Inorganic carbon distribution and CO$_2$ fluxes in a large European estuary (Tagus, Portugal)

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Ten field cruises were carried out in Tagus estuary from 1999 to 2007 to study the dynamics of the inorganic carbon system. Dissolved inorganic carbon (DIC) and total alkalinity (TA) increased with salinity. DIC and TA were generally conservative in the estuarine mixing zone (salinity > 10), while a complex distribution pattern was observed at the upper estuary. DIC values peaked 1786.9 ± 155.8 µmol kg$^{-1}$ at that segment. Estimated annual mean fluxes of DIC were 0.27 Tg C yr$^{-1}$ from the river to the estuary, and 0.37 Tg C yr$^{-1}$ from here to the coastal area. The Tagus estuary was always CO$_2$ supersaturated, with partial pressure of CO$_2$ (pCO$_2$) reaching 9160 µatm in the upper estuary. An average emission of 0.11 Tg C yr$^{-1}$ was estimated from the estuary to the atmosphere, corresponding to 23% of exported DIC. Only 8% of the riverine DIC was ventilated. The non-conservative behaviour of CO$_2$ parameters in the estuary segment under freshwater influence was attributed to alternations in the relevance of riverine/terrestrial runoff, photosynthesis, aerobic respiration, organic matter mineralization and CaCO$_3$ precipitation/dissolution.

Estuaries rank among the most productive and dynamic aquatic ecosystems$^1$. They are frequently characterized by strong physical–chemical gradients, enhanced biological activity and intense sediment dynamics. Nowadays it is unequivocally accepted that inner estuaries act as sources of CO$_2$ to the atmosphere. A recent study$^2$ reports that estuaries emit 20.8 mol C m$^{-2}$ yr$^{-1}$ to the atmosphere, mainly due to their heterotrophic metabolic status, sustained by terrestrial/riverine organic carbon inputs, and also by waste water in populated areas. A fraction of this carbon is exported to the nearby coastal areas mostly as organic particles, but also to the atmosphere in the form of CO$_2$ emissions. Hence, inner estuaries are effective sieves for terrestrial/riverine inputs and provide a by-pass of carbon towards the atmosphere$^3$.

The flux and/or residence of carbon in each of these compartments depend on the characteristics of the estuary, as well as on the season, and even time of day. For example, approximately 60% of the respiratory CO$_2$ in Scheldt estuary is released to the atmosphere, 26% transferred to the sediment, and only 14% remains in the water column$^1$. Moreover, spatial variability plays an important role due to the hydrodynamic and geomorphological complexity of these littoral zones. Thus, fluxes, sources and mechanisms of CO$_2$ transport and transformation are among the most important current issues in marine and freshwater geochemistry.

A compilation$^4$ of available data on water-air CO$_2$ fluxes in inner estuaries shows that the west European inner estuaries have been extensively studied, accounting for 47% of the total results presented. So far, inter-annual and decadal variability of water-air CO$_2$ fluxes is still undocumented in some estuarine environments. Few studies have been undertaken involving CO$_2$ fluxes variability in Portugal, a country at the eastern boundary of the Subtropical North Atlantic. Data of water-air CO$_2$ fluxes are available for just three Portuguese estuarine systems: the Aveiro coastal Lagoon, the Douro and Sado estuaries$^5$. The Douro, Tagus and Sado inner estuaries and their adjacent coastal waters behave as sources of CO$_2$ to the atmosphere$^5$, with fluxes ranging from 31 to 76 mol C m$^{-2}$ d$^{-1}$, which corresponds to an additional source of 0.1% to the CO$_2$ emissions by the near-shore ecosystems$^8$. However, the estuarine inorganic carbon dynamics has never been assessed.

This paper intends to partially fulfil this gap by focusing on the CO$_2$ dynamics along Tagus estuary (Fig. 1), Portugal, one of the largest western European estuaries in surface area. Spatial and temporal CO$_2$ variability is addressed in this estuary based on information obtained from 10 surveys carried out from 1999 to 2007. This...
work also intends to identify and study the dominant factors/mechanisms influencing the inorganic carbon system. In addition, some estimates are advanced on the water-air CO₂ fluxes over the estuary.

Results

General water properties. The range of values for physical, chemical and biological variables from 1999 to 2007 is shown in Table 1. Overall, salinity increased downstream (Fig. 2A) with lower values in winter/autumn (Fig. 3A). The environmental conditions in the estuary end-members indicate that salinity kept reasonably stable at the marine influenced area in most samples (Table 1), the exception being winter seasons and May 2000. In March 2001 the river discharge peaked 1861 m³ s⁻¹ and salinity did not exceed 12.5 in the estuary. A decrease in temperature from the upper to the lower estuary was observed during spring and summer (Fig. 2B). This was in contrast with winter and autumn, when an increase down the estuary was seen (Fig. 2C). While the amplitude of temperature was 12 °C in the river end-member, only 5 °C amplitude was recorded at the marine influenced area.

Due to hydrodynamic conditions imposed by the tidal regime (tidal amplitude of 1.5 to 4.0 m) and the water discharges (Tagus discharges from 33 to 1861 m³ s⁻¹; Table 1), significant amounts of suspended matter spread all over the estuary (Fig. 2D). In general the amount of SPM in the estuary was low to moderate, rarely exceeding 80 mg l⁻¹ (Fig. 2D; Table 1).

Concerning oxygenation conditions, Tagus waters were always well oxygenated, in general displaying saturation levels above 70% (Table 1), with an increase from winter to spring/summer (Fig. 3B). Concentration of phytoplankton biomass (Chl a) reached a maximum of 73.4 mg m⁻³ in May 2006, and hardly attained 3 mg m⁻³ (Fig. 3C; Table 1) in the rest of the periods (winter/autumn). An increase of Chl a towards the fluvial section was generally observed.

Variations of inorganic carbon system parameters. pH values in the marine section were rather constant (amplitude 0.21; Fig. 4A), while the riverine end-member pH varied significantly (amplitude 1.10; Fig. 4A). Seasonally, pH showed scattered patterns and variations were not the same for all sampling periods (Fig. 5A): in autumn/winter more acidic features were noticed upstream (7.13–7.68) and increased downstream (7.83–8.03); in spring/summer, most of the time, more basic values were present upstream than downstream.

TA and DIC values were always lower in the riverine section than in the marine area, ranging between 977 μmol kg⁻¹ in winter and 2587 μmol kg⁻¹ in summer. These parameters displayed less irregular values in the marine influenced area and varied, respectively, from 1469 μmol kg⁻¹ in winter to 2885 μmol kg⁻¹ in summer (Fig. 4B,C). A negative correlation was found between riverine TA and average freshwater discharges (r² = 0.482, p < 0.05). TA and DIC increased from winter to spring/summer (Fig. 3E,F), with values varying from 1401 to
Table 1. Range of physical-chemical and biological properties of surface waters in Tagus estuary for each sampling date. Freshwater flow (Q), salinity (S), temperature (T), suspended particulate matter (SPM), chlorophyll a (Chl a), dissolved oxygen (DO), total alkalinity (TA), dissolved inorganic carbon (DIC) and CO₂ partial pressure (pCO₂). aTagus river flow, taken from Almourol station (the most downstream hydrological station, ~85 km upstream the estuary mouth). On-the-spot water discharge data was not available. Values were obtained from the Portuguese Environment Agency (APA, I.P .) accessed in a public database (http://snirh.apambiente.pt/) bUpwelling was present at the adjacent coastal shelf.

| Season         | Sampling dates | Q (m³ s⁻¹) | S          | T (°C)   | SPM (mg L⁻¹) | Chl a (mg m⁻³) | DO (%) | pH   | TA (µmol kg⁻¹) | DIC (µmol kg⁻¹) | pCO₂ (µatm) |
|----------------|----------------|------------|------------|----------|--------------|----------------|--------|------|---------------|----------------|-------------|
| Summer         | September 1999 | 33         | 4.66–36.00 | 14.1–22.0 | 16.4–39.6    | 1.5–14.4        | 79–106 | 7.23–7.91 | 2307–3381    | 2409–3323 | 922–4575    |
| Spring         | May 2000       | 376        | 0.17–26.96 | 17.8–20.8 | 6.1–71.3     | 1.0–13.5        | 82–103 | 7.82–7.88 | 1401–3535    | 1421–3455 | 906–1592    |
| Winter         | March 2001     | 1861       | 0.09–12.50 | 13.0–14.6 | 19.6–164.7   | 0.7–3.1         | 66–104 | 7.63–7.92 | 977–1834     | 1016–1816 | 873–1998    |
| Summer         | July 2001      | 130        | 0.24–35.10 | 16.1–24.7 | 7.8–42.3     | 3.2–13.0        | 93–126 | 7.91–8.01 | 1918–2827    | 1954–2666 | 714–1326    |
| Summer         | June 2002      | 81         | 0.31–34.27 | 17.7–24.3 | 28.6–135.0   | 1.4–40.1        | 87–104 | 7.70–8.23 | 2573–3330    | 2587–3270 | 1012–2779   |
| Spring         | May 2003       | 233        | 0.20–34.12 | 16.6–23.4 | 5.7–62.0     | 1.6–31.8        | 85–107 | 7.54–7.94 | 1751–2784    | 1875–2672 | 851–3778    |
| Winter         | February 2004  | 264        | 0.18–23.51 | 12.7–15.7 | 11.5–64.5    | 0.2–2.6         | 78–91 | 7.13–8.05 | 1447–2792    | 1476–2639 | 662–9160    |
| Spring         | May 2006       | 125        | 0.58–33.76 | 17.7–21.8 | 37.9–116.3   | 1.0–73.4        | 89–114 | 7.77–8.25 | 1418–3382    | 1422–3145 | 487–2794    |
| Autumn         | November 2006  | 768        | 0.21–32.39 | 17.7–19.0 | 32.3–56.8    | 0.2–1.1         | 72–90 | 7.35–7.90 | 1757–2884    | 1915–2717 | 1058–4552   |
| Spring         | May 2007       | 86         | 9.81–35.23 | 14.8–20.9 | 12.0–45.0    | 1.4–9.4         | 82–101 | 7.89–8.05 | 2371–2528    | 2269–2366 | 1058–4552   |

3535 µmol kg⁻¹ during the productive period and from 977 to 2884 µmol kg⁻¹ during the non-productive period (Table 1).

pCO₂ values were higher in the riverine section, reaching as high as 9160 µatm in February 2004 (Fig. 4D; Table 1), a value ~24 times higher than pCO₂ of atmospheric equilibrium (383.9 µatm). Seasonally average values of pCO₂ remain rather stabilized from winter to spring/summer and increased in autumn (Fig. 3G). Values of pCO₂ dropped rapidly in the upper estuarine zone (Fig. 5D) at salinities below 10. pCO₂ values as high as 9160 µatm (Table 1) were accompanied by low pH (7.13) at salinities below 5. Downstream, pCO₂ in general dropped to values of 620 µatm at the estuary mouth (Fig. 5D).

**CO₂ evasion pattern.** Table 2 shows CO₂ gas transfer velocities at the water-air interface, proposed by different authors and calculated for Tagus estuary, as well as wind speed and tidal current for each season. Daily wind velocity was random and variable, oscillating between 1.7 m s⁻¹ and 3.9 m s⁻¹. The maximum tidal current was lower in summer (58 cm s⁻¹) and reached 122 cm s⁻¹ in autumn depending on the tidal regime, river discharges and bathymetry of the estuary. Two of the algorithms used to estimate gas transfer velocity (k), namely kODIA 7 and kAOD 8, gave the highest values when compared with other algorithms. This was an expected outcome since both approaches are based on the same technique (floating dome) and took into account the water current velocity. The kODIA 7 algorithm led to minimum k values, since it considers water current alone. However, maximum values of k were obtained in spring for all the parameterizations associated with maximum wind speed conditions (Table 2).

When applying a sensitive analysis to the fluxes calculated for each of the various parameterizations, differences emerged varying from 8 to 30%. Hence, in order to minimize any substantial errors in the fluxes estimated due to the use of a single generic relationship, CO₂ fluxes were averaged for the proposed parameterizations (kAOD, kB04, kODIA, kRC01, and kA09). A seasonal pattern of CO₂ fluxes to the atmosphere was revealed in Tagus estuary, values increasing from 80.4 ± 87.7 mmol C m⁻² d⁻¹ in spring to 133.9 ± 89.3 mmol C m⁻² d⁻¹ in autumn (Table 2). Concerning spatial variability, the amplitude of fluxes variability was ~250 mmol C m⁻² d⁻¹ (calculated as the...

![Figure 2. Longitudinal distributions of (A) salinity (S), (B) temperature (T) in spring/summer, (C) temperature (T) in winter/autumn and (D) suspended particulate matter (SPM), during the 10 surveys carried out along Tagus estuary. Riverine end-member: sampling station with lowest salinity; Marine end-member: sampling station nearest the ocean.](image-url)
average of the difference between the least and greatest values observed for each sampling period) for the 10 surveys. Examples of CO\textsubscript{2} fluxes distribution along the estuary in different year seasons (March 2001, July 2001 and May 2006) are shown in Fig. 6.

Overall, Tagus estuary functions as a source of CO\textsubscript{2} to the atmosphere, being estimated an average annual flux of $33.6 \pm 29.7 \text{ mol C m}^{-2} \text{ yr}^{-1}$ and a total CO\textsubscript{2} emission of $0.11 \text{ Tg C yr}^{-1}$.

Figure 3. Box-whisker plot of (A) salinity ($S$), (B) dissolved oxygen (DO), (C) chlorophyll a (Chl a), (D) pH, (E) total alkalinity (TA), (F) dissolved inorganic carbon (DIC) and (G) CO\textsubscript{2} partial pressure ($p_{\text{CO}_2}$) in Tagus estuary during 1999–2007. Median values are represented by line inside boxes, 25th to 75th percentiles are denoted by box edges, 10th to 90th percentiles are depicted by the error bars, and outliers are indicated by circles.
Inorganic carbon balance. The following inorganic carbon fluxes were considered to establish the inorganic carbon balance in Tagus estuary: the riverine DIC input to the estuary, the estuarine DIC output to the adjacent coastal waters and the water-air CO2 flux. Mixing curves of DIC for each sampling period (exception of September 1999 and May 2007) were well reproduced by polynomial equations (Table 3). DIC fluxes and advective export of DIC added during estuarine transport (Internal DIC Flux; Table 3) were estimated10, and the magnitudes and temporal variation of inorganic carbon fluxes examined.

Freshwater end-member DIC concentration (C0; Table 3) did not vary much during all survey periods (1786.9 ± 155.8 μmol kg⁻¹), except during an exceptionally intense river discharge in March 2001, and in June 2002, with low river flow and relatively high photosynthetic activity (Table 1). However, the estimates show that DIC riverine exports to the estuary varied from 16.6 × 10⁶ mol C d⁻¹ (summer 2001) to 179.2 × 10⁶ mol C d⁻¹ (winter 2001) (Table 3), with a mean annual flux of 0.27 Tg C yr⁻¹.

It was observed that during the estuarine transport, generated DIC (C_S - C0) was higher in winter 2001 and lower (sometimes zero) in the other seasons. These internal fluxes ranged from 0 to 167.9 × 10⁶ mol C d⁻¹, being estimated a mean annual internal flux of 0.10 Tg C yr⁻¹ (Table 3). Fluxes from the estuary to the adjacent coastal waters varied from 16.6 × 10⁶ mol C d⁻¹ (in summer 2001) to 347.1 × 10⁶ mol C d⁻¹ (in winter 2001), corresponding to an annual flux of 0.37 Tg C yr⁻¹ (Table 3). Thus, 27% of DIC was generated within the estuary, while the exported DIC to the atmosphere was 0.11 Tg C yr⁻¹, which accounted for approx. 23% of the total DIC exported from the estuary.

Discussion
Tagus waters environmental properties were strongly affected by the river discharge and showed a seasonal variability typical of a mid-latitude system, with most parameter values increasing from winter to spring/summer. Generally, river water carried higher contents of particulate material (Fig. 2D), nutrients (Fig. 7C) and phytoplankton (pers. comm.), than estuarine water. A tendency of a decrease ocean-ward was observed in winter, although high levels of SPM were present during the productive period in the 20–30 salinity range. This predominance of estuarine suspensions in the central/lower estuary can be interpreted as the result of salt marsh particles mixing and/or water circulation in the southern estuary, rather than the occurrence of biogeochemical processes.
SPM values are comparable to values recorded for the Scheldt and the Thames estuaries and much lower (~14 times) than the ones in the highly turbid Gironde

pH values in the marine section were rather constant due to the seawater buffering capacity, while the riverine end-member pH varied largely being such variability attributed to runoff coupled to changes in biological activity. pH seasonal trends can be attributed to more runoff in winter and more intense primary productivity, in particular in spring/summer, upstream. Overall, pH values were higher in spring/summer and lower in autumn/winter (Fig. 3D).

TA and DIC riverine values were similar to those reported for the uppermost sections of other estuaries. TA and DIC plots against salinity (Fig. 5B,C) show values increasing downstream. These trends have also been recorded in other estuaries. The nearly-conservative behaviour can be explained by the counterbalance between sources and consumption of TA and DIC along the salinity gradient. Nevertheless, non-conservative relationships were observed in March 2001 (Fig. 5E,I), June 2002 (Fig. 5F,J), February 2004 (Fig. 5G,K) and May 2006 (Fig. 5H,L).

The Tagus estuary was dominated by supersaturated CO₂ conditions. Observed riverine pCO₂ values (up to 9160 µatm) are similar to other estuaries. The upper Scheldt, for example, revealed values of pCO₂ as high as 9400 µatm and as 15500 µatm. Similar high values are reported for the Saja-Besaya estuary (9728 µatm) at

Figure 5. Mixing curves for (A) pH, (B) total alkalinity (TA), (C) dissolved inorganic carbon (DIC) and (D) CO₂ partial pressure (pCO₂) for all 10 surveys data undertaken in Tagus estuary. TA anomalies in (E) March 2001, (F) June 2002, (G) February 2004 and (H) May 2006. DIC anomalies in (I) March 2001, (J) June 2002, (K) February 2004 and (L) May 2006.
Carbone dissolution as well. In fact, it has been reported the occurrence of dissolution of CaCO3 and consequent
generation of alkalinity in other estuaries, in zones of maximum turbidity, namely in Loire 27 and in the highly
turbid Gironde 31 and Ems32.

Actually, a non-conservative behaviour of TA and DIC in upper estuaries, mostly at salinities below 5, has been
distinguished that other processes are responsible for the inorganic carbon variability in some occasions.

Tem dominated by mixing processes. But comparing the TA/DIC salinity profiles with theoretical mixing lines
drawn between the two end-members, TA/DIC anomalies came out in the upper estuary at salinities below 10. In
March 2001, an exceptional river discharge (1861 m3 s−1; Table 1) occurred, probably not allowing enough

time for biogeochemical reactions to occur in the estuary.29 However, a mechanism involving increase of pCO2
and decrease of pH and DO (Fig. 7A) has been hypothesized to be the aerobic respiration. Such mechanism
would lead, nevertheless, to DIC increase and would have practically no effect on TA. Still, the simultaneous
increase in both parameters (TA and DIC) was observed, pointing to a distinct process responsible for TA pro-
duction, possibly calcium carbonate (CaCO3) dissolution. To assess this possibility, CaCO3 saturation state was

calculated as the ratio kΩCa / (kΩCa + kCalcite) and kΩA / (kΩA + kAragonite) were determined using the thermodynamic
solubility products 29.

Calculations have shown that for this high flow period, the estuary was undersaturated with values of ΩCa and ΩA

typical for calcite and aragonite (respectively ΩCa and ΩA), using the thermodynamic solubility products 29.

As suggested by some authors19,21,23–25, high pCO2 values at riverine waters might be due to organic carbon
mineralization in soils, river waters and sediments. Differences in inorganic carbon variability patterns in the
two end-members indicate, beside the dilution effect, the complexity of interactions between input sources and
processes acting along the estuary. Spatial trends and range of values for this estuary are also similar to those
reported for other estuaries6,5,14,16,19.

Mixing curves are a commonly used approach for the interpretation of source/sink dynamics of estuarine con-
stituents10,13,26. Assuming salinity as a satisfactory mixing indicator, the profiles of water properties as functions
of salinity should be linear, if only mixing processes occur in an estuary. Thus, analysis of correlations between
different parameters was used for identification of other processes in Tagus estuary.

As mentioned above, CO2 parameters behaved conservatively in most of the sampling periods, with the sys-
tem dominated by mixing processes. But comparing the TA/DIC salinity profiles with theoretical mixing lines
drawn between the two end-members, TA/DIC anomalies came out in the upper estuary at salinities below 10. In
June 2002 an anomaly occurred at higher salinities in the middle estuary. Positive anomalies in TA/DIC mixing
curves (TA/DIC concentrations lie above the theoretical mixing line) occurred in March 2001, as well in June
2002 and May 2006, and a negative anomaly occurred in February 2004. Thus, the non-linearity of TA and DIC
distributions indicates that other processes are responsible for the inorganic carbon variability in some occasions.
Actually, a non-conservative behaviour of TA and DIC in upper estuaries, mostly at salinities below 5, has been
referred by some authors27.

In March 2001, an exceptional river discharge (1861 m3 s−1; Table 1) occurred, probably not allowing enough

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duction, possibly calcium carbonate (CaCO3) dissolution. To assess this possibility, CaCO3 saturation state was
calculated for calcite and aragonite (respectively ΩCa and ΩA), using the thermodynamic solubility products29.

Calculations have shown that for this high flow period, the estuary was undersaturated with values of ΩCa and ΩA
varying from 0.01 to 1.02, eventually indicating CaCO3 dissolution. This process has referred to as the generator
of alkalinity in Loire and Godavari estuaries27,30.

In June 2002, a TA/DIC deviation from linearity was noticed in the central part of the estuary, at salinities
approximately 20–30 (Fig. 5F,J). A production of TA of ca. 540 and of ca. 565 µmol kg−1 of DIC was estimated
by comparing the theoretical mixing line to in situ values. The anthropogenic influence of Trancão River (Fig. 1)
in that zone, with high loads of organic carbon and associated mineralization, may explain such increase in TA.
Additionally, the concomitant decrease of pH and DO and increases of pCO2 (Fig. 7C), as well as of SPM and
nitrate, decrease at that respective range of salinities (Fig. 7B), supports the occurrence of organic carbon miner-
alization. The considerable amount of suspended matter attained in that region (Fig. 7C) may have favoured some
carbonate dissolution as well. In fact, it has been reported the occurrence of dissolution of CaCO3 and consequent
generation of alkalinity in other estuaries, in zones of maximum turbidity, namely in Loire27 and in the highly
turbid Gironde1 and Ems31.

A strong decrease of TA/DIC (430 and 640 µmol kg−1, respectively for TA and DIC) was observed during
February 2004 (Fig. 5G,K) in the extremely low range of salinity (from 0 to 1), accompanied by a relatively con-
servative (r2 = 0.765, p < 0.05, n = 12) behaviour downstream. Simultaneously, pCO2 attained extremely high
values (9160 µatm), contrasting with the values obtained in other sampling surveys (hardly attaining 4500 µatm; Table 1). This might be explained by the efflux of CO2 to the atmosphere in the very low salinities region, leading

Table 2. Tagus estuary seasonal values for daily average wind speed, maximum tidal current speed, pCO2
gradient (ΔpCO2), CO2 gas transfer velocity (κ) given by the parameterizations of Carini et al.32 (κCalcite),
Raymond and Cole43 (κRC01), Abril et al.1 (κR014), Borges et al.7 (κB04), and O’Connor and Dobkins13 (κR2004),
water current contribution, water-air CO2 fluxes and CO2 emission. aCalculated as the ratio kΩCalcite / (kΩCalcite + kCalcite)
bAverage CO2 water-air fluxes for the four parameterizations proposed (κCalcite, κRC01, κR014 and κB04) surface area
of 265 km2 computed as the definite integral of bidimensional masks defined from latitude, longitude, and
coastline information, using the ferret software.

| Parameter                  | Winter | Spring | Summer | Autumn |
|----------------------------|--------|--------|--------|--------|
| Wind speed (m s−1)         | 3.7 ± 1.6 | 3.9 ± 1.8 | 3.3 ± 1.3 | 1.7 ± 0.7 |
| Maximum tidal current speed (cm s−1) | 103 | 80 | 58 | 122 |
| ΔpCO2 (µatm)               | 1337.1 ± 1930.8 | 674.2 ± 532.9 | 1147.4 ± 872.6 | 1908.6 ± 1277.8 |
| κCalcite (cm h−1)          | 5.0 ± 2.0 | 7.1 ± 3.7 | 4.9 ± 1.8 | 3.3 ± 1.4 |
| κRC01 (cm h−1)             | 4.8 ± 1.7 | 8.1 ± 6.3 | 4.6 ± 1.3 | 3.3 ± 0.8 |
| κR014 (cm h−1)             | 11.9 ± 3.6 | 14.9 ± 4.8 | 11.6 ± 2.7 | 9.9 ± 3.7 |
| κB04 (cm h−1)              | 10.3 ± 3.6 | 14.1 ± 6.6 | 10.4 ± 3.2 | 7.3 ± 2.4 |
| κR2004 (cm h−1)            | 4.6 ± 1.4 | 4.6 ± 1.5 | 4.0 ± 1.6 | 4.6 ± 2.9 |
| Water current contribution (%)a | 48 | 39 | 45 | 59 |
| Water-air CO2 flux (mmol C m−2 d−1)b | 109.9 ± 83.9 | 80.4 ± 87.7 | 86.9 ± 64.6 | 133.9 ± 89.3 |
| CO2 emission (106 mol C d−1) | 29.0 | 21.2 | 23.0 | 35.3 |
to the consumption of TA/DIC. Moreover, Chl \(a\) values (just up to 2.6 mg m\(^{-3}\); Table 1) reflecting winter conditions, support the above conclusion, since photosynthetic carbon fixation very unlikely would justify TA/DIC consumption. At salinity 20 another decrease of TA/DIC (~270 µmol kg\(^{-1}\)) occurred, which also might correspond to CO\(_2\) degassing reflected in the decrease of \(p\)CO\(_2\) from 920 µatm to 670 µatm.

In May 2006, TA/DIC increase at low salinities seemed to be due to a combination of processes. Even if considerable primary productivity was underway in that region, reflected in elevated Chl \(a\) values (up to 73.4 mg m\(^{-3}\); Table 1), low \(p\)CO\(_2\) (487–650 µatm) and as well as relatively high pH (8.25; Table 1), consumption of TA/DIC did not occur, as expected for high phytoplankton biomass development. As no clear evidence of particulate organic matter mineralization was revealed, a possible explanation for production of DIC in that range of salinity could be mineralization of labile organic material (mainly glicids) produced by phytoplankton exudation and/or lysis. Thus, it means that photosynthetic activity might indirectly contribute to DIC increase, counteracting the
expected decrease under conditions of relatively high productivity. Besides, another mechanism likely acting and leading to generation of alkalinity may have been dissolution of CaCO3, as by this period only slightly supersaturated conditions were present in the estuary.

It should be taken into account that the patterns of TA and DIC could also be related to other processes. As about one third of Tagus estuary surface is composed by intertidal areas, sediments are sites of organic matter degradation. Moreover, salt marshes sediments store carbon and their pore waters enriched in DIC are transferred to the estuary by tidal pumping, also producing DIC. This mechanism has been reported to act in mangrove creeks as well. In addition, denitrification occurs in Tagus, and it is known that such processes were responsible for TA increases in several estuaries. The predominance of CO2 supersaturation conditions in Tagus estuary suggests that the system is dominated by heterotrophy, which is backed by the O2 data (pers. comm.). The highest pCO2 values were noticed at the salinity ranges 0–5 and also 20–30 (Fig. 5D). Upstream pCO2 was most likely originated from riverine waters probably having no time to degas. pCO2 increase observed at higher salinities might be attributed to lateral transport of CO2 from salt marshes mainly located at the southern margin of Tagus in the north margin near the polluted Trancão River.

Studies carried out in Tagus marshes in 2001/2002 revealed CO2 supersaturation, and pCO2 values varying from 877 to 3950 µatm (Oliveira, unpublished data). Besides, other studies suggest that in tidally flooded salt marshes of some estuaries of Georgia/U.S.A, the CO2 supersaturation was controlled by inputs from organic carbon respiration. Also, CO2 supersaturation of three Georgia estuaries were due to CO2 inputs from the intertidal marshes and the rivers. Thus, within Tagus estuary, mechanisms such as mixing of supersaturated freshwater with seawater, CO2 efflux to the atmosphere and carbonate dissolution seem to emerge as the major regulators of pCO2 spatial distribution.

As mentioned in another study, higher CO2 emissions were generally related to more intense wind speed, although no statistical significance was observed (p > 0.05). Tagus estuary water current was found to largely affect the gas transfer velocity over it (~48% on average) (Table 2), an effect estimated by applying the ratio kDICSS/(kDICSS + kDIC).

The value is rather high when compared with estimates for other European estuaries, such as the Scheldt (25%) and Guadalquivir (30%). Assuming that water current and wind speed have an additive effect on k, the water current expression proposed by O’Connor and Dobhins8 was combined with the algorithms from Carini et al. and Raymond and Cole. The outcome of the respective additive effect resulted in kDICSS = kDICSS + kDICSS and kBOH = kBOH + kDICSS. Also, the possibility of a fetch effect on k has been investigated. Since the suspended matter levels present in the estuary were low to moderate (< 165 mg l−1; Table 1) it was assumed that turbidity might have a rather limited effect on k.

Tagus estuary was always CO2 supersaturated inducing effluxes to the atmosphere at an average flux of 33.6 ± 29.7 mol C m−2 yr−1 leading to an average CO2 emission of 0.11 Tg C yr−1. Tagus CO2 fluxes are similar to the ones estimated for some inner estuaries (32.1 mol C m−2 yr−1) and analogous to fluxes of other European estuaries like Sado/Portugal (31.1 mol C m−2 yr−1), Gironde/France (30.8 mol C m−2 yr−1) and Guadalquivir/Spain (31.3 mol C m−2 yr−1). The nearby-conservative DIC distribution observed most of the time along the estuary implies that inputs and outputs are in equilibrium, meaning that the CO2 flux to the atmosphere must be balanced by net CO2 production in the water column or sediment. In fact, several researchers referred the dynamic coupling between CO2 generation and evasion being extremely fast in estuaries.

Table 3. Dissolved Inorganic Carbon (DIC) distributions and fluxes in Tagus estuary. Equations are polynomial equations used to fit the data from DIC versus each sampling transects. All equations have p < 0.05. C0 and C5 are, respectively, freshwater and seawater DIC concentrations. The flux of freshwater DIC is defined as (Q · C0), whereas the flux of internal DIC is (Q · (C5 − C0)) and the estuarine flux is (Q · C5).

| Season     | Sampling dates | DIC (µmol kg−1) as a function of S | r2 | C0 (µmol kg−1) | C5 (µmol kg−1) | Freshwater DIC Flux (106 mol C d−1) | Internal DIC Flux (106 mol C d−1) | Estuarine DIC Flux (106 mol C d−1) |
|------------|----------------|-----------------------------------|----|----------------|----------------|-------------------------------------|----------------------------------|----------------------------------|
| Spring     | May 2000       | 43.1 S + 1540.7 ± 0.774           | 0.774 | 1540.7         | 1540.7         | 51.0                               | 0                                | 51.0                             |
| Winter     | March 2001     | −29.2 S² + 230.0 ± 0.628          | 0.628 | 1110.5         | 2151.2         | 179.2                              | 167.9                            | 347.1                            |
| Summer     | July 2001      | 23.5 S + 1815.0 ± 0.903           | 0.903 | 1815.0         | 1815.0         | 16.6                               | 0                                | 16.6                             |
| Summer     | June 2002      | −1.5 S² + 63.4 ± 0.527            | 0.527 | 2481.5         | 4243.2         | 17.8                               | 12.6                             | 30.5                             |
| Spring     | May 2003       | 14.4 S + 1818.4 ± 0.948           | 0.948 | 1818.4         | 1818.4         | 37.6                               | 0                                | 37.6                             |
| Winter     | February 2004  | 0.7 S² + 6.7 ± 0.602             | 0.602 | 1832.7         | 1445.8         | 42.5                               | −9.0                             | 33.5                             |
| Spring     | May 2006       | −1.3 S² + 59.6 ± 0.629           | 0.629 | 1704.1         | 3018.7         | 18.9                               | 14.6                             | 33.5                             |
| Autumn     | November 2006  | 21.2 S + 2010.5 ± 0.739           | 0.739 | 2010.5         | 2010.5         | 136.4                              | 0                                | 136.4                            |
| Annual mean values (Tg C yr−1) | | | | 0.27 | 0.10 | 0.37 | | |
Freshwater end-member DIC concentration did not vary much during all survey periods. Such near stable values suggest that the concentration of the inorganic carbon entering the estuary is, to a certain extent, independent of the season of the year and very likely independent of the Tagus discharges.

The relative contribution of riverine CO$_2$ to the overall CO$_2$ emission by the estuary (estimated after 45) was ~6% in spring and ~10% in autumn. In fact, these values are very close to those reported for the very productive Scheldt estuary (10%)$^{45}$ and for 11 European estuaries (median value 10%)$^{46}$. Still, that proportion can be highly variable from one estuary to the other, for example for the Randers Fjord the riverine contribution reached a value of 50%$^{46}$, for Guadalquivir estuary 30%$^{41}$ and for Rhine estuary ~300%$^{46}$. Hence, most of the emission of CO$_2$ from Tagus estuary (~90%) was attributed to heterotrophic activity.

Figure 7. Distributions of CO$_2$ partial pressure ($p$CO$_2$), pH and dissolved oxygen (DO) along the salinity gradient in (A) March 2001 and in (B) June 2002. Also, distributions of (C) suspended particulate matter (SPM) and nitrate (NO$_3$) in June 2002 along the salinity gradient in Tagus estuary.
Our study suggests that changes in the Tagus estuary carbonate parameters seemed to be consequence of rather more complex feature than just the result of simple mixing of freshwater and seawater. Riverine/terrestrial runoff and occurrence of specific biogeochemical processes as photosynthesis, aerobic respiration, organic matter mineralization (degradation) and CaCO₃ precipitation/dissolution might be responsible for carbonate variability. Probably, the pore waters rich in DIC transferred to the estuary waters by tidal pumping may also contribute to the occurred changes. The inorganic carbon budget revealed that 0.27 Tg C enter into Tagus estuary annually, while 0.37 Tg C are exported to the adjacent coastal waters. Overall, 23% of the total DIC exported from Tagus estuary is emitted to the atmosphere, and about 8% of riverine DIC is ventilated. Most of the estuarine emissions (average flux of 33.6 ± 29.7 mol C m⁻² yr⁻¹) were attributed to heterotrophy.

Methods

Geographic coverage. Tagus Estuary (Fig. 1) is located at the southwest Portugal (38°36′–39°N, 08°54′–09°24′W) and supports important human communities and natural resources. It is an inundated valley with a submerged area of 320 km² where ~40% are intertidal areas (~20 km² salt marsh vegetation and ~80 km² mudflats). This mesotidal estuary (tidal range 1–4 m) has a narrow and fault-controlled inlet channel separating two distinct regions: an outer wave-dominated area from an inner broad and tide-dominated part. Winds dominate from south and southwest during winter, rotating progressively to the northwest and north directions during spring, and maintaining these directions throughout the summer months. There is a strong seasonal hydrodynamic and biogeochemical variability due to seasonal fluctuations in meteorological conditions and river discharges (mean annual flow of 350 m³ s⁻¹). There is also a strong horizontal gradient inside the estuary as a result of the hydrodynamic conditions, mostly tidally-controlled, with a dominant semidiurnal period and maximum amplitude of 4.8 m in spring tide. Middle estuarine areas, and to a lesser extent upper areas, have more stable and homogenous conditions, displaying a higher residence time. Lower estuarine areas, influenced by the tidal regime, are characterized by high variability. The mean residence time of water in the estuary varies between 26 and 8 days. The system is vertically well-mixed and has a mean tidal prism of 600 × 10⁶ m³, about a third of the mean volume.

Even with recent reduction in organic loadings due to the implementation of considerable sewage treatment plants, the Tagus estuary is under intense anthropogenic disturbance, with a major population centre within its catchment basin (~2.3 million of inhabitants).

Sampling, analysis and calculation methods. The sampling period was from 1999 to 2007, covering an area extending from the estuary mouth to the point where freshwater was encountered. Sampling locations were selected to provide a full coverage of the salinity gradient (from 0 to 35). Surface seawater samples were collected at ebb conditions with Niskin bottles, for a total of 18 sites along a ~50 km stretch of the estuary (Fig. 1). Temperature (T) and salinity (S) parameters were determined in situ with a CTD (Conductivity - Temperature - Depth) Aanderaa probe. Salinity was calibrated with an AutoSal salinometer using IAPSO standard seawater, with a variation coefficient of 0.003%.

Dissolved oxygen (DO) was analysed following the Winkler method using a whole-bottle manual titration. The coefficient of variation associated with the method ranged from 0.08 to 0.25%. pH was measured immediately after sample collection at 25 °C, using a Metrohm 704 pH-meter and a combination electrode (Metrohm) standardised against 2-amino-2-hydroxymethyl-1,3-propanediol seawater buffer (ionic strength of 0.7 M), at a precision of 0.005 pH units. Total alkalinity (TA) samples were filtered through Whatman GF/F (0.7 μm) filters, fixed with HCl, and stored (refrigerated not frozen) until use. Samples were then titrated automatically with HCl (~0.25 M HCl in a solution of 0.45 M NaCl) past the endpoint of 4.5 pH, with an accuracy of ±2 μmol kg⁻¹. The respectively accuracy was controlled against certified reference material supplied by A.G. Dickson (Scripps Institution of Oceanography, San Diego, USA). Chlorophyll a (Chla) was determined by filtering triplicate aliquots of ~150 ml water through Whatman GF/F filters (0.7 μm) under a 0.2 atm vacuum, and immediately frozen and later extracted in 90% acetone for analysis in a fluorometer Hitachi F-7000, calibrated with commercial solutions of Chl a (Sigma Chemical Co.). The variation coefficient was 1.8%. For suspended particulate matter (SPM) determinations, six aliquots of 100–1000 ml water samples were filtered through pre-combusted (2 h at 450 °C) Whatman GF/F filters and determined gravimetrically (drying at 70°C). The respective filters were subsequently used for particulate organic (POC) and inorganic (PIC) carbon determinations using a CHN Fissons NA 1500 Analyser, with acetanilide as the calibration standard. The respectively accuracy was controlled against certified reference material supplied by A.G. Dickson.

Meteorological data. Wind speed and direction were measured in situ with a Vaisala® meteorological station (Datalogger Campbell Scientific CR510) coupled with a MetOne 034 A anemometer. Continuous measurements were acquired with 1-minute intervals at 11 m height. Wind speed was referenced to a height of 10 m (u₁₀). We assume one standard deviation of ±2 m s⁻¹ as wind speed error. Atmospheric CO₂ data was obtained from the Terceira Island’s reference station (Azores, Portugal, 38.77°N 27.38°W), from the network of the National Oceanic and Atmospheric Administration (NOAA)/Climate Monitoring and Diagnostics Laboratory (CMLD)/Carbon Cycle Greenhouse Gases Group (CCGG). Some algorithms were used to convert observed atmospheric CO₂ content in mole fraction (in dry air) to wet air values. Direct measurements of atmospheric CO₂ partial pressure made on-board was only available for some sampling periods. Significant correlations were found out between Terceira data and shipboard data (r² = 0.910, p < 0.05, n = 45) and the discrepancies lied just between 3 and 13 ppm. The impact of using Terceira data on this study was considered negligible.
Estimated parameters. pH values corrected to in situ temperature were calculated from total alkalinity (TA) and in situ pH and temperature. For these calculations the carbon dioxide constants of Millero et al. were applied.

The partial pressure of CO$_2$ in seawater (pCO$_2$) and the dissolved inorganic carbon (DIC) were calculated from the in situ temperature, TA and corrected pH, using the carbonic acid dissociation constants given by Millero et al. and the CO$_2$ solubility coefficient of Weiss. Errors associated with pCO$_2$ and DIC calculations were estimated to be ±10 μatm and ±5 μmol kg$^{-1}$, respectively (accumulated errors on TA and pH).

The water-air CO$_2$ fluxes (CO$_2$ Flux) were computed according to:

$$\text{CO}_2 \text{ Flux} = k \cdot K_o \cdot \Delta \text{pCO}_2$$

where $k$ is the CO$_2$ gas transfer velocity, $K_o$ the solubility coefficient of CO$_2$ and $\Delta \text{pCO}_2$ the water-air gradient of CO$_2$. Positive CO$_2$ flux indicates emission of CO$_2$ from water to the atmosphere and negative flux the opposite direction.

Some authors suggest that $k$--wind speed relationships are site-specific. More recently, it was argued that wind, water current, surface area and turbidity, all significantly affect $k$ in estuaries. Various measurement techniques on the gas transfer velocity in estuaries have been implemented, using methods such as dual tracer addition, natural gas tracer or floating dome technique. The tracer methods involve long term measurement of $k$ over the entire estuary, while the floating dome technique is a short term measurement affected by the system heterogeneity that is typical in estuaries. In any case, the selection of a particular value for $k$ will affect the overall representation of the net ecosystem metabolism. Since $k$ was not determined in situ in Tagus estuary, we based our calculations to the most likely value for $k$ on parameterizations used on similar studies: (1) from a SF6 release experiment in the Parker River and estuary (hereafter referred to as C96), (2) from a compilation of published $k$ values in various rivers and estuaries, using different methodologies (hereafter referred to as RC01), (3) considering the contribution of the water current (hereafter referred to as B04), and (4) based on a generic equation that gives $k$ as a function of water current velocity, wind speed, estuarine surface area and suspended matter content (hereafter referred to as A09). The choice of these formulations was motivated by the relative similarity between the Tagus estuary and the systems studied by the mentioned studies, in their physical characteristics (e.g., shallow, well-mixed, influenced by tides). Water current and tidal height data at Tagus estuary were obtained with hindcast simulations using the MOHID Modelling System (www.mohid.com), based on real forcing for river discharge, tide and wind.

Estimated DIC fluxes. The internal flux of dissolved constituent in the Tagus estuary was estimated based on mixing curves, by quantifying how much DIC was added by net heterotrophy during estuarine transport through DIC versus salinity plots. Whenever the distribution of a dissolved constituent is continuous and predictable using simple polynomial equations, $C_0$ is where the polynomial equation defining DIC concentrations intersects the y-intercept (or here $C_0$ becomes $C_0 - C_s$) and $C_s$ is the concentration of the constituent where the tangent at the seawater end-member crosses the y-intercept. Still, total exported flux from the estuary is given by $(Q \cdot C_S)$, where $Q$ is the freshwater flow, $(Q \cdot (C_S - C_0))$ the internal flux, and $(Q \cdot C_0)$ the flux from the freshwater end-member.

Statistical analysis. Exploratory analysis and statistical procedures were implemented using the statistical software Statistica 6.0 (Statsoft Inc., 2001). Differences between sampling periods in the measured/calculated physical-chemical and biological parameters, were assessed using an analysis of variance (ANOVA), and differences between means have been considered statistically significant for $p < 0.05$. The dominant processes influencing surface water chemistry were identified using linear correlations between the system parameters.

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**Author Contributions**

A.P.O. was responsible for the field work and M.D.M. was responsible for the simulations using MOHID. All authors wrote the main manuscript text. All authors reviewed the manuscript.

**Additional Information**

**Competing Interests:** The authors declare that they have no competing interests.

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