

Extensive evaporation in a modern temperate estuary: Stable isotopic and compositional evidence

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Abstract

Estuaries have long been recognized as sites of major compositional fluctuations that can have a range of effects including mineral growth in the water column and in the underlying estuarine sediment. We have studied chloride and sodium concentrations and stable isotopes (H and O) from a suite of estuarine waters from the temperate Anllóns estuary in NW Spain to assess the complexity of estuarine mixing process. Water samples were collected hourly from in estuary sites over three consecutive days and end-member samples were collected on each sampling day. Evaporative concentration of the estuarine waters is demonstrated by the maximum concentration of geochemically conservative chloride being as much as 17.5% greater in the estuary than in the local seawater. Relative to chloride concentration, both $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values of estuary waters tend to be more enriched than would be expected for the simple physical mixing of river water and seawater. These patterns can only be plausibly accounted for through evaporation affecting the water, concentrating the chloride and causing isotope fractionation. We have modelled the effects of evaporation on chloride concentration and the stable isotopes in the estuary; the results closely match the distribution of analytical data suggesting that up to 40% evaporation has happened. We have demonstrated that two thirds of estuarine water samples analysed underwent between 5% and 40% evaporation. This previously unreported degree of evaporation in estuaries has important implications for any processes that is effected by the consequent degree of elevated solute concentration.

Estuaries are locations of complex water and sediment mixing patterns due to the twice-daily influx of seawater (Berner and Berner 2012). Estuarine sediments and the signatures that result from the competing influences of fluvial and marine systems are of interest in their own right and as analogues to understand ancient, deeply buried estuarine sandstones. Daily variations in water chemistry through tidal cycles result in complex systems of water mixing, and sediment deposition and resuspension (Pritchard 1967; Meade 1972; Liss 1976; Eisma 1986, 1988; Dyer 1994). Understanding the impact of these systems on physical, chemical, and biological processes that govern sediment distribution and mineral deposition, may allow us to unravel mechanisms of early diagenetic carbonate and clay minerals deposition. As 95% of fluvially transported iron gets trapped in estuaries

(Berner and Berner 2012), this approach may also shed light on the deposition of early diagenetic iron phases.

Sedimentation processes (Eisma 1986, 1988), mineral distribution (Edzward and O'Melia 1975) and water compositions (Liss 1976; Costas et al. 2011) have all been studied to various extents in estuaries. Modern estuaries can be used as analogues for estuarine systems in the rock record. The processes that occur in modern environments are similar to those that have resulted in ancient sedimentary successions in the subsurface and at outcrop (Haughton et al. 1991). Provenance studies of drainage basins have long been regarded as a crucial input for the reconstruction of sedimentary basins. Clarifying geochemical processes in modern estuaries and the effects of these processes on sediments may lead to a clearer understanding of mineral and facies distributions in buried sediments in the subsurface. This research is a first step in understanding the role of changing water geochemistry and potential controls on eogenesis in modern environments.

While there have been numerous studies of the stable isotopic ratios ($\delta^2\text{H}$ and $\delta^{18}\text{O}$) of the oceans and rivers (e.g.,

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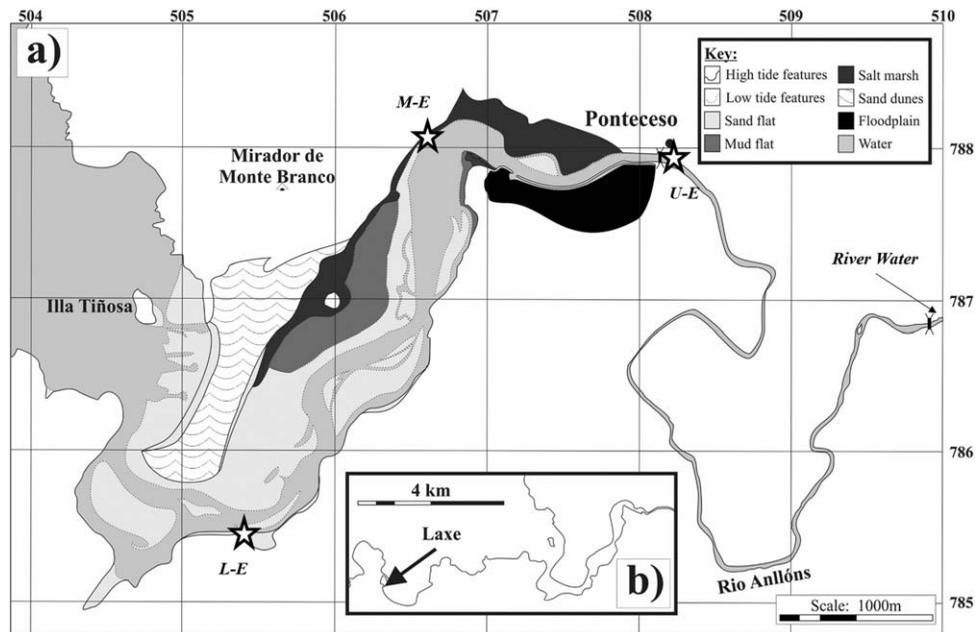


Fig. 1. Sample locations in the Anllóns Estuary, Galicia, North-West Spain. The Anllóns River drains into the Ría de Corme y Laxe, an open bay system under marine influence (Costas et al. 2011). Water samples were collected in April 2010, hourly over full tidal cycles (13 h) for three consecutive days. Samples were collected from the two end-members on each of the three days, from the coastal marine environment in the town of Laxe, 4.5 km away (Fig. 1b), within the Ría system, as well as in the river water beyond the high tide limit (Fig. 1a). In-estuary samples were collected in the lower estuary (L-E), mid-estuary (M-E) and upper estuary (U-E).

Epstein and Mayeda 1953; Dansgaard 1964; Craig and Gordon 1965; Fairbanks 1982; Ferronsky and Brezgunov 1989; Khatiwala et al. 1999; to name but a few), there have been relatively few studies of $\delta^2\text{H}$ and $\delta^{18}\text{O}$ from estuarine waters (Martin and Letolle 1979; Zhang et al. 1990; Surge and Lohmann 2002; Swart and Price 2002; Corlis et al. 2003; Stalker et al. 2009; Price et al. 2012). Evaporation, precipitation, and the mixing of different water bodies over prolonged periods have resulted in the stable isotope compositions ($\delta^2\text{H}$ and $\delta^{18}\text{O}$) of the oceans and rivers that we see today (Epstein and Mayeda 1953; Dansgaard 1964; Craig and Gordon 1965; Fairbanks 1982; Ferronsky and Brezgunov 1989; Khatiwala et al. 1999; Corlis et al. 2003) with the $\delta^{18}\text{O}$ ratio of seawater controlled by long-term rock-water interactions with basalt at mid-ocean ridges (Muehlenbachs and Clayton 1976). In the lower reaches of estuaries, close to the open marine environment, $\delta^{18}\text{O}$ has been reported to have a positive linear correlation with salinity (Martin and Letolle 1979; Zhang et al. 1990). However, few studies have addressed the stable isotope variations through an estuary from the upper limit of marine influence, where river water dominates, to the open sea. The specific research objective being addressed in this article is to determine the extent to which estuaries represent simple physical mixtures of river water and seawater or whether there are other, nonconservative processes that significantly affect their geochemistry.

Study area

The Anllóns River, Galicia, North-West Spain (Fig. 1), is 516 km² (Devesa-Rey et al. 2010) and drains a predominately igneous and metamorphic hinterland (Arribas et al. 2010). The dominant land uses are pastoral and arable agriculture and forestry (Devesa-Rey et al. 2010; Costas et al. 2011). There are two towns in the region, Carballo and Ponteceso, and a small coastal town at Laxe. The Anllóns River flows downstream into the Anllóns Estuary, where it passes into the Ría de Corme y Laxe and then into the mid-Atlantic Ocean (Costas et al. 2011). The river is approximately 60 km in length and is undammed (Devesa-Rey et al. 2010). The average flow of the river is 11.9 m³ s⁻¹ which can vary at the extreme between 80 m³ s⁻¹ and 1 m³ s⁻¹ from the wet season to the dry season (Varela et al. 2005; Costas et al. 2011). During times of high discharge of the Anllóns river waters, salinity concentrations in the Ría are much lower than expected (Varela et al. 2005; Costas et al. 2011). April has been previously reported as the month of greatest fluvial discharge (Costas et al. 2011).

The Anllóns Estuary is a semidiurnal, mesotidal estuary, approximately 10 km long and 1 km wide. The Galician coast is wave-dominated with maximum tides of up to ~ 4.4 m (Arribas et al. 2010). The Anllóns Estuary contains a typical range of estuarine sedimentary environments from

Table 1. Chloride and sodium concentrations and $\delta^2\text{H}$ and $\delta^{18}\text{O}$ data for the end member seawater and river water and the three estuary sites (Fig. 1).

Site	Cl^- (mg/L^{-1})	Na^+ (mg/L^{-1})	$\delta^2\text{H}$ (‰) V-SMOW	$\delta^{18}\text{O}$ (‰) V-SMOW	
Sea Water	12464	7926	5.9	0.2	
	8960	6009	4.8	0	
	11237	6417	9.7	1.4	
	6041	4049	1.7	-0.1	
	6891	4849	5.4	0.2	
	7131	4564	5.4	0	
	11245	6833	6.5	0.9	
	River Water	16	9	-28.3	-5.6
14		10	-29.4	-5.6	
24		12	-28.2	-5.1	
21		11	-27.5	-5.5	
27		15	-30.7	-5.5	
24		14	-29.6	-5.3	
37		27	-28.7	-5.3	
28		16	-29.8	-5.3	
25		15	-29.4	-5.4	
24		14	-30.1	-5.4	
Lower Estuary		17016	9214	4.9	0.1
		8102	4859	-10.1	-2.3
		3821	2110	-9.6	-2.5
		495	661	-11.4	-3
	413	608	-14.5	-3.4	
	2698	1615	-9.5	-2.5	
	2410	1696	1.6	-0.4	
	11299	7020	9.8	0.5	
	11215	6918	8.2	0.5	
	13212	8069	9.9	0.5	
	12722	7702	6.9	0.1	
	5664	3944	5.1	-0.1	
	6313	4218	-2.1	-1.2	
	4769	3342	-6.6	-2.1	
	14538	9123	7.5	0.2	
	4171	2935	8.7	0.5	
	5213	3797	5.2	-0.1	
	7839	5160	6.5	0.3	
Mid Estuary	14182	8213	-3.2	-1	
	14078	8139	-0.8	-0.5	
	2170	1196	-19.5	-4.3	
	1353	801	-22.1	-4.6	
	1061	606	-21.4	-4.7	
	638	395	-20.5	-4.4	
	969	581	-20.8	-4.8	
	1210	862	-16.1	-3.8	
	3138	2607	-3.2	-1.8	
	1580	1323	-11.5	-2.9	
	1087	912	-11	-2.9	

Table 1. Continued

Site	Cl^- (mg/L^{-1})	Na^+ (mg/L^{-1})	$\delta^2\text{H}$ (‰) V-SMOW	$\delta^{18}\text{O}$ (‰) V-SMOW
Upper Estuary	430	438	-19.3	-4.2
	1658	1403	-15.7	-3.2
	10037	5717	0.4	-0.8
	3406	2847	-4.5	-1.2
	717	420	-28.4	-5.3
	446	245	-30.5	-5.8
	455	253	-26.9	-5.2
	366	227	-27.1	-5.1
	360	223	-27.7	-5.4
	261	164	-26.5	-5.3
	109	85	-28	-5.4
	235	150	-27.9	-5.5
	544	307	-27.6	-5.4
	423	272	-25.2	-4.9
	683	422	-28.1	-5.3
	830	496	-26.7	-5.1
	673	476	-24.9	-4.8
	1031	623	-25.4	-5.1
802	498	-25.9	-5.2	
346	220	-27.5	-5.4	
418	366	-23.6	-4.7	
674	441	-26.6	-5	
519	324	-25.4	-5.1	
1083	717	-22.5	-4.7	

sand flats to mud flats, detached and attached bars and flood plains and has a spit and dune system protecting the estuary from the open sea (Fig. 1a). The Anllóns Estuary has a warm, temperate climate with the winter and summer average temperatures of 9°C and 20°C, respectively (Devesa-Rey et al. 2010). The region around the estuary has annual rainfall averaging 1200mm, predominately falling in the autumn and winter months (Lorenzo et al. 2008; Devesa-Rey et al. 2010).

Methods

Lower, mid- and upper estuarine waters were collected at static locations through complete tidal cycles on three consecutive days in April 2010 (Fig. 1a). Local marine and fluvial water samples were also collected on each day. Waters were collected to determine variations in salinity, chloride and sodium concentrations plus oxygen and hydrogen isotopes. Approximately five liters of each sample were collected by wading into the water. All samples were filtered using Whatman 0.2 μm cellulose nitrate filter papers within one hour of sampling and 500mL aliquots of untreated filtered water were stored in Nalgene LDPE sample bottles. Another 500mL aliquot of filtered water was acidified using ultrapure

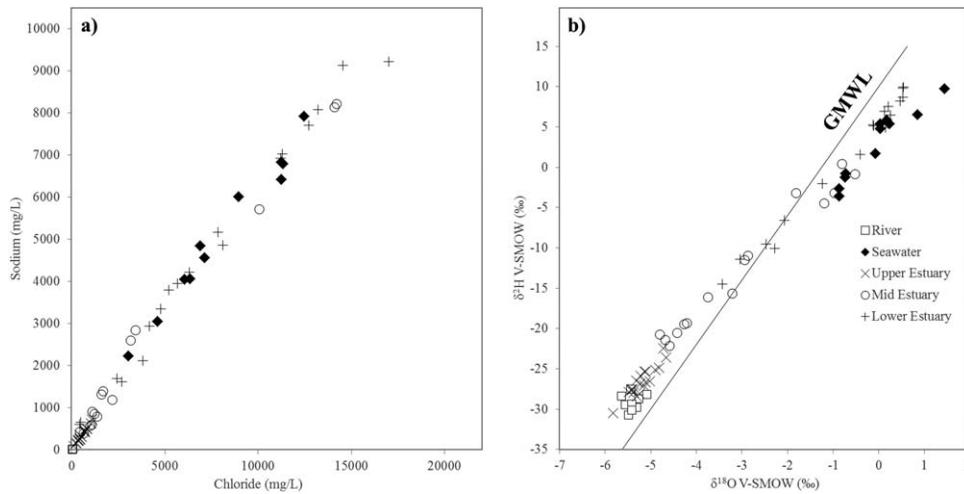


Fig. 2. Apparently conservative trends displayed in the Anllóns estuary waters. When cross-plotted, it appears that chloride and sodium behave conservatively to one another during mixing as a straight line emerges (Fig. 2a). It appears that $\delta^2\text{H}$ and $\delta^{18}\text{O}$ behave conservatively to each other in the Anllóns waters (Fig. 2b). Note that some in-estuary waters have higher chloride and sodium concentrations than the local seawater. Note also that some in-estuary waters are enriched in $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values compared to the local seawater.

15% HNO_3 and stored in a Nalgene vessel. All bottles were filled to overflowing and sealed tight, to prevent air ingress or evaporation, and then stored in cooled, opaque containers until return to Liverpool where samples were then frozen for preservation, as suggested by Kendall and McDonnell (1998). Water samples were fully thawed prior to subsampling for analysis. The estimated air temperature on each day of sampling ranged from 22 °C to 23 °C (WeatherSpark Beta a 2014) and samples were collected during the wet season (WeatherSpark Beta b 2014).

Potentiometric chloride titrations were performed at Liverpool University using a Metrohm 848 Titrino Plus with a 20 mL exchange unit. Waters with expected chloride concentrations up to 1000 mg/L were titrated against 0.01 M AgNO_3 solution while waters with expected chloride concentrations greater than 1000 mg/L were titrated against 0.1 M AgNO_3 . The uncertainty is $\pm 2\%$ for all potentiometric titrations at 95% confidence. ICP-AES was used to determine concentrations of sodium, using a Perkin Elmer DV4300, at Expro ADS, Southampton. Samples were diluted in a solution of 0.2 mM HNO_3 and 0.2 mL of 1000 mM Co solution was added as an internal standard. The relative error for sodium in this technique is $\pm 3\%$. O and H isotope ratios of the waters were measured on a Delta V Plus (Thermo Fisher Scientific) mass spectrometer equipped with a Gas Bench II water equilibration device at the SUERC facility. To equilibrate, all exainers were purged with a flush gas to remove atmospheric gases from between the sample and the lid, prior to analysis. The flush gas used for $\delta^2\text{H}$ equilibration was a mixture of 2% H_2 in He. A platinum rod was added to both speed up the reaction and to insure the procedure gen-

erates usable $\delta^2\text{H}$ numbers within a workable timeframe. The flush gas used for $\delta^{18}\text{O}$ equilibrium was a mixture of 0.5% CO_2 in He which removes any remaining 2% H_2 in He gas and leaves the atmosphere rich in CO_2 . Isotopic measurements were run in triplicate with a standard error of $\pm 2\%$ V-SMOW for $\delta^2\text{H}$ and $\pm 0.5\%$ V-SMOW for $\delta^{18}\text{O}$, based on repeat analyses of standards and natural samples. All isotopic data are presented as per mil (‰) variations relative to the V-SMOW standard.

A geochemical model was derived to assess the role, and quantify the amount, of evaporation in the Anllóns estuarine waters. Isotopic fractionation data from controlled experiments (Cappa et al. 2003), along with the Rayleigh distillation equation (Dansgaard 1964), were used to develop this model.

Results

All of the analytical results are presented in Table 1. Sodium and chloride concentrations in the local seawater reach maximum values of 7926 mg/L and 12,464 mg/L, respectively. In the river water sodium and chloride have maximum concentrations of 27 mg/L and 37 mg/L. In the estuary, chloride concentrations range from 109 mg/L (upper estuary) to 17,016 mg/L (lower estuary), and sodium concentrations range from 85 mg/L to 9214 mg/L.

Chloride is typically assumed to be geochemically conservative as it is not involved in common silicate, carbonate, sulfide, or sulfate mineral dissolution or precipitation reactions (Berner and Berner 2012). In this system, sodium also seems to be conservative as it significantly correlates with

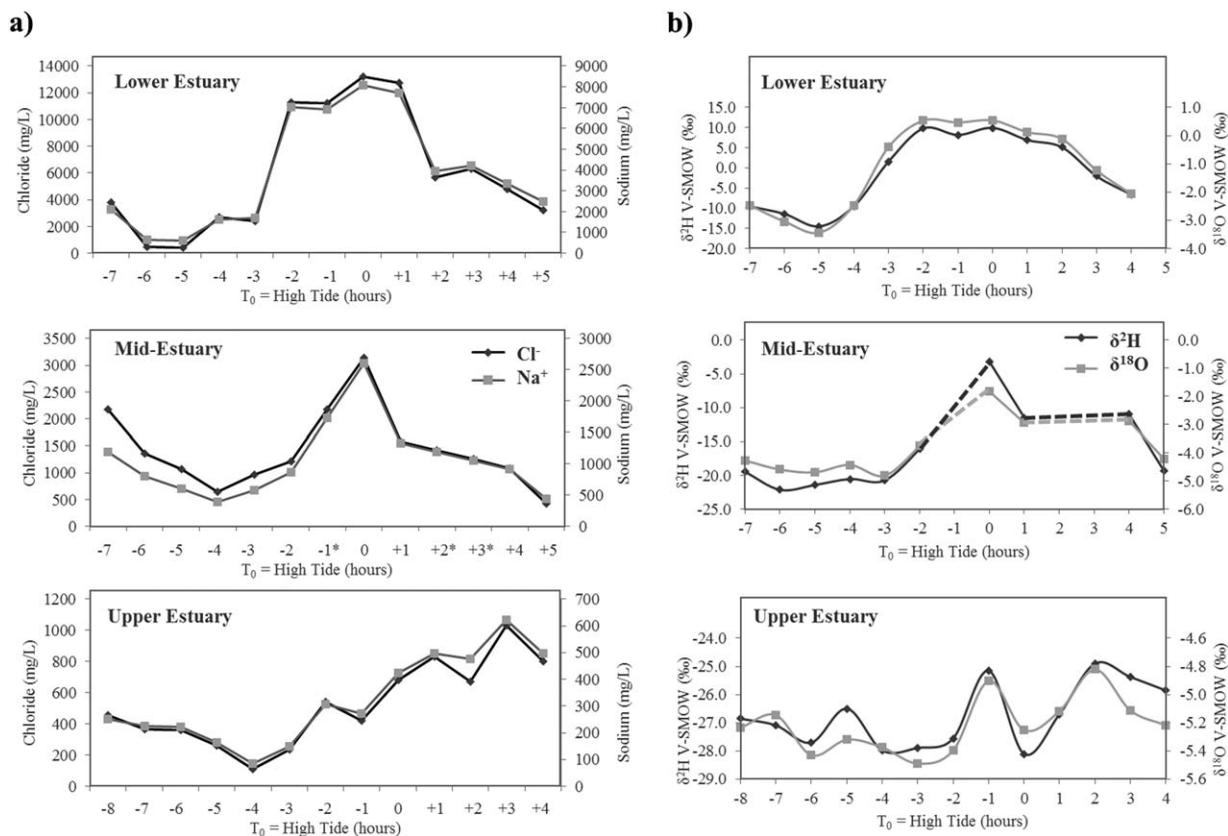


Fig. 3. Tidal cycle time series of chloride, sodium, $\delta^2\text{H}$ and $\delta^{18}\text{O}$. Sampling sites marked on Fig. 1a (U-E, M-E, and L-E), were sampled on different days. Sites were sampled hourly for 13 h through entire tide cycles. High tide marked is noted by T_0 on each day. In each site, it is clear that chloride and sodium concentrations trend similarly, i.e., apparently behaving in a conservative manner. The most saline concentrations are observed in the Lower-Estuary and at high tide. $\delta^2\text{H}$ and $\delta^{18}\text{O}$ compositions also trend similarly to one another through each tidal cycle. Dashed lines in the Mid-Estuary samples were inserted to emphasize the time series. This indicates that although the waters have mixed throughout the tidal cycle, mixing has not resulted in preferential fractionation of one isotopic composition with regards to the other, i.e., $\delta^2\text{H}$ and $\delta^{18}\text{O}$ appear to behave conservatively.

chloride (Fig. 2a). Although chloride and sodium are geochemically conservative, it is notable that lower estuary waters contain enriched concentrations of both ions in Fig. 2a compared to the local seawater end-member. At high tide in the lower estuary, concentrations of both chloride and sodium in the estuary exceed the local seawater end-member concentrations (12,464 mg/L and 7926 mg/L respectively; Fig. 3a; Table 1).

Seawater $\delta^2\text{H}$ is between 1.7‰ and 9.7‰ and $\delta^{18}\text{O}$ ranges from -0.1‰ to 1.4‰. River water $\delta^2\text{H}$ ranges from -30.7‰ to -28.2‰ and $\delta^{18}\text{O}$ ranges from -5.6‰ to -5.1‰. In the estuary, $\delta^2\text{H}$ ranges from -30.5‰ (upper estuary) to 9.9‰ (lower estuary). Also in the estuary, $\delta^{18}\text{O}$ ranges from -5.8‰ (upper estuary) to 0.5‰ (lower estuary). $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values from the waters collected from the Anllóns Estuary form a linear array with a slope less than the global meteoric water line (Fig. 2b). Although there are significant differences in both $\delta^2\text{H}$ and $\delta^{18}\text{O}$ through time (Fig. 3b), they have a positive correlation (Fig. 2b). The waters collected in the lower

estuary have maximum isotopic compositions that are broadly similar to those of the local seawater (Fig. 2b).

Discussion

Comparing chloride concentration and stable isotope ratios

To determine whether $\delta^2\text{H}$ and $\delta^{18}\text{O}$ behave conservatively, the isotopic ratios of the estuary waters were plotted against geochemically conservative chloride. It is highly significant that neither $\delta^2\text{H}$ nor $\delta^{18}\text{O}$ demonstrate conservative behaviour relative to chloride (Fig. 4a,b) as there is an overall curved (convex) trend instead of a straight line for both isotopes vs. chloride. This convex trend suggests that the isotopic ratios are more enriched than they should be compared to the corresponding geochemically conservative chloride concentration in each sample (Berner and Berner 2012). Note that there is no evidence for a discrete third

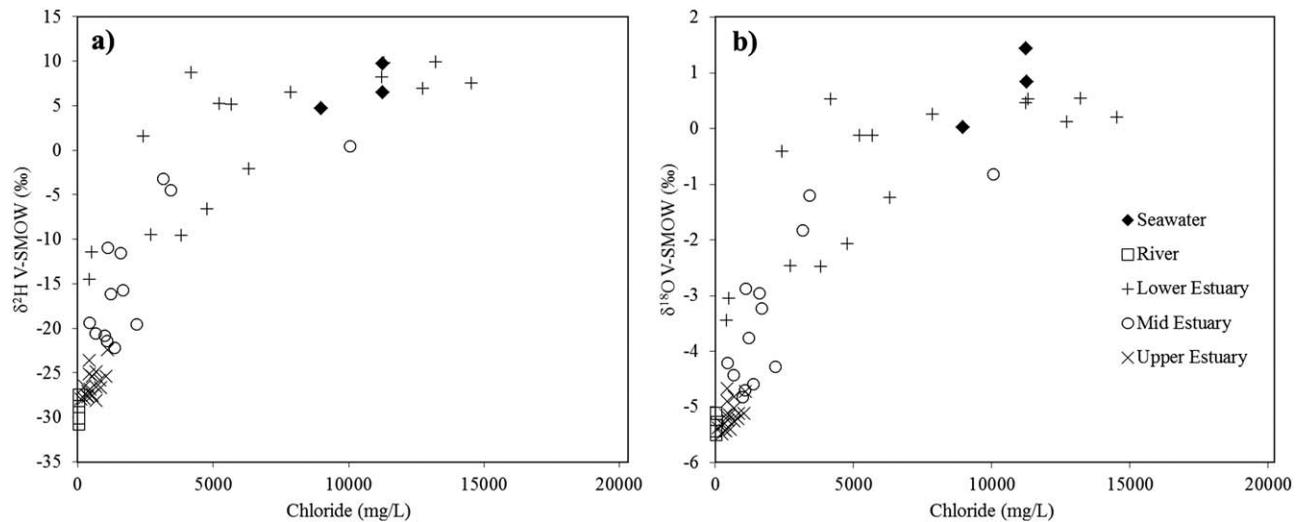


Fig. 4. Cross-plots of (a) hydrogen and (b) oxygen isotopes vs. chloride for the waters in the estuary revealing a non-conservative trend. A positive, or convex upward, trend is observed when the stable isotope compositions of each water sample are cross-plotted against the corresponding chloride composition. This suggests that the $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values are greater than would be expected if they behaved conservatively relative to chloride. As chloride is geochemically conservative, isotopic fractionation must be responsible for the deviation from a simple mixing trend.

end-member component based on the sodium and chloride relationships or the $\delta^{18}\text{O}$ and $\delta^2\text{H}$ relationships.

Cause of the elevated chloride concentration and anomalous stable isotope ratios

The enriched $\delta^{18}\text{O}$ and $\delta^2\text{H}$ isotopic ratios that would be expected for simple physical mixing, based on chloride concentrations from the estuary (Fig. 4a,b), suggests that isotopic fractionation has occurred. The fractionation process responsible for this offset has affected both the hydrogen and oxygen isotopes, more or less equally given the correlation apparent in Fig. 2b, suggesting that mineral dissolution or precipitation processes (e.g., growth or dissolution of small amounts of carbonate or other oxygen-rich and hydrogen-free minerals) cannot be the cause. Furthermore, the higher maximum chloride and sodium concentrations in the Anllóns Estuary than in the local seawater (by close to 40%) must also be accounted for (Fig. 2a). The only plausible explanation is localised evaporation within the estuary basin. As the estuary water is very far from halite saturation, loss of molecular H_2O by evaporation would linearly increase chloride and sodium concentrations with no deviation from an extrapolation of the straight line describing the mixture between seawater and river water.

It is noteworthy that in an estuary where the river water was more saline than seawater (due to evaporation in the warm arid environment of continental Australia), a nonlinear trend of salinity and $\delta^{18}\text{O}$ was reported by Corlis et al. (2003). Significantly, this phenomenon was interpreted by these authors to be a result of local evaporation causing isotopic enrichment.

Evaporation model

We have used fractionation data from Cappa et al. (2003) to simulate the effect of progressive evaporation on the oxygen and hydrogen isotopes of Anllóns Estuary waters. The work of Cappa et al. (2003) was utilised in this study because they presented the experimental derivation of the effective fractionation factor (α^{eff}) for waters as a function of varying humidity. Isotopes will fractionate due to variations in temperature (Faure 1986) as well as humidity (Price et al. 2012) and it is important to consider both of these when deriving a fractionation model. We derived a continuously varying fractionation factor as a function of the degree of evaporation by fitting lines through the experimental data reported by Cappa et al. (2003). The published experiments were performed at 20°C , which is suitable since this is close to the mean temperature for the Anllóns estuary during the sampling period (WeatherSpark Beta 2014). We have used the experimental fractionation factor data from the 20% humidity experiment:

$$\alpha^{18}\text{O} = -0.0184.f + 0.9999 \quad (1)$$

$$\alpha^2\text{H} = -0.0811.f + 0.9936 \quad (2)$$

where f is the fraction of the original water remaining after evaporation and $\alpha^{18}\text{O}$ and $\alpha^2\text{H}$ are the evaporative fractionation factors for oxygen and hydrogen. Equations 1 and 2 are the line equations derived by cross plotting the fraction of sample removed against the experimental values for α^{eff} for each of $\delta^2\text{H}$ and $\delta^{18}\text{O}$ reported by Cappa et al. (2003). The evolving chloride concentration (Cl^{e}) was derived using the following:

Table 2. Values used to represent physical mixtures of river water and ocean water that were subject to evaporation using Eq. 4 with input from either Eq. 1 or 2 (for oxygen and hydrogen isotopes)

Nominal estuary site	Chloride (mg/L ¹)	$\delta^2\text{H}$ (‰) V-SMOW	$\delta^{18}\text{O}$ (‰) V-SMOW
River	20	-30.5	-5.6
Upper	100	-30.3	-5.6
Upper-Mid	1000	-28.7	-5.3
Mid	5000	-21.4	-4.1
Mid-Lower	10000	-12.3	-2.7
Lower	15000	-3.1	-1.2

$$\text{Cl}^e = \text{Cl}^o / f \tag{3}$$

where Cl^o is the initial chloride concentration of the physical mixture of river water and seawater and f is the fraction of water remaining after evaporation. In this model, we started with simple physical mixtures of river water and seawater and calculated the initial chloride concentrations and corresponding $\delta^2\text{H}$ and $\delta^{18}\text{O}$ signatures of a range of river water-seawater mixtures in an estuary. We used the lowest salinity river water compositions from this dataset to represent the river water end-member. This river water sample had 16 mg/L chloride and $\delta^2\text{H}$ and $\delta^{18}\text{O}$ ratios of -30.5‰

and -5.6‰ respectively. The seawater components used in this model for chloride, $\delta^2\text{H}$ and $\delta^{18}\text{O}$ were 19,400 mg/L, 10.0‰ and 0.0‰, respectively which are the typical of open marine conditions (Berner and Berner 2012). The river water was physically mixed with water with fixed amounts of higher chloride concentration seawater with correspondingly elevated $\delta^2\text{H}$ and $\delta^{18}\text{O}$ signatures. We thus derived a range of $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values for estuary waters with a range of initial (pre-evaporation) chloride concentrations (Table 2).

Evaporation of the five simulated, physically mixed, estuary waters (river water end-member, upper estuary, mid-estuary, lower estuary and seawater end-member; Table 2) was then modeled using a Rayleigh distillation equation:

$$R_w/R_{wo} = f^{(\alpha-1)} \tag{4}$$

where R_w is the isotopic ratio of the resulting water; R_{wo} is the initial isotopic ratio of the water; f is the fraction of water remaining and α is the fractionation factor derived using Eqs. 1 and 2 (Dansgaard 1964). Evaporation was modeled in 5% increments (Fig. 5a,b). The output from our model shows that evaporation leads to different behaviour for the isotopes than the dissolved (conservative) ions. While evaporation simply concentrates the dissolved load, the isotopes of oxygen and hydrogen undergo differential evaporation (^{16}O and ^1H undergo evaporation preferentially to ^{18}O and ^2H). The result is an array of remaining-water $\delta^2\text{H}$ and

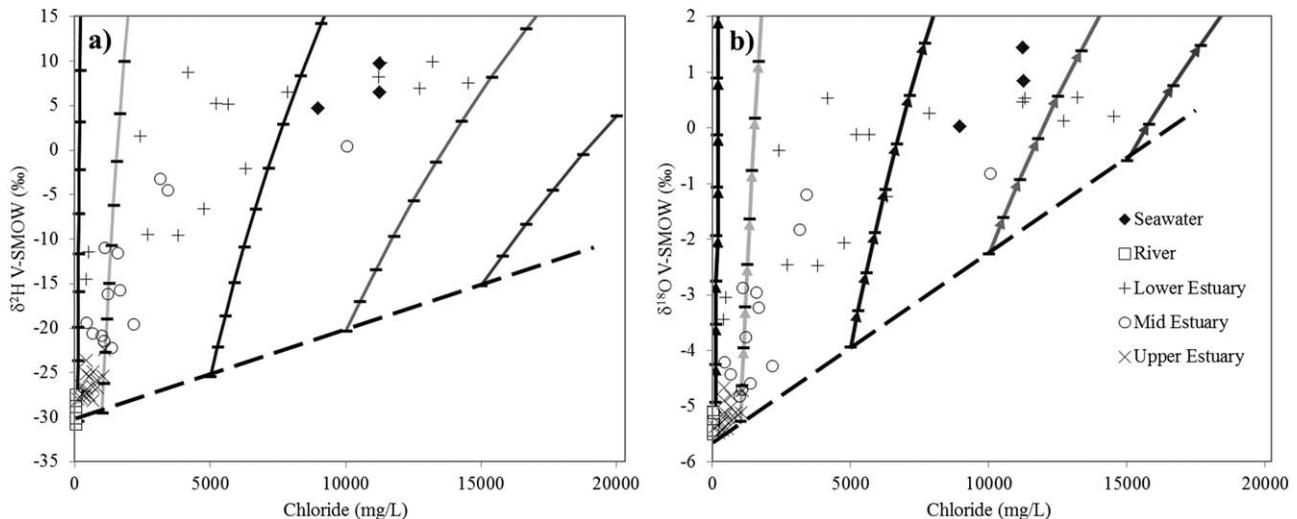


Fig. 5. Models of the effects of evaporation on in-estuary isotopic compositions. A simple evaporation model was derived using fractionation coefficient data from Cappa et al. (2003) where both temperature and humidity were considered. Then model was run starting with hypothetical chloride concentrations and isotope ratios (Table 2) derived from various proportions of river water and oceanic water. The initial hypothetical waters were then evaporated in 5% increments (as defined by increasing chloride concentration) and the effect on the stable isotopes derived. The model indicates that evaporation causes both $\delta^2\text{H}$ and $\delta^{18}\text{O}$ to track off (up) from the simple physical mixing trend (dashed lines on each plot), with a more developed curve in the isotopically enriched starting compositions. When the Anllóns Estuary geochemical data are superimposed on the fractionation model, the pattern suggests that up to 40% evaporation has occurred. Most of this extensive evaporation has occurred in the waters in the mid to lower estuary.

$\delta^{18}\text{O}$ trajectories that deviate strongly (upward) from the theoretical simple mixing line (Fig. 5a,b).

$\delta^2\text{H}$, $\delta^{18}\text{O}$ and chloride concentration values from the estuary waters have been superimposed on the modeled evaporation trajectories (Fig. 5a,b). The concurrence of the model and the analytical data suggests that evaporation can adequately explain the deviation of the chloride and stable isotope data from a simple mixing line. Evaporation changes chloride and sodium equally so the effects of evaporation are effectively invisible in Fig. 2 for the vast majority of the samples. The estuary water samples with unexpectedly higher salinity than the local seawater can be explained by in-estuary evaporation. Evaporation shifts both $\delta^2\text{H}$ and $\delta^{18}\text{O}$ ratios to higher values.

The modeled effects of evaporation on the $\delta^2\text{H}$ and $\delta^{18}\text{O}$ ratios of physically mixed river-water and seawater, shown in Fig. 5a,b, have been cross plotted to assess how the effects of evaporation would manifest on a diagram of $\delta^2\text{H}$ vs. $\delta^{18}\text{O}$. The resulting modeled output lies on a straight line because we started with simple physical mixtures and evaporation seems to have affected the $\delta^2\text{H}$ vs. $\delta^{18}\text{O}$ equally and in parallel to physical mixing. The modeled $\delta^2\text{H}$ and $\delta^{18}\text{O}$ ratios fall close the GMWL but have a slightly shallower slope; the modeled data and the GMWL intersect at a $\delta^{18}\text{O}$ value of about -3‰ . Note that the modeled simulation of the effects of in-estuary evaporation, on $\delta^2\text{H}$ and $\delta^{18}\text{O}$ ratios, has the same slope as the real values reported from the estuary; these also intersect the GMWL at about -3‰ (Fig. 2b). This concurrence (Figs. 2b, 6) supports the interpretation of the occurrence of extensive evaporation and explains why evaporation was not detected when looking at the stable isotope data on their own.

The modeled evaporation trajectories can be used to estimate the amount of evaporation that has occurred for a specific Anllóns estuary sample by comparing all data to the 5% increments in Fig. 5a,b. From this model, it can be concluded that water in the Anllóns Estuary has been evaporated by up to 40% (Fig. 5a,b). Note that this cannot necessarily be detected when looking at either the composition data in isolation, or at the isotope data in isolation. However, it is likely that the majority of estuary waters are evaporated to some degree as most water samples deviate from the simple mixing lines in Fig. 5a,b.

In apparent contrast to the interpretation of significant amounts of evaporation in the Anllóns estuary, the waters collected from the estuaries studied by Martin and Letolle (1979) and Zhang et al. (1990) showed conservative behaviour. However, for these studies, samples were collected from the thalweg of the estuary and relatively far down the estuary system toward the open sea. Interestingly, it was speculated that a nonconservative trend of $\delta^{18}\text{O}$ vs. chlorinity may be observed if the residence time of the water is prolonged (Zhang et al. 1990). In contrast to Zhang et al. (1990), our Anllóns samples were collected from throughout the estuary and away from the main channel. The mixing of

chloride and sodium in our estuary samples appears to be conservative (Fig. 2a); the mixing of $\delta^2\text{H}$ and $\delta^{18}\text{O}$ in our estuary also appear to be conservative (Fig. 2b), yet when $\delta^2\text{H}$ and $\delta^{18}\text{O}$ ratios are cross-plotted with chloride concentrations, it is evident that nonconservative processes have occurred (Figs. 4, 5). It is thus important to compare stable isotopes to conservative dissolved species (chloride preferably) to enable the nonconservative process of evaporation to be detected.

Considerations must therefore be made for the site at which samples are collected as well as the flushing rate at the time of sample collection. Evaporation takes place across the estuary in shallow tidal pools and from water-saturated sediment at low tide. The rising tide would simply pick up and dilute the evaporatively concentrated water with its altered chloride concentration and isotopic signatures. It is interesting to consider whether the evaporatively concentrated water could be considered to be a third end-member in the Anllóns Estuary system. This might be plausible if there were one set of compositional and isotopic characteristics of the evaporatively concentrated water but, as Fig. 5a,b illustrate, there is a rather wide range of compositions and isotope ratios depending on the initial proportions of the physically mixed seawater and river water and the extent of evaporation. While it is certain that there has been back-mixing of the evaporatively concentrated water and the physically mixed seawater and river water it is not possible to deduce the amount of the evaporatively concentrated water as it can have such a wide range of compositions and isotope ratios.

Conclusions

Comparison of chloride concentrations with $\delta^2\text{H}$ and $\delta^{18}\text{O}$ ratios in the Anllóns Estuary, NW Spain, suggest that these estuarine waters are not just simple physical mixtures between river water and seawater in contrast to other interpretations of estuary waters (e.g., Liss 1976; Martin and Letolle 1979; Eisma 1986, 1988; Zhang et al. 1990). Instead the Anllóns Estuary has undergone up to about 40% evaporation explaining why some of the estuary waters have higher chloride concentrations than seawater and the $\delta^2\text{H}$ and $\delta^{18}\text{O}$ ratios are more enriched than would be expected from their chloride concentrations. Evaporative fractionation of in-estuary waters during mixing could easily go unnoticed if ionic concentrations and stable isotope ratios are studied separately. Evaporation of up to 40% will affect all dissolved species, not just chloride and sodium, and this may have implications for environmental, ecological and mineralogical processes in the estuary.

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Acknowledgments

James Utley, Patrick Dowey and Ehsan Daneshvar are thanked for their assistance in sample collection. Reviewers Ray Burgess and anonymous are thanked for their constructive and helpful suggestions that led to a significantly improved manuscript. We would like to thank the sponsors of the BASIC Consortium (also known as the Chlorite Consortium) at the University of Liverpool: (BP, Chevron, ConocoPhillips, ENI, ExxonMobil, Petrobras, Shell, Statoil). Mark Andrew (Expro ADS) is thanked for his advice for water analysis. Stable isotope analyses and training were supported by a Natural Environment Research Council Facility grant to RHW (IP-1242-0511). David Hodgson, Jim Marshall, Andy Thomas, Leta Smith, Rosario Scheerhorn, Pascal Salaün and Simon Poulton are thanked for helpful discussions and advice.

Submitted 3 September 2014

Revised 8 March 2015

Accepted 12 March 2015

Associate editor: Dr. H. Maurice Valett