

# Oxygen depletion in relation to water residence times

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The relationship between residence time and oxygen saturation was investigated in a mesotidal lagoon in southern Portugal. The system receives no significant freshwater input during the summer months and has a high evaporation rate. These features enable an estimate of residence time from the salinity differences between ocean water entering the system and lagoon water. More than 10 000 GPS referenced measurements of oxygen saturation, temperature and salinity were made during large spring tides in September, 2006. The lowest oxygen saturation (~44%) was measured in the waters with the highest calculated residence times (7 days). There was a significant linear decrease in the oxygen saturation with increasing residence time of ~16% per day. This was similar to the rate measured on a neap tide in August, 2005. The high salinity, low oxygen saturated water was spatially confined to one inner channel, except at high water when this water was pushed into other channels. Although the tides investigated were the largest for several years, the oxygen saturation did not exceed 70% in this inner region. It is proposed that the direct discharge of oxygen consuming effluent, including domestic sewage, into this inner channel is responsible for this persistent oxygen deficit.

## Introduction

The oxygen dissolved in marine waters may directly influence the biological species present<sup>1</sup> and the pollution status<sup>2,3</sup> of the local environment. In recent years, episodes of low (hypoxia) or zero (anoxia) oxygen concentrations have increased dramatically in shallow coastal waters around the world.<sup>4</sup> Dissolved oxygen may be reduced after direct discharge of oxygen consuming wastes, such as sewage,<sup>5</sup> or indirectly through eutrophic events fuelled by nutrient additions.<sup>6</sup> In either case, poor water quality may result.

Oxygen consumption and production rates make an important contribution to the water quality and ecological status under the EU Water Framework Directive (WFD, 2000/60/EC), and the USA Clean Water Act.<sup>7</sup> Good water quality status in both the EU and USA depends partly upon measures of inorganic nutrients (*e.g.* nitrogen and phosphorus)<sup>8</sup> and chlorophyll, with oxygen concentrations intimately linked to these controlling variables. Many studies of oxygen, however, only document daytime values, so that night time oxygen sags are not always recorded.<sup>9</sup> Intuitively, it might be expected that the O<sub>2</sub> saturation would fall overnight but be replenished during the day in sunny, phytoplankton rich environments. Additional increased degradable organic matter from waste discharges may upset any balances that do exist and lead to persistent hypoxia or even anoxia.

The amount of oxygen present in waters is normally presented as a concentration (mg l<sup>-1</sup> or μM) or as a percentage of full saturation at specific temperature and salinity conditions. When expressed in the latter form, the diurnal range may be

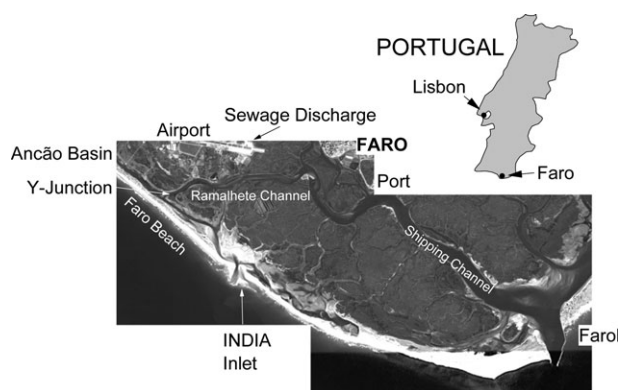
0% near dawn and reach 200% during the day in effected waters (*e.g.* ref. 10). In general, percentage saturation is a more useful unit for comparing oxygen values, where there are large seasonal changes in salinity and temperature values, as is the case in the Ria Formosa. Waters with high residence times in areas of restricted exchange may experience considerable O<sub>2</sub> depletion if oxygen consuming organic matter is present. In their study of regions of restricted exchange, Tett *et al.*<sup>11</sup> outlined a model to estimate the de-oxygenation of the bottom waters. Their water exchange model suggests that the Ria Formosa lagoon in southern Portugal is well flushed with a mean residence time of 0.5 days. This lagoon becomes hypersaline during the summer months, due to high evaporation rates, low rainfall and lack of surface runoff.<sup>8</sup> At the western end of the lagoon, there are only two inlets; the inflowing ocean water is confined to well defined channels and cause the same water to be exchanged with each tide, so that there is little mixing between the ocean water and the water of the inner channels. This was first hypothesized by Newton and Mudge<sup>12</sup> and quantified by Mudge *et al.*<sup>13</sup>

The southern region of Portugal is a popular holiday destination, which results in increased amounts of relatively poorly treated sewage wastes into the lagoon over the summer months.<sup>14</sup> The effluent from the urban waste water treatment plant (Fig. 1) discharges directly into the waters that appear to have the highest residence times, up to 12 days.<sup>13</sup> A preliminary survey undertaken on a neap tide in the summer of 2005 identified an oxygen consumption rate of ~18% day<sup>-1</sup> (0.05 mg l<sup>-1</sup> h<sup>-1</sup>). It is likely that these factors contribute to water quality issues that can occur during the summer months, such as high mortalities of economically important clams. This paper investigates this relationship between the water residence time as calculated from the salinity difference method of Mudge *et al.*<sup>13</sup> and the oxygen content of lagoon water during

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**Fig. 1** Location map of the Ria Formosa Lagoon in southern Portugal.

the large equinoctial spring tides, when flushing is potentially at its greatest.

## Materials and methods

The location of each sampling point was recorded using the track feature of a Garmin GPSMAP 76CS set to record every second. Measurements of salinity and water temperature were made with a calibrated Seabird SBE-19 CTD attached to a small boat. Data were recorded internally every second with the internal clock synchronised to the time from the GPS satellites. Oxygen saturation measurements were made with a calibrated WTW oxygen probe attached to the CTD frame. The O<sub>2</sub> meter was similarly synchronised to the GPS clock. Full oxygen saturation was 6.69 mg l<sup>-1</sup> at a salinity of 37 and temperature of 25 °C. The boat speed was kept between 2.5 to 3.0 m s<sup>-1</sup> to prevent cavitation in the boat wake while covering optimal distance.

Six transects were sampled on the 8th September, 2006, in the Ancão Basin at the western end of the Ria Formosa lagoon (Fig. 1); an early morning mid-ebb, low water, mid-flood, two near high water, and an afternoon mid-ebb. The times of the transects and the corresponding times of sunrise, sunset and predicted tidal times at Faro Bar are presented in Table 1. This period had the highest predicted tides for several years and there was a delay of 30–45 min between times at the bar and in the Ancão Basin, based on previous observations.<sup>15</sup>

**Table 1** Sunrise and sunset times for the two sampling days, together with predicted tidal times and mid-sampling transect times. All times are in UTC

	8th September, 2006	9th September, 2006
Sunrise	06:07	06:08
Sunset	18:50	18:48
Predicted LW at Faro Bar	08:39	09:21
Predicted HW at Faro Bar	14:37	15:19
Survey times		
Mid-ebb	06:30	06:32
Low water	09:10	09:39
Mid-flood	12:17	12:51
High water	15:14 and 16:34	15:38
Mid-ebb	18:10	

Four further transects were conducted on the 9th September, 2006, between the major inlet at Farol and the entrance to Ancão Basin. These transects also included sub-transects to the INDIA inlet that was artificially constructed in 1997 during the Inlet Dynamics Initiative project for the Algarve (INDIA),<sup>16</sup> partly with the aim of improving the water quality in the Ancão Basin (Fig. 1). These transects were longer than the previous days and encompassed the major shipping channel and the region where significant sewage materials were discharged.<sup>14</sup> The sunrise and sunset times, together with the predicted tidal times and mid-survey times, are in Table 1.

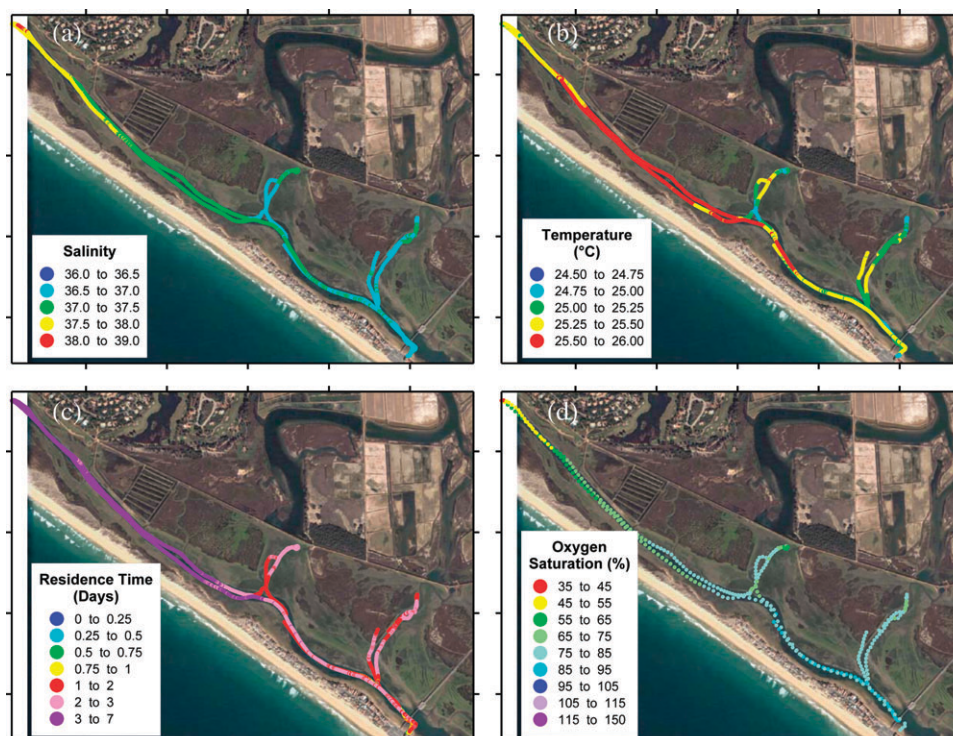
The residence time was calculated according to the method of Mudge *et al.*<sup>13</sup> using the salinity difference at any location with the inlet waters and evaporation rates; these were measured at an adjacent salt extraction pond.

## Results

### Ancão Basin

Each survey within the western end of the lagoon was completed within 40 min, collecting ~2500 data items for the salinity, temperature and location. Due to data storage limitations in the oxygen meter, only 250–450 values were recorded on each run. Although six separate runs were made on one day, only the mid-ebb (morning) figures are reproduced here (Fig. 2). Salinity reached a maximum of 38.35 at low water (mid-morning), while temperature reached 27.87 °C on mid-flood near midday. These values were consistent with other observations in the lagoon, where water temperature was principally related to time of day<sup>12</sup> and salinity was controlled by the state of the tide. The lowest salinities occurred at high water, when new seawater entered the system from the Atlantic Ocean. During these measurements, mean salinity at the inlets was 36.47. The spatial distribution of salinity and temperature in the Ancão Basin on mid-ebb can be observed in Fig. 2a and b, respectively. The derived residence time calculated from the salinity difference and evaporation rate is shown in Fig. 2c. These values were significantly greater than one day, and in the case of pockets of water at the extreme end of the lagoon, were up to 6.6 days. The measured O<sub>2</sub> saturation (Fig. 2d) was below 100% for the entire transect and dipped below 45% at the most westerly point reachable by boat on that tide.

At low water (figures not shown), high salinity water up to 38.3 drained out of the upper channels, although it was also possible to observe less saline waters (minimum salinity = 32.2) draining from the one brackish water source in this area of the lagoon. The spatial effect of these low salinity waters was only in the order of a few hundred metres. The waters behind the embankment (visible in Fig. 2) had relatively high nutrient loads and algal biomass and drained from a small stream that had its origin from the surface of a horticultural site and also received water from a hotel and golf complex sewage treatment plant.<sup>17</sup> These waters had relatively high nutrient loadings and the dam, seen in the images of Fig. 2, had major blooms of algae and became eutrophic. Interestingly, the salinity had an inverse relationship with temperature at this time, since the latter was more of a function of time of



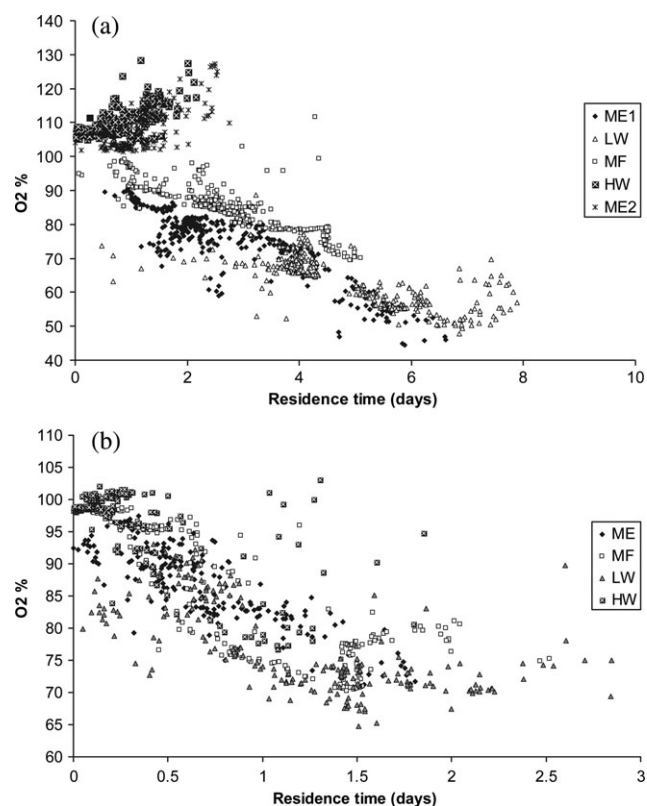
**Fig. 2** Data for the morning mid-ebb survey of the Ancão Basin. (a) The salinity, (b) temperature in °C (c) residence time (in days) calculated from the evaporation rate and salinity difference with the inlet, and (d) oxygen as a percentage of saturation.

day in these shallow upper reaches. The residence time was uniformly high (>3 days), except where the low salinity drainage waters affected this calculation. The oxygen saturation was similar to that of the mid-ebb as the algae had yet to produce sufficient O<sub>2</sub> from photosynthesis to overcome the respiration debt. As the tide flooded into this region, the high salinity water was backed up behind the incoming lower salinity water and forced up into the channels.

The relationship between the calculated residence time and O<sub>2</sub> saturation for all states of the tide can be seen in Fig. 3a. Apart from the data from high water and the afternoon mid-ebb, the O<sub>2</sub> saturation decreased with residence time. The data ( $n = 1060$ ) described a linear decrease of between 6.2 and 7.2% per day, depending on whether the intercept was fixed at 100%. In all cases, the fitted slopes were statistically significant ( $P < 0.001$ ). The afternoon data indicated short residence times based on lower salinity, indicating that this was new water recently advected into the basin. The O<sub>2</sub> saturation was slightly greater than 100%. Not only was this new water from outside the lagoon, but the phytoplankton had been photosynthetically generating O<sub>2</sub> throughout the morning and the early afternoon.

### Farol to Ancão

On the second major survey, four transects taking approximately 110 min each were made with the mid-transect time corresponding to mid-ebb, low water, mid-flood and high water. As the runs were longer, ~6600 measurements were made for each parameter, with a mean speed near 3 m s<sup>-1</sup>. The salinity and temperature distributions for the morning mid-ebb tide can be seen in Fig. 4a and b. The highest salinities and



**Fig. 3** The relationship between the calculated residence time (days) and O<sub>2</sub> saturation for the two regions of the lagoon. (a) The Ancão Basin and (b) Farol to Ancão Basin (ME = mid-ebb; LW = low water; MF = mid-flood; HW = high water).

temperatures were measured in the Ramalhete Channel adjacent to the airport (Fig. 1). The eastern end of the airport is also the site of the sewage discharge into the lagoon from Faro and its surrounding conurbation. The lowest salinities and temperatures were measured in the deep waters at the main inlet at Farol, corresponding to the oceanic boundary conditions.

The greater the distance from the ocean, the higher were the estimates for residence time up the main channel. The residence time scale (Fig. 4c) divides the first day into four, to indicate the components of the past two tidal cycles. The water in the Ramalhete Channel had residence times in the order of 1–2 days and indicated mixing at either end, with new seawater either from the Farol inlet or the relatively new INDIA inlet. The O<sub>2</sub> saturation (Fig. 4d) decreased from nearly 100% at the inlets to a minimum of 71% near the airport.

At low water (figures not shown), the high salinity water (>37) extended down the main shipping channel to within 4 km from the ocean. The residence time for the water draining out of the Ancão Basin was in the order of 3+ days, and due to the nature of the Y-junction, was directed down the Ramalhete Channel, which has a path length from this point to the ocean of ~12 km. The mean O<sub>2</sub> saturation in the Ramalhete Channel was only 71% despite good conditions after 11.00 for generating O<sub>2</sub> from photosynthetic activity.

As the tide flooded back into the lagoon, the warm high salinity water was pushed back up the Ramalhete Channel and into the Ancão Basin, with a small degree of mixing with waters entering through the INDIA inlet. This new ocean water had an oxygen saturation of ~100%. By high water, only the water in the Ramalhete Channel had an oxygen saturation of less than 100%.

The relationship between the residence time and O<sub>2</sub> saturation for this part of the lagoon can be seen in Fig. 3b. The rate of loss of oxygen per day in this region was between 13 and 17%, depending on the form of the regression equation used. In all cases, the fitted slopes were statistically significant

( $P < 0.001$ ). These values were almost identical to those calculated on a neap tide in August, 2005, using the same methodology (18.6%) (unpublished data).

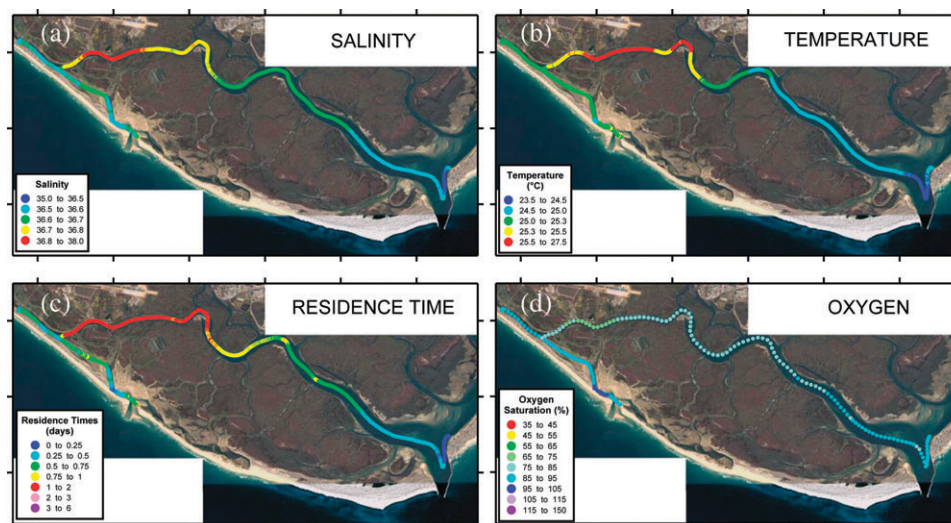
## Discussion

A simple budget for oxygen in the waters of a lagoon, such as the Ria Formosa that receives almost no freshwater input over the summer, can be represented schematically by the following equation:

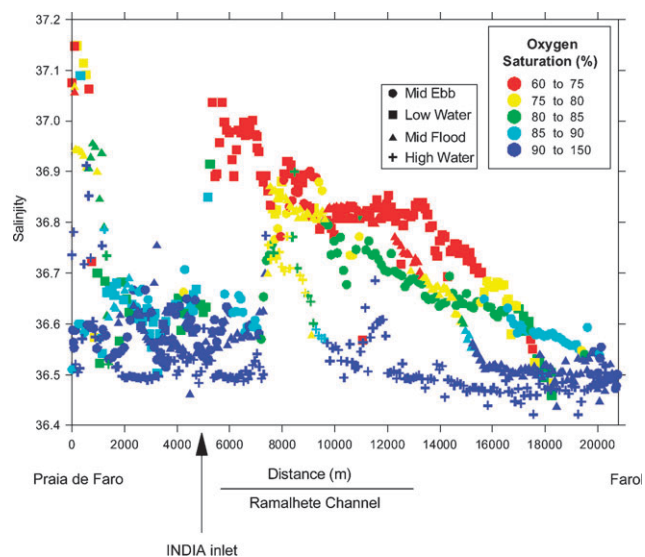
$$[O_2] = [\text{net photosynthetic production} + \text{atmospheric diffusion} + \text{mixing}] - [\text{faunal respiration} + \text{abiotic (sedimentary) oxidation} + \text{organic waste oxidation}]$$

It must be noted that there are also changes in the oxygen carrying capacity of the water in response to the temperature and salinity of the seawater.

The net effect of these processes is an apparent linear depletion of oxygen by ~16% per day (Fig. 3), although the data in Fig. 3b is best described by an exponential decrease asymptotic to ~60% saturation. At equilibrium, the production term in the above scheme is equal to the consumption term. There will be O<sub>2</sub> concentration dependent changes to the atmospheric diffusion term, but it is likely that the main factor determining the rate of decrease would be the aerobic respiration of organic matter. The biochemical oxygen demand (BOD) of water in the channel leading from the airport to the Ramalhete Channel was up to 14 mg l<sup>-1</sup>, based on unpublished data from Wayland and Megson using a three day incubation. They also measured the BOD<sub>3</sub> values of ~8 mg l<sup>-1</sup> in the brackish water draining into the system from the holiday complex to the west. These values do not appear to be particularly high but in several cases the oxygen content after three days incubation was 0.0 mg l<sup>-1</sup> due to the low initial dissolved oxygen content. The co-incident organic carbon contents of the settled sediments along this channel



**Fig. 4** Data for the morning mid-ebb survey from Farol, the entrance to the lagoon, and the Ancão Basin. (a) The salinity (b) temperature in °C (c) residence time (in days) calculated from the evaporation rate and salinity difference with the inlet and (d) oxygen as a percentage of saturated (6.69 mg l<sup>-1</sup> at a salinity of 37 and temperature of 25 °C).



**Fig. 5** The salinity and oxygen saturation (%) as a function of the distance from Praia de Faro. The major inlet at Farol is at the extreme right of the x-axis. All low oxygen regions are in the Ramalhete Channel and have a correspondingly high salinity.

reached 25% and this may explain the low dissolved oxygen content.

It has been shown in previous work with lipid biomarkers<sup>14</sup> that the highest sewage deposition occurs at the location with the lowest oxygen saturation, *i.e.* in the Ramalhete Channel near the junction with the channel from the INDIA inlet. The greater deposition at this site is probably due to the water becoming static as the water is backed up the channel by new water entering through the Farol inlet. As this backed up water meets the flow from the INDIA channel, a small amount of mixing occurs but the suspended load is deposited to the sediment.<sup>14</sup> These organically rich, partly derived from sewage wastes will have a high BOD and may reduce the oxygen saturation in the water. During the sampling programme, the effect of the reducing sediments on the dissolved O<sub>2</sub> concentration was apparent; when the outboard motor propeller was in very shallow water and resuspended the near surface sediments, the water becomes black due to the iron sulfide rich particles and the measured O<sub>2</sub> saturation plummeted. Conversely, at extreme high water, when the boat was above the seagrass beds, saturation levels were significantly greater than 100%.

The spatial relationship between the salinity, distance through the lagoon and oxygen saturation can be seen for the channels from Farol to Ancão in Fig. 5. The fully O<sub>2</sub> saturated waters are confined to the regions near the two inlets, which also have the lowest salinity. The Ramalhete Channel at all states of the tide has lower O<sub>2</sub> and higher salinities. These higher salinities are due to evaporation and exist throughout the lagoon in the summer.

The INDIA inlet to the south east of Faro Beach (Praia de Faro) has migrated further to the south east since it was

constructed in 1997. Satellite images of the area and GPS measurements show that the INDIA inlet had moved by ~500 m by September, 2006. This reflects the general direction of sediment movement along this coast from the west towards the east. Interestingly, the initial location is still reflected in the salinity and oxygen data, indicating that sea-water may be seeping through the sand barrier at this location (see Fig. 4).

## Conclusions

The link between long residence time and low oxygen saturation in the Ria Formosa has been demonstrated. In this particular system, oxygen saturation decreased by 16% per day in response to discharges of high organic carbon content wastes and potentially eutrophic phytoplankton blooms. The approach taken in this study offers a rapid cost effective method for monitoring water quality in other coastal areas with regions of restricted exchange.

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