

## Section 8: Sediment Oxygen Profiles and Fluxes as a Constraint on the Delivery of Organic Matter to Sediments

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Throughout the marine environment, typically more than 90 percent of the organic matter raining down from the upper layers of the ocean is metabolized by organisms living on and in the sea-floor sediments. In the open ocean, oxygen ( $O_2$ ) accounts for about 90 percent of this metabolism of organic matter (Jahnke and Jackson, 1992), while in coastal environments other oxidants can be responsible for a substantial fraction of it. However, because oxygen ultimately reacts with the products of organic matter reactions with oxidants other than  $O_2$ , fluxes of oxygen into the sediments provide a direct measure of the rate of organic matter oxidation (Canfield and others, 1993). In areas of the sea floor where the rate of organic matter deposition increases, there is a similar increase in the oxidation rate (at steady state). Often visible color zones develop in sediments reflecting the sequence in which the different oxidants are used to break down the organic matter at different depths in sediment. Oxidation is first by  $O_2$ , followed by nitrate ( $NO_3^-$ ), nitrite ( $NO_2^-$ ), manganese oxides, iron oxides, and sulfate ( $SO_4^{2-}$ ). The sequence is everywhere similar, with only the depth of the zonation differing in response to organic matter deposition rates. This zonation is of great importance to the fate of metals deposited in the sediments, because the products of reaction with different oxidants have a strong influence upon metal cycling between solid phases and the interstitial waters, and can influence the release of metals from contaminated sediments to the overlying water (see Section 10 on metal recycling).

A critical geochemical boundary in sediments is the depth beneath the water-sediment interface at which the concentration of  $O_2$  drops to 0, marking the onset of oxidations by compounds other than oxygen and reactions that change the partitioning of many metals (and contaminants) between the solids and interstitial waters of the sediments. The depth of  $O_2$  penetration in sediments is related to the organic matter deposition rate, the rate at which the organic matter is metabolized (Cai and Sayles, 1996), and the bottom water  $O_2$  concentration. Hence, changes in the rate of organic matter deposition can be expected to change the  $O_2$  penetration depth. Increases in organic matter deposition rate tend to decrease  $O_2$  penetration depth while lower deposition increases it.

### Sediment $O_2$ Profiles in Massachusetts Bay

The importance of oxygen to both organic matter oxidation and sedimentary metal cycles led to the development of a study to characterize  $O_2$  profiles in the sediments of Massachusetts Bay. The expected responses

of sedimentary  $O_2$  profiles and fluxes to changes in the deposition rate of metabolizable organic matter provided an opportunity to investigate the possible effect of sewage effluent discharge on the  $O_2$  profiles and fluxes in sediments near the new Massachusetts Bay outfall. The hypothesis was that enhanced deposition of metabolizable organic matter would alter the sediment  $O_2$  profiles and fluxes. To this end, studies were undertaken at a site (USGS Station 3, fig. 7.1) characterized by fine-grained sediment in which organic matter is known to accumulate. The field measurements were conducted in the period September 1995–February 2005. With few exceptions, three cruises per year were carried out, one each in February–March, May–June, and September–October, to provide a seasonal perspective to the data collected.

Sediment  $O_2$  profiles were determined in situ with polarographic oxygen electrodes mounted on a profiler (described by Sayles and others, 1996, the approach is similar to that developed by Revsbech and others, 1980). This instrument is a small tripod (fig. 8.1) that is lowered to the sea floor, cast loose from the ship so other activities can be pursued, and retrieved after completion of its preset program (after about 45 minutes). Three electrodes simultaneously collect three profiles during each deployment. The depth increments for the profiles in Massachusetts Bay were 0.54 millimeters (mm) near the interface, increasing to 1.08 mm after 47 steps. Two deployments for each cruise were planned but not always achieved.

Figure 8.2A illustrates the typical distribution of  $O_2$  with depth at the study site. As illustrated here,  $O_2$  is rapidly exhausted below the sediment-water interface.  $O_2$  rarely penetrates below 10 mm and typically reaches  $O_2=0$  at 3 to 6 mm. Figure 8.2B illustrates a complicating effect caused by the activities of burrowing organisms on the distribution of  $O_2$  in the sediment. The rapid increase in  $O_2$  below an  $O_2=0$  depth of 4.5 mm is indicative of the advection of  $O_2$  into the sediment by biological activity. Fewer than 10 percent of the profiles exhibited similar perturbations; these profiles were not used in the determinations of  $O_2=0$  or  $O_2$  fluxes. The two profiles of figure 8.2 illustrate how heterogeneous the sediments are on a small spatial scale. These two profiles are from one deployment; the electrodes were separated by about 9 centimeters (cm). Such variation inevitably enhances scatter in the results. The data from profiles such as figure 8.2A form the basis of our calculations of  $O_2$  fluxes and  $O_2=0$  depths.



**Figure 8.1.** Winter recovery of the profiler on a typical February cruise. The clear plastic shroud in the center of the instrument houses the mobile sensor head on which are mounted the three electrodes and light sensor used to locate the sediment-water interface. Lending invaluable assistance are crew members of the U.S. Coast Guard Cutter *Marcus Hanna*.

## Sediment O<sub>2</sub> Fluxes

The diffusive fluxes of O<sub>2</sub> into the sediment were calculated on the basis of the estimated O<sub>2</sub> gradient at the interface. Gradients at the interface, depth  $x=0$ , were determined by fitting an exponential to the first 5 or 6 points that represent measurements made in the sediment. The algorithm used was

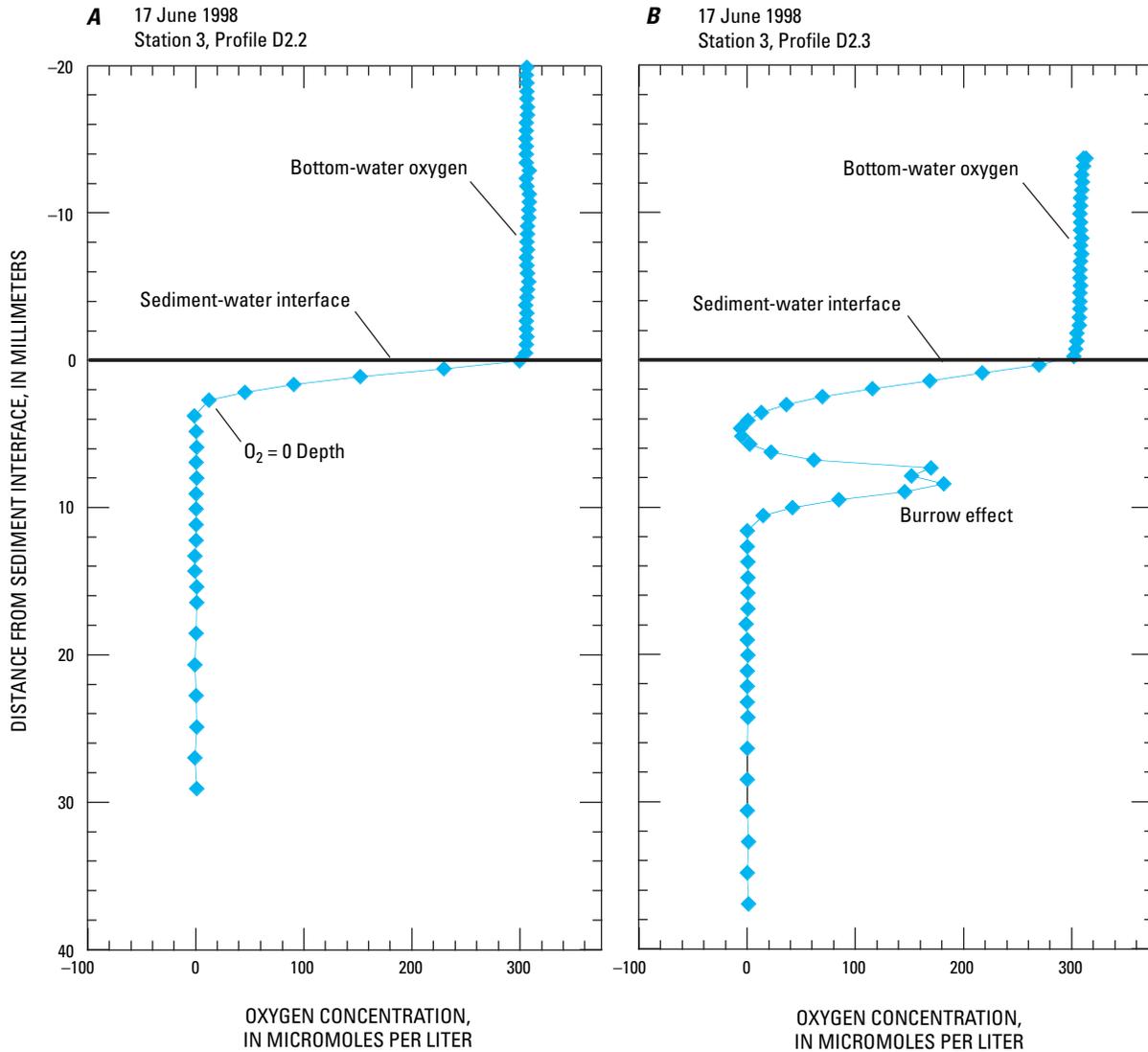
$$C/C_o = a_1 [1 - \exp(-a_2 x)] + a_3, \quad (1)$$

where  $C$  is the electrode response at depth  $x$ ,  $C_o$  is the electrode response in bottom water, and  $a_1$ ,  $a_2$ , and  $a_3$  are fitting parameters. For depth  $x=0$ , the derivative,  $dc/dx$ , of this expression is  $-a_1 * a_2$ . The gradient at the interface in terms of O<sub>2</sub> is  $-a_1 * a_2 * O_2 \text{BW}$ , where O<sub>2</sub>BW

is the bottom water O<sub>2</sub> concentration. The bottom water O<sub>2</sub> data used for the period 1995–2000 were interpolated from data collected during MWRA monthly monitoring cruises before and after our deployments. For the period 2000–2005, O<sub>2</sub> was measured in samples taken at the time of the deployment cruises (W.R. Martin, WHOI, 2005, written commun.). The flux was calculated as

$$J_{O_2} = -por * D_{sw} * (por^{.75}) * (dc/dx)_{x=0}. \quad (2)$$

In this equation  $por$  is the average porosity measured in the upper 3 mm of many sediment cores collected over many years,  $por^{.75}$  is a correction for sediment tortuosity (Klinkenberg, 1961; McDuff and Ellis, 1979) determined in those cores, and  $D_{sw}$  is the diffusion coefficient of O<sub>2</sub> in seawater corrected for ambient temperature.



**Figure 8.2.** (A) Sediment oxygen ( $O_2$ ) concentration profile typical of those used in the estimation of sediment  $O_2$  diffusive fluxes and depths to  $O_2=0$ . Concentration is in units of micromoles per liter ( $\mu\text{mol/L}$ ) and depth in millimeters (mm). This profile is representative of the undisturbed profiles used in the calculations. (B) Sediment  $O_2$  profile that illustrates the strong influence that burrowing organisms can have on  $O_2$  profiles at the study site. Fewer than 10 percent of the profiles collected exhibit recognizable effects from burrowing activities.

The porosity and tortuosity values were supplied by W.R. Martin (WHOI, 2005, written commun.). Estimates of  $O_2$  fluxes for the entire period 1995–2005 are shown in figure 8.3. The data presented are the averages of values obtained from the three profiles typically collected during each deployment; sometimes one electrode failed, reducing the number of profiles to two. On a few occasions, only a single profile was measured. On most cruises, two deployments were carried out. The measurements for each deployment on a given cruise are presented as an average; hence, there are often two values on a given sampling date. The data are grouped into the three time periods (February–March, May–June, and September–October) to reflect any systematic differences in fluxes between these three seasons. Within the variation of the flux data, one standard deviation ranged from 20 to 30 percent, and there was no significant difference between the pre- and post-outfall fluxes. Similarly, a Student t-test yielded no significant difference in the calculated fluxes for the pre- and post-outfall years for any of the three seasons (all t-probabilities were greater than 0.3).

An important qualification to this method of estimating sediment  $O_2$  fluxes should be noted. In coastal environments, diffusive fluxes often do not account for the total  $O_2$  flux; rather, biological activity, often termed irrigation, enhances transport across the sediment-water interface (Aller, 1980, Christensen and others 1984). Fluxes determined with benthic chambers do include both diffusive and biologically mediated exchange, and thus measure the total flux (Sayles and Dickenson, 1991). In eight instances where profiling was done at the same time as chamber deployments, the fluxes estimated from profiling were about 75 percent of the total as determined with the chambers (chamber  $O_2$  data from W.R. Martin, WHOI, 2005, written commun.). These results indicate that a significant  $O_2$  flux is not accounted for by diffusion. It is not possible to say whether or not this additional flux has changed as a result of the initiation of the outfall discharge. A significant change in sediment metabolism, however, would require that a large proportion of this flux be a result of oxidation of outfall material; because of the absence of change in the diffusive flux, this seems unlikely.

A second caveat to the conclusion regarding  $O_2$  fluxes relates to the rates of metabolism of outfall organic matter reaching the sediments. If these rates of metabolism are low, for example less than about 30 percent per year, the effect of enhanced organic matter delivery would not reach the maximum for about 10 years. Should such a slow reaction rate apply, small changes would not be observed for a number of years. A substantial change in delivery (that is an increase of about 50 percent), however, should be readily detectable in the 4 years of post-outfall data available.

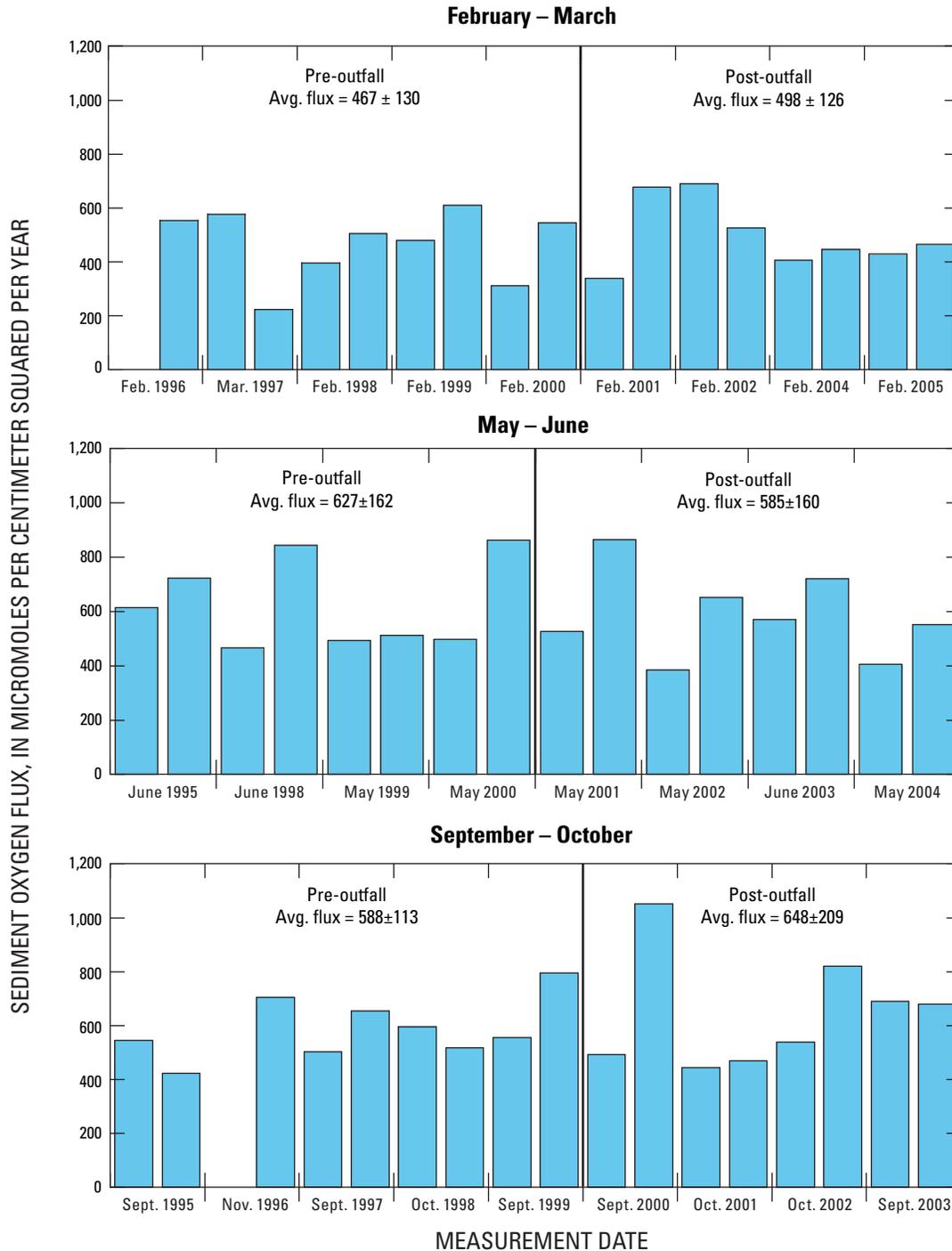
## Sediment $O_2$ Penetration Depths

The depths to  $O_2=0$  are summarized in figure 8.4. As in the case of sediment  $O_2$  fluxes, there were no discernible changes in the depths to  $O_2=0$  from the onset of use of the outfall. A Student t-test of the data from the pre- and post-outfall periods confirms this conclusion (the t-probability was greater than 0.3 for each of the three time periods).

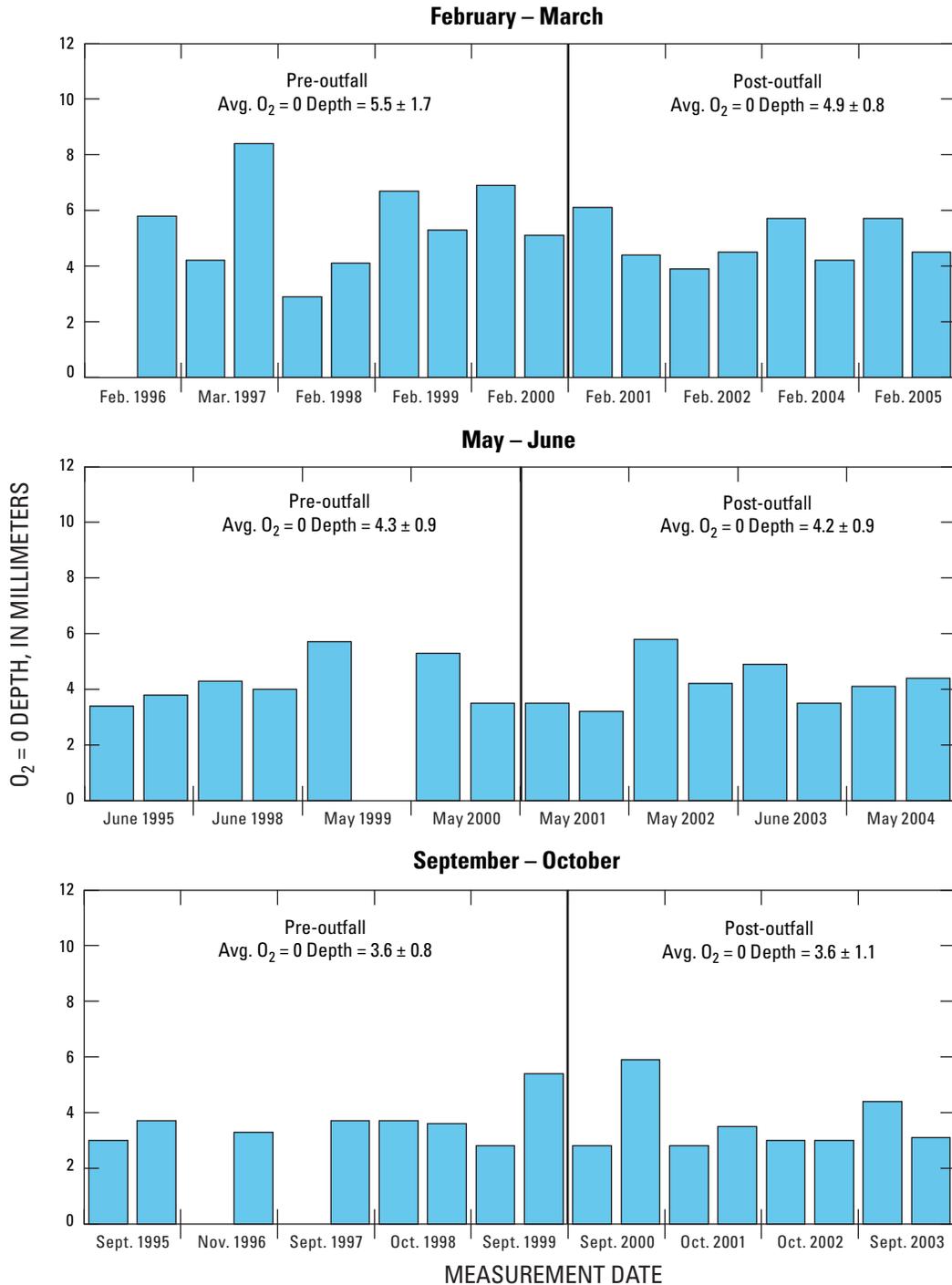
For  $O_2$  fluxes and depth to  $O_2=0$ , the differences between the February–March and September–October data sets are significant (t-probabilities are much less than 0.05). These results are consistent with the warmer temperatures and burn down of the spring–summer bloom material that are expected to enhance organic matter remineralization in the fall period, and thus to increase  $O_2$  fluxes and decrease  $O_2=0$  depths, as observed. Similar seasonal effects are observed in many coastal environments.

## Conclusions

Based on  $O_2$  concentration profiles, and depths to  $O_2=0$  in the surficial sediments at the study site, estimates of  $O_2$  diffusion into surficial bottom sediment provide no evidence of influence from sewage discharge from the Massachusetts Bay outfall. A substantial (about 25 percent) nondiffusive  $O_2$  flux, not detectable with the method used here, seems unlikely to alter this conclusion. A very slow reaction rate for outfall-derived organic matter could, however, delay the onset of detectable changes.



**Figure 8.3.** Average diffusive  $\text{O}_2$  fluxes for each instrument deployment in the three seasonal periods during which cruises were undertaken. The  $\text{O}_2$  fluxes are in units of micromoles per square centimeter per year ( $\mu\text{mol}/\text{cm}^2/\text{year}^1$ ). The height of each bar is the average of the estimates of flux for the three profiles typically collected during a single deployment. In most cases, there are two bars for a given date, representing the two deployments on that date. The heavy black line designates the startup date of the Massachusetts Bay outfall. The average flux (Avg Flux) and standard deviation ( $\pm$ ) for the pre- and post-outfall periods are given at the top of each panel.



**Figure 8.4.** Average depths to the  $O_2=0$  depth for each instrument deployment in the three seasonal periods during which cruises were undertaken. The  $O_2=0$  depths are in millimeters (mm). The height of each bar is the average of the estimates of  $O_2=0$  depth for the three profiles typically collected during a single deployment. In most cases, there are two bars for a given date, representing the two deployments on that date. The heavy black line designates the startup date of the Massachusetts Bay outfall. The average (Avg)  $O_2=0$  depth and standard deviation ( $\pm$ ) for the pre- and post-outfall periods are given at the top of each panel.