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SEASONAL AND DIEL CHANGES IN SALINITY, TEMPERATURE, DISSOLVED OXYGEN AND SULPHIDE AT A STATION IN THE UPPER DERWENT ESTUARY, SOUTHEASTERN TASMANIA

by D.A. Ritz and R.E. Buttermore*
Department of Zoology, University of Tasmania and
Department of the Environment, Hobart.

(with six text-figures)

ABSTRACT

RITZ, D.A. and BUTTERMORE, R.E., 1984 (31 viii): Seasonal and diel changes in salinity, temperature, dissolved oxygen and sulphide at a station in the upper Derwent estuary, southeastern Tasmania. *Pap. Proc. R. Soc. Tasm.*, 118: 109-115. https://doi.org/10.26749/rstpp.118.109 ISSN 0080-4703. Department of Zoology, University of Tasmania and Tasmanian Department of the Environment, Hobart, Tasmania, Australia.

Temperature, salinity, oxygen saturation and sulphide levels fluctuated widely both seasonally and with depth at a station on the upper Derwent estuary just downstream from a pulp and paper mill. In summer (February) oxygen saturation at the bottom reached a minimum of about 20% and sulphide levels peaked at 11 mg L^{-1}. Conditions at this time would be expected to be lethal to a wide variety of organisms. Some of the possible causes for these changes are discussed.

INTRODUCTION

This study was undertaken as part of a wider programme to investigate the effects of discharging paper mill effluent into the upper Derwent estuary (Matthews 1979). During the study it became evident that, at times, the dissolved oxygen decreased to very low levels while sulphide levels increased considerably. Similar changes in dissolved oxygen and sulphide in estuaries have been reported by other workers (e.g. Bella *et al.* 1972) and levels of the order described are known to be hazardous to resident fauna (e.g. Colby & Smith 1967, Theede 1973, Caldwell 1975).

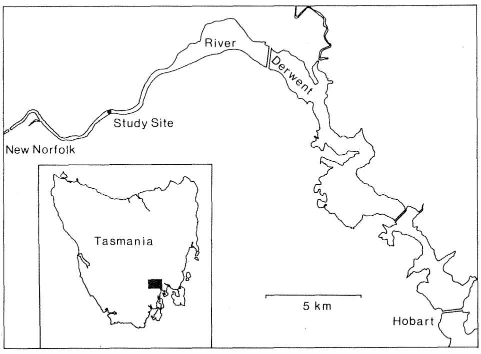
Since the areas of depleted oxygen and enhanced sulphide coincided with benthic faunal depauperation, it was decided to analyse the extent of the seasonal and diel changes in these factors. Changes in temperature and salinity were monitored simultaneously and pH was recorded. Very few studies of Australian estuaries have included diel and seasonal changes in water properties. An early study (Rochford 1953) recorded without comment oxygen and nutrient levels throughout two 24-hour periods at Old Beach on the Derwent River, and at a station on the Tamar River, northern Tasmania.

MATERIALS AND METHODS

One sampling station situated about 1 km downstream of the pulp and paper mill at Boyer (fig. 1) was selected for detailed study. This station occurs in the gradient zone of the estuary (Guiler 1955) and is also located near the average position of the toe of the salt wedge (Matthews 1979).

This station was sampled throughout a 24-hour period on four occasions to represent autumn, winter, spring and summer: 24-25th May 1978, 17-18th August 1978, 28-29th November 1978, 27-28th February 1979. Further limited data were obtained on 16th May 1979. Sampling was carried out from an anchored boat and temperature and salinity were measured hourly at surface, 3 m depth and within 0.5 m of the bottom (5-6 m depth depending on state of tide), using an Autolab salinometer (Yeo-Kal, Environmental Electronics). Dissolved oxygen was also measured hourly using a Yellow Springs oxygen meter. Since the cable length was insufficient for the deeper sampling, water samples were obtained with a Van Dorn closing bottle. Every three hours, 1 L samples of water from the three depths were retained and preserved for later sulphide analysis (A.P.H.A. 1975). At the same time pH was recorded for these samples.

During the first sampling session, it was decided to use a modified Winkler titration (A.P.H.A. 1975) as a check on the performance of the dissolved oxygen meter, and also for measuring dissolved oxygen at 6 m. It was suspected that high concentrations of sulphides and other substances anticipated at this depth might interfere with the probe operation. In practice, the delay between collecting samples and their titration in the laboratory (up to 36 hours) led to results which were obviously inaccurate. High levels of suspended organic matter present in the water at 6 m probably contributed to this error (A.P.H.A. 1975). The Winkler titration was subsequently abandoned and the dissolved oxygen probe was calibrated before use and during operation.



RESULTS

Temperature and Salinity

Temperature and salinity records from the four main sampling dates are given in figures 2 and 3, and figure 4 shows temperature and salinity depth profiles measured in May 1979. The latter sampling occurred at about 2 hours prior to high tide in Hobart. According to Matthews (1979), high tide at Boyer lags behind that at Hobart by about 100 minutes.

In May 1978 when total river discharge was relatively low, i.e. 240×10^6 m^3 (Matthews 1979), salinity fluctuations at 3 m were very marked (fig. 3). The range of salinities experienced at this depth was about 12-24‰ and the cyclical nature of the change was evident to some degree. Surface and bottom salinities remained nearly constant at about 1.5 ‰ and 24.5‰ respectively. Times of high and low tides at Hobart are shown in figure 2 and succeeding figures where appropriate.

The stratification of the river at this time of year is clearly shown in figure 4 where, with a depth change of only 0.5 m, salinity can change by as much as 15‰ and temperature by nearly 7°C.

At times of peak river flow in August 1978, i.e. a total of around 450×10^6 m^3 (Matthews 1979), the water was isothermal and fresh throughout the sampling period (fig. 2). In November when the monthly flow had decreased to less than 200×10^6 m^3 distinct changes in the water characteristics were apparent. The surface water was nearly isohaline and isothermal at around 0.5‰ and 18°C respectively. However, at 3 m there was clear evidence of a tidal current between 1000 and 1600 when the salinity increased from around 2‰ to a maximum of 13‰ at 1400. The deeper water at 6 m remained relatively isohaline and isothermal throughout. It appears from these data as though the tide at Boyer lags behind that at Hobart by rather more than the 100 minutes estimated by Matthews (1979). Because the station was situated in a small bay out of the main river channel the tidal effect could have been further delayed by local eddy circulation.

In February when river flow was at a minimum, 145×10^6 m^3 (Matthews 1979), salinity fluctuations at both 3 m and 6 m were particularly intense (fig. 3). Surface salinity remained uniform at about 1‰ , but that at 3 m showed a cyclic fluctuation between about 2‰ and 14‰. Bottom salinity varied between 18‰ and 24‰ with a less obvious cycle. Temperature varied only between about 16° and 20°C from surface to bottom. Apparently there is little difference in temperature between fresh and salt water at this time of year.

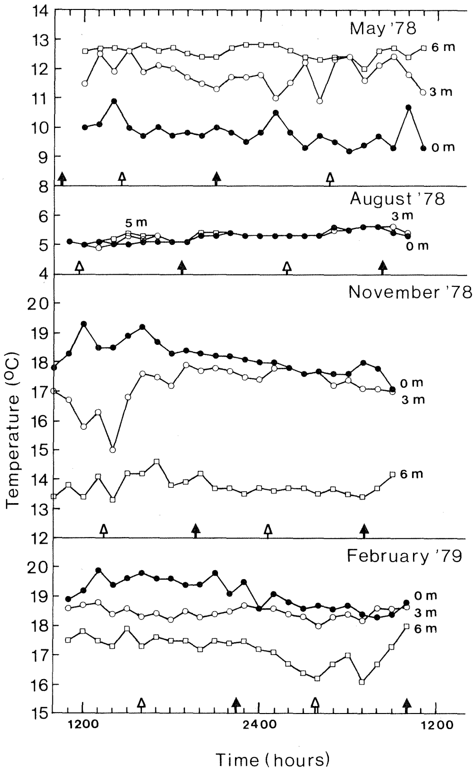


FIG. 2 - Temperatures at study site during four sampling periods and at three depths. ▲ - time of high tide; △ - time of low tide.

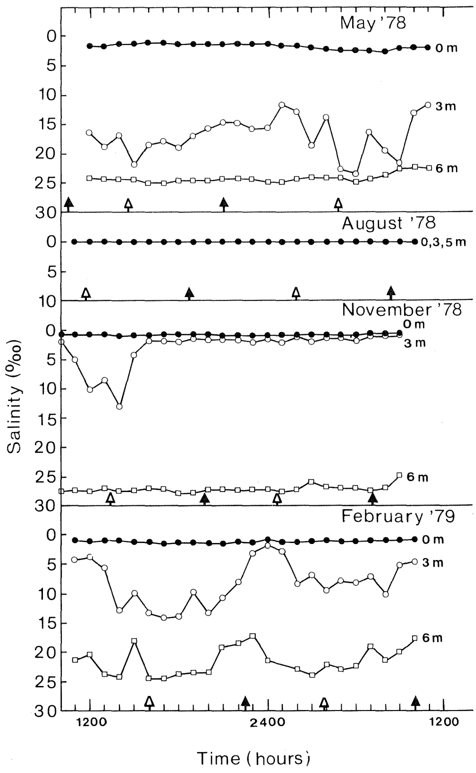


FIG. 3 - Salinity at study site during four sampling periods and at three depths. ▲ - time of high tide; △ - time of low tide.

Dissolved Oxygen

As might be expected the surface oxygen levels remained high, i.e. between 80 and 100% saturation or slightly above throughout the study. However, subsurface oxygen levels were subject to considerable fluctuation. In August when the water column was entirely fresh and about 5°C, oxygen saturation at all depths remained close to 100% (fig. 5). At other times oxygen saturation was usually somewhat lower and values at the surface and at 3 m coincided fairly closely. Occasionally there were departures from this pattern, e.g. at 1400 to 1600 in February and at 0600 to 0900 in May where the values at the surface and at 3 m differed by up to 20%. The reasons for this may have been the sharp discontinuity just below 3 m (fig. 4). Slight displacement of the water sampling bottle either up or down could have resulted in large differences in the measured oxygen. The divergence in oxygen values at 0 m and 3 m could have been the result of tidal influence although they do not coincide with the obviously tidally related salinity cycles (fig. 3). In fact, in February, rising salinities at 3 m and below between 1300 and 2000 suggesting the input of high salinity water on the rising tide, coincided with a drop in oxygen saturation at 3 m.

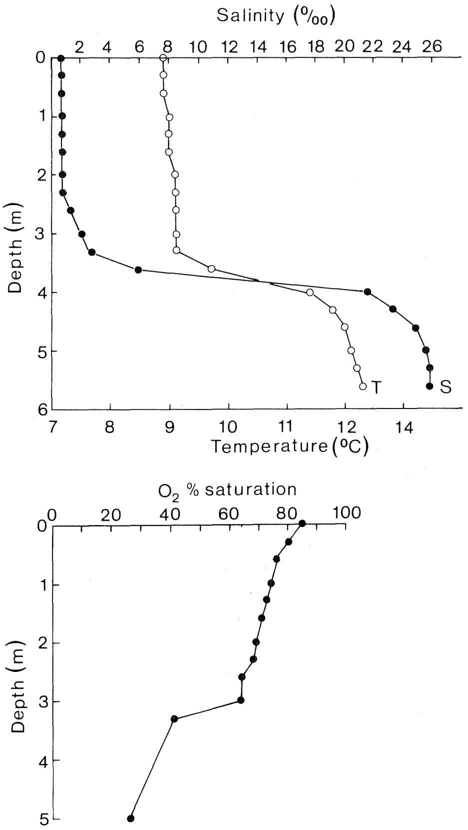


FIG. 4 - A: Temperature and salinity/depth profiles. B: Oxygen saturation/depth profile. All measurements on 16.5.79.

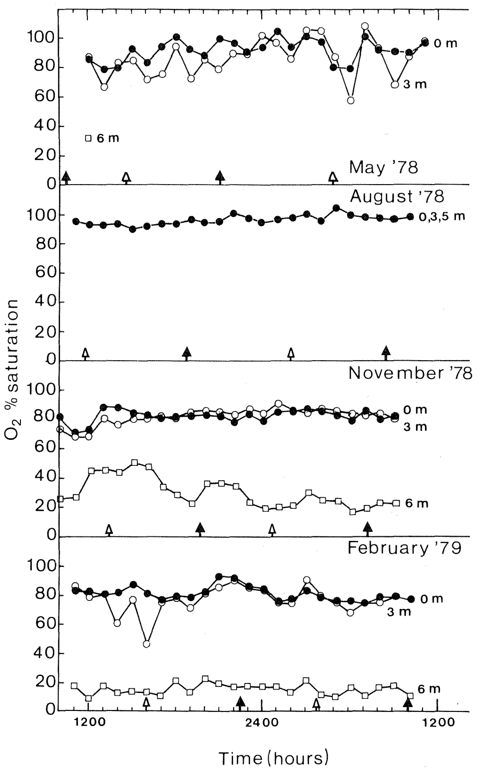


FIG. 5 - Oxygen saturation at study site during four sampling periods and at three depths. ▲ - time of high tide; △ - time of low tide.

Apart from the August samples, oxygen saturation values at 6 m were, with only one exception, less than 50%. The single reading of 32% saturation in May 1978 was supplemented by very similar values recorded in May 1979 (fig. 4).

Oxygen saturation values at 6 m in November showed considerable fluctuation between about 50% and 20%. The period of highest oxygen levels at 6 m, i.e. between 1200 and 1600 coincided with the period of highest salinities at 3 m (fig. 3). Thus oxygen may have been replenished by the rising tide. The oxygen levels at 3 m did not show the same cyclical change but this may have resulted from the inherent instability of the mid-depth (fig. 4) as explained above.

Oxygen saturation values showed no clear diel cycles.

Sulphide Levels

In May the surface and 3 m sulphide levels remained uniformly low whilst those at 6 m reached a maximum of 2.8 mg L^{-1} at 0600 (fig. 6). The slight fluctuations recorded at 6 m could have been tidally related since the sampling routine (3-hourly) may have masked the variation. However, they are not mirrored at 3 m where the greatest salinity fluctuations were experienced (fig. 3).

The August and November sulphide levels were uniformly low at all depths (fig. 6). However, in February, the highest levels and the greatest fluctuations were recorded. Highest concentrations reached were 10 to 11 mg L^{-1} at 6 m at 2100 and 0300 respectively. The period between these two times corresponds roughly to the period of lowest salinity and hence ebbing tide. Conversely the period of lowest sulphide levels corresponds roughly to the period of highest salinities, i.e. 1400 to 2000 and 0400 to 0800. However the inverse correlation between salinity and sulphide concentration at both 3 m and 6 m proved not to be significant ($P > 0.05$).

The fluctuations in sulphide levels do not obviously coincide with similar fluctuations in oxygen saturation although any possible correspondence between the two may have been masked to some extent by the different sampling regimes.

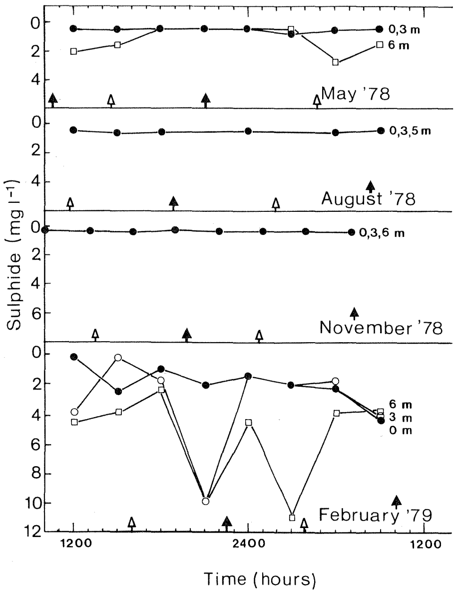


FIG. 6 - Sulphide concentration at study site during four sampling periods and at three depths. ⬆ - time of high tide; ⇧ - time of low tide.

pH

pH was lowest in August, i.e. 6.5 to 6.8, when the site was dominated by fresh water at all depths. At other times the pH varied little with a range from 6.8 to 7.2 with no seasonal trend.

DISCUSSION

Matthews (1979) collated physico-chemical data on the upper Derwent estuary and presented an interpretation of the hydrodynamic regime though his report contains serious errors. His conclusions about tidal exchange and particle transport rates are based on incorrect calculations of volume entering the estuary on a flood tide. The volume of freshwater entering the upper estuary closely matches the tidal prism in winter and the ratio is about 1:3 in summer. Thus the stratification and circulation pattern approach the classical salt-wedge estuary condition in winter but represent a partially mixed condition in summer (Perkins 1974).

One of Matthews' conclusions was that suspended wood fibre in the paper mill effluent entering the river at Boyer could accumulate and be deposited in the region with which the present study is concerned. He proposed a two-layer flow regime though due to the miscalculation assumed that the subsurface landward flow was much weaker than is probably the case. Without knowledge of such processes as waterlogging, flocculation and localized circulation patterns it is not possible to predict where particulate matter from the effluent would be deposited. However, the data on N.F.R. (non-filterable residue) and sediment organic content support the suggestion that the particulate matter is deposited over a region extending at least 10 km downstream from the paper mill (Matthews 1979). Concentration of particulate matter seems to occur particularly over a stretch extending 5 km downstream from the mill except during periods of maximum river discharge when there is effective flushing. Slow decomposition of fibre mats would exert an oxygen demand on the overlying bottom water. Matthews speculated that photosynthetic activity is inhibited by the discolouration of the surface waters. Lack of a diel cycle in dissolved oxygen reported in the present study supports the argument that photosynthetic activity is insignificant in this part of the river. Interestingly the data of Rochford (1953) for dissolved oxygen in Tasmanian rivers shows no clear diel cycle.

According to Bella *et al.* (1972), hydrogen sulphide levels of 1 mg L^{-1} are not uncommon in water overlying sediments in Oregon estuaries. Where poor flushing characteristics are combined with such factors as high organic content, for example wood chips, shallow water depths and low dissolved oxygen, sulphide concentrations in the water were found to be as high as 12-16 mg L^{-1}. Such a description is apt for the station worked in the present paper especially in February when temperatures were highest, dissolved oxygen was lowest, and river flow reduced to a minimum. At this time of year levels of sulphide at the Derwent station were comparable to those reported by Bella *et al.* In fact the odour of hydrogen sulphide was conspicuously strong in February particularly at night.

The fluctuations in sulphide levels at the Derwent sampling station in February appear to be independent of dissolved oxygen. Bella *et al.* (1972) noted an inverse relationship between the two and Wheatland (1954) described how they might interact in a polluted estuary. The latter author described a lag phase in build-up of sulphide following a gradual decline in dissolved oxygen as the water warms up. This is apparently the case at the Derwent sampling station in November where dissolved oxygen levels at the bottom were nearly always less than 50% saturated while sulphide levels were still negligible.

Hydrogen sulphide occurs in solution as part of a pH-dependent system, i.e. $H_2S \rightleftharpoons HS^- \rightleftharpoons S^{2-}$. At pH levels recorded during the present study, i.e. between 6.5 and 7.2, free sulphides are divided between the forms H_2S and HS^- (Bella *et al.* 1972). Increase of the pH towards 8 would increase the toxicity of H_2S because it would shift the equilibrium towards the dissociated species (Theede 1973). Sulphide levels reported for the sampling station examined in this study would almost certainly be lethal to a wide range of organisms. Benthic diatoms succumbed within 48 hours to levels of 0.9-6.8 mM (31-231 mg L^{-1}), showing a high degree of tolerance (Admiraal 1979). On the other hand, the 96 hour LC50 for an amphipod was 0.2 mg L^{-1} and early embryos of *Crassostrea gigas* were drastically affected within 2 hours of exposure to only 0.32 mg L^{-1} (Caldwell 1975). Concentrations of less than 0.075 mg L^{-1} at pH 7.6-8 were reported by Colby & Smith (1967) to be harmful to several fish and particularly so to their eggs and fry.

During spring and summer months, the region of the Derwent estuary described here is almost devoid of macrobenthic organisms exceeding 500 μm (Matthews 1979). With increasing river flow in autumn (May), oxygen levels recover somewhat and sulphide levels are considerably reduced. Recolonization of the site, at least by polychaetes, is apparent at about this time. With maximum river flow in winter the site is flushed completely with fresh water, dissolved oxygen is restored to full saturation and sulphide levels are reduced still further. The steady-state location of the toe of the salt wedge lies in the region of the river investigated in this paper. The variable environmental conditions implicit in such a situation might be expected to suppress the faunal diversity even without the intervention of man-made effluent discharges. Matthews (1979) described a marked decrease in macrobenthic faunal diversity in this region of the river which he acknowledged could be partly attributable to its ecotonal (transitional) nature. Discharge of effluent with high oxygen demand could only exacerbate such a situation. The main source of concern is likely to arise from the aggregation and deposition of wood fibre the subsequent breakdown of which exerts a heavy B.O.D. and C.O.D. on the overlying water. Most severe effects are experienced in summer when dissolved oxygen levels reach a minimum, sulphide production is greatest and hydrogen sulphide gas is released at the surface.

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