Monitoring of oxygen condition in the Ria Formosa coastal lagoon, Portugal†

Alice Newton,[ab] Pedro S. Oliveira,[b] John D. Icely*[c] and Peter A. Foster[d]

Received 15th July 2009, Accepted 3rd November 2009
First published as an Advance Article on the web 25th November 2009
DOI: 10.1039/b914015h

Dissolved oxygen (DO) is one of the most important environmental variables of water quality, especially for marine life. Consequently, oxygen is one of the Chemical Quality Elements required for the implementation of European Union Water Framework Directive. This study uses the example of the Ria Formosa, a meso-tidal lagoon on the south coast of Portugal to demonstrate how monitoring of water quality for coastal waters must be well designed to identify symptoms of episodic hypoxia. New data from the western end of the Ria Formosa were compared to values in a database of historical data and in the published literature to identify long-term trends. The dissolved oxygen concentration values in the database and in the literature were generally higher than those found in this study, where episodic hypoxia was observed during the summer. Analysis of the database showed that the discrepancy was probably related with the time and the sites where the samples had been collected, rather than a long-term trend. The most problematic situations were within the inner lagoon near the city of Faro, where episodic hypoxia (<2 mg dm^{-3} DO) occurred regularly in the early morning. These results emphasise the need for a balanced sampling strategy for oxygen monitoring which includes all periods of the day and night, as well as a representative range of sites throughout the lagoon. Such a strategy would provide adequate data to apply management measures to reduce the risk of more persistent hypoxia that would impact on the ecological, economic and leisure uses of this important natural resource.

Introduction

The number of low oxygen, hypoxic and anoxic zones in estuaries, coastal and marine waters is increasing.[1] Much of this increase is related to the run off of nutrients from land that leads to eutrophication and subsequent decrease in dissolved oxygen (DO) through microbial respiration. Oxygen depletion can also occur in aqueous environments in response to:

- long residence times with low turnover of water, and/or low oxygen diffusion from the atmosphere;
- direct discharge into water of oxygen depleting waste (*e.g.* sewage, industrial and agricultural effluent) with a high biological oxygen demand;
- historical discharges of contaminants that can affect the current dissolved oxygen concentrations in the water column;
- resuspension of sediments that have previously contained or still contain oxygen depleting wastes;
- global changes in climate that may alter the temperature, rainfall and wind forces affecting DO concentrations.

All of these conditions may interact to alter present day DO concentrations, impairing ecosystem function, and resulting in "dead zones".[2]

Indeed, one of the symptoms of eutrophication in transitional and coastal waters is low (hypoxia) or zero (anoxia) DO.[3] The fate of oxygen as an essential element has until now been neglected in global observing and monitoring programmes. The international scientific community is addressing the inadequacy of current observation capabilities for assessing oxygen depletion through, for example, projects of the Group on Earth

[a]*LOICZ, NILU-CEE, Box 100, 2027 Kjeller, Norway*
[b]*IMAR FCT-Gambelas, Universidade do Algarve, 8005-139 Faro, Portugal*
[c]*CIMA, Gambelas, Universidade do Algarve, 8005-139 Faro, Portugal. E-mail: alicely2@gmail.com*
[d]*School of Ocean Sciences, U. Wales Bangor, Menai Bridge, Anglesey, LL59 5AB, UK*

† Part of a themed issue dealing with water and water related issues.

Environmental impact

Dissolved oxygen concentration and saturation are critical for most forms of aquatic life. The European Water Framework Directive includes "oxygen condition" as one of the physico-chemical elements supporting the classification of "Ecological Status". Oxygen concentration and percentage saturation observations are routine in many environmental monitoring programmes and there are abundant data available in the various data bases. However, the usefulness of these data for statistical analysis is limited because of variations in oxygen concentration with the time of day, as well as the effects of salinity and temperature on solubility. Most measurements are taken in the middle of the day and do not reflect conditions at night or early in the morning when an oxygen sag may be observed.

Observation, the Global Earth Observation System of Systems, and the European Union (EU) 7th Framework programme. It is important to improve the capacity for monitoring and predicting oxygen depletion throughout the Earth system and to evaluate the existing and future impacts on ecosystems.

In the EU, oxygen condition is one of the statutory chemical quality elements (CQE) that must be considered under the Water Framework Directive (WFD). An improvement of water quality is the objective of the WFD, including the reduction of eutrophication in both continental and coastal systems.[4] Although screening models can identify systems vulnerable to eutrophication,[5,6] it is also important to carry out monitoring to test and verify the results from these models.[7] The WFD includes three types of monitoring: 1) routine "surveillance" monitoring; 2) "operational" monitoring to assess the extent and gravity of a problem; 3) "investigative" monitoring to determine the causes of the problem.

The present study tests the application of DO condition as a CQE in the Ria Formosa, which is a shallow mesotidal lagoon on the south coast of Portugal (Fig. 1) with natural biogeochemical cycles essentially regulated by tidal exchanges at the seawater boundaries and at the sediment interface.[8,9] The water temperatures in the channels range from 12 °C in winter to 27 °C in summer and the salinity from 13 to 36.5, although much higher values can be observed in saltpans.[10]

Reports of the oxygen condition in the Ria Formosa vary. Screening models and evaluations of eutrophication[6,8] using historical databases indicate no problems with oxygen saturation. Others report the occurrence of oxygen sags.[7,8,11,12] Consequently, in accordance with the WFD, an "operational" monitoring plan has been designed to determine the occurrence, extent and gravity of the problem and to identify the possible onset and extent of hypoxia in the Ria Formosa lagoon. The objective of this paper is to demonstrate how an analysis of historical data for oxygen condition can be useful in the design of a monitoring plan and a programme for implementation of the WFD.

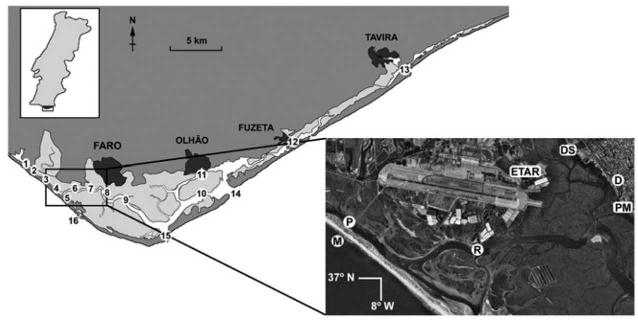

Fig. 1 Map of the Ria Formosa Lagoon showing the sample sites (1–16) used from the historical data set; the sites are described in more detail in Fig. 2. The inset shows the position of the Ria Formosa in southern Portugal. The aerial photograph shows the sites used in the current study including: **D**, Doca; **DS**, Doca Seca; **ETAR**, urban waste water treatment plant (**E** in text); **M**, Mar; **P**, Ponte; **PM**, Portas do Mar; and **R**, Ramalhete.

Alice Newton

Alice Newton was educated in France, Belgium, Portugal and the UK. Her university degrees are a BSc in Marine Biology and Oceanography, an MSc in Biological Oceanography and a PhD in Chemical Oceanography conferred by the University of Wales, Bangor, UK. Alice coordinates the ERASMUS MUNDUS Joint Master in Water and Coastal Management at the University of Algarve, Faro, Portugal and is the current Chairperson of LOICZ (Land-Ocean Interactions in the Coastal Zone), a core project of the International Geosphere-Biosphere Programme and the International Human Dimensions Programme at NILU, the Norwegian Institute for Air Research. Alice's research interests include eutrophication, both "natural" in upwelling zones and "anthropogenic" in coastal and transition waters.

Methods

Historical data

The DO data for the Ria Formosa was analysed from the oceanographic data base Typologies and Reference Conditions (TICOR), that had been compiled for all Portuguese coastal and transitional waters.[13] There were a total of 1052 data for dissolved oxygen in the Ria Formosa, although only 428 of these were selected for this study, as the others had not included the sampling time. The preliminary analysis of the database showed that the most problematic results were the inner stations of the lagoon during the night. Thus, the "operational" monitoring plan was designed to study night time conditions at these stations.

Operational monitoring fieldwork

Initially a spatial survey was carried out. Samples were taken at seven stations in Ria Formosa (aerial photograph in Fig. 1): Doca Seca (**DS**), Doca (**D**), Portas do Mar (**PM**), Ramalhete (**R**), Ponte (**P**), ETAR de Montenegro (**E**), with Mar (**M**) as the control station on the seaward side of the lagoon. The samples were collected at low water, when this coincided with sunrise. These conditions generally coincided with spring tides. Sampling had to be taken on two consecutive days to ensure that the sampling was close to sunrise. Triplicate samples were taken from the stations **DS**, **D**, **PM** on the first day; and from the stations **R**, **P** and **E** on the second day.

Two methods were used to determine dissolved oxygen, the Winkler method in the laboratory[14] and an oxygen electrode (Probe WTW model pH/OXI 340 i/SET) in the field. For the Winkler method, the samples were collected at the surface with a bucket with the minimum of agitation—the lagoon is too shallow to use a Niskin bottle. The temperature was measured with a thermometer. Salinity was determined with a salinometer (LT 320/SET of WTW) calibrated with standard seawater. The oxygen saturation was calculated according to Weiss.[15]

Once the results of this preliminary fieldwork were analyzed, station **PM** was identified as the most problematic, especially in view of its proximity to clam beds. The sampling strategy was designed to test the possible development of an oxygen sag at night. Studies were therefore carried out at this station overnight during the summer, for median tidal cycles (between spring and neap tides). The first sampling period was from 20.50 on the 16th of July to 7.50 on 17th of July and the second period was from 20.37 on 31st of July to 7.39 on 1st of August. Samples were collected every hour, and oxygen was also measured with the WTW oxymeter. Salinity and temperature were measured with the calibrated WTW salinometer every 30 min after sunset until one hour after sunrise. Samples were also taken at slack water.

Results and discussion

In this paper, oxygen condition is shown both as dissolved oxygen concentration (mg dm^{-3}) as well as derived oxygen percentage saturation (%). Both temperature and salinity control oxygen solubility and saturation and these are particularly important for the Ria Formosa in the summer where the warm, hypersaline conditions will markedly reduce oxygen solubility in the lagoon. Essentially, the dissolved oxygen percentage saturation should not fall below 80% to maintain a healthy biota. The effect of hypoxia on the biota has been reviewed by Diaz and Rosenberg[16] and their review has been used to set the threshold for biological stress and hypoxia at the conventional levels at 5 and 2 mg dm^{-3}, respectively. However, Vaquer-Sunyer and Duarte[17] suggest that the level used for hypoxia is below the empirical sublethal and lethal oxygen threshold for half the species tested: they report a median lethal concentration of 1.6 mg dm^{-1}, but show that fish and crustaceans have a higher requirement for oxygen and are also more sensitive to short term exposure than annelids.

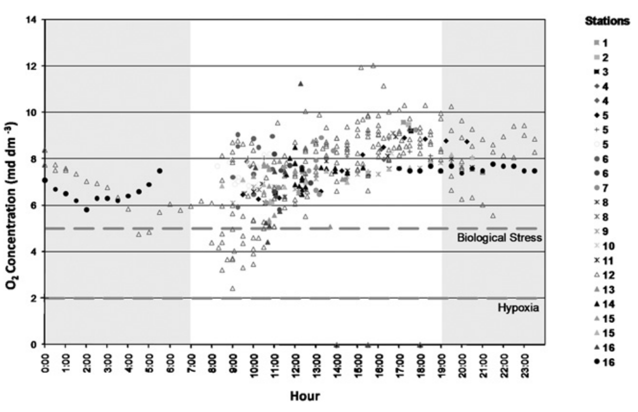

Fig. 2 Oxygen concentration of samples from the TICOR database. The approximate location of the sampling stations are shown in the map of Fig. 1 and are described as: **1**, Anção foot bridge; **2**, Ancão basin adjacent to golf course; **3**, Ponte; **4**, junction between Ramalhete and Barra channels; **5**, Barra channel; **6**, Ramalhete channel near village; **7**, Ramalhete channel near outlet of ETAR; **8**, Portas do Mar; **9**, Buoy in Faro Channel; **10**, Bouy in Olhão channel; **11**, outside Olhão harbour; **12**, Fuzeta quay; **13**, Tavira inlet; **14**; Armona inlet; **15**, Faro inlet; **16**, Barra Nova inlet. The shading on the figure demonstrates unequal distribution of samples over 24 h, with the time period 19.00 and 07.00 h (shaded) containing much fewer samples than the period between 07.00 and 19.00 (unshaded).

Results of the analysis of the historical data in the TICOR database

Fig. 2 shows the values of dissolved oxygen at the different stations in the lagoon. Most of the values are above biological

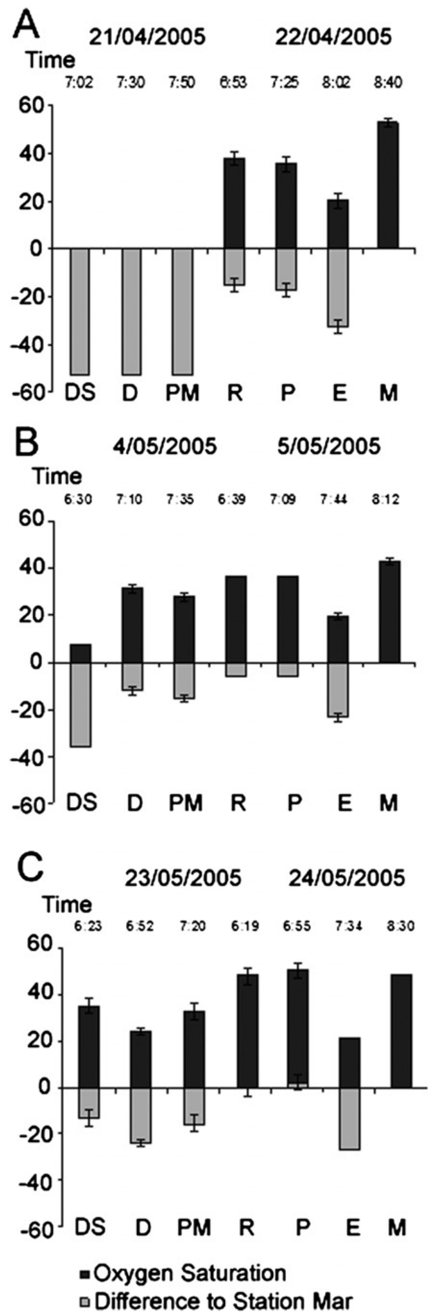

Fig. 3 Histograms in dark grey are of % oxygen saturation at the stations in the aerial image of Fig. 1 sampled at specific times close to, or at, sunrise. Histograms in light grey show the difference in % oxygen saturation between the lagoon sites and the site **M** on the open sea. **A**, 21st & 22nd April; **B**, 4th & 5th May; **C**, 23rd & 24th May. Abbreviations: **D**, Doca; **DS**, Doca Seca; **E**, Urban Waste Water Treatment plant; **M** Mar; **P**, Ponte, **PM**; Portas do Mar; and **R**, Ramalhete.

stress level (5.0 mg dm^{-3}) mainly between 6 and 10 mg dm^{-3} and reaching a maximum of 12 mg dm^{-3}. The average value of dissolved oxygen from all 428 samples is 7.5 mg dm^{-3}.

Assuming the day light period to be 07.00 to 19.00 h, the unshaded area in Fig. 2 shows that 84% of the data for oxygen are from daylight hours whilst the shaded area representing the night (19.00–07.00) contains only 16% of the data. This difference in the number of day and night samples creates a biased estimate of DO condition, since episodic hypoxia is more likely to occur at night.

The eutrophication screening model applied to the Ria Formosa by Nobre *et al.*[6] shows a mean dissolved oxygen value of 5 mg dm^{-3} based on all 1052 data for oxygen from the TICOR data base. The time of the day of sampling apparently produces an overestimation of the average concentration of dissolved oxygen, as observed by Cachola and Sampayo[18] who register values of dissolved oxygen between 7.3 mg dm^{-3} (high water) and 12.8 mg dm^{-3} (low water) at station **D**. However, other authors have identified lower values. For example, Dionísio *et al.*[11] have values of 2.5–7.2 mg dm^{-3}, at the station **PM**, in summer and spring and 5.3–10.7 mg dm^{-3} at the station **P**, in winter and spring. In both cases, the sampling time is prior to 12.00 pm. Newton and Mudge[19] report a morning oxygen sag of 48% saturation and oxygen super-saturation reaching 140% during the day. Loureiro *et al.*[7] report values of oxygen saturation between 81–111% at station **R** and 76–108% at station **P**, and emphasise that the results for oxygen concentrations essentially reflect the time of day when the samples are collected. In a more wide ranging study of the western lagoon, Mudge *et al.*[12] observe that oxygen saturation does not exceed 70% at some inner regions of the lagoon and that the lowest oxygen saturation (~44%) occurs in waters with the highest calculated residence time (7 days).

Results and analysis of the "operational monitoring"

In the current study, the dark grey histograms in Fig. 3A–C show the relative difference in oxygen saturation between the stations in the lagoon compared to the open sea (**M**) over three different tidal cycles during late spring and early summer. At dawn, all values are undersaturated for oxygen including those for the open sea (**M**). However, those in the inner lagoon (**DS**, **D**, **PM**, **E**) are always negative relative to the sea, with oxygen saturations between 0% to 40%. Even stations **R** and **P** have periodic phases of oxygen sag at sunrise relative to oxygen concentrations in **M**: this is particularly evident between the 21st and 22nd April when there is a difference of –15% (light grey histograms in Fig. 3A). During the 4th and 5th May, this difference is much less, at around –5% (Fig. 3B) whilst, during the 23rd and 24th May, **R** shows no difference and **P** is even slightly positive (Fig. 3C). In general, when oxygen saturation in the outer lagoon (**R** and **P**) is similar to that of the open sea (**M**), the relative oxygen sag at the inner stations improves from 0–20% (dark grey histograms for **DS**, **D**, **PM**, **E** in Fig. 3A) to 5–35% (Fig. 3B, C).

Most of the sampling events, including those not shown in this paper, indicate that the DO condition at night is worst at Portas do Mar (**PM**). Fig. 4 shows a more detailed analysis of oxygen condition between sunset and sunrise at **PM** (Fig. 1) over two different occasions overnight during the summer of 2005. The

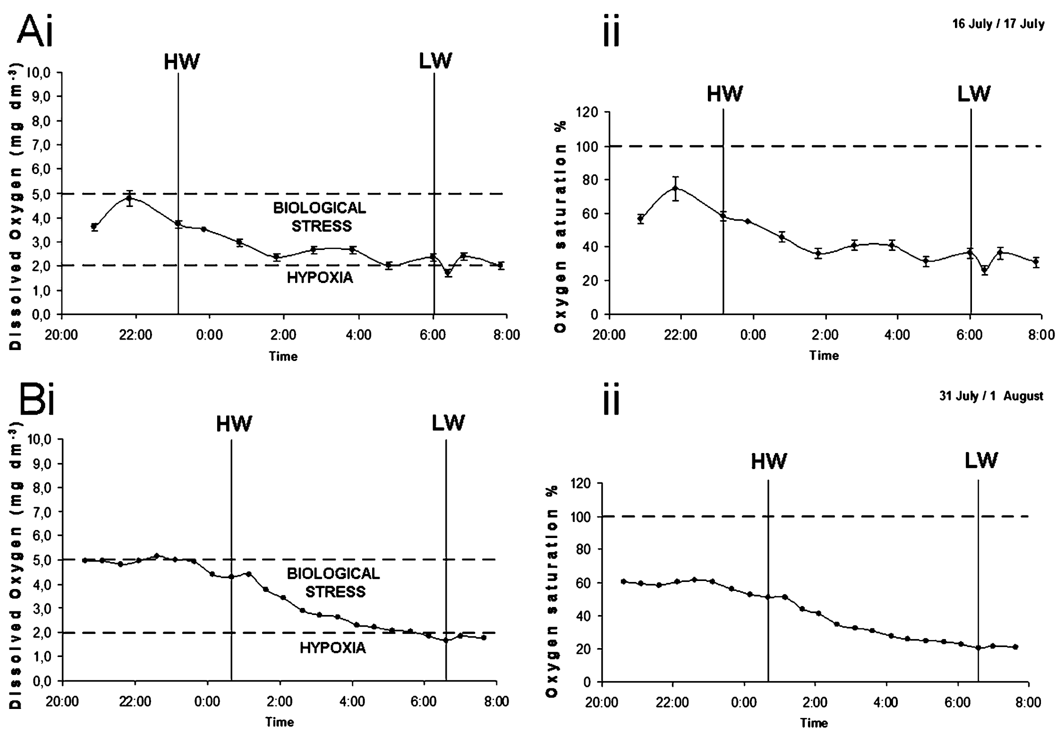

Fig. 4 Curves showing change in oxygen condition during the night at Portas do Mar (**PM** in Fig. 1). **A**, 16th to the 17th July 2005; **B**, 31st July to the 17th July 2005, **i**, dissolved oxygen concentration, upper and lower ——— show the limits below which biological stress and hypoxia occur, respectively; **ii**, % oxygen saturation, single ——— marks the 100% saturation. HW and LW show the time for high and low water over the sampling period.

values of DO are all below the biological stress concentration with a decrease from sunset until sunrise, with the lowest values at <2.0 mg dm^{-3} that are effectively hypoxic conditions (Fig. 4Ai, Bi).

Over the same two sampling periods, **PM** has a maximum saturation of 74.7% and a minimum of 20.3%, with an average of 47.5% (Fig. 4Aii, Bii). These figures support the observations of Mudge *et al.*[12] (2007) that oxygen saturation is reduced by increasing residence time of water masses within the inner regions of the western lagoon during the dry summer months, when the lagoon is effectively hypersaline.[10,20]

Summer hypoxia is a common problem. A well known example is the Chesapeake Bay[21] where extensive seasonal hypoxia in bottom waters of the main water body lasts about three months of the year. The northern Gulf of Mexico is currently the largest zone of oxygen-depleted coastal waters in the Atlantic Ocean. The extent of the hypoxic zone has varied in size from year to year since 1985 when the first systematic surveys were conducted.[2] Hypoxic bottom waters have extended at times over 20 000 km^2 in the summer.[2]

The results of the study from the Ria Formosa show that the oxygenation of the waters in the inner part is of concern, particularly, for the aquaculture industry and fisheries. Nevertheless, oxygenation in this lagoon is not as poor as in other similar systems: the dissolved oxygen in the Adyar Mangrove at night is between 0.1 and 8.8 mg dm^{-3},[22] compared to 1.7 and 5.2 mg dm^{-3} in the Ria Formosa.

Other examples of hypoxia and or anoxia in the literature are for: Italy, the Sacca di Goro lagoon;[23,24] Croatia, Erka Estuary;[25] China, the Pearl River estuary;[26] Australia, the Swan River;[27] many locations in the United Stated of America, York River,[28] Virginia estuaries,[29] New York Bight,[30] Long Island Sound,[31] Pamlico River Estuary,[32] Florida Keys.[33]

Conclusions

1. In the European context, dissolved oxygen (DO) "condition" is an important Chemical Quality Element of the WFD,[4] but one that has been somewhat neglected, with a dependency on historical data bases to provide the necessary data for screening models (*e.g.* for the Ria Formosa).[6,8]

2. DO measurements from data bases should be used with caution as each datum point should be assessed for quality. For example, missing data for temperature, date, time or coordinates of the sampling site invalidate the use of these measurements.

3. The sampling regime is of particular importance as the most deleterious changes in DO occur during periods that are the most inconvenient for sampling. Furthermore, location of sampling sites is important for addressing localised problems, such as inadequate water exchange (*e.g.* for the Ria Formosa).[12]

4. The somewhat technical issues raised by points 1–3 have important consequences for environmental monitoring and management. Eutrophication has been identified as the major threat to the Ecological Quality of the Ria Formosa in view of the land use in the catchment of the lagoon.[8] Portugal, as a member of the EU, has adopted the WFD[4] which aims at the prevention, protection and the improvement of the quality of the environment, the protection of the human health, and the rational and cautious use of natural resources.

5. The night time oxygen sags at the inner stations of the Ria Formosa detected in this study and others are one of the symptoms of the onset of hypoxia (<2 mg dm^{-3} DO). This is an important environmental problem causing grave perturbations in the structure and function of aquatic ecosystems,[2] and is a situation that should be carefully monitored and management measures applied to reduce the risk of more persistent hypoxia.

6. Global change has shown the research community that long term monitoring and observation are important tools to understanding changes in carbon dioxide (CO_2). A similar data effort with monitoring stations around the world that have documented recent increase in atmospheric CO_2 is needed for documenting changes in DO. Model predictions indicate that global changes could lead to a depletion of the oxygen in many earth systems.[34] Models rely on the availability of good quality data for model calibration and testing. Although there is a lot of data on DO in many data bases, these are not always available, or not in a coherent format.

Acknowledgements

This work was partially funded by the Instituto da Água (INAG), Portugal within the auspices of the RECITAL project. We thank the two anonymous reviewers for their suggestions to improve this paper.

References

1 R. J. Diaz, *J. Environ. Qual.*, 2001, **30**, 275–281.
2 R. E. Turner, N. N. Rabalais and D. Justic, *Mar. Pollut. Bull.*, 2006, **52**, 139–148.
3 J. E. Cloern, *Mar. Ecol.: Prog. Ser.*, 2001, **210**, 223–253.
4 E.C., *Official J.E.C.*, 2000, **L327**, 1e73(22.12.2000).
5 S. B. Bricker, J. G. Ferreira and T. Simas, *Ecol. Modell.*, 2003, **169**, 39–60.
6 A. M. Nobre, J. G. Ferreira, A. Newton, T. Simas, J. D. Icely and R. Neves, *J. Mar. Syst.*, 2005, **56**, 375–390.
7 S. Loureiro, A. Newton and J. D. Icely, *Estuarine, Coastal Shelf Sci.*, 2006, **67**, 382–398.
8 A. Newton, J. D. Icely, M. Falcão, A. Nobre, J. P. Nunes, J. G. Ferreira and C. Vale, *Cont. Shelf Res.*, 2003, **23**, 1945–1961.
9 L. Murray, S. M. Mudge, A. Newton and J. D. Icely, *Biogeochemistry*, 2006, **81**, 159–178.
10 A. Newton and S. M. Mudge, *Estuarine, Coastal Shelf Sci.*, 2003, **57**, 73–85.
11 L. P. O. C. Dionisio, G. Rheinheimer and J. J. Borrego, *Mar. Pollut. Bull.*, 2000, **40**, 186–193.
12 S. M. Mudge, J. D. Icely and A. Newton, *J. Environ. Monit.*, 2007, **9**, 1194–1198.
13 A. M. Bettencourt, S. B. Bricker, J. G. Ferreira, A. Franco, J. C. Marques, J. J. Melo, A. Nobre, L. Ramos, C. S. Reis, F. Salas, M. C. Silva, T. Simas and W. J. Wolff, *Typology and reference conditions for Portuguese transitional and coastal waters*, ed. INAG and IMAR, Ideias Virtuais, Portugal, 2004, pp. 1–98.
14 K. Grasshoff, M. Ehrhard, K. Kremlingand L. G. Anderson, *Methods of Seawater Analysis*, Wiley-VCH FR Germany, 3rd edn., 1999, pp. 1–632.
15 R. F. Weiss, *Deep Sea Res.*, 1970, **17**, 721–735.
16 R. Diaz and R. Rosenberg, *Oceanog. Mar. Biol. Ann. Rev.*, 1995, **33**, 245–303.
17 K. Vaquer-Sunyer and Carlos M. Duarte, *Proc. Natl. Acad. Sci. U. S. A.*, 2008, **105**, 15452–15457.
18 R. Cachola and M. A. A. Sampayo, *Pesca e Navegação*, 1984, **45**, 24–27.
19 A. Newton and S. M. Mudge, *Estuarine, Coastal Shelf Sci.*, 2005, **62**, 405–414.
20 S. M. Mudge, J. D. Icely and A. Newton, *Estuarine, Coastal Shelf Sci.*, 2008, **77**, 278–284.

21 D. F. Boesch, *Ecol. Eng.*, 2006, **26**, 6–26.
22 V. Selvam, V. Hariprasad, R. Mohan and R. Ramasubramanian, *Ind. J. Mar. Sci.*, 1994, **23**, 94–97.
23 S. Vincenzi, G. Caramori, D. Rossi, R. Leoa and A. Giulio, *Ecol. Modell.*, 2006, **193**, 90–104.
24 J. M. Zaldıvar, E. Cattaneo, M. Plus, C. N. Murray, G. Giordani and P. Viaroli, *Cont. Shelf Res.*, 2003, **23**, 1847–1875.
25 T. Legovic, D. Petriciolo and V. Zutic, *Mar. Chem.*, 1991, **32**, 347–359.
26 K. Yin, Z. Lin and Z. Ke, *Cont. Shelf Res.*, 2004, **24**, 1935–1948.
27 H. Astill and P. S. Lavery, *Hydrol. Processes*, 2001, **15**, 2387–2399.
28 R. J. Diaz, R. J. Neubauer, L. C. Schaffner, L. C. Pihl, S. P. Baden in Marine Coastal Eutrophication, ed. R. A. Volenweider, R. Marchetti and R. Viviari *Proceedings of International Conference, Bologna 1990 in Science of the Total Environment*, Special Supplement, 1992, 1055–1068.
29 A. Y. Kuo and B. J. Neilsen, *Estuaries*, 1987, **10**, 277–283.
30 R. Waldhauer, A. F. J. Draxler, D. G. McMillan, C. A. Zetlin, S. Leftwich, A. Matte and J. E. O'Reilly, *Estuaries*, 1985, **8**, 129A.
31 B. L. Welsh and F. C. Eller, *Estuaries*, 1991, **14**, 265–278.
32 D. W. Stanley, *37th Conference of the International Association for the Great Lakes Research and Estuarine Research Federation Program and Abstracts*. IAGLR, Buffalo NY (USA), p. 165.
33 B. E. Lapointe and W. R. Matzie, *Estuaries*, 1996, **19**, 422–435.
34 IPCC. *Technical Paper on Climate Change and Water*, 2007.