# Comparisons of Measured Productivity and the Composite Parameter $BZ_pI_0$ in Massachusetts Bay 2001-2010

Massachusetts Water Resources Authority

Environmental Quality Department Report 2013-10



# Citation

Keay, KE, Taylor DI, Hall MP, Leo WS, Libby PS. 2013. Comparisons of Measured Productivity and the Composite Parameter  $BZ_pI_0$  in Massachusetts Bay: 2001-2010. Boston: Massachusetts Water Resources Authority. Report 2013-10. 15 p. + Appendices.

# COMPARISONS OF MEASURED PRODUCTIVITY AND THE COMPOSITE PARAMETER BZ<sub>P</sub>I<sub>0</sub> IN MASSACHUSETTS BAY 2001-2010

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> > **June 2013**

**Report No: 2013-10** 

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# 1.0 Introduction

Revisions to MWRA's Ambient Monitoring Plan for the MWRA Effluent Outfall (MWRA 2010) were approved by regulators and became effective in December 2010; the changes included ending laboratory measurements of primary productivity, which is the rate of growth of marine plants in the presence of sunlight and nutrients. However, the Ambient Monitoring Plan Revision 2 does require MWRA to produce two reports on estimates of primary production. The first report (Keay et al. 2012) summarizes comparisons made between field measurements of primary productivity and those modeled using MWRA's water quality model, the Bays Eutrophication Model (BEM). This report fulfills the second requirement, and evaluates the relationship between productivity measurements and the Cole and Cloern (1987) light-biomass model  $BZ_pI_0$ .

# 2.0 Approach

Between 1992 and 2010, MWRA measured primary productivity by phytoplankton at three locations; station F23 at the mouth of Boston Harbor, station N18 a kilometer south of the Mass Bay outfall, and station N04, several kilometers to the northeast of the outfall. Methods and results from MWRA's primary productivity study are in numerous technical reports available on MWRA's website <a href="MWRA">MWRA</a> Environmental Quality Department Technical Reports List (for method details see Libby et al. 2005 Appendix C; results are reported in the annual Water Column Monitoring reports, for example, Libby et al. 2000). Primary production was measured using a small volume/short incubation time method (Lewis and Smith,1983) using procedures from Strickland and Parsons (1972).

In addition to making direct measurements of productivity, MWRA has previously evaluated the performance of light-biomass model  $BZ_pI_0$  (Cole and Cloern 1987) developed to estimate productivity in estuaries. In the  $BZ_pI_0$  model, chlorophyll biomass (B) integrated over the photic depth<sup>1</sup> ( $Z_p$ ) is multiplied by the amount of sunlight hitting the ocean surface ( $I_0$ ). In many well mixed estuaries where the amount of available light limits algal growth, the  $BZ_pI_0$  parameter tracks measured algal growth rates well enough to be used as a surrogate for measurements of primary productivity (Cole and Cloern 1987, Keller, 1988).

Comparisons of the modeled BZpI<sub>0</sub> parameter to measured productivity for the 1992 through 2000 monitoring years are contained in Kelly and Doering (1995, 1997), Cibik et al. (1996, 1998a, 1998b), and Libby et al. (1999, 2000, 2001). Results of these comparisons have been inconsistent, with measured productivity from some years and stations showing a better fit to the model than others.

A preliminary analysis of more recent data was performed by Shen (2009) who also found that the model fit varied between seasons, years, and stations.

After a thorough review of the previous reports and of the data, we decided to evaluate the relationship between productivity and  $BZ_pI_0$  for the years 2001 through 2010. There were two main reasons for this choice:

- The relationship between the parameters had been evaluated for 1992-2000;
- There are potential comparability issues between the 1992 to 2000 results and the 2001 to 2010 monitoring data for all parameters involved in the evaluation. Among them:

<sup>1</sup> Sunlight is fairly rapidly absorbed as it penetrates seawater, especially in turbid coastal systems. The photic depth is the depth to which enough sunlight penetrates to allow photosynthesis to occur.

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- Primary productivity methods changed multiple times during the 1990s. Any comparison for data before 1998 would entail using productivity data generated using very different protocols.
- Chlorophyll and calibrated fluorescence from most of 1998 through the end of 2000 are identified as "use with caution."<sup>2</sup>
- o Incident light (Irradiance) data measured by MWRA at the Deer Island Treatment plant roof were only available after 1996.

<sup>2</sup> This issue was discussed with regulators and the Outfall monitoring Science Advisory Panel in April 2001 (<a href="http://www.epa.gov/region1/omsap/omsap0401.html">http://www.epa.gov/region1/omsap/omsap0401.html</a>). After identifying the problems, chlorophyll data (and the calibrated fluorescence data that depend on them) were corrected to the extent feasible, but some uncertainties remained.

#### 3.0 Data Selection

In preparation for this report, all light data obtained by MWRA at the Deer Island Treatment Plant were reviewed in their entirety. Several data quality issues were identified, and the entire dataset was calibrated to improve year-to-year comparability in the incident light component of  $BZ_pI_0$  (Appendix A). Since the Deer Island light data were used in the original computation of the areal productivity data from MWRA's ambient monitoring, productivity data were recalculated using the recalibrated light data (Appendix B). Corrected areal productivity data were nearly identical to those originally calculated (Appendix B).

Computation of  $BZ_pI_0$  for the years 2001 through 2010 and pairing those results with concurrent measurements of areal productivity is detailed in Appendix C. That dataset included 325 concurrent determinations of areal productivity and  $BZ_pI_0$ . For 24 of those samples, calculated photic zone depth was greater than average water depth for the station. Equation 4 from Brush and Brawley (2009) provides a formula for correcting  $BZ_pI_0$  in these cases.

This correction was evaluated for the MWRA samples but was not applied, because for all 24 cases in which the measured water depth was less than the photic zone depth, the result of the Brush and Brawley (2009) correction was over 95% of the original  $BZ_pI_0$  computation.

Correlation and linear regression analyses between areal productivity and  $BZ_pI_0$  were run using SPSS release 19. Analyses were run on:

- The entire dataset.
- All samples split by year (2001 through 2010)
- All samples split by station (F23, N04, N18)
- All samples split by season (Winter-spring, Summer, and Autumn<sup>3</sup>)
- All data split by season and then station

SPSS version 19 was used for the exploratory data analyses. Both  $BZ_pI_0$  and areal productivity showed significant departures from assumptions of normality using the Shapiro-Wilk and Kolmogorov-Smirnov statistics. Log-transformed data also showed departures from normality. The correlation and regression analyses reported below were conducted using both the untransformed and ln-transformed data. Results were similar enough that only the untransformed results are discussed below.

Because of the exploratory nature of these analyses, no attempt has been made to correct for multiple comparisons, and significance levels for the statistics have not been tabulated. The large number of regressions run, coupled with the variability in the data, suggest that few if any of the regression slopes determined would differ significantly following a correction for multiple comparisons. Therefore, these slopes are neither tabulated nor discussed.

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Seasons are defined as follows: Winter-spring = January-April; Summer = May-August; Autumn = September-December.

# 4.0 Results

Relationships are discussed as "weak" if the  $r^2$  for the linear regression is less than 0.3, "moderate" if it is between 0.3 and 0.5, and "strong" if the  $r^2$  is greater than 0.5.

Published relationships between  $BZ_pI_0$  and areal productivity tend to be "strong" by these criteria. For example, Cole and Cloern (1987) document  $r^2$  ranging from 0.60 to 0.94. Keller (1988) documented relationships between the parameters in MERL mesocosm experiments and in Narragansett Bay ranging from 0.56 to 0.85. Finally, for the first three years of the MWRA monitoring, Kelly and Doering (1997) documented regressions between these parameters whose  $r^2$  ranged from 0.46 to 0.73.

By these criteria, nine (35%) of the regressions on untransformed data reported in Table 1 were weak, ten (38%) of the regressions were moderate, and seven (27%) of the regressions showed a strong relationship between the parameters.

All samples The regression of  $BZ_pI_0$  on areal productivity for all 325 samples taken together was moderate, with an  $r^2$  of 0.34 (Table 1). As expected for a relationship that explains only 34% of the variability in the data, there is a substantial amount of scatter around the best fit line (Figure 1).

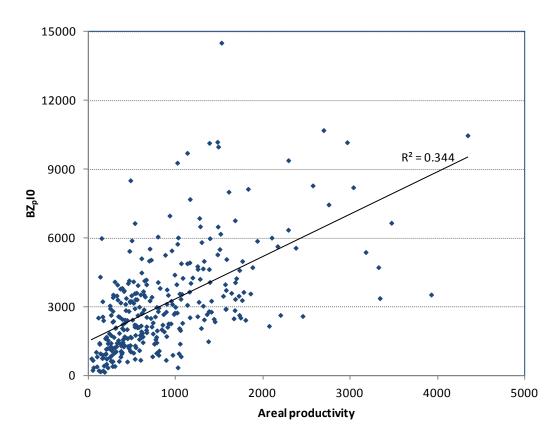


Figure 1. Scatterplot of areal productivity and  $BZ_pI_0$  for all samples and all surveys between 2001 and 2010 (325 samples). Best fit line and  $r^2$  from a linear regression are included. In all plots, areal productivity data have units of mg  $C^*m^{-2}*day^{-1}$  and  $BZ_pI_0$  has units of  $\mu$ g chl  $L^{-1}$  \* m \* einsteins m - 2day - 1.

 $\label{eq:condition} \textbf{Table 1. Correlation coefficients (r) and coefficients of determination (r^2) between Areal productivity and BZpI0 for 2001 to 2010 MWRA monitoring data.}$ 

		Raw		Log-transformed		
		r	r <sup>2</sup>	r	r <sup>2</sup>	n
All data		0.587	0.344	0.637	0.406	325
by Year						
2001		0.732	0.535	0.736	0.541	40
2002		0.7	0.49	0.8	0.639	38
2003		0.676	0.457	0.486	0.236	40
2004		0.791	0.626	0.874	0.763	30
2005		0.668	0.446	0.766	0.587	30
2006		0.604	0.364	0.765	0.585	30
2007		0.37	0.137	0.472	0.223	29
2008		0.319	0.102	0.432	0.187	29
2009		0.321	0.103	0.583	0.34	29
2010		0.772	0.595	0.712	0.507	30
By Station	By Station					
F23		0.7	0.491	0.726	0.527	60
N04		0.451	0.204	0.53	0.281	133
N18		0.68	0.462	0.672	0.452	132
By Season						
Spring		0.725	0.525	0.705	0.497	111
Summer		0.326	0.106	0.43	0.184	116
Autumn		0.623	0.388	0.653	0.427	98
By Season and Station						
Spring	F23	0.894	0.8	0.75	0.563	30
	N04	0.566	0.32	0.628	0.395	41
	N18	0.767	0.588	0.673	0.453	40
Summer	F23	0.376	0.141	0.436	0.19	20
	N04	0.33	0.109	0.365	0.133	48
	N18	0.415	0.172	0.598	0.358	48
Autumn	F23	0.655	0.429	0.832	0.692	10
	N04	0.432	0.186	0.556	0.31	44
	N18	0.789	0.623	0.751	0.564	44

Split by year When split by year, most data show moderate to strong regressions, with  $r^2$  ranging between 0.36 and 0.63 for 7 of the 10 years. 2007 through 2009 depart from this pattern, with weak relationships ( $r^2$  less than 0.15) between production and  $BZ_0I_0$  for those years (Table 1, Figure 2).

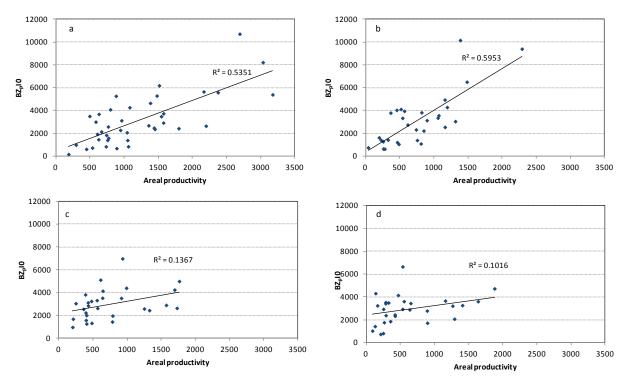


Figure 2. Scatterplots of areal productivity and BZ<sub>p</sub>I0 for selected years. In 2001(a) and 2010(b) the linear regression was strong, with an  $r^2 > 0.5$ . In contrast, in 2007(c) and 2008(d), the linear regression was extremely weak, with an  $r^2 < 0.15$ .

Split by station When split by station, the data show that across all years, regressions for stations F23 and N18 have an  $r^2$ at the high end of the "moderate" range (>0.45). In contrast, the regression for data from station N04 is weak, with an  $r^2 = 0.20$  (Table 1, Figure 3).

Split by season When split by season, the data show that spring and fall tend to have moderate to strong relationships between productivity and  $BZ_pI_0$ , while the regression for summer data is weak, with the regression explaining only about 10% of the variability in the data (Table 1 Figure 4). This observation is buttressed by the results of the season by station split. All three stations have regressions on summer only data with an  $r^2 < 0.2$  (Table 1).

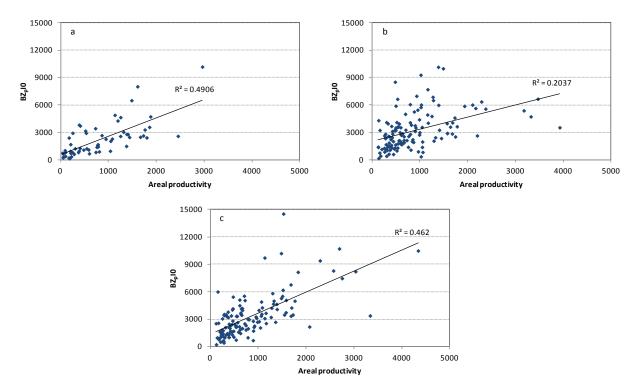


Figure 3. Scatterplots of areal productivity and  $BZ_pI0$  for individual stations. (a) F23(Harbor) (b) N04 (NE Nearfield) (c) N18 (near outfall).

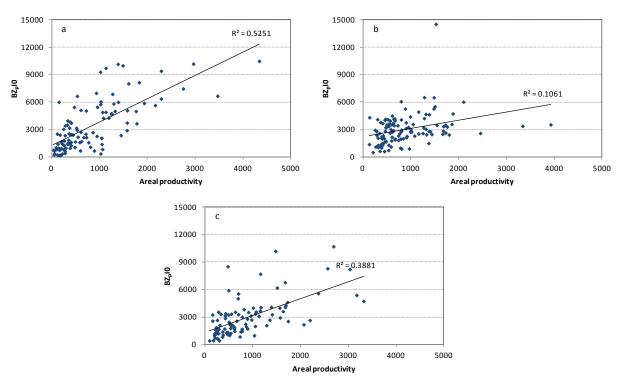


Figure 4. Scatterplots of areal productivity and  $BZ_pI0$  for monitoring seasons. (a) Winter-spring, February to April. (b) Summer, May to August. (c) Autumn, September-December.

Exclusion of summer data After inspecting the results of the split by season and the split by season and by station, the data were filtered to exclude the 116 samples from summer surveys, and the regressions between  $BZ_pI_0$  and areal productivity were repeated for all data, data split by year, and data split by station. These results are presented in Table 2.

The regression between  $BZ_pI_0$  and areal productivity for only winter-spring plus autumn samples for all stations and all years included 209 samples. The strength of the regression was moderate, with an  $r^2 = 0.45$  (Table 2, Figure 5), but was stronger than the regression that included all data (Table 1, Figure 1). A similar result can be observed for the regressions on data split by year and split by station. For all years with moderate or strong regressions between the parameters, the relationship between productivity and  $BZ_pI_0$  is improved by removing the summer data from the regressions. For 2004 the exclusion of summer data results in a substantial improvement in the fit of the data, increasing the  $r^2$  of the regression from 0.63 to 0.90 (Figure 6). In contrast, weak regressions seen between parameters for years 2007 through 2009 for all samples (Table 1) remained weak following the removal of summer data (Table 2).

Table 2. Correlation coefficients (r) and Coefficient of Determination  $(r^2)$  between areal productivity and  $BZ_pI0$  for 2001 to 2010 winter-spring and autumn MWRA monitoring data.

	Raw		Log-transformed		n
	r	r <sup>2</sup>	r	r <sup>2</sup>	
All data	0.675	0.456	0.685	0.47	209
by Year					
2001	0.823	0.677	0.846	0.716	26
2002	0.852	0.726	0.857	0.734	22
2003	0.717	0.514	0.544	0.295	26
2004	0.95	0.902	0.935	0.875	20
2005	0.692	0.479	0.755	0.57	20
2006	0.73	0.533	0.83	0.688	20
2007	0.496	0.246	0.562	0.315	19
2008	0.288	0.083	0.48	0.23	19
2009	0.296	0.088	0.567	0.321	19
2010	0.863	0.745	0.759	0.577	18
By Station					
F23	0.846	0.715	0.708	0.501	40
N04	0.485	0.235	0.592	0.35	85
N18	0.772	0.596	0.7	0.49	84

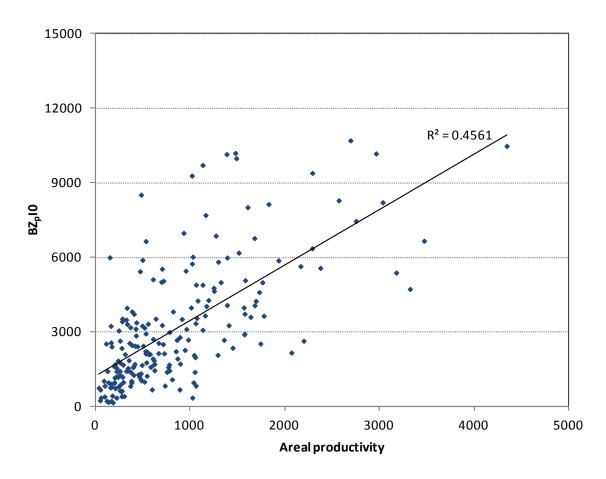
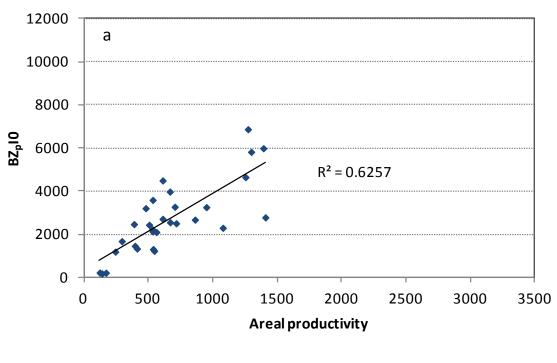


Figure 5. Scatterplot of areal productivity and  $BZ_pI0$  for all samples and all surveys between 2001 and 2010, after the exclusion of summer survey data (209 samples).

Similarly, the removal of summer data noticeably improved the fit between productivity and  $BZ_pI_0$  for results at stations F23 and N18. Regressions on data from those stations both have moderate  $r^2$  when all data are included (Table 1). When summer data are excluded, the regression for station F23 data has a strong relationship with an  $r^2$  of 0.72, while that for data from station N18 has an  $r^2$  of 0.60 (Table 2). The weak relationship between the parameters for data from station N04 is not substantially improved by the removal of summer data, with the  $r^2$  increasing only from 0.20 to 0.24.



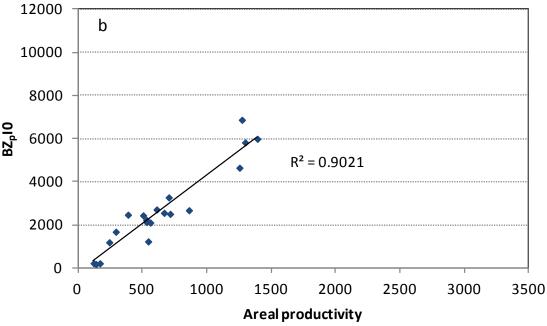


Figure 6. Scatterplot of areal productivity and  $BZ_pI0$  data from 2004, documenting the improvement in the regression when summer data are excluded. (a) All data,  $r^2 = 0.63$ . (b) Winter-spring and Autumn data only,  $r^2 = 0.90$ .

#### 5.0 Discussion

In general, the results of this evaluation are consistent with those observed in prior evaluations in MWRA water column monitoring reports, as well as those reported by Shen (2009). Regression model fits vary among seasons, years, and stations, and the coefficients of determination  $(r^2)$  are commonly not high enough to use calculated  $BZ_pI_0$  values as a proxy for primary productivity.

Some additional observations can be made from the analyses. First, as mentioned above, the moderate to strong relationships that exist between  $BZ_pI_0$  and productivity for most stations, years, and seasons is not evident for summer data. It is interesting to note that the  $BZ_pI0$  parameter was formulated for well-mixed estuaries, and in Massachusetts Bay during summer the water column is stratified. The lack of relationships observed during summer may reflect water column conditions very different from those in which the composite parameter  $BZ_pI_0$  was developed. When summer data are excluded from the regressions, over half of the regressions in Table 2 show strong  $r^2$  in the ranges reported by other researchers (e.g. Cole and Cloern 1987, Keller 1988).

Another observation is that moderate to strong relationships exist between the parameters for most winterspring and autumn data from the Harbor station F23 and station N18 in the nearfield. At N04, in contrast, only moderate (spring) to weak (summer, fall) relationships between productivity and  $BZ_pI_0$  were observed. Station N04 at the northeast corner of the nearfield is about 50m deep and somewhat further offshore than N18, which is about 30m deep. Stratification at N04 begins sooner and persists longer As with summer data, it is possible that the general failure of the  $BZ_pI_0$  parameter to reproduce patterns seen in the productivity data from this station may reflect an offshore water column at N04 very different from the systems in which the light-biomass model was developed.

The final observation is that the  $BZ_pI_0$  fit to productivity data is quite variable among years. Even after the exclusion of summer data, the  $r^2$  of annual regressions between productivity and  $BZ_pI_0$  ranged between a low of 0.08 in 2008 to a high of 0.90 in 2004 (Table 2).

The 10-year dataset of paired  $BZ_pI_0$  and primary productivity generated for this review highlights some interesting features of the water column processes in Boston Harbor and Massachusetts Bay. For example, data from station F23 (Figure 4a) show a number of samples with somewhat higher  $BZ_pI_0$  for the measured areal productivity than the "main" cluster of points (Figure 7). These samples were investigated to determine if they might share other distinguishing characteristics. Most of these samples came from winter-spring surveys, though four are from summer surveys. They tend to represent samples that simultaneously contained relatively high chlorophyll and were exposed to relatively high irradiance compared to other samples with similar levels of areal productivity. In other words, the relatively high  $BZ_pI_0$  seen for those samples does not appear to result from any one component in its formulation. Other questions include whether differences in the phytoplankton community (for example, the development or senescence of the *Phaeocystis pouchetii* blooms that tended to occur in late winter-spring) are associated with characteristic differences in  $BZ_pI_0$  or in the areal productivity calculations.

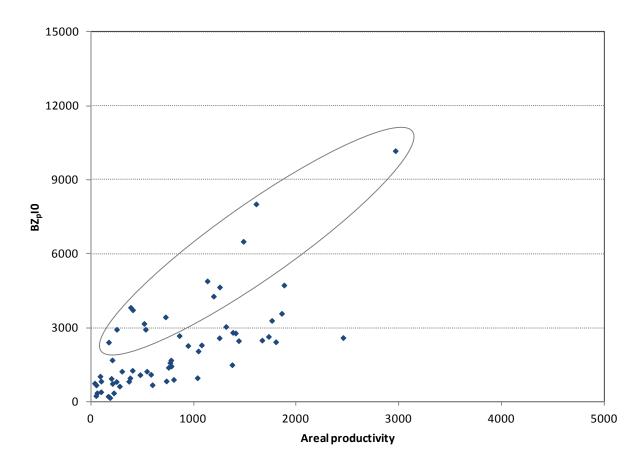


Figure 7. Scatterplot of areal productivity and  $BZ_pI0$  data from Boston Harbor station F23, 2001 to 2010. Samples subjected to additional evaluation are circled.

Other questions include whether differences in the phytoplankton community (for example, the development or senescence of the *Phaeocystis pouchetii* blooms that tended to occur in late winter-spring) are associated with characteristic differences in  $BZ_pI_0$  or in the areal productivity calculations.

#### 6.0 Conclusions

This review was based on the most recently and most comparably obtained light, biomass, photic zone depth and productivity data measured under MWRA's monitoring program. The relationship between areal productivity and the composite parameter  $BZ_pI_0$  does not appear to be consistently strong enough to rely on  $BZ_pI_0$  as a proxy for primary productivity at any given station for a single survey. It does however, show promise for helping evaluate the water column monitoring data.

The variability in the goodness of fit observed in these evaluations is not surprising. The  $BZ_pI_0$  model (Cole and Cloern 1987) is a simple model that uses light and biomass alone to predict phytoplankton production. The model assumes nutrient-replete conditions, and also assumes that phytoplankton biomass is mixed equally through the photic zone. 20 years of MWRA monitoring data document that these assumptions are at least seasonally violated by the waters in Boston Harbor and Massachusetts Bay. The fact that the  $r^2$  values especially during certain years, seasons and at certain stations were so low suggest that at least during certain years, stations and seasons, factors other than light availability and biomass regulated production. These factors might include nutrient availability, or phytoplankton grazing. It makes sense that the model does not track the actual measurements well during summers – when grazing is likely greatest and phytoplankton production in surface waters (in the bay, and maybe in the harbor) is likely nutrient limited.

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# 8.0 Appendices

Appendix A: Correction of 2PI irradiance data from Deer Island meteorological station

Appendix B: Recalculating productivity using revised light data.

Appendix C: Calculating BZpI0.

# $\frac{\text{Appendix A}}{\text{Correction of } 2\pi \text{ Irradiance Data From Deer Island Meteorological Station}}$

# **Background:**

While investigating the applicability of the " $BZ_pI_0$ " model as a proxy for 14C measurements of productivity, it became clear to MWRA ENQUAD staff that measurements of incident light ( $I_0$ ) made from the roof of Deer Island, suffered from instrument drift and mis-calibration, such that the light "envelope" over the year varied from year to year when it would be expected to be consistent (Fig. A-1). The difference can be up to about 20% of the light.

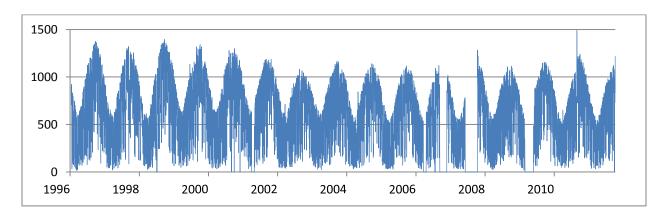


Figure A-1. Daily average  $2\pi$  irradiance measurements at Deer Island, showing instrument drift

In particular, the 2PI\_IRRAD sensor was deployed for longer than the one year recommended between calibrations. Degradation of sensor performance was determined and corrected as described in this document. In addition, calibrations prior to 11/6/2003 16:45 were high compared with all subsequent years possibly due to incorrectly applied calibration factors; these data were corrected by multiplying by factors that brought the data in line with the annual irradiance envelope from recent years when the instrument was better maintained.

#### **Procedure:**

# 1) Account for nonlinear instrument response

Based on empirical representations of radiative transfer equations, the Bird clear sky model (Bird and Hulstrom, 1981) estimates insolation based on solar angle and the cumulative effects of aerosols, water vapor, ozone and other gases, and Rayleigh (molecular) scattering upon sunlight reaching Earth's surface. A spreadsheet copy of the model was downloaded from the National Renewable Energy Laboratory website

at <a href="http://rredc.nrel.gov/solar/models/clearsky/">http://rredc.nrel.gov/solar/models/clearsky/</a>. The model was parameterized using the latitude and longitude of the sensor on Deer Island, and the default values for light-scattering parameters suggested in Bird and Hulstrom (1981).

The model provides, for each zenith angle, modeled solar insolation in watts/m<sup>2</sup>. These model outputs were used as a normalizing value with which to divide the measured irradiance. The normalizing function is plotted in Figures A-2 and A-3.

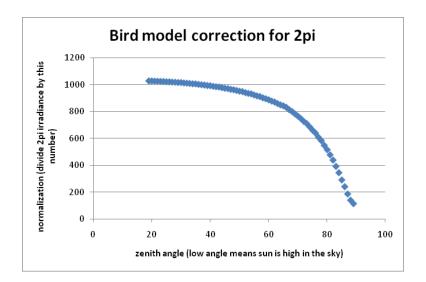


Figure A-2. Bird model correction: Normalize the data by dividing by the correction appropriate to the zenith angle corresponding to the date and time of each measurement.

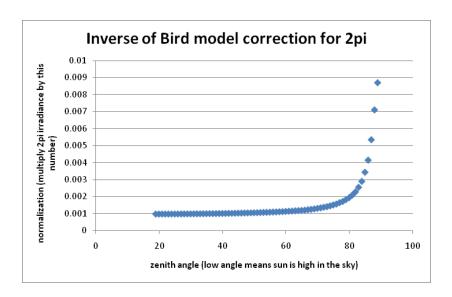


Figure A-3. Inverse of Bird model correction shown in Figure A-2, showing that at night/low light levels, the correction goes to infinity. Therefore, we only normalize relatively low zenith angles (mid-day data) to keep the values from blowing up.

We determined the zenith angle, and the resulting Bird model correction, for each year-day and hour. This allowed us to normalize the measured irradiance time-series for the time of year and time of day.

# 2) Determine deployments (segments)

In theory, each new deployment of an instrument should be a new EVENT\_ID in the database. However, some EVENT\_IDs actually correspond to multiple deployments. Records of when instrument was replaced, and what the correct calibration was, were spotty in early years.

Seeing when the values suddenly jump up enabled us to determine when the sensors were really replaced, because of the drift as described below. The start and end date of each segment were determined. There turned out to be eight segments, shown with different colors in Figure A-4.

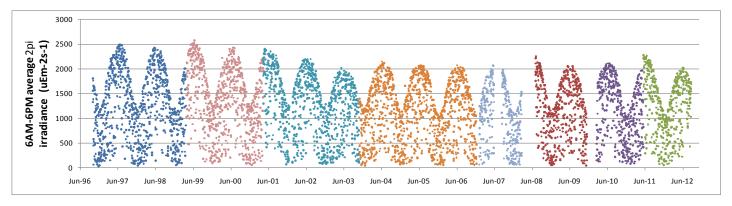


Figure A-4. Uncorrected  $2\pi$  irradiance data (daytime average) showing the different segments corresponding to sensor deployments.

# 3) Determine drift

Instruments are supposed to be cleaned regularly and replaced every 2 years. Normalizing for sensor response to solar angle, choosing sunny days only, and then filtering out noise, allows the trend to be determined. A proportionate decline per day was subtracted from the data to "level" them.

We determined the leveling in the following way. For each segment/deployment, we selected the uncorrected 2PI\_IRRAD data along with the Bird model correction value for the corresponding day-of-year and hour, just for <a href="https://linear.com/high solar altitude">high solar altitude</a> (zenith angles <= 65) and just for <a href="https://linear.com/clear-sky days">clear-sky days</a> were defined as those with percent monotonic change in irradiance > 90%, i.e. excluding those with "spiky" light time series. To reduce noise, we excluded cases where the ratio of 2pi irradiance to Bird model correction was not between 2 and 3, although we found that the results were similar without this restriction.

The resulting data were fit with a separate linear regression for each segment. The resulting slope was divided by the change in the Bird-model-normalized value over the number of days in each segment, to get a percentage change over the segment, or the "drift", for that segment.

The drift per day is applied to each raw datum, along with the number of days since the deployment/segment began, to get the "leveled" value as shown in Figure A-5.

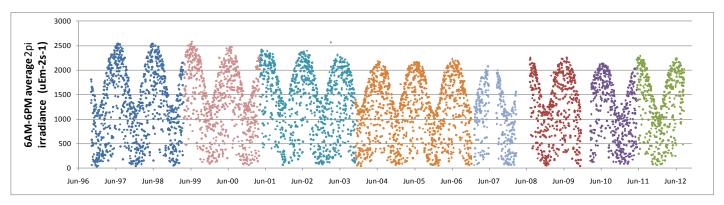


Figure A-5. "Leveled"  $2\pi$  irradiance data (daytime average) showing the different segments corresponding to sensor deployments.

# 4) Determine calibration adjustment

Raw data are supposed to have a calibration factor applied (based on factory calibration sheets.) This is just a multiplier for all the data. We know that recent deployments (segments 4 to 8) have been correctly calibrated, so it is possible to determine what to multiply each segment by, to get the clear-day, relatively-high-solar-angle average values to be the same over time – across all segments. This is the "calibration adjustment" for each segment.

The drift per day is applied to each raw datum, along with the number of days since the deployment/segment began, to get the leveled value, which is then multiplied by the calibration adjustment to get the final adjusted value for  $2\pi$  irradiance.

# 5) Review results, and update MOORING table with corrected data

The corrected values replaced the uncorrected values in the MOORING table. Maury Hall compared the daily average corrected data, with the record of sunny/cloudy days from Logan Airport as a reality check. These values can now be used for recalculating AREAL\_PROD and BZpIO.

The changes in  $2\pi$  irradiance are very small; they are larger in earlier years, than in 2001-2010. The daytime average daily  $2\pi$  irradiance before and after correction is shown in Figure A-6.

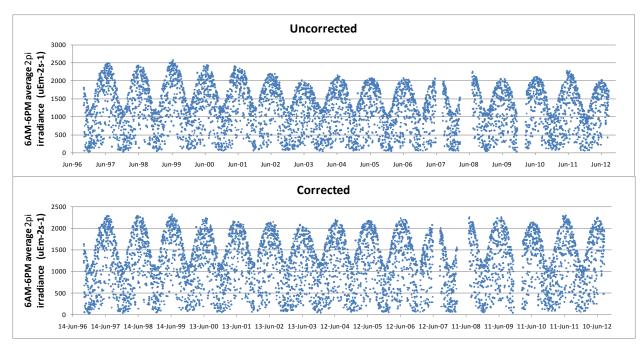


Figure A-6. Daily daytime average  $2\pi$  irradiance measurements at Deer Island, before and after correction.

# 6) Correct drift in future deployments

We will use the incoming, or "dirty" calibration in the future to correct for sensor drift.

# References

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# Appendix B Recalculating Productivity Using Revised Light Data

# **Background:**

From 1995-2010, the outfall monitoring program included a productivity study. Massachusetts Bay samples collected from three stations, several times per year, were spiked with <sup>14</sup>C, incubated under varying light levels to determine the productivity vs. irradiance response. The resulting P vs. I curve fit parameters (Platt *et al.*, 1980 or Webb *et al.*, 1974) were convoluted with incident light and extracted chlorophyll data, to calculate daily and areal productivity, potential productivity, and chlorophyll-normalized productivity (See *e.g.* Libby *et al.*, 2001 and Libby *et al.*, 2011 for discussion of results.)

The Outfall Monitoring Science Advisory Panel (OMSAP) recommended that, as these measurements were being dropped, alternative ways of estimating productivity be evaluated (OMSAP, 2009). One such alternative (MWRA, 2010) is the "BZ $_p$ I $_0$ " model of Cole and Cloern (1987). While investigating the applicability of this model, it became clear to MWRA ENQUAD staff that measurements of incident light (I $_0$ ) made from the roof of Deer Island, suffered from instrument drift and mis-calibration, such that the light "envelope" over the year varied from year to year when it would be expected to be consistent. The difference can be up to about 20% of the light.

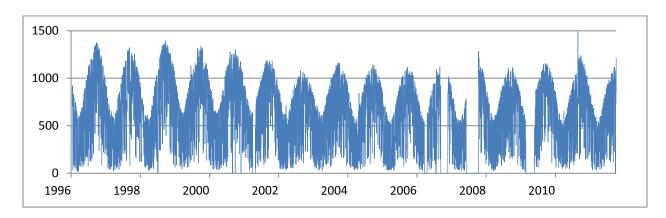


Figure B-1. Uncorrected daily average  $2\pi$  irradiance measurements at Deer Island, showing instrument drift

The irradiance measurements have been corrected as described in Appendix A.

 $BZ_pI_0$  was calculated using the corrected Deer Island light data, along with good estimates of B (chlorophyll biomass in the photic zone) and  $Z_p$  (photic depth.) It is also advisable to correct the calculated values of areal production, which will be compared with the  $BZ_pI_0$  results. Changes in  $I_0$  also affect areal production although not in a linear way. To avoid any confounding factors in comparing the  $BZ_pI_0$  model to the productivity data, we decided to recalculate productivity using the reported curve-fit parameters and the revised  $I_0$ , as described in this appendix.

# **Prerequisites:** Need to have available in the project database:

- A) Survey: EVENT, STATION, SAMPLE, DEPTH\_CLASS records for the BWQM study and relevant EVENT ID.
- B) In situ data: PROFILE and PROFILE\_DOWNCAST records for that EVENT\_ID. In situ light data should have been reviewed and qualified as usual.
- C) Light model: from each in situ irradiance profile, we have fit the exponential decay of light with depth and obtained an extinction coefficient. This is stored in the LIGHT\_MODEL\_FOR\_FLU\_CALIB table.
- D) For daily incident light data: <u>revised</u> MOORING data for study\_id = 'MET' from two weeks before and two weeks after each survey. Code to determine the clear-sky date to use for calculating potential productivity is included in the recalc\_areal\_prod.sql script.
- E) Pigments: ANALYTICAL RESULTS chlorophyll (CHLA) data for that EVENT ID.
- F) Curve fit parameters: ALPHA, BETA, PMAX, and PSB from the BWQM\_PROD\_MODEL\_XTAB view.

#### **Procedure:**

This procedure is essentially the same as described in MWRA ENQUAD SOP-79 "Calculating Productivity", starting at step 5. The revised irradiance data from Deer Island and good modeled light from each station (see step 4 of SOP-79) are assumed to be available.

# 1) Calculate daily primary production

Daily primary production and potential production for each sample is calculated by SQL script, using the estimated light at each sample depth and at the surface from the light attenuation curve convoluted with the measured incident light at Deer Island.

The SQL script **RECALC\_AREAL\_PROD.SQL** does this calculation. We neglect reflection loss at the sea surface, and assume that the modeled extinction of light with depth applies over the day with  $I_{0-} = 2\pi$  irradiance from the Biospherical sensor on the roof of Deer Island.

a. Light at depth over the day

# Percent light at each sample depth

There are five sample depths, from near-surface (A) to near-bottom (E) as described in Libby et al. 2010.

Assuming that the modeled<sup>1</sup> extinction of light with depth applies over the day, for each sample depth we can calculate the percent of surface light on that day (neglecting reflection):

<sup>&</sup>lt;sup>1</sup> Although we are using one term in the exponential, the script is written to allow up to three terms.

```
I_{pct}(z) = 100\% [I(z) / I(0-)] = [A1 exp(-k1 z) + A2 exp(-k2 z) + A3 exp(-k3 z)] / [I(0-)]
```

The first step in RECALC\_AREAL\_PROD.SQL is to put the percent light, at each sample depth, in a global temporary table PP\_PCT\_LIGHT\_GT.

# Incident light every 15 min over the day

Incident irradiance ( $2\pi$  irradiance), measured on the roof of the Deer Island administration building with a Biospherical hemispherical sensor, is available from Deer Island from late October 1996 through the present, with some gaps. These data were corrected in 2012, as noted in the "Background" section above.

There remain several data gaps, where the instrument was not functioning or had been taken down due to construction activities. For these dates we substitute a light curve derived by interpolating shipboard light measurements taken at sampling stations. Generally there are about 10 station visits during a day that can be interpolated. We made this calculation for the following days (surveys):

```
21-APR-2007 (WF074)
19-JUN-2007 (WF077)
24-JUL-2007 (WN079)
22-AUG-2007 (WF07B)
06-MAR-2008 (WF082)
24-MAR-2008 (WN083)
11-APR-2008 (WF084)
21-MAY-2008 (WN086)
13-JUN-2008 (WF087)
03-FEB-2010 (WF101)
```

The substitution is done with a COALESCE statement on-the-fly in the next insert statement.

# <u>Light at each sample depth every 15 min over the day</u>

Multiply the percent light by the incident irradiance to obtain the light at each depth for each 15 minute interval over the sampling day. Ignore times before 0600h and after 1800h.

```
RECALC_AREAL_PROD.SQL stores this in the global temporary table PP_LIGHT_PROD_AT_DEPTH_GT. For each time, 6 am to 6 pm, in the mooring record we have
```

```
(ffu.gvl(m.value, m.val_qual) * p.PCT_LIGHT / 100 ) as I_Z_T, null as P_Z_T, -- will be filled in next step
```

For surface light, RECALC\_AREAL\_PROD.SQL also inserts values for depth = 0, percent light = 1 (representing 100%; as noted above this ignores reflection.)

# b. Productivity at depth over the day

Daily primary production and potential production for each sample is calculated by SQL script, using the estimated light at each sample depth and at the surface from the light attenuation curve convoluted with the measured incident light at Deer Island.

# Productivity at each sample depth every 15 minutes over the day

For each sample, we have the modeled relation between hourly volumetric production and irradiance in the laboratory incubation experiment, in the form of curve fit parameters ALPHA, BETA, Pmax, and Psb. Since when BETA = 0, the Platt model reduces to the Webb model, we can use the more general formulation of Platt:

$$P(I_{incub}) = Psb * (1 - exp (-ALPHA * I_{incub} / Psb)) * exp (-BETA * I_{incub} / Psb)$$

Assume that the lab relation applies in the field and is unchanged over the day. Then we can calculate  $P(I(z_i, t))$  at each of the 15-minute intervals, 0600h to 1800h.

The calculated hourly volumetric production is added to the global temporary table, with a correlated subquery, in RECALC\_AREAL\_PROD.SQL.

## Estimated productivity at the surface every 15 minutes over the day

Here we use the P versus I curve determined for the near-surface (A) depth sample but we use the light from the surface, and we assign the result to our dummy sample at 0 m, which we call '<STAT ID> SURF'.

**NOTE**: We have cases where there is no good curve fit for the "A" depth, for whatever reason. In this case, we use the curve parameters from the shallowest available sample (B or even C). This way we will always have a surface value, at least, and can integrate to the surface, unless there are NO valid values at any depth (as for WN093 station N04.)

# Productivity at each sample depth summed over the day

Next, in RECALC\_AREAL\_PROD.SQL, we sum the values of P(I(zj, t)) over the day, and divide the sum by 4 (because there are four 15-minute intervals in one hour) to obtain daily volumetric production at depth  $z_i$ , in mgC m<sup>-3</sup> day<sup>-1</sup>.

DAILY 
$$PROD(z_i) = \{ P(I(z_i, 0600h) + P(I(z_i, 0615h) + ... + P(I(z_i, 1800h)) \}/4 \}$$

Use yet another global temporary table PP\_DAILY\_PROD\_GT.

Check that the value of N is the expected number of 15-minute increments in 12 hours (48). Note that STAT\_ARRIV represents the time the station was visited, but the DAILY\_PROD value actually represents that whole day.

# Estimation of productivity at the air-sea interface

The previous section should also yield a result for DAILY\_PROD at the surface (depth = 0), with a dummy "sample\_id" that is STAT\_ID concatentated with "\_SURF". This value is not stored in the database but is used in the calculation of vertically integrated productivity (AREAL PROD).

# Chlorophyll normalized productivity

For calculating chlorophyll-normalized productivity, we use the average of all fit-for-use results for the param\_code 'CHLA' from the corresponding sample (in ug/L), from BWQM\_PROD\_MODEL\_XTAB view. In the few cases where there is no valid CHLA data for a sample, we substitute the corresponding calibrated fluorescence profile data. The chlorophyll values are included in the PP\_PROD\_SAMPLES\_GT table.

Chlorophyll-normalized DAILY\_PROD is inserted into the PP\_DAILY\_PROD\_GT table for each depth:

DAILY\_PROD\_B (z) = DAILY\_PROD (z) / CHLA (z)
$$\frac{mgC}{mg chl} = \frac{mgC}{m^3 day} / \frac{mg chl}{m^3}$$

For the surface dummy sample, we use the 'A' depth chlorophyll -- even if there are no productivity results from the 'A' depth.

The chlorophyll-normalized daily production will not be stored in the database but will be used to calculate depth-integrated chlorophyll normalized areal production in a subsequent step.

c. Potential productivity at each sample depth

# Nearby sunny day

For the calculation of potential productivity, it is necessary to choose a nearby sunny (clear-sky) day, or use a theoretical light curve<sup>2</sup>. We determine clear sky days by the percent of times between sunrise and sunset that irradiance increases monotonically between sunrise and solar noon or decreases monotonically after solar noon. From the set of clear sky days (in the CLEAR\_SKY\_DAYS table), code in RECALC\_AREAL\_PROD.SQL chooses the day with the highest percent monotonic irradiance, brightest, and nearest to sampling dates, for each event. There is

PP POTENTIAL DAY GT global temporary table.

The sunny day chosen, is recorded in the comments for each potential productivity value.

only one "sunny day" selected for each event, and these are inserted in the

<sup>&</sup>lt;sup>2</sup> In the originally-reported data, the investigators visually examined the light data to choose a nearby sunny day (see SOP-79 for more information.)

There are a few surveys for which it was not possible to determine a nearby sunny day: WF077, WN079, WN083, WF084, WN086, WF087, WF101.

# Calculate potential productivity

Use the sunny day's irradiance in place of that from the survey day, and repeat the calculations above to determine DAILY\_PROD\_POT for each sample depth and for the surface.

Percent light at each sample depth is the same as for measured productivity – thus we can use the same table PP\_PCT\_LIGHT\_GT.

The POTENTIAL light at each sample depth (and the surface) every 15 min over the day and the resulting POTENTIAL productivity every 15 minutes are stored in the global temporary table PP\_LIGHT\_PROD\_AT\_DEPTH\_POT\_GT.

# Potential productivity at each sample depth summed over the day

DAILY\_PROD\_POT at each sample depth and for the surface "dummy" sample are calculated in the same way as DAILY\_PROD, and inserted into the global temporary table PP\_DAILY\_PROD\_POT\_GT.

Chlorophyll normalized potential productivity DAILY\_PROD\_POT\_B is likewise stored in the global temporary table. It will not be stored in the database but will be used to calculate depth-integrated chlorophyll normalized potential areal production in a subsequent step.

d. Insert the data into ANALYTICAL RESULTS PROD 2012

RECALC\_AREAL\_PROD.SQL inserts DAILY\_PROD and DAILY\_PROD\_POT into the table ANALYTICAL\_RESULTS\_PROD\_2012 and fills in the event, unit, method, anal\_lab\_id etc, except for depth = 0, because productivity was not measured there - we just calculated it so we can include it in the areal integration of the next step.

# 2) Calculate integrated areal production at each station

The script RECALC\_AREAL\_PROD.SQL uses data in the same global temporary tables to do the remaining calculations. We use a trapezoidal integration of daily production from the deepest sample to the surface. For the surface (depth = 0) value, use zero depth with the curve fit parameters from the 'A' sample. (This "virtual" sample result, DAILY\_PROD( $z_0$ ), is used in the calculation, but is not written to the database, the same as has been done historically.)

a. Integrated areal production

Sum DAILY\_PROD(z<sub>i</sub>) from the air-sea interface to depth z<sub>E</sub> using

```
\begin{split} \text{AREAL\_PROD} = \\ & \{ \text{DAILY\_PROD}(z_0) + \text{DAILY\_PROD}(z_A) \} / 2 * (0 - z_A) + \\ & \{ \text{DAILY\_PROD}(z_A) + \text{DAILY\_PROD}(z_B) \} / 2 * (z_A - z_B) + \\ & \{ \text{DAILY\_PROD}(z_B) + \text{DAILY\_PROD}(z_C) \} / 2 * (z_B - z_C) + \\ & \{ \text{DAILY\_PROD}(z_C) + \text{DAILY\_PROD}(z_D) \} / 2 * (z_C - z_D) + \\ & \{ \text{DAILY\_PROD}(z_D) + \text{DAILY\_PROD}(z_E) \} / 2 * (z_D - z_E) \end{split}
```

In RECALC\_AREAL\_PROD.SQL, we first insert samples, bottles, and depth class records, for the samples representing the whole station, as well as composite table records. The sample\_depth\_code and ordered\_depth\_code of this virtual sample are both zero ('0'), and the depth is the depth of the deepest sample.

The data from the global temporary table that stores the daily production for all depths (PP\_DAILY\_PROD\_GT) are used in the trapezoidal integration, and the integrated value inserted into ANALYTICAL\_RESULTS\_PROD\_2012.

A similar calculation yields potential areal production, but using data from PP DAILY PROD POT GT.

For the integration, we select from just the non-missing rows in PP\_DAILY\_PROD\_GT or PP\_DAILY\_PROD\_POT\_GT. If there are no valid curve fit parameters for a sample, and thus no daily production value, that sample is skipped in the trapezoidal depth integration to calculate areal production. For example if there is no 'B' depth one integrates from 'A' to 'C'. If the near surface sample ('A' depth) yields no valid result, the curve fit parameters from the shallowest available sample are applied to the surface (0 depth) virtual sample, along with the light estimated for zero depth, to determine the value to use for zero depth in the trapezoidal integration.

# 7) Calculate chlorophyll-specific parameters

Chlorophyll normalized areal production and potential production are calculated in the same way, using the chlorophyll value measured in each sample (or in the 'A' sample, in the case of the zero depth virtual sample.)

```
\begin{split} PROD\_CHLA\_Z &= \\ (1/z_E) * & [ \\ & & \{DAILY\_PROD^B(z_0) + DAILY\_PROD^B(z_A)\}/2 * (0 - z_A) + \\ & & \{DAILY\_PROD^B(z_A) + DAILY\_PROD^B(z_B)\}/2 * (z_A - z_B) + \\ & & \{DAILY\_PROD^B(z_B) + DAILY\_PROD^B(z_C)\}/2 * (z_B - z_C) + \\ & & \{DAILY\_PROD^B(z_C) + DAILY\_PROD^B(z_D)\}/2 * (z_C - z_D) + \\ & & \{DAILY\_PROD^B(z_D) + DAILY\_PROD^B(z_E)\}/2 * (z_D - z_E) \\ \end{bmatrix} \end{split}
```

Note: DAILY\_PROD<sup>B</sup> (z) is not stored in the EM&MS database but is in the global temporary table PP\_DAILY\_PROD\_GT.

Depth-averaged chlorophyll-specific primary production PROD\_POT\_CHLA\_Z is calculated similarly but using DAILY\_PROD\_POT\_B from the PP\_DAILY\_PROD\_POT\_GT table.

The units of PROD\_CHLA\_Z and PROD\_POT\_CHLA\_Z are mgC(mg Chla)-1d-1.

8) Insert the data into ANALYTICAL\_RESULTS\_PROD\_2012

RECALC\_AREAL\_PROD.SQL uses the SAMPLE\_ID and BOTTLE\_ID and ANAL\_LAB\_ID of the existing AREAL\_PROD records and inserts AREAL\_PROD, AREAL\_PROD\_POT, PROD\_CHLA\_Z, and PROD\_POT\_CHLA\_Z into ANALYTICAL\_RESULTS\_PROD\_2012. The METH\_CODE is set to 'PROD\_2012'. Records are created for the rare case where there are no productivity results at any depth. Comments are added for cases where incident light data are obtained from interpolating shipboard measurements rather than from the Deer Island MET station.

Figure B-2 shows that the correction and recalculation, has only a negligible effect on the AREAL PROD values.

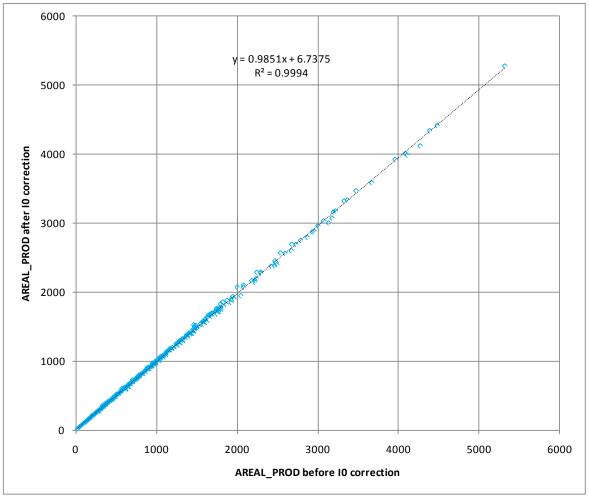


Figure B-2. Comparison of AREAL\_PROD recalculated from curve-fit parameters and using corrected Deer Island light data, with that originally reported.

# Appendix C Calculating BZpI0

# **Background:**

From 1995-2010, the outfall monitoring program included a productivity study. Massachusetts Bay samples collected from three stations, several times per year, were spiked with <sup>14</sup>C, incubated under varying light levels to determine the productivity vs. irradiance response. The resulting P vs. I curve fit parameters (Platt et al., 1980 or Webb et al., 1974) were convoluted with incident light and extracted chlorophyll data, to calculate daily and areal productivity, potential productivity, and chlorophyll-normalized productivity (See e.g. Libby et al., 2001 and Libby et al., 2011 for discussion of results.)

The Outfall Monitoring Science Advisory Panel (OMSAP) recommended that, as these measurements were being dropped, alternative ways of estimating productivity be evaluated (OMSAP, 2009). One such alternative (MWRA, 2010) is the "BZ $_p$ I $_0$ " model of Cole and Cloern (1987). While investigating the applicability of this model, it became clear to MWRA ENQUAD staff that measurements of incident light (I $_0$ ) made from the roof of Deer Island, suffered from instrument drift and mis-calibration, such that the light "envelope" over the year varied from year to year when it would be expected to be consistent. The difference can be up to about 20% of the light.

While investigating the applicability of this model, it became clear to MWRA ENQUAD staff that measurements of incident light ( $I_0$ ) made from the roof of Deer Island, suffered from instrument drift and mis-calibration, such that the light "envelope" over the year varied from year to year when it would be expected to be consistent. The difference can be up to about 20% of the light. The irradiance measurements have been corrected as described in detail in Appendix A.

 $BZ_pI_0$  will be calculated using the corrected Deer Island light data, along with good estimates of B (chlorophyll biomass in the photic zone) and  $Z_p$  (photic depth.) It is also advisable to correct the calculated values of areal production, which will be compared with the  $BZ_pI_0$  results. Changes in  $I_0$  also affect areal production although not in a linear way. To avoid any confounding factors in comparing the  $BZ_pI_0$  model to the productivity data, we decided to recalculate productivity using the reported curve-fit parameters and the revised  $I_0$ . This is described in Appendix B. As it happens, the changes to AREAL\_PROD from this correction are negligible.

This appendix describes the third and final step: calculating  $BZ_pI_0$  and pairing it with AREAL\_PROD so that the relationship between the two can be examined. Results are obtained for 2001-2010, as earlier years were evaluated in HOM water column annual reports through 2000. In addition, chlorophyll data from 1998-2000 had to be corrected for a laboratory error and they, and calibrated fluorescence from the same period, may not be completely comparable to more recent data.

#### **Procedure:**

The procedure uses the corrected Deer Island light data and the revised areal productivity data.

The result is written to a list file that can then be parsed into Excel.

# 1) Calculation script to use new irradiance data

The script **BZpIO\_calculation.sql** does the calculation. Variables in the script can be edited to use original or corrected irradiance, and original or corrected productivity values.

#### 2) Data used in the calculation

# Attenuation coefficient and 1% light level (photic depth)

These results are from the LIGHT\_MODEL\_FOR\_FLU\_CALIB table – the photic depth is calculated from the attenuation coefficient k, for each station visit. Profiles without a good light fit are excluded, but these do not happen to include any productivity station visits.

# Station mean chlorophyll value for each station visit

The vertically averaged fluorescence value, for all depths above the 1% light level is "B" in the model. Since the fluorescence measurements are every 0.5 m, averaging and integrating are equivalent. All profiles reach near the bottom. Some profiles have bottom (or max. profile) depths shallower than the calculated photic depth, in which case of course we integrate to the bottom of the profile.

# Incident light every 15 min over the day

Incident irradiance ( $2\pi$  irradiance), measured on the roof of the Deer Island administration building with a Biospherical hemispherical sensor, is available from Deer Island from late October 1996 through the present, with some gaps. These data were corrected in 2012, as noted in the "Background" section above.

There remain several data gaps, where the instrument was not functioning or had been taken down due to construction activities. For these dates we substitute a light curve derived by interpolating shipboard light measurements taken at sampling stations. Generally there are about 10 station visits during a day that can be interpolated. These results are stored in the table PP\_15MIN\_INTERP, which contains substitute data for the following days (surveys):

21-APR-2007 (WF074)

19-JUN-2007 (WF077)

24-JUL-2007 (WN079)

22-AUG-2007 (WF07B)

06-MAR-2008 (WF082)

24-MAR-2008 (WN083)

11-APR-2008 (WF084)

21-MAY-2008 (WN086)

13-JUN-2008 (WF087)

03-FEB-2010 (WF101) 23-FEB-2010 (WF102)

The substitution is done with a UNION of data selected from MOORING but excluding days with only a few light measurements, and data selected from PP 15MIN INTERP.

The measurements are averaged over the whole day (IO\_24), and separately from 6 am – 6 pm (IO), and converted to units of Einsteins per meter squared per day.

3) Calculate BZpIO and get the corresponding AREAL PROD.

Running the script BZpIO\_calculation.sql will produce a list file BZpIO\_CALCULATION.lis. Open this in Excel and parse the fields into different columns (start import at row 10). Years from 2001 are included.

Note that the following surveys and days will not be included:

- surveys prior to 2001 or after 2010
- surveys with no valid fluorescence data (WN02G)

# BZpI0

The product of integrated chlorophyll fluorescence, photic depth, and daily average irradiance is the model parameter BZpIO. In the results, BZpIO uses the 12-hour light and BZpIO\_24 uses the 24 hour light.

#### AREAL PROD

This is the recalculated AREAL\_PROD from the ANALYTICAL\_RESULTS\_PROD\_2012 table.

# ZP > AVG WATER DEPTH

There are a few records where the photic depth  $Z_p$  is deeper than the water depth. It is not clear how the model should be applied to these stations. From one point of view,  $B^*Z_p$  is a measure of the amount of chlorophyll available for production (and thus for those stations one should instead use  $B^*Z_{bottom}$ ). From another point of view,  $Z_pI_0$  is "an index of light availability in the photic zone" (Cole and Cloern, 1987), and the model could be used without modification. It may be simplest to exclude those 24 stations from the analysis, as they are a small percentage of the 326 data points for 2001-2010.

The following fields are included in the spreadsheet:

YEAR	year
EVENT	event (survey) identifier
STAT	station identifier
STAT_ARRIV	station arrival time (Eastern Standard Time)
AVG WATER DEPTH	average water depth for that station (over many surveys) (m)
R2_OF_LIGHT_	R^2 of the light model fit for that station visit
REGRESSION	
В	"Biomass": calibrated fluorescence averaged over the photic depth (or
	over the profile, if photic depth > water depth) (ug/L)
ZP	1% light level depth (m)
10	average incident 2pi light measured at Deer Island, from 6 am to 6 pm
	(uEm-2sec-1). Corrected for drift and miscalibration
BZPI0	model parameter: B * ZP * IO
10_24	average incident 2pi light measured at Deer Island, from midnight-
	midnight (uEm-2sec-1). Corrected for drift and miscalibration
BZPI0_24	alternate model parameter: B * ZP * I0_24
AREAL_PROD	areal production (mgCm-2d-1) from C-14 experiments, recalculated
	from P vs. I curve fit parameters using 6 am-6 pm corrected IO values
COMMENTS	Indicates source of IO data (some stations had shipboard light
	substituted for missing Deer Island data)
ZP >	"X" if photic depth > average water depth (both rounded to nearest
AVG_WATER_DEPTH	meter). May wish to exclude these from analysis.

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