Supplement of

Benthic alkalinity and dissolved inorganic carbon fluxes in the Rhône River prodelta generated by decoupled aerobic and anaerobic processes

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S1. Linear increase of TA and DIC concentrations with time in the benthic chamber

Figure S1: Temporal evolution of DIC and total alkalinity concentrations in the benthic chamber at stations A, Z (measured during two deployments), and E. Error bars represent analytical uncertainties determined from triplicate measurements. The benthic fluxes and their standard deviations are provided in the text, in Figure 4 and in Table 2.

S2. Ion activity product for FeS precipitation

The ionic activity product (IAP) for the precipitation of FeS\(_{(s)}\) was calculated using following Beckler et al. (2016),

\[
\text{pIAP} = \log\left(\frac{\gamma_{\text{Fe}(II)}[\text{Fe}^{2+}][\gamma_{\text{HS}}]_{\text{HS}}}{\{\text{H}^+\}}\right)
\]

where \(\gamma_{\text{Fe}(II)}\) and \(\gamma_{\text{HS}}\) represent the activity coefficients of Fe\(^{2+}\) and HS\(^-\),

\[
\alpha_{\text{HS}} = \frac{(H^+)^2}{(H^+)^2 + (H^+)K_{a1} + K_{a1}K_{a2}}
\]

is calculated with the acid dissociation constant of H\(_2\)S (\(K_{a1} = 10^{-6.88}\)) and HS\(^-\) (\(K_{a2} = 10^{-17}\)) (Davison, 1991), and \(\{\text{H}^+\}\) is the activity of the proton. Activity coefficients of Fe\(^{2+}\) (Millero and Schreiber, 1982) and HS\(^-\) (Millero, 1983) were calculated using Pitzer parameters. The measured Fe\(^{2+}\) concentrations were used as ‘free’ available Fe\(^{2+}\), as Fe\(^{2+}\)
does not form strong complexes, and $\sum H_2S$ concentrations were used to calculate the speciation of sulfide species (assuming no elemental sulfur or polysulfide were present in the pore waters).

The ion activity products (pIAPs) calculated at most stations indicate that pore waters were either undersaturated, as a result of the low concentrations (stations AK, B, and K) or complete absence (stations A and Z) of dissolved sulfides, or close to the solubility of amorphous FeS or mackinewite (Fig. S2). These findings are surprising given the presence of significant concentrations of nanoparticulate FeS ($FeS_0$) in the pore waters at each of these stations (Fig. 6). The large $FeS_0$ concentration in the pore waters suggests that iron sulfide particles were already aggregated at the time of sampling but not totally precipitated as $FeS_{(s)}$. These findings therefore indicate that these sediments were not at equilibrium and provide another piece of evidence for a highly dynamic system.
Figure S2: Calculated pIAP values as a function of depth into the sediment compared to the pK\textsubscript{sp} of amorphous FeS and mackinawite. Due to the lack of dissolved sulfide, the pIAP values in the pore waters of station A and Z could not be calculated.

References


