337.8
Jul-09	effluent 2	0.1	bdl	9.5	285.5	320.9	100.2	28.5	11.5	5.2	7.0	bdl	0.03	9.6	292.8
Aug-09	effluent 2	0.2	bdl	8.4	320.4	327.4	95.1	25.5	11.3	4.9	6.6	bdl	bdl	8.4	323.0
Sep-09	effluent 2	0.9	bdl	10.5	340.5	373.1	119.3	25.7	13.1	7.0	9.3	0.05	bdl	11.0	345.5
Oct-09	effluent 2	0.7	bdl	10.7	349.2	430.0	138.3	29.5	13.8	7.8	11.6	bdl	bdl	9.8	424.8

SURFACE WATER

Date	Sample	Al T	Zn T	Si T	S T	Ca	Mg	Na	K	Fe	Mn	Al	Zn	Si	S
Apr-08	overflow 2	1.3	0.4	nm	128.0	97.4	39.0	14.8	6.0	15.0	2.1	0.40	0.40	nm	127.0
Apr-08	overflow 2	nm	nm	nm	nm	157.7	69.0	23.1	9.8	33.2	4.3	0.83	0.72	11.2	253.9
May-08	overflow 2	2.0	0.6	11.4	249.8	157.1	67.3	30.9	9.6	29.5	3.9	0.31	0.63	10.3	229.7
May-08	overflow 2	48.6	1.6	18.5	474.7	244.4	117.0	30.8	12.8	44.9	9.7	47.60	1.56	18.0	475.3
Jun-08	overflow 2	49.8	1.5	16.9	440.0	240.7	108.3	29.5	13.9	11.8	10.5	52.92	1.53	17.8	479.7
Jul-08	overflow 2	22.0	1.1	16.0	358.5	209.2	98.2	29.8	11.9	3.8	7.4	20.59	1.13	15.9	339.3
Sep-08	overflow 2	17.1	1.0	14.5	296.7	201.5	93.2	30.6	11.3	14.2	6.9	17.76	1.11	15.8	323.8
Oct-08	overflow 2	19.9	1.2	15.7	311.9	192.2	92.3	24.3	11.7	39.8	6.7	16.45	1.18	15.3	310.6
Nov-08	overflow 2	3.1	0.8	11.8	254.1	155.8	71.2	25.6	10.0	37.3	4.8	0.70	0.75	11.5	255.6
Jan-09	overflow 2	9.4	1.0	13.4	306.0	163.6	77.4	22.6	9.4	50.8	4.6	7.16	0.90	12.4	285.5
Feb-09	overflow 2	3.0	0.8	11.6	253.8	182.6	78.2	25.9	9.8	46.3	4.5	0.98	0.73	11.6	260.1
Mar-09	overflow 2	30.1	1.3	15.8	444.2	231.8	108.5	28.6	11.8	78.8	8.2	28.59	1.91	16.3	427.5
Apr-09	overflow 2	53.1	1.7	19.4	478.3	242.8	118.3	29.7	13.0	46.8	10.0	51.87	1.83	20.2	477.2
May-09	overflow 2	28.6	1.2	15.1	353.0	211.2	101.1	25.9	11.0	27.7	8.2	30.47	1.30	15.8	389.0
Jun-09	overflow 2	2.2	0.1	9.0	90.1	84.5	34.7	12.9	6.2	11.0	1.7	0.38	0.27	8.9	95.9
Jul-09	overflow 2	1.1	0.2	10.4	165.1	146.0	62.7	22.6	9.1	15.0	2.2	bdl	0.70	9.8	160.8
Aug-09	overflow 2	41.8	1.5	17.8	389.6	222.6	110.2	28.3	11.3	8.6	8.9	41.58	1.46	17.6	390.6
Sep-09	overflow 2	51.5	1.6	18.4	412.4	233.2	121.5	28.5	13.6	9.2	10.2	50.54	1.72	19.7	406.9
Oct-09	overflow 2	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf	nf

LEGEND
TOTAL SEDIMENT CONCENTRATIONS

Parameter	Abbreviation	Unit
Al	aluminium	g kg^{-1}
bdl	below detection limit	
C	carbon	g kg^{-1}
Ca	calcium	g kg^{-1}
depth	average depth below surface	cm
Fe	iron	g kg^{-1}
K	potassium	g kg^{-1}
Mg	magnesium	g kg^{-1}
Mn	manganese	g kg^{-1}
Na	sodium	g kg^{-1}
nd	not determined	
S	sulfur	g kg^{-1}
Si	silicium	g kg^{-1}
TOC	total organic carbon	g kg^{-1}
Zn	zinc	g kg^{-1}

TOTAL ELEMENT CONCENTRATIONS IN REACTIVE SEDIMENT (DRY WEIGHT)

RAPS 1

Core	Depth	S	C	TOC	Al	Ca	Fe	K	Mg	Mn	Na	Si	Zn
3	4.5	7.42	161.6	141.4	48.2	79.5	32.4	11.15	6.13	1.31	1.99	bdl	0.28
3	4.5	nd	nd	122.6	nd	nd	nd	nd	nd	nd	nd	nd	nd
3	7.5	8.11	146.2	95.1	42.0	124.9	23.7	11.08	7.04	0.64	1.88	bdl	0.08
3	7.5	8.23	147.3	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
3	16.5	9.95	158.7	nd	40.4	129.3	21.9	11.08	7.16	0.48	1.78	bdl	0.04
3	16.5	10.82	152.0	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
3	25.5	8.55	125.0	82.7	38.9	138.7	21.6	10.91	7.39	0.47	1.81	bdl	0.01
3	25.5	8.57	115.5	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
3	28.5	9.25	136.4	91.8	37.7	162.5	21.2	10.66	7.62	0.47	1.71	bdl	bdl
3	28.5	8.95	132.4	nd	39.5	149.2	22.0	10.75	7.51	0.47	1.76	bdl	bdl
3	28.5	10.14	141.0	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
3	34.5	7.53	130.9	113.4	35.5	146.7	18.6	10.81	8.11	0.48	2.13	0.03	0.02
3	34.5	8.78	139.8	85.9	34.9	138.5	19.8	10.86	8.45	0.47	1.76	0.03	bdl
4	4.5	6.36	146.3	74.7	39.7	113.0	19.2	11.67	6.70	0.71	1.78	bdl	3.71
4	4.5	3.23	77.2	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
4	7.5	4.83	138.0	122.2	41.2	153.0	15.8	11.38	12.68	0.60	1.81	bdl	0.07
4	7.5	4.70	149.5	88.6	53.1	105.3	25.7	12.51	8.08	0.77	2.20	bdl	0.05
4	7.5	nd	nd	nd	48.9	78.1	23.2	12.65	6.89	0.71	1.90	bdl	0.12
4	13.5	3.74	146.2	nd	43.6	108.2	21.2	14.32	7.16	0.77	1.94	0.24	3.49
4	13.5	4.05	147.5	115.8	35.8	119.0	19.9	13.69	6.32	0.76	2.16	6.21	3.44
4	16.5	4.16	165.0	106.0	42.1	119.8	20.1	14.25	7.67	0.83	1.92	bdl	0.11
4	16.5	3.19	122.1	99.3	41.6	117.7	21.3	14.21	6.89	0.81	1.93	bdl	0.08
4	28.5	3.56	132.0	98.5	41.9	95.2	20.9	15.35	7.00	0.86	2.47	0.04	2.87

TOTAL ELEMENT CONCENTRATIONS IN REACTIVE SEDIMENT (DRY WEIGHT)

RAPS 2

Core	Depth	S	C	TOC	Al	Ca	Fe	K	Mg	Mn	Na	Si	Zn
1	10.5	31.79	86.5	73.6	134.5	12.1	134.6	5.50	2.02	0.26	1.30	0.01	0.45
1	10.5	30.71	89.3	78.0	130.7	12.0	125.3	5.54	2.07	0.26	0.75	0.01	0.46
1	16.5	5.88	172.9	65.0	48.1	99.7	26.7	10.21	7.12	0.60	1.75	bdl	0.22
1	16.5	4.31	109.8	182.1	52.6	111.4	28.7	11.62	7.85	0.67	1.84	0.68	0.25
1	19.5	5.77	146.4	103.8	36.4	129.4	20.4	9.27	6.98	0.64	1.57	0.01	0.18
1	19.5	4.73	111.9	94.5	37.8	156.4	23.3	10.32	7.41	0.76	1.62	0.14	0.26
1	28.5	5.38	163.1	76.3	32.8	133.0	18.2	9.63	7.39	0.74	1.47	bdl	0.04
1	28.5	3.86	115.3	83.3	36.2	131.4	19.4	10.23	7.37	0.79	1.49	bdl	0.05
1	34.5	4.03	128.2	87.2	38.9	140.8	21.5	10.80	8.41	0.92	1.56	0.40	0.04
1	34.5	4.37	136.9	83.4	48.9	116.9	20.0	12.67	7.99	0.76	1.45	0.07	0.05
2	4.5	12.23	135.9	127.6	45.5	33.8	71.5	6.87	3.57	0.30	1.35	bdl	0.24
2	4.5	13.48	169.5	119.5	45.0	29.7	72.8	6.78	3.16	0.33	1.34	0.11	0.21
2	7.5	11.45	278.6	258.3	nd	nd	nd	nd	nd	nd	nd	nd	nd
2	10.5	10.58	203.8	188.1	30.3	62.4	23.3	7.62	4.54	0.61	1.39	bdl	0.13
2	10.5	19.76	221.1	187.1	33.5	65.1	25.9	8.62	5.62	0.68	1.86	bdl	0.15
2	13.5	3.30	208.9	221.1	nd	nd	nd	nd	nd	nd	nd	nd	nd
2	16.5	6.37	249.5	192.6	31.92	36.87	19.74	9.674	4.578	0.861	3.71	0.14	bdl
2	19.5	5.83	183.6	130.4	49.3	44.8	28.3	12.91	5.43	0.72	2.20	2.11	0.56
2	19.5	5.18	163.8	157.6	56.1	40.7	30.4	13.78	5.48	0.82	2.24	2.52	0.04
2	25.5	3.70	150.6	166.8	40.3	71.3	19.4	12.99	5.95	0.64	1.95	0.05	0.07
2	25.5	2.88	146.1	125.7	42.5	62.8	18.2	11.30	5.98	0.61	1.94	0.01	0.05
2	28.5	3.90	172.4	162.9	35.4	91.2	72.1	12.82	6.17	1.27	1.98	0.11	0.06
2	28.5	3.76	160.7	191.8	41.1	92.2	19.9	14.02	6.62	0.75	2.31	bdl	0.04
2	31.5	1.45	141.1	88.7	nd	nd	nd	nd	nd	nd	nd	nd	nd

LEGEND
SEQUENTIAL EXTRACTION OF SULFUR

Parameter	Abbreviation	Unit
AS	adsorbed sulfate	g kg^{-1}
ASS	acid soluble sulfate	g kg^{-1}
ASS-Fe	iron concentrations determined in ASS extraction step	g kg^{-1}
AVS	acid volatile sulfur	g kg^{-1}
CRS	chromium reducible sulfur	g kg^{-1}
depth	average depth below surface	cm
ES	elemental sulfur	g kg^{-1}
nd	not determined	
orgS	organic sulfur	g kg^{-1}
TS	total sulfur (average)	g kg^{-1}
WSS	water soluble sulfur	g kg^{-1}
WSS-Fe	iron concentrations determined in WSS extraction step	g kg^{-1}

SEQUENTIAL EXTRACTION OF SULFUR

RAPS 1

Core	Depth	TS	WSS	ES	AVS	CRS	ASS	AS	orgS	WSS-Fe	ASS-Fe
3	4.5	7.42	0.93	0.50	0.06	1.43	0.81	0.01	1.99	0.02	27.02
3	4.5	7.42	0.88	0.91	0.06	1.40	0.86	0.01	1.15	0.02	27.26
3	4.5	7.42	nd	0.70	0.05	0.20	nd	nd	nd	nd	nd
3	4.5	7.42	nd	0.67	2.50	1.44	nd	nd	nd	nd	nd
3	7.5	8.17	nd	0.60	0.12	1.07	nd	0.01	nd	nd	nd
3	7.5	8.17	0.89	0.61	0.09	1.73	nd	0.02	nd	0.01	nd
3	7.5	8.17	0.97	0.18	0.16	1.51	0.57	nd	nd	0.02	12.90
3	7.5	8.17	nd	0.81	0.37	1.55	0.76	nd	1.75	nd	16.38
3	16.5	10.39	1.89	1.09	0.43	0.27	0.55	0.01	nd	0.01	9.92
3	16.5	10.39	1.46	0.63	0.12	3.28	0.51	nd	nd	0.03	13.97
3	16.5	10.39	nd	0.48	0.09	3.04	nd	nd	1.68	nd	nd
3	16.5	10.39	nd	0.23	0.10	3.44	nd	nd	nd	nd	nd
3	16.5	10.39	nd	2.01	0.09	1.91	nd	nd	3.63	nd	nd
3	25.5	8.56	1.30	1.40	0.11	2.05	0.41	0.01	nd	0.01	13.60
3	25.5	8.56	0.93	1.56	0.11	1.99	0.41	0.01	nd	0.04	15.87
3	25.5	8.56	nd	1.10	0.10	2.05	nd	nd	1.84	nd	nd
3	25.5	8.56	nd	0.97	0.05	1.29	nd	nd	1.94	nd	nd
3	25.5	8.56	nd	0.70	0.06	0.26	nd	nd	nd	nd	nd
3	28.5	9.45	1.33	1.77	0.11	2.25	0.44	0.01	2.69	0.02	13.48
3	28.5	9.45	1.59	1.51	0.07	2.19	0.40	0.01	nd	0.01	12.82
3	28.5	9.45	nd	1.21	0.18	2.68	nd	nd	nd	nd	nd
3	28.5	9.45	nd	1.68	0.06	2.21	nd	nd	1.95	nd	nd
3	28.5	9.45	nd	1.46	0.06	1.04	nd	nd	nd	nd	nd
3	34.5	8.16	0.73	1.62	0.04	0.45	0.40	0.01	nd	0.02	14.00
3	34.5	8.16	0.73	1.75	0.05	2.01	0.43	0.01	nd	0.04	14.87
3	34.5	8.16	nd	1.75	0.02	2.47	nd	nd	2.22	nd	nd
3	34.5	8.16	nd	2.10	0.04	1.95	nd	nd	2.13	nd	nd
3	34.5	8.16	nd	1.75	0.04	2.13	nd	nd	nd	nd	nd
4	4.5	4.79	0.59	0.92	0.22	1.25	0.59	0.01	nd	0.01	17.01
4	7.5	4.77	0.31	0.61	0.03	0.97	0.53	0.01	nd	0.07	17.25
4	7.5	4.77	0.31	0.69	0.05	1.26	0.52	0.01	nd	0.07	18.08
4	7.5	4.77	0.31	0.62	0.01	1.35	0.50	0.01	2.19	0.08	18.39
4	7.5	4.77	0.31	0.61	0.01	1.46	0.51	bdl	nd	0.08	15.58
4	7.5	4.77	0.32	1.19	0.17	1.23	0.53	0.01	nd	0.06	19.46
4	13.5	3.89	0.10	0.15	0.08	0.36	0.51	0.01	nd	0.03	15.92
4	16.5	3.67	0.14	0.30	0.02	1.39	0.75	0.01	2.37	0.14	20.66
4	16.5	3.67	0.13	0.35	nd	nd	nd	nd	nd	0.10	nd
4	16.5	3.67	nd	0.45	nd	nd	nd	nd	nd	nd	nd
4	28.5	3.56	0.08	0.11	0.06	0.59	0.43	0.01	nd	0.03	18.48

SEQUENTIAL EXTRACTION OF SULFUR

RAPS 2

Core	Depth	TS	WSS	ES	AVS	CRS	ASS	AS	orgS	WSS-Fe	ASS-Fe
1	10.5	31.79	2.76	7.91	lost	0.39	10.01	0.01	4.04	0.02	117.4
1	16.5	5.10	0.44	1.12	0.06	1.11	nd	0.00	nd	0.01	nd
1	16.5	5.10	0.49	1.53	nd	nd	nd	0.01	nd	0.01	nd
1	16.5	5.10	nd	1.65	0.10	1.48	0.52	nd	nd	nd	20.46
1	16.5	5.10	nd	1.56	0.11	1.63	0.50	nd	nd	nd	18.67
1	16.5	5.10	nd	1.30	0.12	1.62	nd	nd	nd	nd	nd
1	19.5	5.25	0.27	1.50	0.03	1.23	0.36	0.00	1.77	0.03	13.93
1	19.5	5.25	0.25	1.41	0.05	1.40	nd	0.01	2.24	0.03	nd
1	19.5	5.25	nd	1.10	0.05	1.41	0.39	nd	nd	nd	15.94
1	19.5	5.25	nd	1.33	0.12	1.42	nd	nd	nd	nd	nd
1	28.5	4.62	0.12	0.68	0.01	1.80	0.39	0.01	1.65	0.02	12.89
1	28.5	4.62	0.13	0.60	0.08	1.94	0.29	0.00	2.06	0.04	11.30
1	28.5	4.62	nd	0.73	0.03	1.86	nd	nd	nd	nd	nd
1	28.5	4.62	nd	0.79	0.04	1.78	nd	nd	nd	nd	nd
1	34.5	4.20	0.13	0.49	0.01	2.08	0.26	0.00	1.47	0.04	14.32
1	34.5	4.20	0.15	0.61	0.02	1.83	0.30	0.00	1.71	0.06	14.50
1	34.5	4.20	nd	0.64	0.01	1.83	nd	nd	nd	nd	nd
1	34.5	4.20	nd	0.73	0.01	1.72	nd	nd	nd	nd	nd
2	4.5	12.85	2.94	3.03	0.16	0.82	2.56	0.01	3.02	0.24	70.54
2	4.5	12.85	2.73	2.74	0.21	0.94	2.67	0.01	2.83	0.18	67.57
2	10.5	15.17	1.30	2.75	0.23	1.58	0.67	0.01	3.56	0.18	21.74
2	10.5	15.17	1.22	2.10	0.18	1.07	0.61	0.01	3.73	0.14	15.42
2	19.5	5.50	0.71	0.83	0.02	0.75	0.46	0.01	1.90	0.08	24.11
2	19.5	5.50	0.80	0.91	nd	0.84	0.42	0.01	0.01	0.06	25.08
2	19.5	5.50	nd	0.88	nd	0.86	nd	nd	nd	nd	nd
2	19.5	5.50	nd	0.92	nd	0.04	nd	nd	nd	nd	nd
2	25.5	3.29	0.19	0.51	0.03	0.74	0.24	0.01	2.23	0.08	15.89
2	25.5	3.29	0.18	0.33	0.05	0.14	0.24	0.01	2.04	0.07	16.69
2	25.5	3.29	nd	0.30	nd	0.77	nd	nd	nd	nd	nd
2	25.5	3.29	nd	0.46	nd	0.53	nd	nd	nd	nd	nd
2	28.5	3.83	0.17	0.32	0.00	0.92	0.25	0.01	1.43	0.04	15.05
2	28.5	3.83	0.18	0.33	0.04	0.97	0.25	0.01	2.34	0.07	12.50
2	28.5	3.83	nd	0.20	0.03	0.91	nd	nd	nd	nd	nd
2	28.5	3.83	nd	0.14	0.04	0.52	nd	nd	nd	nd	nd

LEGEND
SEQUENTIAL EXTRACTION OF IRON

Parameter	Abbreviation	Unit
bdl	below detection limit	
CarbFe	carbon bound iron	g kg^{-1}
depth	average depth below surface	cm
HydFe	hydroxide iron	g kg^{-1}
MagFe	magnetite iron	g kg^{-1}
nd	not determined	
OxFe	oxide iron	g kg^{-1}
ResFe	residual iron	g kg^{-1}
TFe	total iron	g kg^{-1}
WSFe	water soluble iron	g kg^{-1}

SEQUENTIAL EXTRACTION OF IRON

RAPS 1

Core	Depth	TFe	WSFe	CarbFe	HydFe	OxFe	MagFe	ResFe
3	4.5	32.39	0.04	3.92	9.21	13.14	5.16	5.16
3	7.5	23.66	0.08	3.66	4.95	9.49	5.26	5.26
3	25.5	21.55	0.04	3.16	3.84	7.24	5.91	5.91
3	25.5	nd	0.14	4.18	3.56	8.54	5.18	5.18
3	28.5	21.17	0.05	4.57	3.49	11.37	4.75	4.75
3	34.5	18.58	0.02	3.61	3.54	6.06	1.37	1.37
3	34.5	19.79	0.17	3.92	3.28	6.12	nd	22.10
4	4.5	19.22	0.07	4.14	4.35	7.82	nd	nd
4	7.5	15.77	0.05	4.15	4.07	10.63	4.83	4.83
4	7.5	25.73	0.05	4.79	4.20	9.70	4.97	4.97
4	13.5	21.16	0.04	2.36	3.66	11.22	7.11	7.11
4	16.5	20.14	0.11	2.20	3.41	11.11	5.20	5.20
4	16.5	21.26	0.06	3.97	3.56	12.06	5.15	5.15
4	28.5	20.86	0.01	2.63	3.91	13.29	6.83	6.83

RAPS 2

Core	Depth	TFe	WSFe	CarbFe	HydFe	OxFe	MagFe	ResFe
1	10.5	134.59	0.20	45.66	63.29	17.12	2.12	2.12
1	10.5	125.26	0.31	49.58	67.19	18.56	2.02	2.02
1	16.5	26.67	0.05	8.91	3.74	12.36	4.35	4.35
1	16.5	28.66	0.09	8.48	3.90	12.37	4.88	4.88
1	19.5	20.41	0.08	6.22	2.88	9.95	nd	nd
1	19.5	23.33	0.04	6.35	2.91	nd	4.88	4.88
1	28.5	18.17	0.04	4.62	2.42	8.52	4.80	4.80
1	28.5	19.44	0.04	4.49	2.63	8.61	4.34	4.34
1	34.5	21.55	0.03	3.84	2.66	9.65	5.38	5.38
1	34.5	20.00	0.02	4.41	2.94	10.40	5.91	5.91
2	4.5	71.52	0.19	16.01	43.44	9.69	3.56	3.56
2	4.5	72.85	0.35	23.89	45.57	9.99	3.59	3.59
2	10.5	23.28	0.20	7.39	10.19	4.41	2.47	2.47
2	10.5	25.91	0.18	7.37	10.54	5.01	2.67	2.67
2	19.5	28.30	0.07	4.17	9.24	9.88	5.02	5.02
2	19.5	30.35	0.14	4.29	9.58	10.30	4.44	4.44
2	25.5	19.40	0.03	2.28	5.46	10.49	4.88	4.88
2	25.5	18.23	0.16	2.05	4.17	9.83	5.22	5.22
2	28.5	72.13	0.04	2.21	4.73	8.30	5.15	5.15
2	28.5	19.92	0.05	2.38	4.38	8.47	5.41	5.41

SEQUENTIAL EXTRACTION OF IRON

RAPS 1

		WSFe Extraction					CarbFe Extraction				
Core	**Depth**	**Al**	**Mn**	**S**	**Si**	**Zn**	**Al**	**Mn**	**S**	**Si**	**Zn**
3	4.5	0.05	0.11	0.27	0.11	bdl	1.45	0.73	0.20	1.40	0.25
3	7.5	0.13	0.24	1.11	0.34	bdl	1.76	0.64	0.39	2.42	0.27
3	25.5	0.08	0.16	0.93	0.23	bdl	0.38	0.23	0.14	0.40	0.06
3	25.5	0.19	0.19	1.11	0.54	bdl	0.57	0.24	0.16	0.73	0.06
3	28.5	0.10	0.17	1.11	0.31	bdl	0.61	0.24	0.17	0.92	0.07
3	34.5	0.05	0.16	0.85	0.15	bdl	0.39	0.23	0.14	0.47	0.04
3	34.5	0.24	0.18	1.03	0.74	bdl	0.61	0.25	0.16	0.90	0.05
4	4.5	0.10	0.25	0.89	0.24	bdl	0.45	0.37	0.17	0.49	3.04
4	7.5	0.07	0.19	0.20	0.12	0.01	0.67	0.44	0.11	0.57	0.07
4	7.5	0.07	0.19	0.18	0.17	0.01	0.73	0.47	0.13	0.68	0.07
4	13.5	0.05	0.16	0.21	0.18	bdl	0.35	0.50	0.12	0.43	2.15
4	16.5	0.16	0.13	0.15	0.37	0.00	0.38	0.35	0.17	0.45	0.05
4	16.5	0.10	0.14	0.16	0.30	0.00	0.66	0.51	0.22	bdl	0.04
4	28.5	0.03	0.17	0.19	0.12	1.12	0.40	0.50	0.12	0.64	2.05

RAPS 2

		WSFe Extraction					CarbFe Extraction				
Core	**Depth**	**Al**	**Mn**	**S**	**Si**	**Zn**	**Al**	**Mn**	**S**	**Si**	**Zn**
1	10.5	0.06	0.10	11.60	0.08	bdl	145.63	0.07	3.35	bdl	0.20
1	10.5	0.12	0.12	11.67	0.09	bdl	147.28	0.07	3.14	bdl	0.20
1	16.5	0.11	0.15	0.59	0.11	bdl	8.83	0.32	0.24	bdl	0.14
1	16.5	0.16	0.15	0.55	0.17	bdl	8.02	0.35	0.32	bdl	0.16
1	19.5	0.13	0.14	0.28	0.15	bdl	1.94	0.42	0.26	bdl	0.16
1	19.5	0.11	0.15	0.29	0.13	0.17	2.30	0.44	0.29	bdl	0.17
1	28.5	0.06	0.14	0.18	0.11	0.12	0.53	0.58	0.21	bdl	0.06
1	28.5	0.06	0.14	0.18	0.14	bdl	0.62	1.01	0.20	bdl	0.06
1	34.5	0.05	0.16	0.13	0.10	bdl	0.46	0.46	0.17	bdl	0.04
1	34.5	0.05	0.16	0.14	0.11	bdl	0.57	0.45	0.15	bdl	0.04
2	4.5	0.07	0.16	4.85	0.06	bdl	14.42	0.09	0.69	bdl	0.18
2	4.5	0.13	0.16	5.05	0.08	0.01	19.10	0.10	0.71	bdl	0.23
2	10.5	0.12	0.35	1.60	0.14	bdl	2.68	0.21	0.19	bdl	0.13
2	10.5	0.11	0.34	1.66	0.12	bdl	2.81	0.22	0.20	bdl	0.12
2	19.5	0.07	0.20	0.60	0.10	bdl	1.39	0.34	0.12	bdl	0.07
2	19.5	0.12	0.21	0.62	0.16	bdl	1.47	0.36	0.14	bdl	0.07
2	25.5	0.04	0.19	0.23	0.10	bdl	0.55	0.50	0.44	0.37	0.11
2	25.5	0.14	0.21	nd	0.19	bdl	0.43	0.51	0.82	0.35	0.10
2	28.5	0.05	0.18	0.21	0.13	bdl	0.40	0.59	0.78	0.42	0.09
2	28.5	0.05	0.17	0.19	0.10	bdl	0.33	0.57	0.56	0.31	0.09

SEQUENTIAL EXTRACTION OF IRON

RAPS 1

		HydFe Extraction					OxFe Extraction			
Core	**Depth**	**Al**	**Mn**	**S**	**Si**	**Zn**	**Al**	**Mn**	**Si**	**Zn**
3	4.5	1.97	0.16	0.23	0.95	0.09	0.62	0.06	0.57	0.02
3	7.5	1.04	0.07	0.16	0.79	0.02	0.36	0.04	0.40	bdl
3	25.5	0.67	0.05	0.17	0.54	0.02	0.31	0.04	0.31	0.01
3	25.5	0.75	0.04	0.12	0.65	0.02	0.27	0.04	0.26	0.01
3	28.5	0.65	0.05	0.14	0.43	0.01	0.29	0.03	0.26	0.01
3	34.5	0.67	0.06	0.15	0.45	0.01	0.26	0.04	0.23	0.01
3	34.5	0.83	0.09	0.12	0.96	bdl	0.22	0.04	0.24	0.01
4	4.5	0.98	0.06	0.23	0.63	0.33	0.33	0.03	0.23	0.01
4	7.5	1.01	0.06	0.20	0.61	0.03	0.58	0.05	0.57	0.02
4	7.5	1.06	0.06	0.19	0.65	0.03	0.45	0.04	0.43	0.02
4	13.5	0.77	0.07	0.16	0.48	0.11	0.40	0.05	0.30	0.02
4	16.5	1.16	0.05	0.19	0.73	0.02	0.47	0.07	0.48	0.04
4	16.5	1.13	0.06	0.20	0.61	0.02	0.73	0.06	1.01	0.02
4	28.5	0.86	0.09	0.15	0.57	0.11	0.47	0.05	0.41	0.02

RAPS 2

		HydFe Extraction					OxFe Extraction			
Core	**Depth**	**Al**	**Mn**	**S**	**Si**	**Zn**	**Al**	**Mn**	**Si**	**Zn**
1	10.5	12.56	0.03	0.57	1.92	0.09	1.01	0.04	0.32	0.02
1	10.5	13.41	0.03	0.46	1.09	0.10	0.95	0.04	0.27	0.02
1	16.5	4.00	0.10	0.40	2.71	0.04	0.96	0.06	1.09	0.02
1	16.5	2.54	0.05	0.22	0.61	0.03	0.72	0.07	0.62	0.02
1	19.5	1.28	0.09	0.19	0.48	0.09	0.56	0.05	0.61	0.01
1	19.5	1.21	0.02	0.14	0.36	0.04	nd	nd	nd	nd
1	28.5	0.24	bdl	0.11	0.21	0.01	0.25	0.04	0.35	0.01
1	28.5	0.18	bdl	0.11	0.56	0.00	0.26	0.04	0.36	0.02
1	34.5	0.68	0.06	0.19	0.42	0.13	0.43	0.02	0.46	0.01
1	34.5	0.80	0.05	0.18	0.53	0.03	0.40	0.03	0.40	0.01
2	4.5	8.08	0.02	0.53	1.37	0.03	0.87	0.02	0.27	0.01
2	4.5	8.57	0.02	0.55	1.35	0.02	0.93	0.02	0.36	0.01
2	10.5	3.11	0.01	0.10	0.55	0.04	0.72	0.01	0.87	0.02
2	10.5	3.35	0.02	0.09	0.95	0.03	0.56	0.01	0.43	0.01
2	19.5	2.32	0.05	0.22	0.52	0.04	0.64	0.04	0.33	0.03
2	19.5	2.48	0.04	0.23	0.50	0.03	0.75	0.04	0.50	0.02
2	25.5	1.18	0.03	0.00	0.50	bdl	0.59	0.05	0.45	0.02
2	25.5	0.88	0.01	-0.04	0.37	bdl	0.53	0.04	0.42	0.02
2	28.5	0.97	0.02	-0.04	0.47	bdl	0.48	0.04	0.40	0.03
2	28.5	0.83	0.04	-0.08	0.37	bdl	0.57	0.04	0.58	0.03

MOISTURE CONTENT

Core	Depth, cm below surface	Water content, %
3	4.5	53.6
3	7.5	42.1
3	16.5	42.1
3	25.5	32.9
3	28.5	33.3
3	34.5	30.4
4	4.5	27.9
4	13.5	24.8
4	28.5	24.9
1	10.5	80.6
1	16.5	36.2
1	19.5	35.4
1	28.5	27.4
1	34.5	29.2
2	4.5	84.0
2	10.5	72.9
2	19.5	65.0
2	25.5	54.1
2	28.5	56.8

SULFUR AND OXYGEN ISOTOPE RATIOS OF DISSOLVED SULFATE AND SULFIDE

Sample	Date	d34S-SO4, ‰	d18O-SO4, ‰	d34S-H2S, ‰
RAPS 1 inf (np)	Apr-08	10.2	-1.5	
RAPS 1 eff* (np)	Apr-08	14.7	3.8	
RAPS 1 ov (np)	Apr-08	11.3	1.0	
RAPS 2 inf (np)	Apr-08	10.0 / 10.1	0.1	
RAPS 2 eff* (np)	Apr-08	12.7 / 12.5 / 12.1 / 11.7	4.3	
RAPS 2 ov (np)	Apr-08	11.1 / 10.5	-0.1	
RAPS 1 inf (np)	May-08	11.8 / 10.4	nm	
RAPS 1 eff* (np)	May-08	15.4 / 15.6	nm	
RAPS 1 eff (np)	May-08	15.6	nm	
RAPS 2 inf (np)	May-08	9.6 / 13.9 / 10.2 / 8.7 / 10.1	nm	
RAPS 2 eff* (np)	May-08	13.0 / 12.3	nm	
RAPS 2 eff (np)	May-08	13.2	nm	
RAPS 2 ov (np)	May-08	10.8 / 10.4 / 8.5/10.4	nm	
RAPS 1 inf (np)	May-08	10.4	nm	
RAPS 1 eff* (np)	May-08	21.5 / 21.2	nm	
RAPS 1 eff (np)	May-08	22.1	nm	
RAPS 2 inf (np)	May-08	10.1	nm	
RAPS 2 eff* (np)	May-08	13.0 / 9.6	nm	
RAPS 2 eff (np)	May-08	11.6	nm	
RAPS 2 ov (np)	May-08	9.5 / 10.3 / 10.8	nm	
RAPS 1 inf (np)	Jun-08	10.8	nm	
RAPS 1 eff* (np)	Jun-08	27.8 / 25.7	nm	
RAPS 1 eff (np)	Jun-08	27.9 / 28.3 / 27.2	nm	
RAPS 2 inf (np)	Jun-08	10.4 / 10.5	nm	
RAPS 2 eff* (np)	Jun-08	12.3 / 12.3	nm	
RAPS 2 eff (np)	Jun-08	12.2/12.3 / 11.9	nm	
RAPS 2 ov (np)	Jun-08	10.9 / 10.2	nm	
RAPS 1 inf (np)	Jul-08	10.3	-1.0	
RAPS 1 eff* (np)	Jul-08	22.8 / 22.4	nm	
RAPS 1 eff (np)	Jul-08	23.7	nm	-25.3
RAPS 2 inf (np)	Jul-08	9.9	nm	
RAPS 2 eff* (np)	Jul-08	13.2 / 12.8	nm	
RAPS 2 eff (np)	Jul-08	12.8	2.5	
RAPS 2 ov (np)	Jul-08	10 / 9.9	-0.7	
RAPS 1 inf	Sep-08	10.2	nm	
RAPS 1 eff	Sep-08	20.1	nm	-27.6
RAPS 1 eff (np)	Sep-08	19.8 / 19.2	nm	
RAPS 2 inf	Sep-08	10.7 / 10.1	nm	
RAPS 2 eff	Sep-08	13.6 / 13.6	nm	-32.3 / -36.9
RAPS 2 eff (np)	Sep-08	13.2/13.5 / 14.0	nm	
RAPS 2 ov	Sep-08	10.7 / 10.7/10.1	nm	
RAPS 1 inf	Oct-08	11.3 / 10.0	nm	
RAPS 1 eff	Oct-08	17.7 / 16.9	nm	-32.6
RAPS 2 inf	Oct-08	11.0	nm	
RAPS 2 eff	Oct-08	12.6 / 13.1	nm	-38.1
RAPS 2 ov	Oct-08	9.9	nm	

SULFUR AND OXYGEN ISOTOPE RATIOS OF DISSOLVED SULFATE AND SULFIDE

Sample	Date	d34S-SO4, ‰	d18O-SO4, ‰	d34S-H2S, ‰
RAPS 1 inf	Nov-08	10.7	nm	nm
RAPS 1 eff	Nov-08	13.9 / 13.9	nm	-39.0
RAPS 2 inf	Nov-08	10.2 / 9.3	nm	nm
RAPS 2 eff	Nov-08	11.5/12.6	nm	-39.9/-40.9 / -41.2
RAPS 2 ov	Nov-08	9.9	nm	nm
RAPS 1 inf	Jan-09	10.9	-0.4	nm
RAPS 1 eff	Jan-09	15.0 / 13.5	5.9	-41.0
RAPS 2 inf	Jan-09	9.9	-0.3	nm
RAPS 2 eff	Jan-09	12.0	1.6	1.0
RAPS 2 ov	Jan-09	10.4 / 10.2	-0.7	nm
RAPS 1 inf	Feb-09	8.5/10.4	nm	nm
RAPS 1 eff	Feb-09	12.9	nm	-47.6
RAPS 1 ov	Feb-09	10.8/10.9	nm	nm
RAPS 2 inf	Feb-09	9.9	nm	nm
RAPS 2 eff	Feb-09	11.8/12.4	nm	1.0
RAPS 2 ov	Feb-09	9.4	nm	nm
RAPS 1 inf	Mar-09	10.4	nm	nm
RAPS 1 eff	Mar-09	17.0	nm	lost
RAPS 2 inf	Mar-09	10.6/9.8/9.6	nm	nm
RAPS 2 eff	Mar-09	11.6/12.0	nm	lost
RAPS 2 ov	Mar-09	10.1/10.2	nm	nm
RAPS 1 inf	Apr-09	10.6	-0.2	nm
RAPS 1 eff	Apr-09	21.8 / 21.7	12.5	-34.5
RAPS 2 inf	Apr-09	9.4	-0.9	nm
RAPS 2 eff	Apr-09	12.0 / 12.7	2.0	-40.5 / -40.0 / -40.3
RAPS 2 ov	Apr-09	10.6	nm	nm
RAPS 1 inf	May-09	11.6	nm	nm
RAPS 1 eff	May-09	21.9/22.9/23.1	nm	-31.6 / -31.3
RAPS 2 inf	May-09	4.1/10.7	nm	nm
RAPS 2 eff	May-09	11.9/12.2	nm	-40.2
RAPS 2 ov	May-09	11.2 / 10.2	nm	nm
RAPS 1 inf	Jun-09	10.4	0.5	nm
RAPS 1 eff	Jun-09	21.5	14.0	-24.9
RAPS 1 ov	Jun-09	11.0/11.1	1.8	nm
RAPS 2 inf	Jun-09	10.6/10.3	0.5	nm
RAPS 2 eff	Jun-09	12.9	4.3	-38.5
RAPS 2 ov	Jun-09	10.4	-0.5	nm
RAPS 1 inf	Jul-09	11.1	-1.2	nm
RAPS 1 eff	Jul-09	17.4	5.8	-23.0
RAPS 1 ov	Jul-09	10.7 / 11.6	0.3	nm
RAPS 2 inf	Jul-09	10.2	-0.2	nm
RAPS 2 eff	Jul-09	14.1 / 13.5	2.9	-36.5 / -35.3
RAPS 2 ov	Jul-09	10.2	-0.3	nm
RAPS 1 inf	Aug-09	10.9	-0.1	nm
RAPS 1 eff	Aug-09	24.1	10.5	-30.1 / -31.0
RAPS 2 inf	Aug-09	9.8	-0.8	nm
RAPS 2 eff	Aug-09	13.5	3.1	-34.6
RAPS 2 ov	Aug-09	10.3	-0.9	nm

SULFUR AND OXYGEN ISOTOPE RATIOS OF DISSOLVED SULFATE AND SULFIDE

Sample	Date	d34S-SO4, ‰	d18O-SO4, ‰	d34S-H2S, ‰
RAPS 1 inf	Sep-09	11.3	-0.3	nm
RAPS 1 eff	Sep-09	31.9	15.3	-22.4
RAPS 2 inf	Sep-09	10.8 / 10.4	-0.6	nm
RAPS 2 eff	Sep-09	12.7	0.9	-37.8
RAPS 2 ov	Sep-09	10.4	-0.7	nm
RAPS 1 inf	Oct-09	14.6 / 11.2	-0.3	nm
RAPS 1 eff	Oct-09	40.3 / 42.7	18.2	-19.8 / -17.8
RAPS 2 inf	Oct-09	11.3 / 10.4	-0.4	nm
RAPS 2 eff	Oct-09	13.7	1.5	-39.9

nm…not measured
np...no preservation
*…sample taken at discharge point into the polishing wetland

WATER ISOTOPES

Sample	Date	dD, ‰	d18O, ‰
RAPS 1 eff	Jul-09	-54	-8
RAPS 1 inf	Jul-09	-52	-8
RAPS 1 ov	Jul-09	-53	-8
RAPS 2 eff	Jul-09	-47	-7
RAPS 2 inf	Jul-09	-53	-8
RAPS 2 ov	Jul-09	-51	-8
RAPS 1 eff	Aug-09	-48	-8
RAPS 1 inf	Aug-09	-52	-8
RAPS 2 eff	Aug-09	-50	-7
RAPS 2 inf	Aug-09	-53	-8
RAPS 2 ov	Aug-09	-51	-8
RAPS 1 inf	Sep-09	-51	-8
RAPS 1 eff	Sep-09	lost	lost
RAPS 2 eff	Sep-09	-48	-7
RAPS 2 inf	Sep-09	-52	-8
RAPS 2 ov	Sep-09	-49	-7
RAPS 1 eff	Oct-09	-49	-7
RAPS 1 inf	Oct-09	-52	-8
RAPS 2 eff	Oct-09	-45	-7
RAPS 2 inf	Oct-09	-54	-8

CARBON ISOTOPE RATIOS OF TOTAL DISSOLVED INORGANIC CARBON

Sample	Date	d13C, ‰	n	stdev, ‰
RAPS 1 inf	Jul-08	-19	7	5
RAPS 1 inf	Sep-08	-13	6	3
RAPS 1 inf	Oct-08	-9	6	1
RAPS 1 inf	Nov-08	-7	6	2
RAPS 1 inf	Jan-09	-4	6	3
RAPS 1 inf	Feb-09	-14	4	1
RAPS 1 inf	Mar-09	-13	6	1
RAPS 1 inf	Apr-09	-3	7	1
RAPS 1 inf	May-09	-4	6	3
RAPS 1 inf	Jun-09	-10	6	2
RAPS 1 inf	Jul-09	-15	2	0
RAPS 1 inf	Aug-09	-4	4	0
RAPS 1 inf	Sep-09	-2	2	0
RAPS 1 inf	Oct-09	7	2	0
RAPS 1 eff	May-08	-12	5	1
RAPS 1 eff	Jun-08	-12	7	3
RAPS 1 eff	Jul-08	-17	10	1
RAPS 1 eff	Sep-08	-15	3	1
RAPS 1 eff	Oct-08	-13	6	1
RAPS 1 eff	Nov-08	-12	16	0
RAPS 1 eff	Jan-09	-11	23	0
RAPS 1 eff	Feb-09	-11	13	0
RAPS 1 eff	Mar-09	-11	8	0
RAPS 1 eff	Apr-09	-10	12	1
RAPS 1 eff	May-09	-12	10	1
RAPS 1 eff	Jun-09	-13	23	3
RAPS 1 eff	Jul-09	-13	2	0
RAPS 1 eff	Aug-09	-15	2	0
RAPS 1 eff	Sep-09	-14	2	1
RAPS 1 ov	Feb-09	-10	6	3
RAPS 1 ov	Jun-09	-15	6	0
RAPS 1 ov	Jul-09	-15	2	0
RAPS 2 inf	Jun-08	-19	5	4
RAPS 2 inf	Sep-08	-16	4	0
RAPS 2 inf	Nov-08	-15	6	0
RAPS 2 inf	Jan-09	-16	3	0
RAPS 2 inf	Mar-09	-18	3	1
RAPS 2 inf	Apr-09	-16	6	0
RAPS 2 inf	May-09	-16	4	0
RAPS 2 inf	Jun-09	-18	5	0
RAPS 2 inf	Jul-09	-14	2	0
RAPS 2 inf	Aug-09	-14	2	0
RAPS 2 inf	Sep-09	-14	2	0
RAPS 2 inf	Oct-09	-13	4	0

CARBON ISOTOPE RATIOS OF TOTAL DISSOLVED INORGANIC CARBON

Sample	Date	d13C, ‰	n	stdev
RAPS 2 eff	May-08	-9	6	1
RAPS 2 eff	Jun-08	-7	7	3
RAPS 2 eff	Jul-08	-9	12	1
RAPS 2 eff	Sep-08	-12	4	5
RAPS 2 eff	Mar-09	-8	12	1
RAPS 2 eff	Jun-09	-6	20	4
RAPS 2 eff	Aug-09	-8	4	0
RAPS 2 eff	Sep-09	-5	2	0
RAPS 2 eff	Oct-09	-5	2	0
RAPS 2 ov	Oct-08	-22	2	0
RAPS 2 ov	Nov-08	-12	6	3
RAPS 2 ov	Jan-09	-15	6	3
RAPS 2 ov	Feb-09	-14	8	0
RAPS 2 ov	Mar-09	-25	5	2
RAPS 2 ov	Apr-09	-31	3	4
RAPS 2 ov	May-09	-22	6	4
RAPS 2 ov	Jun-09	-16	4	0
RAPS 2 ov	Jul-09	-12	4	0
RAPS 2 ov	Aug-09	-21	2	1
RAPS 2 ov	Sep-09	-24	4	1

n = number of replicates and duplicates
stdev = standard deviation

CARBON ISOTOPE RATIOS AND CARBON CONTENT OF THE ORGANIC SUBSTRATE AND TYPHA SPECIES

Core	Depth, cm	d13C, ‰	d13C, duplicate	C, wt %	C, wt % Duplicate
3	4.5	-28.73		13.78	
3	28.5	-27.92		12.18	
3	34.5	-28.54		8.86	
4	7.5	-26.1		11.49	
4	16.5	-26.76		11.58	
1	16.5	-27.76		9.09	
1	19.5	-27.28	-28.21	11.92	11.08
1	28.5	-28.21	-28.07	10.21	11.08
2	19.5	-28.27	-27.7	17.35	15.53
2	25.5	-28.37		8.84	
2	28.5	-28.34		10.55	
Typha roots		-27.69	-27.22	39.80	39.71
Typha leaves		-28.01	-28.01	42.14	42.23

SULFUR ISOTOPE RATIOS OF INORGANIC SEDIMENT SULFUR

Step	RAPS	Core	Depth, cm	d34S, ‰
ASS	1	3	4.5	3.8
ASS	1	3	4.5	5.7
ASS	1	3	16.5	5.9
ASS	1	3	25.5	7.4
ASS	1	3	28.5	7.6
ASS	1	3	34.5	7.0
ASS	1	4	4.5	4.6
ASS	1	4	4.5	10.6
ASS	1	4	4.5	4.6
ASS	1	4	16.5	1.9
ASS	2	1	10.5	10.7
ASS	2	1	16.5	5.6
ASS	2	1	19.5	7 / 0.4
ASS	2	1	34.5	12.6
ASS	2	2	10.5	11.7
ASS	2	2	19.5	0.4
AVS	1	3	4.5	-1.6
AVS	1	3	4.5	nm
AVS	1	3	16.5	-8.7
AVS	1	3	25.5	-12.4
AVS	1	3	28.5	-8.6
AVS	1	3	34.5	nm
AVS	1	4	4.5	nm
AVS	1	4	7.5	nm
AVS	1	4	7.5	5.9
AVS	1	4	7.5	nm
AVS	1	4	13.5	nm
AVS	1	4	16.5	nm
AVS	1	4	28.5	nm
AVS	2	1	10.5	nm
AVS	2	1	16.5	-4.8
AVS	2	1	19.5	-3.0
AVS	2	1	28.5	-2.9
AVS	2	1	34.5	nm
AVS	2	2	4.5	nm
AVS	2	2	10.5	-8.7
AVS	2	2	19.5	-5.2
AVS	2	2	25.5	nm
AVS	2	2	28.5	nm
CRS	1	3	4.5	-20.9 / -20.6 / -22.7
CRS	1	3	7.5	-21.4 / -23.6 / -24.8 / -20.7
CRS	1	3	16.5	-20.7 / -19.2
CRS	1	3	25.5	-22.0 / -22.4
CRS	1	3	28.5	-21.8 / -20.5
CRS	1	3	34.5	-24.5 / -24.0

SULFUR ISOTOPE RATIOS OF INORGANIC SEDIMENT SULFUR

Step	RAPS	Core	Depth, cm	d34S, ‰
CRS	1	4	4.5	-25.3 / -23.7 / -25.3
CRS	1	4	4.5	-23.7
CRS	1	4	7.5	-12.6 / -9.3 / -13.0 / -13.4
CRS	1	4	7.5	-13.4 / -14.7 / -14.7
CRS	1	4	7.5	-15.2 / -15.1
CRS	1	4	13.5	nm
CRS	1	4	16.5	-20.2 / -23.1
CRS	1	4	28.5	-29. / -29.66
CRS	2	1	10.5	nm
CRS	2	1	16.5	-21.9 / 23.9
CRS	2	1	19.5	-22.2 / -22.0
CRS	2	1	28.5	-21.0 / -25.2
CRS	2	1	34.5	-15.8 / -21.6
CRS	2	2	4.5	-21.0 / -24.2
CRS	2	2	10.5	-11.0 / -11.4
CRS	2	2	19.5	-7.2 / -6.5
CRS	2	2	25.5	-11.0 / -13.0 / -14.1
CRS	2	2	28.5	-16.7 / -18.9
ES	1	3	4.5	-11.8 / -5.6 / -4.1
ES	1	3	7.5	-12.4 / -9.1 / -8.0
ES	1	3	16.5	-3.0 / -9.9 / -8.9 / 12.0 / -8.6
ES	1	3	25.5	-9.5 / -10.8 / -11.7
ES	1	3	28.5	-11.2 / -2.2 / -11.8 / -11.0 / -10.5
ES	1	3	34.5	-14.2 / -13.6
ES	1	4	4.5	4.2 / 4.2
ES	1	4	7.5	7.8 / 7.6 / 9.9
ES	1	4	7.5	7.4 / 7.9 / 9.5
ES	1	4	7.5	8.4 / 8.9
ES	1	4	13.5	nm
ES	1	4	16.5	-3.2 / -2.0
ES	1	4	28.5	nm
ES	2	1	10.5	-12.4
ES	2	1	16.5	-6.6 / -7.4 / -4.9
ES	2	1	19.5	5.6 / -0.9
ES	2	1	28.5	-1.0 / -3.3
ES	2	1	34.5	-3.7 / -3.0 / -3.8
ES	2	2	4.5	-22.5 / -25.0
ES	2	2	10.5	-1.0 / -5.4 / -4.9
ES	2	2	19.5	-0.5 / -0.7
ES	2	2	25.5	3.7 / -1.9
ES	2	2	28.5	-5.1 / -25.9

nm...not measured
AVS…acid volatile sulfur
ES…elemental sulfur
CRS…chromium reducible sulfur
ASS…acid volatile sulfur
depth… cm below surface

ADDITIONAL INFORMATION FOR CHAPTER 1

CORRELATION MATRICES OF PHYSICOCHEMICAL PARAMETERS AND ELEMENT CONCENTRATIONS

INFLUENT 1

	T	pH	EC	Eh	Alk	Q	Cl	SO4	Ca	Mg	Na	K	Fe	Mn	Al	Zn	Si	Acd
T		.397**	0.1	-.411**	-.431**	-.649**	0.0	-0.1	.465**	0.2	0.0	0.2	-0.1	0.1	-0.1	-0.2	-0.1	-0.1
		0.0	0.3	0.0	0.0	0.0	0.9	0.3	0.0	0.2	0.7	0.2	0.3	0.5	0.5	0.1	0.4	0.4
		64.0	64.0	64.0	64.0	61.0	63.0	63.0	63.0	63.0	63.0	63.0	63.0	63.0	63.0	63.0	43.0	63.0
pH		1.0	-0.2	-.738**	.668**	-.350**	0.2	-.594**	0.1	-0.1	.292*	.541**	-0.1	-.498**	-0.1	-.574**	-0.3	-0.1
			0.1	0.0	0.0	0.0	0.1	0.0	0.5	0.3	0.0	0.0	0.4	0.0	0.4	0.0	0.1	0.3
			64.0	64.0	64.0	61.0	63.0	63.0	63.0	63.0	63.0	63.0	63.0	63.0	63.0	63.0	43.0	63.0
EC			1.0	.391**	-0.1	-.387**	0.2	.547**	.648**	.577**	.325**	.393**	-0.1	.544**	0.0	.417**	0.2	0.0
				0.0	0.4	0.0	0.1	0.0	0.0	0.0	0.0	0.0	0.5	0.0	0.8	0.0	0.1	1.0
				64.0	64.0	61.0	63.0	63.0	63.0	63.0	63.0	63.0	63.0	63.0	63.0	63.0	43.0	63.0
Eh				1.0	-.503**	.381**	0.2	.523**	-0.1	0.1	0.1	-0.2	-0.1	.395**	0.0	.388**	0.2	0.0
					0.0	0.0	0.2	0.0	0.7	0.5	0.4	0.2	0.5	0.0	1.0	0.0	0.2	1.0
					64.0	61.0	63.0	63.0	63.0	63.0	63.0	63.0	63.0	63.0	63.0	63.0	43.0	63.0
Alk					1.0	-.425**	0.1	-.465**	0.2	0.0	0.1	0.2	-0.1	-.438**	-0.1	-.550**	-0.2	-0.1
						0.0	0.3	0.0	0.2	0.8	0.5	0.1	0.3	0.0	0.4	0.0	0.1	0.3
						61.0	63.0	63.0	63.0	63.0	63.0	63.0	63.0	63.0	63.0	63.0	43.0	63.0
Q						1.0	0.1	-0.2	-.755**	-.610**	0.0	-.691**	-0.1	-.314*	-0.1	-0.1	-0.1	-0.1
							0.5	0.1	0.0	0.0	0.8	0.0	0.5	0.0	0.3	0.5	0.4	0.4
							60.0	60.0	60.0	60.0	60.0	60.0	60.0	60.0	60.0	60.0	43.0	60.0
Cl							1.0	-.358**	-0.1	-0.2	.914**	.442**	-.293*	-.329**	-0.2	-.332**	-0.2	-0.2
								0.0	0.4	0.1	0.0	0.0	0.0	0.0	0.2	0.0	0.3	0.1
								63.0	63.0	63.0	63.0	63.0	63.0	63.0	63.0	63.0	43.0	63.0
SO4								1.0	.468**	.531**	-.264*	-0.1	0.2	.733**	0.2	.742**	.421**	.250*
									0.0	0.0	0.0	0.6	0.1	0.0	0.1	0.0	0.0	0.0
									63.0	63.0	63.0	63.0	63.0	63.0	63.0	63.0	43.0	63.0
Ca									1.0	.786**	0.1	.370**	0.2	.518**	.287*	.300*	.412**	0.2
										0.0	0.7	0.0	0.2	0.0	0.0	0.0	0.0	0.1
										63.0	63.0	63.0	63.0	63.0	63.0	63.0	43.0	63.0
Mg										1.0	-0.2	0.1	0.1	.604**	0.2	.437**	0.3	0.1
											0.2	0.4	0.6	0.0	0.2	0.0	0.1	0.4
											63.0	63.0	63.0	63.0	63.0	63.0	43.0	63.0

ADDITIONAL INFORMATION FOR CHAPTER 1

CORRELATION MATRICES OF PHYSICOCHEMICAL PARAMETERS AND ELEMENT CONCENTRATIONS

	T	pH	EC	Eh	Alk	Q	Cl	SO4	Ca	Mg	Na	K	Fe	Mn	Al	Zn	Si	Acd
Na											1.0	.671**	-0.1	-.265*	0.0	-.283*	0.2	-0.1
												0.0	0.3	0.0	0.8	0.0	0.3	0.4
												63.0	63.0	63.0	63.0	63.0	43.0	63.0
K												1.0	0.0	-0.1	0.0	-0.2	0.1	-0.1
													0.7	0.3	0.8	0.2	0.4	0.7
													63.0	63.0	63.0	63.0	43.0	63.0
Fe													1.0	0.0	.948**	.289*	.862**	.984**
														0.7	0.0	0.0	0.0	0.0
														63.0	63.0	63.0	43.0	63.0
Mn														1.0	0.1	.715**	.372*	0.1
															0.4	0.0	0.0	0.4
															63.0	63.0	43.0	63.0
Al															1.0	.306*	.875**	.987**
																0.0	0.0	0.0
																63.0	43.0	63.0
Zn																1.0	.474**	.328**
																	0.0	0.0
																	43.0	63.0
Si																	1.0	.886**
																		0.0
																		43.0

INFLUENT 2

	T	pH	EC	Eh	Alk	Q	Cl	SO4	Ca	Mg	Na	K	Fe	Mn	Al	Zn	Si	Acd
T		-.451**	.599**	.413**	-.444**	-.467**	0.1	.598**	.627**	.600**	.568**	.557**	.628**	.565**	.588**	.573**	.645**	.594**
		0.0	0.0	0.0	0.0	0.0	0.7	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
		63.0	63.0	63.0	63.0	62.0	62.0	62.0	62.0	62.0	62.0	62.0	61.0	62.0	61.0	62.0	42.0	61.0
pH		1.0	-.785**	-.585**	.822**	.802**	-0.1	-.791**	-.754**	-.759**	-.540**	-.617**	-.808**	-.737**	-.750**	-.765**	-.668**	-.779**
			0.0	0.0	0.0	0.0	0.5	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
			63.0	63.0	63.0	62.0	62.0	62.0	62.0	62.0	62.0	62.0	61.0	62.0	61.0	62.0	42.0	61.0

ADDITIONAL INFORMATION FOR CHAPTER 1

CORRELATION MATRICES OF PHYSICOCHEMICAL PARAMETERS AND ELEMENT CONCENTRATIONS

	T	pH	EC	Eh	Alk	Q	Cl	SO4	Ca	Mg	Na	K	Fe	Mn	Al	Zn	Si	Acd
EC			1.0	.580**	-.672**	-.785**	0.2	.964**	.931**	.982**	.874**	.861**	.973**	.951**	.931**	.957**	.854**	.971**
				0.0	0.0	0.0	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
				63.0	63.0	62.0	62.0	62.0	62.0	62.0	62.0	62.0	61.0	62.0	61.0	62.0	42.0	61.0
Eh				1.0	-.526**	-.495**	0.2	.665**	.557**	.616**	.388**	.489**	.628**	.635**	.633**	.642**	.527**	.667**
					0.0	0.0	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
					63.0	62.0	62.0	62.0	62.0	62.0	62.0	62.0	61.0	62.0	61.0	62.0	42.0	61.0
Alk					1.0	.723**	0.0	-.663**	-.629**	-.631**	-.520**	-.515**	-.693**	-.630**	-.660**	-.669**	-.653**	-.676**
						0.0	0.7	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
						62.0	62.0	62.0	62.0	62.0	62.0	62.0	61.0	62.0	61.0	62.0	42.0	61.0
Q						1.0	-0.2	-.749**	-.729**	-.753**	-.609**	-.623**	-.768**	-.757**	-.742**	-.771**	-.665**	-.756**
							0.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
							61.0	61.0	61.0	61.0	61.0	61.0	60.0	61.0	60.0	61.0	42.0	60.0
Cl							1.0	0.2	0.2	0.2	0.2	.276*	0.2	0.2	0.2	0.2	0.2	0.2
								0.1	0.2	0.1	0.1	0.0	0.2	0.1	0.1	0.1	0.3	0.1
								62.0	62.0	62.0	62.0	62.0	61.0	62.0	61.0	62.0	42.0	61.0
SO4								1.0	.901**	.978**	.842**	.842**	.951**	.964**	.946**	.964**	.862**	.974**
									0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
									62.0	62.0	62.0	62.0	61.0	62.0	61.0	62.0	42.0	61.0
Ca									1.0	.935**	.856**	.929**	.960**	.836**	.835**	.850**	.870**	.888**
										0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
										62.0	62.0	62.0	61.0	62.0	61.0	62.0	42.0	61.0
Mg										1.0	.897**	.888**	.970**	.971**	.952**	.970**	.884**	.980**
											0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
											62.0	62.0	61.0	62.0	61.0	62.0	42.0	61.0
Na											1.0	.883**	.839**	.846**	.825**	.832**	.785**	.837**
												0.0	0.0	0.0	0.0	0.0	0.0	0.0
												62.0	61.0	62.0	61.0	62.0	42.0	61.0
K												1.0	.890**	.802**	.788**	.789**	.862**	.823**
													0.0	0.0	0.0	0.0	0.0	0.0
													61.0	62.0	61.0	62.0	42.0	61.0

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	T	pH	EC	Eh	Alk	Q	Cl	SO4	Ca	Mg	Na	K	Fe	Mn	Al	Zn	Si	Acd
Fe													1.0	.919**	.930**	.936**	.927**	.962**
														0.0	0.0	0.0	0.0	0.0
														61.0	60.0	61.0	41.0	61.0
Mn														1.0	.979**	.988**	.909**	.980**
															0.0	0.0	0.0	0.0
															61.0	62.0	42.0	61.0
Al															1.0	.982**	.927**	.992**
																0.0	0.0	0.0
																61.0	41.0	60.0
Zn																1.0	.894**	.984**
																	0.0	0.0
																	42.0	61.0
Si																	1.0	.923**
																		0.0
																		41.0

EFFLUENT

	T	pH	EC	Eh	Alk	Q	Cl	SO4	Ca	Mg	Na	K	Fe	Mn	Al	Zn	Si	Acd
T		.372**	.563**	-0.1	.612**	-.423**	-0.2	.497**	.518**	.519**	.472**	0.2	-.336**	.429**	-0.2	-0.1	-0.2	-0.2
		0.0	0.0	0.5	0.0	0.0	0.1	0.0	0.0	0.0	0.0	0.2	0.0	0.0	0.2	0.5	0.2	0.2
		63.0	63.0	63.0	63.0	61.0	62.0	62.0	62.0	62.0	62.0	62.0	62.0	62.0	62.0	62.0	42.0	62.0
pH		1.0	.346**	-0.1	.575**	-0.2	0.1	.252*	.294*	.312*	.327**	0.1	-.500**	0.0	-.474**	-.345**	-.452**	-.525**
			0.0	0.3	0.0	0.2	0.5	0.0	0.0	0.0	0.0	0.2	0.0	0.7	0.0	0.0	0.0	0.0
			63.0	63.0	63.0	61.0	62.0	62.0	62.0	62.0	62.0	62.0	62.0	62.0	62.0	62.0	42.0	62.0
EC			1.0	0.1	.781**	-.717**	0.1	.972**	.973**	.978**	.809**	.622**	-.408**	.681**	-0.2	0.0	-0.3	-0.1
				0.6	0.0	0.0	0.5	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.2	0.8	0.1	0.4
				63.0	63.0	61.0	62.0	62.0	62.0	62.0	62.0	62.0	62.0	62.0	62.0	62.0	42.0	62.0
Eh				1.0	0.1	0.0	0.2	0.1	0.1	0.1	0.1	.270*	-0.1	0.2	-0.1	-0.1	0.0	-0.1
					0.5	0.8	0.1	0.5	0.4	0.4	0.4	0.0	0.3	0.1	0.5	0.4	0.9	0.6
					63.0	61.0	62.0	62.0	62.0	62.0	62.0	62.0	62.0	62.0	62.0	62.0	42.0	62.0

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	T	pH	EC	Eh	Alk	Q	Cl	SO4	Ca	Mg	Na	K	Fe	Mn	Al	Zn	Si	Acd
Alk					1.0	-.533**	0.2	.679**	.749**	.750**	.705**	.527**	-.552**	.529**	-.368**	-0.2	-.555**	-.359**
						0.0	0.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.0	0.0
						61.0	62.0	62.0	62.0	62.0	62.0	62.0	62.0	62.0	62.0	62.0	42.0	62.0
Q						1.0	0.1	-.694**	-.700**	-.688**	-.516**	-.568**	.272*	-.569**	0.0	0.0	.380*	0.0
							0.3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.7	0.8	0.0	0.7
							60.0	60.0	60.0	60.0	60.0	60.0	60.0	60.0	60.0	60.0	42.0	60.0
Cl							1.0	0.1	0.1	0.1	.419**	.572**	-0.1	0.2	-0.1	-0.1	-0.2	-0.1
								0.6	0.4	0.3	0.0	0.0	0.4	0.1	0.3	0.6	0.2	0.5
								62.0	62.0	62.0	62.0	62.0	62.0	62.0	62.0	62.0	42.0	62.0
SO4								1.0	.987**	.983**	.792**	.642**	-.332**	.722**	-0.1	0.0	-0.2	0.0
									0.0	0.0	0.0	0.0	0.0	0.0	0.4	0.9	0.3	0.8
									62.0	62.0	62.0	62.0	62.0	62.0	62.0	62.0	42.0	62.0
Ca									1.0	.988**	.809**	.698**	-.388**	.752**	-0.2	0.0	-0.3	-0.1
										0.0	0.0	0.0	0.0	0.0	0.2	0.7	0.1	0.4
										62.0	62.0	62.0	62.0	62.0	62.0	62.0	42.0	62.0
Mg										1.0	.836**	.701**	-.352**	.731**	-0.1	0.0	-0.2	-0.1
											0.0	0.0	0.0	0.0	0.2	0.9	0.2	0.6
											62.0	62.0	62.0	62.0	62.0	62.0	42.0	62.0
Na											1.0	.734**	-.380**	.671**	-0.2	0.0	-0.2	-0.1
												0.0	0.0	0.0	0.1	0.9	0.3	0.3
												62.0	62.0	62.0	62.0	62.0	42.0	62.0
K												1.0	-.258*	.695**	-0.2	-0.1	-.484**	-0.1
													0.0	0.0	0.1	0.6	0.0	0.6
													62.0	62.0	62.0	62.0	42.0	62.0
Fe													1.0	-0.2	.735**	.400**	.707**	.860**
														0.1	0.0	0.0	0.0	0.0
														62.0	62.0	62.0	42.0	62.0
Mn														1.0	-0.1	0.0	-0.2	0.1
															0.6	0.9	0.2	0.5
															62.0	62.0	42.0	62.0

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	T	pH	EC	Eh	Alk	Q	Cl	SO4	Ca	Mg	Na	K	Fe	Mn	Al	Zn	Si	Acd
Al															1.0	0.2	.628**	.937**
																0.1	0.0	0.0
																62.0	42.0	62.0
Zn																1.0	.431**	.387**
																	0.0	0.0
																	42.0	62.0
Si																	1.0	.707**
																		0.0
																		42.0

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CORRELATION MATRICES OF ELEMENT LOADS

REMOVAL RATES

Alk	Cl	SO4	Ca	Mg	Na	K	Fe	Mn	Al	Zn	Si	Acd	H
Alk	.513(**)	0.1	.428(**)	.249(*)	.471(**)	.640(**)	-0.1	0.2	-0.1	-0.2	0.0	-0.2	-0.1
	0.0	0.6	0.0	0.0	0.0	0.0	0.3	0.1	0.3	0.2	0.8	0.1	0.7
	64.0	64.0	64.0	64.0	64.0	64.0	64.0	64.0	64.0	64.0	47.0	64.0	63.0
Cl	1.0	.408(**)	.645(**)	.559(**)	.928(**)	.637(**)	.290(*)	.504(**)	.292(*)	0.2	.745(**)	0.2	0.1
		0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.0	0.1	0.5
		64.0	64.0	64.0	64.0	64.0	64.0	64.0	64.0	64.0	47.0	64.0	63.0
SO4		1.0	.851(**)	.933(**)	.623(**)	.529(**)	.805(**)	.889(**)	.735(**)	.398(**)	.807(**)	.791(**)	0.2
			0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.2
			64.0	64.0	64.0	64.0	64.0	64.0	64.0	64.0	47.0	64.0	63.0
Ca			1.0	.957(**)	.795(**)	.795(**)	.567(**)	.897(**)	.635(**)	.309(*)	.895(**)	.524(**)	0.1
				0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.5
				64.0	64.0	64.0	64.0	64.0	64.0	64.0	47.0	64.0	63.0
Mg				1.0	.748(**)	.686(**)	.735(**)	.945(**)	.728(**)	.374(**)	.879(**)	.704(**)	0.1
					0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.5
					64.0	64.0	64.0	64.0	64.0	64.0	47.0	64.0	63.0
Na					1.0	.662(**)	.450(**)	.689(**)	.482(**)	.267(*)	.904(**)	.405(**)	0.1
						0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.4
						64.0	64.0	64.0	64.0	64.0	47.0	64.0	63.0
K						1.0	.303(*)	.672(**)	.294(*)	0.1	.747(**)	0.2	0.0
							0.0	0.0	0.0	0.3	0.0	0.1	0.9
							64.0	64.0	64.0	64.0	47.0	64.0	63.0
Fe							1.0	.683(**)	.676(**)	.323(**)	.603(**)	.959(**)	0.2
								0.0	0.0	0.0	0.0	0.0	0.2
								64.0	64.0	64.0	47.0	64.0	63.0
Mn								1.0	.726(**)	.384(**)	.852(**)	.668(**)	0.0
									0.0	0.0	0.0	0.0	0.8
									64.0	64.0	47.0	64.0	63.0
Al									1.0	.384(**)	.916(**)	.731(**)	0.2
										0.0	0.0	0.0	0.1
										64.0	47.0	64.0	63.0
Zn										1.0	.438(**)	.340(**)	0.0
											0.0	0.0	0.8
											47.0	64.0	63.0
Si											1.0	.594(**)	0.1
												0.0	0.4
												47.0	46.0

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Alk	Cl	SO4	Ca	Mg	Na	K	Fe	Mn	Al	Zn	Si	Acd	H
Acd												1.0	0.2
													0.1
													63.0

INFLUENT 1

Cl	SO4	Ca	Mg	Na	K	Fe	Mn	Al	Zn	Si	Acd	Alk	H
Cl	.354(**)	.489(**)	.584(**)	.985(**)	.617(**)	.302(*)	.379(**)	.254(*)	.335(**)	.794(**)	.284(*)	0.2	0.1
	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.3
	64.0	64.0	64.0	64.0	64.0	64.0	64.0	64.0	64.0	47.0	64.0	64.0	63.0
SO4	1.0	.921(**)	.897(**)	.453(**)	.788(**)	.842(**)	.924(**)	.821(**)	.946(**)	.925(**)	.882(**)	0.0	.700(**)
		0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.8	0.0
		64.0	64.0	64.0	64.0	64.0	64.0	64.0	64.0	47.0	64.0	64.0	63.0
Ca		1.0	.988(**)	.596(**)	.942(**)	.822(**)	.940(**)	.774(**)	.911(**)	.960(**)	.816(**)	0.2	.440(**)
			0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.0
			64.0	64.0	64.0	64.0	64.0	64.0	64.0	47.0	64.0	64.0	63.0
Mg			1.0	.679(**)	.958(**)	.784(**)	.922(**)	.739(**)	.888(**)	.957(**)	.779(**)	0.2	.419(**)
				0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.0
				64.0	64.0	64.0	64.0	64.0	64.0	47.0	64.0	64.0	63.0
Na				1.0	.714(**)	.407(**)	.489(**)	.355(**)	.440(**)	.865(**)	.384(**)	.251(*)	0.2
					0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.2
					64.0	64.0	64.0	64.0	64.0	47.0	64.0	64.0	63.0
K					1.0	.709(**)	.822(**)	.643(**)	.784(**)	.915(**)	.677(**)	.390(**)	.259(*)
						0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
						64.0	64.0	64.0	64.0	47.0	64.0	64.0	63.0
Fe						1.0	.818(**)	.945(**)	.840(**)	.843(**)	.977(**)	0.0	.517(**)
							0.0	0.0	0.0	0.0	0.0	0.9	0.0
							64.0	64.0	64.0	47.0	64.0	64.0	63.0
Mn							1.0	.788(**)	.944(**)	.940(**)	.828(**)	0.0	.483(**)
								0.0	0.0	0.0	0.0	0.9	0.0
								64.0	64.0	47.0	64.0	64.0	63.0
Al								1.0	.827(**)	.816(**)	.980(**)	0.0	.563(**)
									0.0	0.0	0.0	0.7	0.0
									64.0	47.0	64.0	64.0	63.0
Zn									1.0	.921(**)	.866(**)	0.0	.563(**)
										0.0	0.0	1.0	0.0
										47.0	64.0	64.0	63.0

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Cl	SO4	Ca	Mg	Na	K	Fe	Mn	Al	Zn	Si	Acd	Alk	H
Si										1.0	.848(**)	0.2	.517(**)
											0.0	0.2	0.0
											47.0	47.0	46.0
Acd											1.0	0.0	.645(**)
												0.7	0.0
												64.0	63.0
Alk												1.0	-0.2
													0.1
													63.0

INFLUENT 2

Alk	Cl	SO4	Ca	Mg	Na	K	Fe	Mn	Al	Zn	Si	Acd	H
Alk	.804(**)	0.2	.509(**)	.456(**)	.667(**)	.651(**)	0.2	0.1	0.1	0.1	.423(**)	0.1	-.331(**)
	0.0	0.1	0.0	0.0	0.0	0.0	0.2	0.4	0.6	0.5	0.0	0.3	0.0
	66.0	66.0	66.0	66.0	66.0	66.0	66.0	66.0	66.0	66.0	47.0	66.0	63.0
Cl	1.0	.507(**)	.747(**)	.713(**)	.863(**)	.839(**)	.482(**)	.440(**)	.393(**)	.434(**)	.813(**)	.456(**)	-.259(*)
		0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
		66.0	66.0	66.0	66.0	66.0	66.0	66.0	66.0	66.0	47.0	66.0	63.0
SO4		1.0	.901(**)	.927(**)	.793(**)	.797(**)	.952(**)	.936(**)	.806(**)	.924(**)	.776(**)	.959(**)	.407(**)
			0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
			66.0	66.0	66.0	66.0	66.0	66.0	66.0	66.0	47.0	66.0	63.0
Ca			1.0	.991(**)	.964(**)	.970(**)	.900(**)	.872(**)	.784(**)	.865(**)	.925(**)	.882(**)	0.1
				0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.6
				66.0	66.0	66.0	66.0	66.0	66.0	66.0	47.0	66.0	63.0
Mg				1.0	.948(**)	.945(**)	.935(**)	.913(**)	.797(**)	.899(**)	.885(**)	.925(**)	0.1
					0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.4
					66.0	66.0	66.0	66.0	66.0	66.0	47.0	66.0	63.0
Na					1.0	.985(**)	.786(**)	.762(**)	.680(**)	.748(**)	.923(**)	.767(**)	-0.1
						0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.5
						66.0	66.0	66.0	66.0	66.0	47.0	66.0	63.0
K						1.0	.794(**)	.769(**)	.709(**)	.758(**)	.954(**)	.765(**)	-0.1
							0.0	0.0	0.0	0.0	0.0	0.0	0.5
							66.0	66.0	66.0	66.0	47.0	66.0	63.0
Fe							1.0	.964(**)	.800(**)	.944(**)	.778(**)	.988(**)	.263(*)
								0.0	0.0	0.0	0.0	0.0	0.0
								66.0	66.0	66.0	47.0	66.0	63.0

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Alk	Cl	SO4	Ca	Mg	Na	K	Fe	Mn	Al	Zn	Si	Acd	H
Mn								1.0	.901(**)	.986(**)	.812(**)	.974(**)	.264(*)
									0.0	0.0	0.0	0.0	0.0
									66.0	66.0	47.0	66.0	63.0
Al									1.0	.936(**)	.854(**)	.825(**)	.250(*)
										0.0	0.0	0.0	0.0
										66.0	47.0	66.0	63.0
Zn										1.0	.846(**)	.957(**)	.273(*)
											0.0	0.0	0.0
											47.0	66.0	63.0
Si											1.0	.754(**)	0.0
												0.0	0.9
												47.0	46.0
Acd												1.0	.303(*)
													0.0
													63.0

EFFLUENT

Alk	Cl	SO4	Ca	Mg	Na	K	Fe	Mn	Al	Zn	Si	Acd	H
Alk	.877(**)	.499(**)	.659(**)	.646(**)	.850(**)	.766(**)	.387(**)	.416(**)	0.1	-0.1	.542(**)	.262(*)	0.0
	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.6	0.5	0.0	0.0	1.0
	65.0	65.0	65.0	65.0	65.0	65.0	65.0	65.0	65.0	65.0	47.0	65.0	63.0
Cl		.586(**)	.726(**)	.728(**)	.944(**)	.803(**)	.499(**)	.483(**)	0.2	0.1	.845(**)	.409(**)	.277(*)
		0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.6	0.0	0.0	0.0
		65.0	65.0	65.0	65.0	65.0	65.0	65.0	65.0	65.0	47.0	65.0	63.0
SO4			.970(**)	.971(**)	.709(**)	.693(**)	.750(**)	.928(**)	.527(**)	0.2	.891(**)	.729(**)	.560(**)
			0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.0	0.0	0.0
			65.0	65.0	65.0	65.0	65.0	65.0	65.0	65.0	47.0	65.0	63.0
Ca			1.0	.992(**)	.800(**)	.809(**)	.743(**)	.892(**)	.483(**)	0.2	.895(**)	.696(**)	.490(**)
				0.0	0.0	0.0	0.0	0.0	0.0	0.2	0.0	0.0	0.0
				65.0	65.0	65.0	65.0	65.0	65.0	65.0	47.0	65.0	63.0
Mg				1.0	.813(**)	.788(**)	.777(**)	.880(**)	.507(**)	0.2	.904(**)	.726(**)	.499(**)
					0.0	0.0	0.0	0.0	0.0	0.1	0.0	0.0	0.0
					65.0	65.0	65.0	65.0	65.0	65.0	47.0	65.0	63.0
Na					1.0	.722(**)	.580(**)	.600(**)	.312(*)	0.1	.950(**)	.501(**)	.318(*)
						0.0	0.0	0.0	0.0	0.4	0.0	0.0	0.0
						65.0	65.0	65.0	65.0	65.0	47.0	65.0	63.0

ADDITIONAL INFORMATION FOR CHAPTER 1

CORRELATION MATRICES OF ELEMENT LOADS

Alk	**Cl**	**SO4**	**Ca**	**Mg**	**Na**	**K**	**Fe**	**Mn**	**Al**	**Zn**	**Si**	**Acd**	**H**
K						1.0	.522(**)	.645(**)	.264(*)	0.1	.791(**)	.448(**)	.347(**)
							0.0	0.0	0.0	0.6	0.0	0.0	0.0
							65.0	65.0	65.0	65.0	47.0	65.0	63.0
Fe							1.0	.643(**)	.741(**)	.258(*)	.892(**)	.936(**)	.362(**)
								0.0	0.0	0.0	0.0	0.0	0.0
								65.0	65.0	65.0	47.0	65.0	63.0
Mn								1.0	.518(**)	0.2	.840(**)	.677(**)	.589(**)
									0.0	0.1	0.0	0.0	0.0
									65.0	65.0	47.0	65.0	63.0
Al									1.0	0.2	.615(**)	.922(**)	.506(**)
										0.1	0.0	0.0	0.0
										65.0	47.0	65.0	63.0
Zn										1.0	0.2	.284(*)	.430(**)
											0.3	0.0	0.0
											47.0	65.0	63.0
Si											1.0	.814(**)	.460(**)
												0.0	0.0
												47.0	46.0
Acd												1.0	.500(**)
													0.0
													63.0

data show:

r = correlation coefficient

p = significance

n = number of samples

Acd = acidity

Alk = alkalinity

**	Correlation is significant at the 0.01 level (2-tailed).
*	Correlation is significant at the 0.05 level (2-tailed).