

EXTENDED ABSTRACT

Tracking dominant Alkalinity Sources in a Passive Mine Water Treatment System with stable Carbon Isotopes

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Extended Abstract

In addition to metal removal, passive systems designed to treat net-acidic mine waters strive to increase pH by generating alkalinity. In the past, carbonate minerals were used for this purpose (e.g. $\text{CaCO}_3 + \text{H}^+ \leftrightarrow \text{Ca}^{2+} + \text{HCO}_3^-$). However, treatment under oxic conditions, for instance in Oxic Limestone Drains, often led to a rapid decline in alkalinity generation because elevated iron and aluminium concentrations caused an armouring of the limestone gravel by formation of secondary hydroxide precipitates. This was soon followed by a complete failure of the treatment system with dramatic effects on local ecosystems.

In order to address this problem, Anoxic Limestone Drains (ALD) were developed to create reducing conditions that prevent the oxidation and hydrolysis of ferrous iron. However, reducing conditions alone are not effective for aluminium removal since this element is not redox sensitive. Consequently, in order to be able to treat net-acidic waters with elevated iron and aluminium concentrations, ALD and sub-surface wetlands were combined in one vertical flow pond (VFP) consisting of a reactive substrate of limestone and organic matter.

In addition to limestone as an alkalinity source, organic matter generates reducing conditions by promoting initially aerobic respiration ($\text{CH}_2\text{O} + \text{O}_2 \leftrightarrow \text{CO}_2 \uparrow + \text{H}_2\text{O}$) thereby hampering the oxidation of Fe^{2+} . Furthermore, bicarbonate is generated by anaerobic respiration processes via microbial oxidation of organic matter using iron and sulphate as terminal electron acceptors (bacterial iron reduction: $4\text{Fe(OH)}_3 + \text{CH}_2\text{O} + 7\text{H}^+ \rightarrow 4\text{Fe}^{2+} + \text{HCO}_3^- + 10\text{H}_2\text{O}$; bacterial sulphate reduction: $\text{SO}_4^{2-} + 2\text{CH}_2\text{O} \rightarrow 2\text{HCO}_3^- + \text{H}_2\text{S} + \text{H}_2\text{O}$; CH_2O = organic matter). Some workers (e.g. Younger et al. 2002, Kepler and Mc Cleary 1994) have suggested that the oxidation of organic matter is a dominant bicarbonate source in organic-rich VFP designed for passive mine water treatment, thus protecting limestone from dissolution and enhancing system performance and longevity.

In an 18 months monitoring of influents and effluents of two parallel operating VFP (80 cm deep reactive substrate composed of 50 vol.% limestone gravel, 50 vol.% compost and manure) treating two net-acidic drainages of the Durham coalfield (UK), we aimed to unravel the predominant bicarbonate generating processes with the help of stable carbon isotope ratios of total dissolved inorganic carbon ($\delta^{13}\text{C-TDIC}$ in ‰; Figure 1). Because of the distinct isotopic differences between the dominant C isotope reservoirs (i) limestone ($1.8 \pm 0.3\text{‰}$) and (ii) organic matter ($-28.5 \pm 2.4\text{‰}$), carbon isotopes of TDIC are good tracers to track the contribution of bicarbonate from both end members.

Through the passive treatment, average pH of the two mine waters (influents) were raised from $\approx 5.1 - 6.0$ to $\approx 6.9 - 7.2$ (effluents). Alkalinities, close to detection limit in the mine waters, were raised to $\approx 190 - 200 \text{ mg L}^{-1} \text{ CaCO}_3 \text{ eq}$ in the effluents (Figure 1). Water that did not pass through the reactive substrate but short-circuited the system as surface flow (i.e. overflow) commonly showed lower pH (4.8–6.6) than in influents as a result of proton acidity generation from iron and aluminium hydrolysis. Carbon isotope ratios of TDIC in the effluents (effluent 1: $-13 \pm 2\text{‰}$, n=14; effluent 2: $-8 \pm 2\text{‰}$, n=9) were surprisingly constant over the course of the monitoring, despite significant seasonalities observed for alkalinities. $\delta^{13}\text{C}_{\text{TDIC}}$ suggest both limestone dissolution and the microbial degradation of organic substrate contributed to the alkalinity generation.

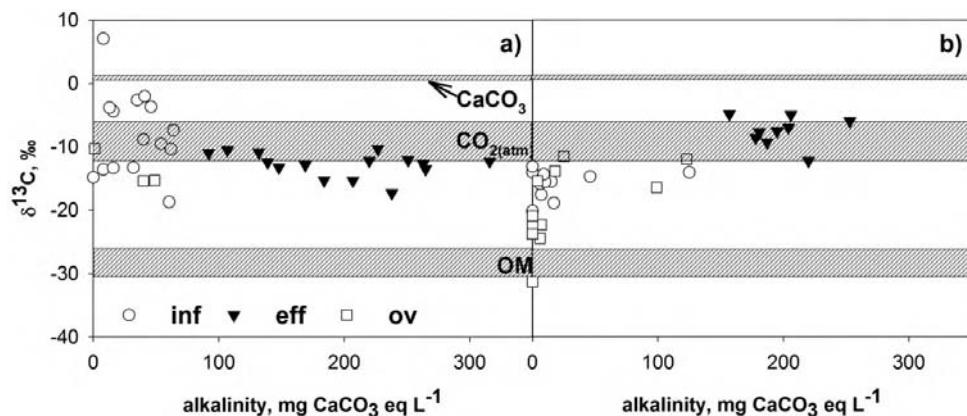


Figure 1 Alkalinity concentrations and carbon isotope ratios in influents (i.e. mine waters), effluents (i.e. water that has percolated through the reactive substrate) and overflows (water that is short-circuiting over the reactive substrate) of VFP 1 (a) and 2 (b); shaded areas=δ¹³C of organic matter (OM), limestone (CaCO₃) and atmospheric carbon dioxide (CO_{2(atm)})

The relative contributions of organic matter and CaCO₃ dissolution to alkalinity were assessed via two mass balances. Approach one compared total alkalinity generation and total acidity consumption (equation 1).

$$(1) \quad Acd_{tot} = 1.75\Delta Fe + 2.25\Delta Al + \Delta H^+_{bic} + \Delta H^+_{DO}$$

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 (basaluminate), 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

In a second approach, carbon isotope ratios of the two end members (limestone and organic matter) were used to explain the carbon isotope ratios measured in TDIC of the effluents (equation 2).

$$(2) \quad \delta^{13}C_{TDIC} = x(\delta^{13}C_{lst} + \varepsilon_{bic}) + (1-x)(\delta^{13}C_{OM} + \varepsilon_{OM} + \varepsilon_{bic})$$

δ¹³C in per mil, lst=limestone (δ¹³C≈ 1.8‰), OM=organic matter (δ¹³C≈ -28.5‰), ε=enrichment factor during limestone dissolution and mineralization of organic matter

Results from approach one suggest that 21±11% (VFP 1, n=15) and 15±15% (VFP 2, n=16) of the alkalinity generated (i.e. acidity consumed) derives from limestone dissolution, whilst the majority of the alkalinity derives from microbial oxidation of organic matter. Using mass balance two, 26±6% of the alkalinity was generated by limestone dissolution in VFP 1, whilst in VFP 2 it was 43±8%. In our poster presentation we will elaborate on the likely reasons of these differences, and on the potentially deleterious effects on the alkalinity generation and pH buffering potential of the VFP that will have significant effects on the treatment performance of both systems over long-term.

References

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