



Benthic alkalinity and DIC fluxes in the Rhône River prodelta

generated by decoupled aerobic and anaerobic processes

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## Abstract

2 Estuarine regions are generally considered a net source of atmospheric CO<sub>2</sub> as a result of the high 3 organic carbon (OC) mineralization rates in the water column and their sediments. Yet, the intensity of anaerobic respiration processes in the sediments tempered by the reoxidation of reduced 4 metabolites controls the net production of alkalinity from sediments that may partially buffer the 5 metabolic CO<sub>2</sub> generated by OC respiration. In this study, a benthic chamber was deployed in the 6 Rhône River prodelta and the adjacent continental shelf (Gulf of Lions, NW Mediterranean) to assess 7 the fluxes of total alkalinity (TA) and dissolved inorganic carbon (DIC) from the sediment. 8 Concurrently, in situ O2 and pH microprofiles, electrochemical profiles, pore water and solid 9 composition were measured in surface sediments to identify the main biogeochemical processes 10 controlling the net production of alkalinity in these sediments. The benthic fluxes of TA and DIC, 11 ranging between 14 and 74 mmol m<sup>-2</sup> d<sup>-1</sup> and 18 and 78 mmol m<sup>-2</sup> d<sup>-1</sup>, respectively, were up to 8 times 12 higher than the DOU fluxes  $(10.4 \pm 0.9 \text{ mmol m}^{-2} \text{ d}^{-1})$  close to the river mouth, but their intensity 13 decreased offshore, as a result of the decline in OC inputs. Low nitrate concentrations and strong pore 14 water sulfate gradients indicated that the majority of the TA and DIC was produced by sulfate and 15 iron reduction. Despite the complete removal of sulfate from the pore waters, dissolved sulfide 16 concentrations were low due to the precipitation and burial of iron sulfide minerals (12.5 mmol m<sup>-2</sup> 17  $d^{-1}$  near the river mouth), while soluble organic-Fe(III) complexes were concurrently found 18 throughout the sediment column. The presence of organic-Fe(III) complexes togeth zero ith low sulfide 19 concentrations and high sulfate consumption suggests a dynamic system driven by the variability of 20 the organic and inorganic particulate nput originating from the river. By preventing reduced 21 substances from being reoxidized, the precipitation and burial of iron sulfide decouples the iron and 22 sulfur cycles from oxygen, therefore allowing a flux of alkalinity out of the sediments. In these 23 conditions, the sediment provides a source of alkalinity to the bottom waters which mitigates the 24 effect of the benthic DIC flux on the carbonate chemistry of coastal waters 25





## Keywords

26 Carbon cycle; alkalinity flux; iron reduction; sulfate reduction; coupled element cycles

## 27 1. Introduction

28 As a link between continental and marine environments, the coastal ocean plays a key role in the global carbon cycle (Bauer et al., 2013). In particular, large fluxes of dissolved and particulate organic 29 carbon (POC) are delivered by rivers to neighbouring continental shelves (Bianchi and Allison, 2009). 30 In fact, even though shelf regions only occupy around 7 % of the global ocean surface area (Jahnke, 31 2010), they account for more than 40 % of POC burial in the oceans of which about half is buried in 32 river deltas and estuaries (Hedges and Keil, 1995; McKee et al., 2004; Muller-Karger et al., 2005; 33 Chen and Borges, 2009). River-dominated ocean margins receive substantial amounts of 34 35 allochthonous and authigenic POC that settle to the sea floor (Rabouille et al., 2001; Burdige, 2005; Andersson et al., 2006), therefore increasing the organic carbon content of the sediments and 36 enhancing mineralization rates (Canfield et al., 1993a; Mckee et al., 2004; Muller-Karger et al., 2005; 37 38 Aller et al., 2008; Burdige, 2011). These processes allow estuarine and deltaic regions to constitute a net source of CO<sub>2</sub> to the atmosphere (Chen and Borges, 2009, Cai, 2011). In these river-dominated 39 40 margins, high sedimentation rates of material containing large concentrations of POC decrease the 41 residence time of organic carbon in the oxic sediment layers (Hartnett et al., 1998) and increase the relative contribution of anaerobic compared to aerobic degradation pathways of organic carbon 42 43 (Canfield et al., 1993a). Anaerobic respiration processes, including denitrification, dissimilatory nitrate reduction to ammonium (DNRA), manganese reduction, iron reduction, and sulfate reduction 44 cr are total alkalinity (TA) (Berner, 1970; Dickson, 1981; Wolf-Gladrow et al., 2007, Table 1) that 45 increases the buffer capacity of pore waters (Ben-Yaakov, 1973; Soetaert et al., 2007), drives the 46 carbonate saturation state of the pore waters towards oversaturation, and potentially trigger carbonate 47 precipitation (Gaillard et al., 1989; Mucci et al., 2000; Jørgensen and Kasten, 2006; Soetaert et al., 48 49 2007; Burdige, 2011). In turn, the precipitation of carbonate species, such as calcite and aragonite,





50 consumes alkalinity within the sediments (Table 1, Eq. 1; Berner, 1970; Soetaert et al., 2007; Krumins et al., 2013; Brenner et al., 2016). Anaerobically produced alkalinity may also be consumed close to 51 the sediment-water interface (SWI) by the aerobic reoxidation of reduced species such as  $NH_4^+$ ,  $Mn^{2+}$ , 52 53 Fe<sup>2+</sup>, and dissolved sulfide (Table 1, Eq. 2-4; Jourabchi et al., 2005; Krumins et al., 2013; Brenner et al., 2016). However, the precipitation and ultimate burial of iron sulfide minerals may prevent 54 reoxidation of dissolved sulfide and Fe<sup>2+</sup> and result in the net production of alkalinity in sediments 55 Thus, the net TA flux across the SWI depends on the type and intensity of anerobic respiration, on 56 57 carbonate precipitation/dissolution and whether reduced species are reoxidized by dissolved oxygen after diffusion upwards or trapped in anaerobic sediment layers by precipitation (Hu and Cai, 2011a; 58 Krumins et al., 2013; Łukawska-Matuszewska et al., 2018). 59 60 To characterize the biogeochemical conditions in which sediments provide an alkalinity source to coastal waters, it is crucial to relate this reaction network to net benthic fluxes of alkalinity and 61

dissolved inorganic carbon (DIC) measured *in situ*. A high ratio (> 1) of benthic TA to DIC fluxes
would increase the buffer capacity of the bottom waters. This could influence the coastal carbon cycle

64 by increasing the storage capacity of CO<sub>2</sub> in coastal waters over long time scales (Thomas et al., 2009;

Andersson et al., 2012; Brenner et al., 2016). The objectives of this study were to investigate if 65 sediments from deltaic regions exposed to large riverine inputs of carboniand minerals represent an 66 alkalinity source to the bottom waters and identify the biogeochemical processes responsible for the 67 net production of alkalinity in these sediments. To achieve these objectives, TA and DIC benthic 68 69 fluxes, dissolved oxygen uptake (DOU) fluxes, burial fluxes of reduced substances and the main 70 biogeochemical processes involved in organic carbon mineralization in sediments were determined along a gradient of organic carbon and mineral inputs to the sea floor in the Rhône River delta 71 72 (France).

Gettes





## 73 2. Study site and methods

### 74 2.1 The Rhône River delta

75 The Rhône River subaqueous delta, also called prodelta due to its prograding characteristics, is a wave-dominated delta located in the Gulf of Lions (France), a microtidal continental margin. The 76 Rhône River is the main source of freshwater, sediments (including iror ex des), and POC to the 77 Mediterranean Sea (Sempéré et al., 2000). The river plume is generally oriented southwestward due 78 to the combined effects of wind forcing and the Coriolis effect (Estournel et al., 1997). The Grand 79 Rhône River mouth is characterized by a prodeltaic lobe (Got et al., 1990) that can be divided into 80 three main areas based on bathymetry and sedimentation rates: the proximal domain within a 2 km 81 82 radius of the river outlet and with water depths between 10 and 30 m; the prodelta domain between 2 83 and 5 km with water depths ranging from 30 to 70 m; and the distal domain further offshore with water depths greater than 70 m. The sediments of the three domains are characterized by a strong 84 85 biogeochemical gradient from the Rhône River mouth to the Gulf of Lions continental slope (Lansard et al., 2009). 86

87 Most of the riverine particles settle in the vicinity of the river mouth leading to mean apparent accumulation rates of up to 37-48 cm yr<sup>-1</sup> (Charmasson et al., 1988), including about 80 % of the 88 particles deposited during flood events (Maillet et al., 2006; Cathalot et al., 2010). Thus, sediments 89 from the proximal domain are dominated by the periodic accumulation of terrestrial organic-rich 90 91 particles (Radakovich et al., 1999; Roussiez et al., 2005). Offshore, sedimentation rates decrease rapidly and reach typical values for shelf regions ( $< 0.1 \text{ cm yr}^{-1}$ ), in the distal domain (Miralles et al., 92 2005). The sediments in all the study area are fine grained and of cohesive nature (Roussiez et al., 93 2005). Their total organic carbon content is higher than 2 % close to the river mouth and decreases 94 offshore (Lansard et al., 2008). The sedimentary inorganic carbon content ranges between 2 and 95 38 % (Roussiez et al., 2005) and is mostly composed of calcite and magnesian calcite (Rassmann et 96 al., 2016). Sediment respiration rates are high in the proximal domain and decrease offshore (Lansard 97





et al., 2009; Pastor et al., 2011; Cathalot et al., 2013; Rassmann et al., 2016). These sediments are
characterized by strong anaerobic production of TA and DIC (Rassmann et al., 2016), but whether
this alkalinity is consumed in the oxic sediment layer or released to the bottom waters has yet to be
determined.

102 2.2 Bottom water sampling and analyses

103 The AMOR-B-Flux cruise took place on-board the RV Tethys II (CNRS-INSU) in September 2015. The investigated stations were located in the river plume along a nearshore-offshore transect 104 (Fig. 1 and Table 2). Bottom water samples were collected with 12-L Niskin<sup>®</sup> bottles as close as 105 106 possible to the sea floor. The seawater temperature was measured using a thermometer with a 107 precision of 0.1 °C and the salinity with a conductivity based thermosalinometer with a precision of 108 0.1. Triplicate pH measurements, reported on the total proton scale  $(pH_T)$ , were carried out within 1 hour after sampling by spectrophotometry with unpurified m-cresol purple as indicator dye (Clayton 109 110 and Byrne, 1993) and a precision of  $\pm 0.01$  pH units. Dissolved oxygen concentrations were analysed by Winkler titration (Grasshoff et al., 1983) within twelve hours after sampling with a precision of  $\pm$ 111 112 0.5 µM.

113 2.3 In situ benthic chamber deployments

114 Benthic fluxes and sediment depth profiles of the main redox species involved in the remineralization of organic carbon were determined with an autonomous benthic lander (Jahnke et 115 116 and Christiansen, 1989). The lander was equipped with a single benthic chamber, water syringe sampling system, and retrofitted with a programmable, battery-powered ISEA IV In Situ 117 Electrochemical Analyzer and a SUBMAN-1 in situ micromanipulator from Analytical Instrument 118 119 Systems, Inc. (AIS, Inc.) to simultaneously obtain depth profiles of redox chemical species with 120 mercury/gold (Hg/Au) amalgam voltammetric microelectrodes (Luther et al., 2008; Tercier-Waeber 121 and Taillefert, 2008). The chamber encloses a 30 x 30 cm sediment surface area with a certain volume





of overlying water determined by measuring the oncentration of two tracers (iodide and bromide) injected immediately after closure of the chamber. Homogenization of the overlying waters was assured with a stirrer integrated in the chamber lid. TA and DIC concentrations were determined in the benthic chamber water samples collected as a function of time he slopes of the concentrationtime plots were estimated using a restricted maximum likelihood estimator (REML) that takes uncertainties of individual measurements into account. Finally, benthic fluxes across the SWI (F<sub>i</sub>) were calculated from the slopes of these concentration-time-plots and the chamber height (Eq. 1),

$$F_i = H \cdot \frac{dC_i}{dt} \tag{1}$$

where H is the overlying water height in the benthic chamber,  $C_i$  represents the concentration of the analyte i (TA or DIC) and t is time.

## 131 2.4 In situ microprofiling of dissolved oxygen and pH

132 A separate benthic lander, carrying a benthic microprofiler (Unisense<sup>®</sup>), was deployed to measure in situ microprofiles of dissolved oxygen and pH (Cai and Reimers, 1993; Rabouille et al., 2003, 133 Rassmann et al., 2016 and references therein). Up to five oxygen and two pH microelectrodes were 134 simultaneously deployed, and vertical depth profiles were measured with a 200 µm resolution. As 135 their response to variations in oxygen concentrations is linear, the O<sub>2</sub> microelectrodes were calibrated 136 with a two-point calibration technique using the bottom water  $O_2$  concentration determined by 137 Winkler titration and the anoxic pore waters. The pH microelectrodes were calibrated using NBS 138 139 buffers (pH 4.00, 7.00 and 9.00 at 20°C) and the spectrophotometrically determined pH of the bottom 140 waters was used to correct for the difference in the liquid junction potential between seawater and the NBS buffers signal drift of O<sub>2</sub> and pH microelectrodes during profiling was checked to be less than 141 142 5%.





#### 143 2.5 Sediment sampling, porosity measurements, and ex situ voltammetric profiling

At each sampling station, sediment cores were collected using an UWITEC<sup>®</sup> single corer (length 60 cm, inner diameter 9 within 30 m from the site where the landers were deployed and processed within 30 minutes after collection. Sediment porosity profiles were determined by slicing one of the cores with a 2 mm resolution until 10 mm depth, a 5 mm resolution until 60 mm, and a 10 mm resolution down to the bottom of the cores. Porosity was calculated from the bottom water salinity, an average sediment density of 2.65 g cm<sup>-3</sup> and the weight difference between the wet and dried sediment after one week at 60 °C.

151 Ex situ voltammetric profiles were obtained in a separate core with a AIS, Inc. DLK-70 152 potentiostat in a three electrode configuration, including Hg/Au working microelectrode constructed 153 from Pyrex glass pulled to a tip of 0.4 mm diameter to minimize particle entrainment during the profiles (Luther et al., 2008), an Ag/AgCl reference electrode, and a platinum counter electrode. The 154 155 Hg/Au voltammetric electrode was deployed in the sediment using a DLK MAN-1 micromanipulator (AIS, Inc). Using a combination of linear sweep and anodic and cathodic square wave voltammetry, 156 Hg/Au voltammetric microelectrodes are able to simultaneous quantify dissolved  $O_2$ ,  $Mn^{2+}$ , Fe<sup>2+</sup>, 157 total dissolved sulfide ( $\Sigma H_2 S = H_2 S + HS^2 + S^0 + S_x^{2-}$ ), as well as organic complexes of Fe(III) (org-158 Fe(III)) and iron sulfide clusters (FeS<sub>aq</sub>), which are not quantifiable but reported in normalized current 159 intensities (Tercier-Waeber and Taillefert, 2008). Hg/Au microelectrodes were calibrated for 160 161 dissolved O<sub>2</sub> using *in situ* temperature and salinity of the overlying waters to determine the dissolved O2 concentrations at saturation (Luther et al., 2008). They were also calibrated externally with MnCl2 162 to quantify all other species according to the pilot ion method (Luther et al., 2008). All voltammetric 163 data was integrated using VOLTINT, a semiautomated Matlab® script with peak recognition software 164 (Bristow and Taillefert, 2008). 165





#### 166 2.6 Pore water and solid phase extractions and analyses

167 Sediment pore waters were extracted using rhizon filters with a mean pore size of 0.1 µm (Seeberg-Elverfeldt et al., 2005) in a glove bag that was extensively flushed with  $N_2$  to create an 168 anaerobic atmosphere pre waters were analyzed immediately onboard for dissolved phosphate 169 concentrations using the paramolybdate method (Murphy and Riley, 1962) as well as for dissolved 170  $Fe^{2+}$  and total dissolved iron concentrations using the ferrozine method (Stookey, 1970)  $\mathbb{P}_{d}$  re water 171 and bottom water fractions were poisoned with HgCl2 for TA and DIC, acidified for sulfate, and stored 172 173 at 4 °C until analysis in the laboratory. Total alkalinity was measured by open cell titration with 0.01 M HCl (Dickson et al., 2007). DIC concentrations were analyzed with a DIC analyzer 174 175 (Apollo/SciTech<sup>®</sup>) on 1 ml samples as previously described (Rassmann et al., 2016). The TA and DIC 176 methods were calibrated using certified reference materials for oceanic CO<sub>2</sub> measurements provided by the Scripps Institution of Oceanography (batch n°136). The relative uncertainty for both DIC and 177 TA was  $\pm$  0.5 % of the final value. Sulfate concentrations were quantified after dilution by ion 178 179 chromatography on an ICS 1000 chromatograph (Dionex) with an IonPac AS 9 HC column and AG 9 HC guard by suppressed conductivity with an AERS 500 suppressor (ThermoFisher Scientific). A 180 9 mM solution of Na<sub>2</sub>CO<sub>3</sub>, at a flow rate of 1 ml min<sup>-1</sup> was used as the eluent. The relative uncertainty 181 of this method was  $\pm$  1.6 %. Separate pore water fractions were frozen at -18 °C for sulfate analysis 182 by high performance liquid chromatography using a Waters, Inc. 1525 binary pump with Waters 2487 183 184 absorbance detector at 215 nm and a Metrohm Metrosep A Supp 5 anion exchange column (150 mm x 4.0 mm) with a 1.0 mM NaHCO<sub>3</sub> / 3.2 mM Na<sub>2</sub>CO<sub>3</sub> eluent at a flow rate of 0.7 ml min<sup>-1</sup> (Beckler 185 et al., 2014). To measure ammonium (NH<sup>+</sup><sub>4</sub>) concentrations, samples were diluted and analysed using 186 the indophenol blue method (Grasshof et al., 1983). The uncertainty of the method was about 5 %. 187 Pore water fractions were also acidified with 2 % HCl for Ca<sup>2+</sup> analysis by inductively-coupled 188 plasma atomic emission spectroscopy (Ultima 2, Horiba Scientific). The method was validated with 189 190 mono-elemental standards and standard solutions (IAPSO, CASS-4, and NASS-6 seawater reference materials) and displayed an external relative uncertainty of  $\pm 2$ . 5, depending on the sample series. 191





192 Close to the Rhône River mouth, at station A, Z, and AK, one core was subsampled from the side with 1cm diameter corers made of cut 10-ml syringes every 5 cm through pre-drilled holes. The 193 content of these subsamples was carefully inserted in gas tight vials containing deionized water and 194 HgCl<sub>2</sub> solution and kept at 4°C until methane analysis. Dissolved methane was quantified after 195 degassing of the pore waters into the headspace and quantified by gas chromatography with a relative 196 uncertainty of  $\pm$  5 % (Sarradin and Caprais, 1996). The position of the sulfate-methane transition zone 197 (SMTZ) was determined as the zone around the depth where  $[SO_4^{2-}] = [CH_4]$  (Komada et al., 2016). 198 Finally, acid volatile sulfur (AVS) for the determination of FeS<sub>s</sub> was extracted from the same sediment 199 200 used for the pore water extractions and conducted in triplicate by cold acid distillation of  $H_2S$  (g) under anoxic conditions that was trapped by NaOH and quantified voltammetrically (Henneke et al., 201 202 1991).

#### 203 2.7 Nanoparticulate FeS and ion activity product for FeS precipitation

As a significant fraction of FeS nanoparticles may pass through the rhizon filters (0.1 $\mu$ m) used to extract pore waters (Nakayama et al., 2016) and the ferrozine method is well known to dissolve FeS nanoparticles (Davison et al., 1998), the difference between spectrophotometrically-determined Fe<sup>2+</sup> concentrations ([ $\Sigma Fe^{2+}$ ]<sub>FR</sub>) and electrochemically-determined Fe<sup>2+</sup> concentrations ([ $Fe^{2+}_{echem}$ ]) in the pore waters was attributed to FeS nanoparticles (FeS<sub>0</sub>), as demonstrated previously (Bura-Nakic et al., 2009; Eq. 2).

$$[FeS_0] = [\sum Fe^{2+}]_{FR} - [Fe^{2+}_{echem}]$$
<sup>(2)</sup>

210 In this interpretation,  $FeS_0$  nanoparticles encompass both the molecular clusters of FeS ( $FeS_{aq}$ ) 211 detected electrochemically, which must be smaller than 5 nm in diameter to diffuse to the electrode 212 (Buffle, 1988), and the larger FeS nanoparticles that are not detected voltammetrically. The ionic 213 activity product (IAP) for the precipitation of FeS was calculated using Eq. 3 (Beckler et al., 2016),

$$pIAP = \log(\frac{\gamma_{Fe(II)}[Fe^{2+}]\gamma_{HS}\alpha_{HS}\Sigma H_2S}{\{H^+\}})$$
(3)





214 where  $\gamma_{\text{Fe(II)}}$  and  $\gamma_{\text{HS}}$  represent the activity coefficients of Fe<sup>2+</sup> and HS<sup>-</sup>,  $\alpha_{HS} = \frac{\{H^+\}K_{a1}}{\{H^+\}^2 + \{H^+\}K_{a1} + K_{a1}K_{a2}}$ 

- 215 is calculated with the acid dissociation constant of  $H_2S$  ( $K_{a1} = 10^{-6.88}$ ) and  $HS^-$  ( $K_{a2} = 10^{-17}$ ) (Davison,
- 216 1991), and  $\{H^+\}$  is the activity of the proton. Activity coefficients of Fe<sup>2+</sup> (Millero and Schreiber,
- 217 1982) and HS<sup>-</sup> (Millero, 1983) were calculated using Pitzer parameters.
- 218 2.8 Calculations of oxygen uptake and AVS burial rates

219 Diffusive oxygen uptake (DOU) fluxes were calculated using Fick's first law (Berner, 1980, Eq.
220 4),

$$DOU = -\phi \cdot D_s \cdot \frac{d[o_2]}{dz}\Big|_{z=0}$$
(4)

221 where  $\phi$  is the sediment porosity, D<sub>s</sub> is the apparent diffusion coefficient in the sediments, and 222  $\frac{d[O_2]}{dz}\Big|_{z=0}$  is the oxygen gradient at the SWI. The D<sub>s</sub> coefficients were adjusted for diffusion in a porous 223 environment according to:  $D_s = \frac{D_0}{(1+3\cdot(1-\phi))}$  with the diffusion coefficient in free water (D<sub>0</sub>) chosen 224 according to Broecker and Peng (1974) and recalculated to *in situ* temperature by the Stokes-Einstein 225 relation (Li and Gregory, 1974). 226 AVS burial fluxes were estimated using available sedimentation rates ( $\omega$  from Charmasson et al.

227 (1998) and Miralles et al. (2005)), average AVS concentrations and porosities of each sediment core,
228 according to Eq. 5,

$$AVS_{burial} = (1 - \emptyset) \cdot \omega \cdot AVS \cdot \rho \tag{5}$$

229 where  $\phi$  is the sediment porosity,  $\omega$  the sedimentation rate, and  $\rho$  the sediment dry bulk density.

## 230 2.9 Stoichiometric ratios

To determine the relationship between net TA and DIC production and to establish whether sulfate reduction represents the main source of TA and DIC in these sediments, stoichiometric ratios of the relative production of TA compared to DIC ( $r_{AD}$ ), as well as TA ( $r_{AS}$ ) and DIC ( $r_{DS}$ ) compared to sulfate consumption, were calculated from the pore water data and compared to theoretical ratios





from the reaction stoichiometries (Table 1). Experimental stoichiometric ratios were obtained from the slope and standard deviation is the linear regression of TA, DIC, and sulfate property-property plots of concentration changes with respect to bottom water concentrations at each depth in the pore waters ( $\Delta$ TA,  $\Delta$ DIC and  $\Delta$ SO<sub>4</sub><sup>2-</sup>) relative to each other after correcting for differences in TA, DIC and sulfate diffusion in the sediments (Berner, 1980, Eq. 6),

240 
$$r_{ij} = \frac{D_i \cdot \Delta i}{D_j \cdot \Delta j} \tag{6}$$

where i is the concentration of either TA or DIC, j the concentration of  $SO_4^{2-}$  or DIC and D<sub>i</sub> and D<sub>j</sub> are the corresponding diffusion coefficients in the pH of the pore waters (pH ~ 7.5), more than 95 % of DIC and carbonate alkalinity are composed of bicarbonate ion (HCO<sub>3</sub>). Given the relatively small difference in the diffusion coefficients of HCO<sub>3</sub><sup>-</sup> and CO<sub>3</sub><sup>2-</sup> (11.8 and 9.55 x 10<sup>-6</sup> cm<sup>2</sup> s<sup>-1</sup> at 25°C, Li and Gregory, 1974) and the high proportion of HCO<sub>3</sub><sup>-</sup> relative to CO<sub>3</sub><sup>2-</sup>, the diffusion coefficient of HCO<sub>3</sub><sup>-</sup> was adopted for both TA<sup>-</sup> DIC diffusion.

The effect of the precipitation or dissolution of calcium carbonate on The and DIC variations was 247 also accounted for by considering the Ca<sup>2+</sup> concentration gradients in the pore waters. For these 248 calculations, the absolute value of the  $Ca^{2+}$  concentration relative to its bottom water concentration 249  $(\Delta Ca^{2+})$  was added to the  $\Delta TA$  or  $\Delta DIC$  after taking the corresponding diffusion coefficients into 250account ( $D_{TA}\Delta$  TA +  $2D_{Ca}|\Delta Ca^{2+}|$  for alkalinity and  $D_{DIC}\Delta$  DIC +  $D_{Ca}|\Delta Ca^{2+}|$  for DIC) and plotted 251 against D<sub>SO42</sub>-ΔSO<sub>4</sub><sup>2-</sup>. The calculated slope provided a stoichiometric ratio corrected for the 252 precipitation of calcium carbonate ( $r_{IIc}$ ). Pore water saturation states, regarding Calcite ( $\Omega_{Ca}$ ), were 253 calculated according to the equation proposed by Mucci (1983) and Millero (1995). 254

## 255 3.Results

#### 256 3.1 Bottom water and surface sediment characteristics

At all stations, bottom water salinities ranged from 37.5 to 38.0 and temperatures varied from 14.7 to 20.6 °C (Table 2). Total alkalinity and DIC concentrations (average  $TA = 2.60 \pm 0.01$  mM and





average DIC =  $2.30 \pm 0.02$  mM, Table 2) were relatively high compared to the Mediterranean Sea average, but common for the Gulf of Lions (Cossarini et al., 2015). The pH<sub>T</sub> of the bottom waters varied from 8.05 to 8.09 with the highest value observed at station AK and the lowest at station E. Although the oxygen concentration decreased with water depth, bottom waters were always well ventilated, with dissolved O<sub>2</sub> concentrations higher than 220 µmol L<sup>-1</sup>. Sediment porosity ranged between 0.7 and 0.8 at the SWI, and they were similar at all stations between 20 and 400 mm depth (Table 2).

#### 266 3.2 Benthic total and diffusive fluxes

267 The *in situ* pH and O<sub>2</sub> microprofiles reflected the differences between the three study domains 268 under the influence of the Rhône River plume (Fig. 2). In the proximal zone (stations A and Z), the oxygen penetration depth was only 1.5 to 2.5 mm into the sediment as also indicated by separate 269 voltammetric measurements (Fig. 5) The oxygen penetration depth increased from 2 to 6 mm at 270 271 station K and reached 8 to 11 mm at the most offshore station E. As a result of bad weather conditions, no exploitable in situ microprofiles were recorded at stations AK and B, though ex situ voltammetric 272 profiles determined oxygen penetration depths of 4 and 2 mm, respectively (Fig. 5). All pH microfiles 273 274 indicated a pH minimum between 7.2 and 7.4 just below the OPD followed by an increase to between 7.5 and 7.6 in the manganous/ferruginous layers of the sediment around 5 mm inshore and below 12 275 mm offshore (Fig. 2). Below this depth, pH stabilizes. 276

The benthic chamber was deployed once at stations A and E and twice at station Z (Z' is the replicate). Total alkalinity and DIC concentrations increased linearly with time in the chamber, but concentration changes decreased along the nearshore-offshore transect (Fig. 3). The highest benthic fluxes were recorded for the two deployments at station Z, with TA fluxes of  $73.9 \pm 20.6$  and  $56.0 \pm$ 17.8 mmol m<sup>-2</sup> d<sup>-1</sup> and DIC fluxes of  $78.3 \pm 10.9$  and  $37.2 \pm 7.2$  mmol m<sup>-2</sup> d<sup>-1</sup> (Fig. 4, Table 2). At station A, the benthic TA and DIC fluxes reached lower values of  $14.3 \pm 1.6$  and  $17.8 \pm 1.6$  mmol m<sup>-</sup> 28 d<sup>-1</sup>, respectively, while benthic fluxes were lowest at station E, with a TA flux of  $3.7 \pm 0.9$  mmol m<sup>-</sup>





<sup>2</sup> d<sup>-1</sup> and a DIC flux of  $9.9 \pm 0.9$  mmol m<sup>-2</sup> d<sup>-1</sup>. In parallel, DOU fluxes reached  $10.2 \pm 1.3$  and 10.4<sup>2</sup> d<sup>-1</sup> and a DIC flux of  $9.9 \pm 0.9$  mmol m<sup>-2</sup> d<sup>-1</sup>. In parallel, DOU fluxes reached  $10.2 \pm 1.3$  and 10.4<sup>2</sup> d<sup>-1</sup> at stations A and Z and decreased offshore to  $5.9 \pm 1.0$  mmol m<sup>-2</sup> d<sup>-1</sup> at station K <sup>2</sup> and  $3.6 \pm 0.6$  mmol m<sup>-2</sup> d<sup>-1</sup> at station E (Fig. 4, Table 2). Although the relative importance of DOU <sup>2</sup> compared to TA and DIC fluxes increased offshore, the TA and DIC fluxes were always between 2 <sup>2</sup> and 8 times larger than the DOU fluxes (Fig. 4).

# 289 3.3 Electrochemistry profile

290 Dissolved  $Fe^{2+}$  concentrations as a function of depth in the sediment mirrored the voltammetric 291 signals of soluble organic-Fe(III) complexes at stations A, Z, AK, B, and K (Fig. 5). High concentrations of dissolved Fe<sup>2+</sup> were observed in the proximal domain at stations A (341 ± 22  $\mu$ M) = 292 293 and Z ( $234 \pm 25 \mu$ M), where dissolved  $\Sigma$ H<sub>2</sub>S was not detected (Fig. 5). At station AK, the shallowest station in the prodelta domain, dissolved Fe<sup>2+</sup> increased to a maximum concentration of 255  $\mu$ M 294 around 2 cm depth, then decreased with sediment depth as FeSaq below 6.5 cm and small 295 296 concentrations of dissolved  $\Sigma H_2S$  around 17 cm were produced (Fig. 5). The two deeper prodelta stations, B and K, displayed lower Fe<sup>2+</sup> concentrations, including one peak not exceeding 81 µM 297 (station B) or 73  $\mu$ M (station K) in the top 2 cm of the sediment and a second peak not exceeding 50 298 299  $\mu$ M between 12-14 cm (station B) and 86  $\mu$ M between 5-7.5 cm (station K) in the sediment. Although  $FeS_{aq}$  was only detected below 15 cm at station K,  $\Sigma H_2S$  was produced in low concentrations (< 5 300  $\mu$ M) around 6.5 cm at stations B and K (Fig. 5). A peak of Fe<sup>2+</sup> was initially formed in the top 5 cm 301 302 of the distal domain (station E) but decreased to a minimum value with depth and did not correlate with the organic-Fe(III) voltammetric signals, which also remained low throughout the profile (Fig. 303 5). Finally, station E displayed generally low concentrations of  $\Sigma H_2S$  in the pore waters (< 6  $\mu$ M), 304 though the onset of  $\Sigma$ H<sub>2</sub>S production was much shallower (2.5 cm) and  $\Sigma$ H<sub>2</sub>S concentrations were 305 consistently higher throughout the profile than at any other stations. 306





#### 307 3.4 Geochemical characteristics of the pore waters and sediments

308 Both TA and DIC concentrations increased rapidly within the pore waters (Fig. 6), likely reflecting the intensity of organic carbon mineralization rates in these sediments. At all stations, DIC pore water 309 concentrations correlated well with TA (overall slope:  $1.01 \pm 0.006$ , r<sup>2</sup>=0.995, n=134). The TA and 310 DIC gradients were highest at stations A and Z, where maximum concentrations of both species 311 reached around 55 mM. At station AK, TA and DIC concentrations reached a maximum of 15 mM at 312 25 cm depth but decreased to 6 mM at the bottom of the core. The maximum concentrations of TA 313 314 and DIC of 35 mM observed at station B, were more comparable to the stations in the vicinity of the river mouth (stations A and Z) than other stations located in the prodelta domain (stations AK and K). 315 316 At station K, TA and DIC concentrations reached 10 mM, whereas the lowest TA and DIC gradients 317 were measured at station E, with concentrations reaching only 4.6 mM at the bottom of the cores (30 cm). Sulfate was completely removed from the pore waters at depths of 35, 24, and 45 cm at station 318 A, Z, and B, respectively (Fig. 6). In turn, sulfate concentrations decreased to a minimum 319 320 concentration of 20 mM at 29 and 24 cm depth at stations AK and K, whereas sulfate consumption was much smaller at station E with a minimum concentration of 28 mM (bottom water sulfate 321 concentration was 31.4 mM). As a result, TA and DIC changes in concentration at a given depth were 322 highly inversely correlated ( $r^2 > 0.97$ ) with sulfate changes in concentration at stations A, Z, AK, B, 323 and K (Table 3). At station E, sulfate variations in the observed depth were in the same order of 324 325 magnitude as the measuring uncertainties. Simultaneously, TA and DIC demonstrated strong correlations ( $r^2 > 0.97$ ) at stations A, Z, AK, B, and K (Table 3). In the proximal domain (stations A 326 and Z), ammonium increased with sediment depth to concentrations > 3 mM (Fig. 6). At station B, 327 ammonium reached concentrations > 2 mM with depth, whereas ammonium concentrations did not 328 329 exceed 1.5 mM at station AK, 0.6 mM at station K, and 0.3 mM at station E. At all stations nitrite plus nitrate concentrations were less than 20 µM (data not shown). Significant methane 330 331 concentrations (> 50  $\mu$ M) were detected at the bottom of the sediment core at stations A, Z, and AK (Fig. 6), and a SMTZ was identified between 28 and 39 cm at station A and between 19 and 39 cm at 332





333 station Z. As methane was  $< 50 \,\mu$ M throughout the profile at station K and sulfate was not completely 334 consumed inside the sediment core at station AK, the SMTZ was not determined at these two stations. 335 Methane analyses were not carried out for the other stations.

The sediment pore waters were oversaturated with respect to calcite ( $\Omega_{Ca} > 1$ ) at all stations. At 336 stations A, Z, and B, decreasing Ca<sup>2+</sup> concentrations in the pore waters indicated precipitation of 337 CaCO<sub>3</sub>, whereas Ca<sup>2+</sup> concentrations remained close to the bottom water Ca<sup>2+</sup> concentrations (11.2 338 mM in Mediterranean waters) at the other stations (Fig. 6). Dissolved phosphate concentrations 339  $(\Sigma PO_4^{3-})$  were relatively high (50-100  $\mu$ M) throughout the profiles at stations A, AK, K and Z, and a 340 large increase in concentration (up to 160  $\mu$ M at station Z) was observed at station AK. K and Z 341 between 15 and 22 cm. In turn,  $\Sigma PO_4^{3-}$  production was minimal throughout station E pore waters (< 342 10 µM). Dissolved phosphate was not measured at station B and diment samples were analyzed for 343 AVS as a function of depth at stations A, AK, and E to assess one station in each domain (Fig. 6). At 344 station A, a peak in AVS (65  $\mu$ mol g<sup>-1</sup>) was measured around 8.0 cm followed by a second, smaller 345 peak (22 µmol g<sup>-1</sup>) at 14 cm, after which AVS decreased with depth. The AVS concentrations were 346 low in the top portion of the sediment at station AK but increased with depth to 100 µmol g<sup>-1</sup> around 347 15 cm. At station E, only a small AVS peak of 20 µmol g<sup>-1</sup> was observed at 14 cm. Finally, large 348 349 concentrations of FeS nanoparticles (FeS<sub>0</sub>) were found in the proximal and prodelta stations, 350 including two broad peaks and maximum concentrations around 1 mM at stations A and Z and a large 351 subsurface maximum up to 6 mM at 145 mm at station AK. These FeS<sub>0</sub> concentrations increased as a function of depth to a relatively constant 0.5 mM below 4.5 cm at station B and below 12 cm at 352 353 station K, whereas they remained mostly negligible at station E (Fig. 6).

#### 354 4. Discussion

In this study, we want to relate biogeochemical processes in the sediment to the observed TA and DIC fluxes. Firstly, benthic TA and DIC fluxes in the Rhône River prodelta are compared to other similar systems to evaluate their relative importance. In the following sections, the most likely





biogeochemical processes responsible for the high TA flux are identified based on the sediment depth profiles collected. In particular, the role of iron sulfide mineral precipitation on the benthic TA flux is established using a variety of analytical techniques, speciation calculations, and a mass balance approach. Finally, the link between inputs to the sediment, carbon mineralization processes, sulfide mineral burial, and the benthic TA flux is provided using a conceptual model.

363 4.1 DIC and alkalinity fluxes from the sediment

364 The sediments of the Rhône proximal and prodelta zones represent important sources of both 365 DIC and TA to the bottom waters (Fig. 4). The DIC fluxes observed in the proximal domain (18-78 mmol  $m^{-2} d^{-1}$  at station A and Z; Fig. 4) are in the range of previously measured fluxes in other deltas 366 367 where anaerobic mineralization processes are dominant, including Mississippi delta sediments from core incubations (15-20 mmol m<sup>-2</sup> d<sup>-1</sup>; Lehrter et al., 2012) or benthic chambers (36-53 mmol m<sup>-2</sup> d<sup>-1</sup>) 368 <sup>1</sup>; Rowe et al., 2002), benthic chamber measurements of the Po River delta sediments and the Adriatic 369 shelf (15-25 mmol m<sup>-2</sup> d<sup>-1</sup>; Hammond et al., 1999), or the Fly River delta during the most active 370 season (35-42 mmol m<sup>-2</sup> d<sup>-1</sup>; Aller et al., 2008) and near the Guadalquivir River estuary (36-46 mmol 371  $m^{-2} d^{-1}$ , Ferron et al., 2009). In contrast, fewer alkalinity fluxes were measured in river deltas, though 372 373 those obtained from benthic chambers in the Danube and Dniester deltas in the Northwest Black Sea (21-67 mmol m<sup>-2</sup> d<sup>-1</sup>, Friedl et al., 1998), are within the range of values reported in this study (14-74 374 mmol m<sup>-2</sup> d<sup>-1</sup>). Benthic TA fluxes obtained in the Guadalquivir estuary (24-30 mmol m<sup>-2</sup> d<sup>-1</sup>; Ferron 375 et al., 2009) and the Adriatic shelf sediments off the Po River delta (0.5-10.4 mmol m<sup>-2</sup> d<sup>-1</sup>; Hammond 376 et al., 1999) are in the lower range of TA fluxes measured in the present study. The biogeochemical 377 origin of these TA benthic fluxes is discussed in the next sections. 378

## 379 4.2 The relative importance of nitrification/denitrification on the TA budget

380 Denitrification is known as a benthic TA source to the bottom waters as 0.8 moles of TA are 381 produced for 1 mole of organic carbon oxidized by nitrate and the product  $N_2$  does not react further





with dissolved oxygen (Table 1, Eq. 5; Thomas et al., 2009; Krummins et al., 2013; Brenner et al., 382 2016). Published estimates of total denitrification rates in Rhône prodelta and shelf sediments range 383 between 4 mmol m<sup>-2</sup> d<sup>-1</sup> in the proximal zone to 1 mmol m<sup>-2</sup> d<sup>-1</sup> in the continental shelf (Pastor et al., 384 lom 2011). Conversion to alkalinity flux would provide a range between 0.8 and 3.2 mmol TA m<sup>-2</sup> d<sup>-1</sup>. As 385 such, denitrification would account for < 10% of the TA flux in the proximal zone where substantial 386 fluxes were measured by *in situ* benthic chambers (Fig. 4). Furthermore, the only net production of 387 388 TA by denitrification must be related to external nitrate sources as nitrification (overall oxidation of ammonium to nitrate) consumes 2 moles of TA per mole of ammonium transformed into nitrate (Table 389 390 1, Eq. 2; Hu et al., 2011a). As coastal sediments mostly display coupled nitrification-denitrification, this process does only represent a small source of TA to the bottom waters (Brenner et al., 2016). It 391 can therefore be concluded that the contribution of denitrification to TA fluxes is minimal in the 392 proximal zone and could be proportionally more important on the shelf where TA fluxes are much 393 394 lower.

#### 395 4.3 DIC and TA produced by sulfate reduction

396 Sulfate reduction typically represents a major organic carbon mineralization pathway in organic-397 rich sediments that simultaneously produces two moles of total alkalinity (TA) and two moles of DIC per mole of sulfate (Table 1, Eq. 6) (Canfield et al., 1993b; Burdige, 2011). Dissimilatory iron 398 399 reduction (Table 1, Eq. 7) in turn produces 1/4 moles of DIC and consumes 7/4 moles of H<sup>+</sup>, resulting 400 in two moles of TA produced per mole of Fe. As these two processes equally produce two moles of TA per mole of terminal electron acceptor (Table 1, Eq.6 for  $SO_4^{2-}$  and Eq. 7 for Fe(OH)<sub>3</sub>), they can 401 both contribute significantly to the bulk alkalinity production in sediment pore waters. The low 402 concentration of nitrate, relatively low production of reduced metals in the pore waters (Fig. 5), and 403 intense ammonium and DIC production in parallel with sulfate consumption at depth (Fig. 6) confirm 404 that sulfate reduction is one of the dominant mineralization pathways in the Rhône prodelta sediments 405 (Pastor et al., 2011; Rassmann et al., 2016). Experimentally-derived stoichiometric ratios of the 406





407 relative production of DIC and TA compared to sulfate consumption may indicate the dominant reaction pathways responsible for the high alkalinity generated in these sediments (Burdige and 408 Komada, 2011). Factoring carbonate precipitation using the pore water  $Ca^{2+}$  data, the  $r_{DSc}$  were 409 determined to range between -2.05 and -1.86, except for one value at -1.37 (station B), whereas the 410  $r_{ASc}$  ratios ranged between -2.35 and -1.89 with the exception of station B at -1.58 (Table 3). 411 Theoretically, the  $r_{DS}$  and  $r_{AS}$  should equal -2.0 if sulfate reduction is the only control on DIC and TA 412 413 production (Table 1, Eq. 6), suggesting that, except at station B, the influence of other diagenetic 414 processes on  $r_{ASc}$  and  $r_{DSc}$  is limited. At station B, however the higher  $r_{DSc}$  ratio (Table 3) may indicate significant anaerobic oxidation of methane (AOM Table 1, Eq. 8) which generates a theoretical  $r_{DS}$ 415 of -1 (Borowsi et al., 1996; Komada et al., 2016). Unfortunately, methane sampling was not 416 performed at station B, preventing precise identification of AOM at this station. 417

## 418 4.4 Formation of iron sulfide species

419 Although the complete depletion of sulfate in the first 30 cm of the sediment at stations A, Z, and B implies an equivalent production of dissolved sulfide ( $\Sigma H_2S$ ) (Table 1, Eq. 6), pore waters displayed 420 little to no  $\Sigma H_2S$  (Fig. 5). If all of the produced  $\Sigma H_2S$  diffused upward and reacted in the oxic sediment 421 layer, the alkalinity produced by sulfate reduction would be consumed by the oxidation of  $\Sigma H_2S$  by 422 dissolved  $O_2$  and the pH should be lowered significantly given the large acidity generated by this 423 reaction (Table 1, Eq. 4). Although  $\Sigma$ H<sub>2</sub>S was nearly absent of the pore waters (Fig. 5), the pH 424 425 minimum was never lower than 7.2 and the observed alkalinity fluxes across the SWI were substantial (Fig. 4), indicating that  $\Sigma H_2S$  was removed from the pore waters below the oxic layer pointic 426 reduction of Fe(III) oxides by  $\Sigma H_2 S$  (Table 1, Eq. 9), followed by precipitation of FeS in the anoxic 427 zone (Table 1, Eq. 10; Berner, 1970; Pyzik and Sommer, 1981; Carman and Rahm, 1997, Soetaert et 428 429 al., 2007), and eventually formation of pyrite (Table 1, Eq. 11; Rickard and Luther, 1997) may represent a significant  $\Sigma H_2S$  removal pathway. As the abiotic reduction of Fe(III) oxides by  $\Sigma H_2S$ 430 coupled with either FeS or FeS and pyrite precipitation (Table 1, Eq. 9-11) does overall not alter 431





432 alkalinity, bacterial sulfate reduction followed by abiotic precipitation of iron and sulfide from the pore waters to either FeS or pyrite (Table 1, Eqs. 12 and 13) should result in  $r_{AD} = 1$  and  $r_{DS} = r_{AS} = -$ 433 2. Formation of pyrite is accompanied by the consumption of molecular  $H_2$  by sulfate-reducing 434 bacteria, resulting in a slight increase in the r<sub>AD</sub> and r<sub>DS</sub> to 1.1 and -1.8% for the overall reaction while 435 the rAS ratio should not change (Table 1, Eq. 14). Another possible pathway includes the concomitant 436 production of Fe<sup>2+</sup> by dissimilatory iron reduction (Table 1, Eq. 7) and  $\Sigma H_2S$  by sulfate reduction 437 followed by precipitation of FeS. In this case, the net r<sub>AD</sub> and r<sub>DS</sub> ratios should decrease to 0.89 and -438 2.25, whereas the  $r_{AS}$  ratio should remain at -2 (Table 1, Eq. 15). With ensuing formation of pyrite, 439 theoretical mole ratios may change slightly to  $r_{AD} = 0.94$  and  $r_{DS} = -2.13$  without H<sub>2</sub> reoxidation (Table 4401, Eq. 16), whereas rAD and rDS ratios of 1.06 and -1.89 should be reached with H2 reoxidation by 441 sulfate-reducing bacteria (Table 1, Eq. 17). In both cases, the rAS ratio should remain at -2. 442

443 The observed range of rADe (1.06 to 1.15) and rDSe (-2.05 to -1.86) ratios in the proximal and prodelta stations, except at station B (Table 3), is fully compatible with sulfate reduction coupled to 444 iron reduction and FeS precipitation (possibly followed by pyritization), though rADe and rDSe ratios 445 are not able to distinguish abiotic and microbial pathways of iron reduction. The occurrence of 446 dissimilatory iron reduction in the proximal and prodelta domains, however, is substantiated by 447 448 several other pieces of evidence. First, the production of soluble organic-Fe(III) complexes deeper than the oxygen penetration depths (Fig. 5) indicates that these species did not result from the 449 oxidation of  $Fe^{2+}$  by dissolved O<sub>2</sub> in the presence of organic ligands (Taillefert et al., 2000). Second, 450 451 as soluble organic-Fe(III) complexes are produced as intermediates in the reduction of Fe(III) oxides by iron reducing bacteria (Taillefert et al., 2007; Jones et al., 2010), their concomitant detection with 452 Fe<sup>2+</sup> at all the stations in the proximal and prodelta domains (Fig. 5) suggests they were produced 453 during dissimilatory iron reduction. Third, the positive correlation between the current intensities of 454 organic-Fe(III) complexes and Fe<sup>2+</sup> concentrations is in line with the same correlation obtained in 455 iron-rich deep-sea sediments (Fig. 7) here sulfate reduction was not significant (Beckler et al., 456 2016). Finally, as these organic-Fe(III) complexes are readily reduced by  $\Sigma H_2S$  (Taillefert et al., 457

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2000), their presence in zones of sulfate reduction suggest these sediments are highly dynamic with
periods of intense sulfate reduction alternating with periods during which sulfate reduction is
repressed and replaced by microbial iron reduction. These dynamics may be controlled by the input
of organic and inorganic material from the Rhône River in the proximal domain, especially during
floods when most of the solid material is deposited on the seafloor (Cathalot et al., 2010; Pastor et
al., 2018).

464 4.5 FeS precipitation

465 The discrepancy between sulfate consumption and the low concentration of  $\Sigma H_2 S$  along with the high TA fluxes clearly suggest that much of the sulfur was precipitated in the solid phase. Indeed, 466 AVS measurements show precipitation of FeS in the proximal and prodelta domains (Fig. 6). In 467 468 addition, the large phosphate concentrations observed at depth in the proximal and prodelta domains 469 (Fig. 6) suggest that  $\Sigma PO_4^{3-}$  adsorbed to Fe(III) oxides was released in the pore waters during 470 secondary conversion of Fe(III) oxides to FeS (Anschutz et al., 1998; Rozan et al., 2002). More importantly, large concentrations of nanoparticulate FeS (FeS<sub>0</sub> in the range of 1-6 mM) were 471 identified in the proximal and prodelta stations that decreased with distance from shore (Fig. 6). The 472 existence of FeS<sub>0</sub> suggests that large fractions of  $Fe^{2+}$  and  $\Sigma H_2S$  were actively removed from the pore 473 waters at the time of measurements and eventually immobilized under the form of sulfide minerals. 474 Although soluble FeSad clusters detected electrochemically when the system is oversaturated with 475 respect to FeS (Theberge and Luther, 1997) are considered good indicators of the active precipitation 476 of iron sulfide minerals (Luther and Ferdelman, 1993; Davison et al., 1998; Taillefert et al., 2000), 477 they were rarely observed in the Rhône River delta (Fig. 5). Indeed, the ion activity products (pIAPs) 478 calculated at most stations indicate that pore waters were either undersaturated, as a result of the low 479 concentrations (stations AK, B, and K) or complete absence (stations A and Z) of dissolved sulfides, 480 or close to the solubility of amorphous FeS or mackinewite (Fig. 8). Collectively, the large 481 concentrations of dissolved  $FeS_0$  compared to the small electrochemically active  $FeS_{aq}$  complexes 482



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and the generally low saturation state of the pore waters indicate that FeS was much more aggregated during this time period. Overall, the presence of soluble organic-Fe(III) complexes along with dissolved Fe<sup>2+</sup> throughout the profiles, the absence of  $\Sigma$ H<sub>2</sub>S and FeS<sub>aq</sub>, and the large concentrations of dissolved FeS<sub>0</sub> found in the pore waters despite complete removal of sulfate in the proximal and some of the prodelta stations provide strong evidence of large FeS precipitation in a context where uses sulfate-reducing conditions may alternate with iron-reducing conditions already observed seasonally in estuarine sediments (Taillefert et al., 2002).

490 4.6. Benthic alkalinity flux as a result of iron sulfide burial

As the extreme sedimentation rates (> 30 cm yr<sup>-1</sup>)  $\frac{1}{100}$  he proximal domain prevent short-term 491 492 reoxidation of  $\Sigma$ H<sub>2</sub>S, the burial of FeS should represent a net source of alkalinity in the pore waters 493 (Berner, 1982; Hu and Cai, 2011a; Brenner et al., 2016). With the precipitation of FeS, about 2 to 3 moles of alkalinity equivalent should be produced for each mole of sulfur precipitated (Table 1, Eqs. 494 495 12 and 15). Assuming concomitant dissimilatory iron and sulfate reduction dominate in the proximal and prodelta zones, a conservative ratio of 2 moles of TA equivalent per mole of FeS precipitated can 496 be estimated (Table 1, Eq. 15). In this calculation, the alkalinity production flux was estimated from 497 the average AVS burial fluxes using Eq.  $\delta$ , with the caveat that these flux comparisons are made 498 UN-Mer assuming steady-state which is questionable in such a dynamic system. Nonetheless, the average AVS 499 concentration of the proximal station (station A) was used, as the sedimentation rate at this station is 500 so high (>30 cm y<sup>-1</sup>) that the entire sediment layer investigated is buried rapidly in a year. The 501 calculated AVS burial flux provides an alkalinity-equivalent flux of  $25.0 \pm 7.7$  mmol m<sup>-2</sup> d<sup>-1</sup> in the 502 proximal domain (Table 4), which falls within the range of benthic alkalinity fluxes measured by 503 benthic chamber at stations A and Z (14.3 - 73.9 mmol m<sup>-2</sup> d<sup>-1</sup>; Fig. 4 and Table 4). In the prodelta, 504 the alkalinity-equivalent flux is estimated at  $9.8 \pm 2.8$  mmol m<sup>-2</sup> d<sup>-1</sup> at station AK (Table 4), which 505 unfortunately cannot be compared to benthic alkalinity fluxes as they were not measured. In the distal 506 domain, however, a low alkalinity-equivalent flux of  $0.04 \pm 0.1$  mmol m<sup>-2</sup> d<sup>-1</sup> is estimated from the 507





average AVS burial flux at station E. This flux is much lower than the  $3.7 \pm 0.9$  mmol m<sup>-2</sup> d<sup>-1</sup> flux measured by benthic chamber (Fig. 4), a difference that could be due to denitrification and shallow carbonate dissolution.

511 4.7. Benthic alkalinity flux as a result of carbonate dissolution

512 Calcium carbonate dissolution below the sediment-water interface as a result of the acidity generated by aerobic respiration may represent another possible contributor to TA fluxes as 513 514 demonstrated in carbonate-rich permeable sediments (Burdige and Zimmerman, 2002; Cyronak et al., 2013; Rao et al., 2014). Both the water column ( $\Omega_{Ca} = 5.5$ ) and the pore waters ( $\Omega_{Ca} > 1$ ) of the 515 proximal zone are largely oversaturated with respect to calcite (Rassmann et al., 2016; Fig. 6). These 516 findings are corroborated by a large decrease in  $Ca^{2+}$  concentration in the pore waters, indicating 517 CaCO<sub>3</sub> precipitation at depth in proximal zone sediments. Yet, the intense consumption of dissolved 518 oxygen in the first millimeters below the sediment-water interface generates a large pH decrease (Fig. 519 520 2) that may induce carbonate dissolution at this scale. Calcium carbonate saturation states at a millimeter scale near the SWI were calculated from pH profiles and an interpolation of the centimetre-521 scale DIC profiles using the SeaCarb software (Fig. 9). They show that in the proximal zone, the 522 523 saturation state with respect to calcite, which is the most abundant detrital carbonate in these sediments (Rassmann et al., 2016), is always above 1.5. Such saturation state precludes massive 524 525 carbonate dissolution at the sediment surface and discounts shallow carbonate dissolution as playing 526 a large role on the benthic alkalinity fluxes observed in the proximal sediments. Minor quantities of 527 calcium carbonate may be dissolved in microniches where the pH could be lower than 7.4 or less 528 abundant carbonate forms (aragonite) may dissolve in the millimetric layers where this mineral is 529 close to undersaturation. These processes, however, surely represent an insignificant flux in the proximal zone compared to the large alkalinity generated by sulfate reduction and subsequent FeS 530 burial. At the distal station on the shelf (Station E, Fig. 9c), the saturation state was close to 1 which 531 may indicate a potential contribution of calcium carbonate dissolution to the benthic alkalinity flux. 532





#### 533 4.8. Linking TA and DIC fluxes to mineralization processes

534 Overall, the present findings indicate that FeS burial modifies the alkalinity budget in the proximal and prodelta sediments (Brenner et al., 2016). As the order of magnitude of the measured 535 benthic alkalinity fluxes is compatible with the alkalinity generated during the reduction of Fe(III) 536 oxides, sulfate, and subsequent FeS burial in the proximal zone, these processes are likely responsible 537 for the large alkalinity fluxes reported in this high-sedimentation delta and, potentially, other similar 538 systems (Hu and Cai, 2011a). 539 540 The biogeochemical cycling of C, Fe, S, and TA close to the Rhône River mouth can be theoretically summarized as follows (Fig. 10): (i) the high pore water DIC concentrations resulting 541

542 from the production of metabolic CO<sub>2</sub> during organic carbon mineralization lead to benthic DIC 543 fluxes that are only modulated by the precipitation of carbonate minerals; (ii) the high pore water TA concentrations result from intense iron and sulfate reduction as a result of the high supply of organic 544 545 matter and Fe(III) oxides to the sediment; (iii) the precipitation of FeS and the high sedimentation rates near the river mouth  $\pi_{2}$  erve the majority of reduced iron and  $\Sigma H_{2}S$  buried in the form of FeS 546 minerals and potentially pyrite within the anoxic sediments (Aller et al., 1986); and (iv) ultimately, 547 the TA-consuming reoxidation of reduced metabolites (i.e.,  $NH_4^+$ ,  $\Sigma H_2S$ ,  $Fe^{2+}$ ) is not important in the 548 oxic sediment layers, and a significant fraction of the anaerobically-produced TA is transferred across 549 the SWI (Fig. 10, red dashed line). In these conditions, anaerobic and aerobic processes are 550 551 decoupled, and the consumption of oxygen no longer reflects the overall respiration rates within these sediments (Pastor et al., 2011) as observed by the relatively lower contribution of DOU fluxes 552

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553 compared to TA and DIC fluxes in the proximal domain (Fig. 4).

In contrast, sedimentation rates (Table 2), overall respiration rates (Fig. 4), and the intensity of iron and sulfate reduction (Fig. 6) decrease in the distal domain (station E), and as a consequence the relative proportion of aerobic processes increases (Pastor et al., 2011). Despite the relatively small decrease in pore water sulfate concentrations with depth and low  $\Sigma$ H<sub>2</sub>S concentrations (< 10 µmol L<sup>-</sup> 558<sup>-1</sup>) at the most offshore station E,  $\Sigma$ H<sub>2</sub>S concentrations were the highest of all the stations. These





findings likely reflect the fact that less riverine Fe(III) oxides were available for FeS precipitation. With low sedimentation rates (0.1 to 1 cm yr<sup>-1</sup>) and thus low input of organic matter and Fe(III) oxides, the overall carbon turnover is decreased and the reduced by-products of sulfate and/or iron reduction may be transported back to the oxic sediment layers to be reoxidized by dissolved oxygen. In this case, the alkalinity generated by <u>anaerobic respiration processes is consumed by reoxidation</u> of the reduced metabolites, and the flux of alkalinity near the SWI decreases to weak values at station E (Fig. 4 and Fig. 10, black line).

566 The strong TA flux to the overlying waters measured in the Rhône River delta, may contribute, along with riverine inputs, to the overall high alkalinity of the Gulf of Lions waters compared to the 567 Mediterranean average (Cossarini et al., 2015). However, the influence of the benthic TA flux on the 568 water column pH and ultimately on the absorption of atmospheric CO2 depends mainly on the TA to 569 DIC benthic flux ratio ( $F_{TA}/F_{DIC}$ ), vertical mixing in the water column, and thus the residence time of <u>570</u> the bottom waters (Hu and Cai, 2011b, Andersson and Mackenzie, 2012). The F<sub>TA</sub>/F<sub>DIC</sub> ratios, ranging <u>571</u> between 0.8 and 1 in the proximal and prodelta zones of the Rhône River delta (Fig. 11), are in the 572 high range of a compilation of TA to DIC flux ratios obtained in different coastal systems and 573 continental shelves (expanded from Hu and Cai, 2011b). As these ratios do not exceed 1, alkalinity 574 575 generated in the sediments will not decrease  $pCO_2$  in the bottom waters and thus not draw atmospheric CO<sub>2</sub> into the coastal ocean. Yet, the large benthic TA fluxes generated from deltaic sediments and the 576 577 elevated  $F_{TA}/F_{DIC}$  (>0.8), which were unknown in the Rhône River prodelta before this study, may modify the carbonate cycle paradigm in these coastal regions. 578

## 579 5. Conclusion

In this study, benthic respiration, as well as benthic alkalinity and DIC fluxes were quantified in the Rhône River delta using benthic landers. These measurements demonstrated that sediments from the proximal and prodelta domains represent a strong source of alkalinity to the water column. The highest alkalinity and DIC fluxes were detected in the vicinity of the Rhône River mouth and were



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584 much stronger than fluxes of dissolved oxygen, indicating the decoupling of oxic and anoxic biogeochemical processes. As pore water oversaturation with respect to calcite prevented carbonate 585 dissolution to occur over the entire sediment column, the high benthic alkalinity fluxes resulted from 586 the high intensity of anaerobic respiration processes, mainly via sulfate reduction and precipitation 587 of iron sulfide minerals, but also with some contributions from dissimilatory iron reduction and AOM. 588 The intensity of sulfate reduction in the proximal domain also resulted in the consumption of a 10-589 20% fraction of the alkalinity and DIC by the precipitation of authigenic carbonates. As the reduced 590 metabolites Fe<sup>2+</sup> and  $\Sigma$ H<sub>2</sub>S produced by the mineralization of organic matter were buried in the solid 591 phase, alkalinity was not consumed by their reoxidation in the oxic sediment layers. Consequently, a 592 significant fraction of the total alkalinity generated in the pore waters was transferred to the bottom 593 waters (benthic flux of 14-74 mmol m<sup>-2</sup> d<sup>-1</sup>). Although sulfate reduction dominated the proximal and 594 prodelta domains, evidence for dissimilatory reduction of Fe(III) oxides was simultaneously observed 595 in the depth profiles, suggesting that anaerobic processes in the Rhône River prodelta are dynamic 596 and potentially controlled by pulsed sediment accumulations. The intensity of the alkalinity and DIC 597 fluxes decreased offshore as the sedimentation rate and the relative importance of anaerobic 598 mineralization pathways compared to aerobic processes decreased. In these conditions the more 599 600 "classical" coupling between aerobic and anaerobic reactions occurs, hence producing much lower benthic alkalinity fluxes. Overall, these findings suggest that deltaic sediments exposed to large 601 riverine inputs of inorganic and organic material may provide a large source of alkalinity to the 602 overlying waters and thus weaken the increase in pCO2 more significantly than previously thought in 603 604 coastal waters.

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### 860 Figure Captions

- 861 Figure 1: Map of the Rhône River prodelta with the stations investigated during the AMOR-B-Flux
- 862 cruise in September 2015.

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**Figure 2:** Dissolved oxygen and pH microprofiles recorded *in situ* at the sediment-water interface at stations A, Z, K, and E. Stations A and Z are located in the proximal zone, K in the prodelta, and E in the distal zone (i.e. continental shelf).

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**Figure 3:** Figure 3: Figure 3: Figure 4 and in Table 2.

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**Figure 4:** DIC and TA fluxes measured with the benthic chamber and diffusive oxygen uptake (DOU) rates calculated from *in situ* microelectrode depth profiles at stations A, Z (measured during two deployments), and E. Error bars represent either uncertainties about the linear regression of the benthic DIC and TA gradients taking into account individual error bars of each data point or error propagation and standard deviations of multiple DOU measurements. Fluxes out of the sediment are positive and fluxes into the sediment are negative.

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**Figure 5:** Depth profiles of dissolved  $O_2$ ,  $Mn^{2+}$ ,  $Fe^{2+}$ , org-Fe(III),  $FeS_{aq}$ , and  $\Sigma H_2S$  concentrations measured electrochemically in intact sediment cores at stations A, Z, AK, K, B, and E. Org-Fe(III) and  $FeS_{aq}$  are reported in normalized current intensities (nA).

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**Figure 6:** Depth profiles of pore water TA, DIC,  $SO_4^{2-}$ ,  $NH_4^+$ ,  $CH_4$ ,  $Ca^{2+}$ , nanoparticulate FeS (FeS<sub>0</sub>), 885  $\Sigma PO_4^{3-}$ , and AVS concentrations along with the calcium carbonate (calcite) saturation state of the pore





waters ( $\Omega_{Ca}$ ) at stations A, Z, AK, K, B, and E. Alternating symbol shapes indicate data collected from duplicate long and short sediment cores. The calcium carbonate (calcite) saturation state ( $\Omega_{Ca}$ ) and pore water FeS<sub>0</sub> concentrations were calculated whereas AVS was determined from solid phase extractions. The two horizontal lines identify the sulfate-methane transition zone (SMTZ) found at stations A and Z. Error bars represent standard deviations of multiple measurements for the concentrations and error propagation for  $\Omega$ . Concentrations of CH<sub>4</sub> were not measured tations B, K, and E.

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Figure 7: Current intensities of organic-Fe(III) complexes as a function of Fe<sup>2+</sup> concentrations
measured at each depth at stations A, Z, AK, B, and K compared to the same data obtained from ironrich deep-sea sediments (Beckler et al., 2016).

897

**Figure 8:** Calculated pIAP values as a function of depth into the sediment compared to the  $pK_{sp}$  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.

901

902 Figure 9: Average pore water saturation states with respect to calcite in the oxic sediment layers at 903 stations: a- Proximal (St. A, Z), b- prodelta (St. K), and c- distal (St. E) calculated using the DIC 904 gradients at the SWI together with the average measured pH microprofiles.

905

906 **Figure 10:** Conceptual model to visualize the link between the burial of iron sulfide minerals and 907 benthic alkalinity fluxes. The total alkalinity (TA) produced under anaerobic conditions at depth 908 diffuses upwards towards the aerobic sediment layer where it is consumed during reoxidation of Fe<sup>2+</sup> 909 and  $\Sigma$ H<sub>2</sub>S by dissolved oxygen (black). If the precipitation of sulfide minerals is significant, the 910 reduced iron and sulfide metabolites produced during anaerobic respiration are not reoxidized by





911 dissolved oxygen, and the TA produced is able to reach the bottom waters (red). The intensity of the

- 912 alkalinity flux into the bottom waters is indicated by the thickness of the arrow at the SWI.
- 913

914 Figure 11: TA to DIC benthic flux ratios as a function of depth at stations A, Z, and E of the Rhône River delta compared to different coastal regions of water depth < 100 m where this ratio was 915 916 quantified from in situ benthic flux measurements (modified from Hu and Cai, 2011b). Other coastal regions include Cadiz Bay and the Guadalquivir continental shelf (Spain; Ferron et al., 2009), the 917 Rio Tinto estuary (Spain; Ortega et al., 2008), the Po river delta and nearby Adriatic shelf (Italy; 918 919 Hammond et al. 1999), San Francisco Bay (USA; Hammond et al., 1985), and the California shelf (USA; Berelson et al., 1996). The global coastal average TA to DIC flux ratio predicted from Krumins 920 et al., 2013 is also reported for reference. Note that this average is different from that reported by Hu 921 and Cai (2011b) which was corrected in their later publication (Hu and Cai, 2013). 922

## 923 Table captions

924 Table 1: Individual and consecutive microbial and abiotic reactions that affect the theoretical

925  $\Delta TA/\Delta DIC$  (r<sub>AD</sub>),  $\Delta DIC/\Delta SO_4$  (r<sub>DS</sub>), and  $\Delta TA/\Delta sulfate$  (r<sub>AS</sub>) stoichiometric ratios. Note that Eq. 14

926 and 17 include oxidation of  $H_2$  produced by pyritization (Eq. 11) by sulfate-reducing bacteria.

927

**Table 2:** Sampling sites during the AMOR-B-Flux cruise in September 2015 and main characteristics of bottom waters; dist. = distance to the Rhône River mouth;  $\omega$  = sedimentation rate; Station Z was sampled twice (Z on 09/08/15 and Z' on 09/14/15) to investigate temporal variability; n.d. = not determined.

932

933 **Table 3:** Diffusion-corrected stoichiometric ratios corrected ( $r_{ADc}$ ,  $r_{DSc}$ , and  $r_{ASc}$ ) or not ( $r_{AD}$ ,  $r_{DS}$ , and 934  $r_{AS}$ ) for carbonate precipitation along with their associated determination coefficients ( $r^2$ ) from linear 935 regression coefficients.





# 936

- 937 Table 4: Calculated FeS burial fluxes and their TA-equivalent production at each station compared
- 938 to TA benthic fluxes measured; n.d. = not determined.

939













Figure 3: Figure 3



Figure 4: Figure 4



















Figure 7: Figure 7







Figure 8: Figure 8



Figure 9: Figure 9







Figure 10: Figure 10







Figure 11: Figure 11





|      | Individual Reactions   | $r_{\mathrm{AD}}$                        | $r_{\rm DS}$                  | ras                  |
|------|--|--|-------------------------------|----------------------|
| (1)  | $Ca^{2+} + HCO_3^- \rightarrow CaCO_3 + H^+$   | $\frac{-2}{-1} = 2$                      |                               | ·                    |
| (2)  | $NH_4^+ + 2O_2 \rightarrow NO_3^- + 2H^+ + H_2O$   | $\frac{-2}{0}$                           |                               |                      |
| (3)  | $Fe^{2+} + \frac{1}{4}O_2 + \frac{5}{2}H_2O \to Fe(OH)_3 + 2H^+$   | $\frac{-2}{0}$                           |                               |                      |
| (4)  | $H_2S + 20_2^- \rightarrow S0_4^{2-} + 2H^+$   | $\frac{-2}{0}$                           |                               | $\frac{-2}{+1} = -2$ |
| (2)  | $CH_2O + \frac{4}{5}NO_3^2 - \frac{2}{5}H^+ \rightarrow HCO_3^- + \frac{2}{5}N_2 + \frac{2}{5}H_2O$  | $\frac{+4/5}{+1} = 0.8$                  |                               |                      |
| (9)  | $2CH_2O + SO_4^{2-} \rightarrow 2HCO_3^{-} + H_2S$   | $\frac{+2}{+2} = 1$                      | $\frac{+2}{-1} = -2$          | $\frac{+2}{-1} = -2$ |
| (2)  | $CH_2O + 4 \ Fe(OH)_3 + 7H^+  ightarrow HCO_3^- + 4 \ Fe^{2+} + 10 \ H_2O$   | $\frac{+8}{+1} = 8$                      |                               |                      |
| (8)  | $CH_4 + SO_4^{2-} + H^+ \rightarrow HCO_3^- + H_2S + H_2O_3$   | $\frac{+2}{+1} = 2$                      | $\frac{+1}{-1} = -1$          | $\frac{+2}{-1} = -2$ |
| (6)  | $Fe(OH)_{3(s)} + \frac{1}{2}H_2S + 2H^+ \rightarrow Fe^{2+} + \frac{1}{2}S(0) + 3H_2O$   | 0 + 2                                    |                               |                      |
| (10) | $Fe^{2+} + H_2 S \rightarrow Fe S_{(s)} + 2H^+$  | $\frac{-2}{0}$                           |                               |                      |
| (11) | $FeS_{(s)} + H_2S \rightarrow FeS_{2(s)} + H_2$  | 010                                      |                               |                      |
|      | Consecutive Reactions  | ſAD                                      | $r_{\rm DS}$                  | TAS                  |
|      | Sulfate reduction, abiotic reduction of Fe(III) oxides, and precipitation of sulfide minerals $\frac{1}{2}$  | +2                                       | +2                            | +7                   |
| (12) | $2CH_2O + SO_4^{2-} + \frac{2}{3}Fe(OH)_{3(5)} \to 2HCO_3^{-} + \frac{2}{3}S(0) + \frac{2}{3}FeS_{(5)} + 2H_2O$  | +2<br>= 1<br>= 1                         | $\frac{12}{-1} = -2$          | $\frac{12}{-1} = -2$ |
| (13) | $2CH_2O + SO_4^2 - \frac{2}{5}Fe(OH)_{3(S)} \to 2HCO_3^2 + \frac{1}{5}S(0) + \frac{2}{5}FeS_{2(S)} + \frac{6}{5}H_2O + \frac{2}{5}H_2$   | $\frac{+2}{+2} = 1$                      | $\frac{+2}{-1} = -2$          | $\frac{+2}{-1} = -2$ |
| (14) | $\frac{20}{11}CH_2O + SO_4^{2-} + \frac{4}{11}Fe(OH)_{3(s)} + \frac{2}{11}H^+ \rightarrow \frac{20}{11}HCO_3^- + \frac{2}{11}S(0) + \frac{4}{11}FeS_{2(s)} + \frac{1}{11}H_2S + \frac{16}{11}H_2O_{1-} + \frac{1}{11}H_2O_{1-} + \frac{1}{1$ | $\frac{+2}{+20/11} = 1.1$                | $\frac{+20/_{11}}{-1} = -1.8$ | $\frac{+2}{-1} = -2$ |
|      | Concomitant dissimilatory iron and sulfate reduction with precipitation of sulfide minerals  |  |                               |                      |
| (15) | $\frac{9}{4}CH_2O + SO_4^{2-} + Fe(OH)_{3(S)} \to \frac{9}{4}HCO_3^{-} + \frac{1}{4}H^+ + FeS_{(S)} + \frac{5}{2}H_2O$   | $\frac{+2}{+9/4} = 0.89$                 | $\frac{+9/4}{-1} = -2.25$     | $\frac{+2}{-1} = -2$ |
| (16) | $\frac{17}{8}CH_2O + SO_4^{2-} + \frac{1}{2}Fe(OH)_{3(s)} \rightarrow \frac{17}{8}HCO_3^{-} + \frac{1}{8}H^+ + \frac{1}{2}FeS_{2(s)} + \frac{5}{4}H_2O + \frac{1}{2}H_2$   | $\frac{+2}{+17/8} = 0.94$                | $\frac{+17}{-1} = -2.13$      | $\frac{+2}{-1} = -2$ |
| (17) | $\frac{17}{9}CH_2O + SO_4^{2-} + \frac{4}{9}Fe(OH)_{3(s)} + \frac{1}{9}H^+ \rightarrow \frac{17}{9}HCO_3^- + \frac{4}{9}FeS_{2(s)} + \frac{1}{9}H_2S + \frac{14}{9}H_2O$   | $\frac{+2^{\circ}}{+1^{\circ}/9} = 1.06$ | $\frac{+17}{-1} = -1.89$      | $\frac{+2}{-1} = -2$ |





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| Table 2. Sampling sites during the AMOR-B-Flux cruise in September 2015 and main characteristics of            |
|--|
| bottom waters; dist. = distance to the Rhône River mouth; $\omega$ = sedimentation rate; Station Z was sampled |
| twice (Z on 09/08/15 and Z' on 09/14/15) to investigate temporal variability; n.d. = not determined.           |

| Domain                   |                 | Proximal                               |                 |               | Prodelta           |               | Distal               |
|--------------------------|-----------------|--|-----------------|---------------|--------------------|---------------|----------------------|
| Stations                 | Α               | Z                                      | Z'              | AK            | В                  | K             | Е                    |
| Long. ° E                | 4.850           | 4.868                                  | 4.868           | 4.853         | 4.833              | 4.858         | 4.684                |
| Lat. °N                  | 43.311          | 43.318                                 | 43.318          | 43.307        | 43.305             | 43.301        | 43.220               |
| Dist. [km]               | 2.1             | 2.2                                    | 2.2             | 2.8           | 3                  | 3.3           | 14.3                 |
| Depth [m]                | 20              | 20                                     | 20              | 42            | 50                 | 58            | 72.5                 |
| Temp. [°C]               | 16.3            | 19.6                                   | 14.7            | 16.2          | 20.6               | 14.7          | 14.3                 |
| Salinity                 | 37.5            | 37.6                                   | 37.7            | 37.7          | 38.0               | 37.7          | 37.8                 |
| O <sub>2</sub> [µM]      | $253.1\pm0.3$   | $249.5\pm0.3$                          | $242.6\pm0.2$   | $250.2\pm0.1$ | n.d.               | $241.8\pm0.2$ | $221.5\pm0.3$        |
| DIC [mM]                 | $2.29\pm0.01$   | $2.31\pm0.01$                          | n.d.            | $2.28\pm0.01$ | $2.27\pm0.01$      | $2.31\pm0.01$ | $2.33\pm0.01$        |
| TA [mM]                  | $2.61\pm0.02$   | $2.60\pm0.01$                          | n.d.            | $2.60\pm0.02$ | $2.60\pm0.01$      | $2.60\pm0.02$ | $2.61\pm0.01$        |
| pH <sub>T</sub>          | $8.08 \pm 0.01$ | $8.06\pm0.01$                          | $8.09\pm0.01$   | $8.09\pm0.01$ | $8.07\pm0.01$      | $8.08\pm0.01$ | $8.05\pm0.01$        |
| mean ø                   | $0.69\pm0.04$   | $0.65\pm0.04$                          | $0.65\pm0.04$   | $0.68\pm0.02$ | $0.66\pm0.03$      | $0.65\pm0.05$ | $0.64\pm0.04$        |
| w [cm yr <sup>-1</sup> ] |                 | 30 - 40ª                               |                 |               | 1 - 4 <sup>b</sup> |               | 0.1 - 1 <sup>c</sup> |
|                          | Benthic fluxes  | s (mmol m <sup>-2</sup> d <sup>-</sup> | 1)              |               |                    |               |                      |
| TA flux                  | $14.3\pm1.6$    | $73.9\pm20.6$                          | $56.0 \pm 17.8$ | n.d.          | n.d.               | n.d.          | $3.7\pm0.9$          |
| DIC flux                 | $17.8 \pm 1.6$  | $78.3 \pm 10.9$                        | $37.2\pm7.2$    | n.d.          | n.d.               | n.d.          | $9.9\pm0.9$          |
| DOU                      | $10.2\pm1.3$    | $10.4\pm0.9$                           | n.d.            | n.d.          | n.d.               | $5.9 \pm 1.0$ | $3.6 \pm 0.6$        |

a. Data from Charmasson et al., 1998

b. Data from Lansard et al., 2009

c. Data from Miralles et al., 2005





| Table 3. Diffusion-corrected stoichiometric ratios $r_{AD}$ , $r_{DS}$ , and $r_{AS}$ and their correspond     | ling ratios |
|--|-------------|
| corrected for carbonate precipitation ( $r_{ADc}$ , $r_{DSc}$ , and $r_{ASc}$ ) along with their associated de | termination |
| coefficients $(r^2)$ from linear regression; n.d = not determined.   |             |

| Stations         | Α                         | Z                         | AK                        | В                         | K                         | Е             |
|------------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------|
| r <sub>AD</sub>  | $0.99\pm0.01$             | $1.08\pm0.02$             | $1.02\pm0.02$             | $1.02\pm0.01$             | $0.98\pm0.05$             | $0.90\pm0.04$ |
| r <sup>2</sup>   | 0.998                     | 0.997                     | 0.998                     | 0.999                     | 0.986                     | 0.984         |
| r <sub>ADc</sub> | $1.10\pm0.01$             | $1.16\pm0.03$             | $1.07\pm0.02$             | $1.15\pm0.02$             | $1.06\pm0.07$             | $1.15\pm0.11$ |
| $r^2$            | 0.999                     | 0.997                     | 0.996                     | 0.998                     | 0.974                     | 0.885         |
| r <sub>DS</sub>  | $\textbf{-1.67} \pm 0.06$ | $\textbf{-1.87} \pm 0.17$ | $\textbf{-1.85} \pm 0.05$ | $\textbf{-1.18} \pm 0.05$ | $\textbf{-1.72} \pm 0.03$ | n.d.          |
| $r^2$            | 0.990                     | 0.969                     | 0.995                     | 0.988                     | 0.997                     | n.d.          |
| $r_{DSc}$        | $\textbf{-1.88} \pm 0.05$ | $\textbf{-2.05} \pm 0.18$ | $\textbf{-1.95} \pm 0.05$ | $\textbf{-1.37} \pm 0.05$ | $\textbf{-1.86} \pm 0.07$ | n.d.          |
| $r^2$            | 0.994                     | 0.972                     | 0.996                     | 0.990                     | 0.994                     | n.d.          |
| r <sub>AS</sub>  | $\textbf{-1.66} \pm 0.07$ | $\textbf{-2.03} \pm 0.17$ | $\textbf{-1.89} \pm 0.06$ | $\textbf{-1.21} \pm 0.04$ | $\textbf{-1.69} \pm 0.07$ | n.d.          |
| $r^2$            | 0.986                     | 0.973                     | 0.992                     | 0.994                     | 0.991                     | n.d.          |
| r <sub>ASc</sub> | $-2.07\pm0.05$            | $-2.35\pm0.14$            | $\textbf{-2.01} \pm 0.06$ | $\textbf{-1.58} \pm 0.05$ | $\textbf{-1.89} \pm 0.14$ | n.d.          |
| $r^2$            | 0.994                     | 0.977                     | 0.989                     | 0.992                     | 0.958                     | n.d.          |





Table 4. Calculated FeS burial fluxes and their TA-equivalent production at each station compared to alkalinity fluxes measured; n.d. = not determined.

| Stations   | A and Z  | AK            | Ε             |
|--|--|---------------|---------------|
| ω [cm yr <sup>-1</sup> ]   | 30   | 3             | 0.1           |
| φ  | 0.67   | 0.68          | 0.64          |
| Mean [AVS] [µmol g <sup>-1</sup> ]                                 | $19.5\pm4.9$   | $45.0\pm11.3$ | $9.0\pm2.3$   |
| sediment density [g cm <sup>-3</sup> ]                             | 2.5  | 2.5           | 2.5           |
| FeS burial flux [mmol S m <sup>-2</sup> d <sup>-1</sup> ]          | $12.5\pm3.8$   | $4.9 \pm 1.4$ | $0.02\pm0.01$ |
| TA-equivalent prod. (=2.0 FeS) [mmol TA $m^{-2} d^{-1}$ ]          | $25\pm 8$  | $9.8\pm2.8$   | $0.04\pm0.1$  |
| Measured TA flux at SWI [mmol TA m <sup>-2</sup> d <sup>-1</sup> ] | $\begin{array}{l} A:14.3\pm1.6\\ Z:73.9\pm20.6\\ Z':56.0\pm17.8 \end{array}$ | n.d.          | $3.7\pm0.9$   |