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Interactive comment on “Sargasso Sea phosphorus biogeochemistry: an important role for dissolved organic phosphorus (DOP)” by M. W. Lomas et al.

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This manuscript describes the cycling of the dissolved and particulate phosphorus pools over the upper 200–500 m in the Sargasso Sea, with time-series data extending backwards to 2004. While there have been a number of studies that have suggested the importance of DOP cycling in this region based on transect and modeling results, this paper is the first to provide a full mass balance of phosphorus to really investigate the specific sources and sinks of P in detail. It is a marvelous addition to the literature on P in the Sargasso Sea. I have only a few comments that should be addressed prior

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to publication.

Methods: Many of the techniques used in the manuscript are for extremely low levels of P. Therefore, please provide more information on the blank corrections used for each technique?

This was a concern raised by one of the other reviewers. We have added more details on blank corrections for all of the chemical measurements. We hope the reviewers find these corrections suitable.

For the particulate P analyses (pg 10142) please provide an estimate of the possible contribution of DOP adsorption to the particulate P measurements - is it 10%? 50%?

We have added text to speak to this point as follows:

“Particulate phosphorus (PPhos) samples were analyzed using the ash-hydrolysis method of Solarzano and Sharp (1980). No efforts were made to separate particulate inorganic from organic phosphorus so data are simply referred to as particulate phosphorus. In addition, there is some evidence that the use of GF/F filters, in comparison with polycarbonate filters of similar pore size, may lead to overestimation of PPhos concentrations, presumably due to adsorption of DOP to the filter (Ammerman, unpubl. Data; ~34% overestimation), although our own testing found the overestimation to be much lower (~5-10%) following rinsing with MgSO₄ as described here. No corrections were made to PPhos concentrations for this possible overestimation. For analysis, sample filters were placed in acid-cleaned (10% HCl) and pre-combusted glass scintillation vials along with 2 ml of 0.017 M MgSO₄, dried down at 80-90°C and then combusted at 500°C for 2 h. After cooling to room temperature, 5 ml of 0.2 M HCl was added to each vial and hydrolyzed at 80°C for 30 minutes. After cooling to room temperature, SRP mixed reagent was added (Parsons et al., 1984), sample was clarified by centrifugation, and absorbance read at 885 nm. Samples were calculated against a potassium monobasic phosphate standard following subtraction of a “field blank”, triplicate pre-combusted filters flushed with ~5ml of 0.17 M Na₂SO₄ at sea and

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then treated identically to the samples. Field blanks were generally < 10% of the lowest sample concentrations. Oxidation efficiency and standard recovery was tested with each sample run using an ATP standard solution and a certified phosphate standard (Ocean Scientific International Ltd. Phosphate Nutrient Standard Solution). In our laboratory, the precision of this method is ~9% at 2.5 nmol l⁻¹ (the lowest concentrations typically observed well below the euphotic zone), and ~1% at 15 nmol l⁻¹ (typical euphotic zone concentrations). The method detection limit, defined herein as three times the standard deviation of the lowest standard (2.5 nmol l⁻¹) is ~0.1 nmol l⁻¹."

APA is based on what % of labeling?

We are not sure what the reviewer is referring to here, we did not use the ELF labeling method for APA, so as to detect the reported rates. Substrate additions were saturating (10uM), based on kinetic studies performed in the region, and the reported rates are maximal potential rates.

Please also provide more information on how P was measured in Case (2001) (Not listed in the References) in order to fully evaluate the time series discussion?

This also was a comment of another reviewer. We don't know with 100% certainty that the decrease in DOP with time is due to net export of P. It is possible that the HTC method used by Case et al. and the PO method used in this manuscript resulted in different oxidation efficiencies for DOP, and therefore is a confounding effect. However, the methods review by Monaghan and Ruttenberg 1999, suggest that for most compounds there is no difference in the oxidation efficiency between ash hydrolysis methods and acid persulfate methods. Moreover, the recoveries for standard compounds given by Torres-Valdes et al 2009 for the UV oxidation method are virtually identical to the recoveries that we observe for the acid persulfate method (unpubl. Data). This suggests to us that any method differences are likely to be minor. That said in the original manuscript we state the decrease in time due to export is 'plausible' and not a firm conclusion. This section has been amended as follows:

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“Two phosphorus time-series records exist at BATS, this study and that of Case (2001), and they provide a unique assessment of the role of DOP in the western subtropical North Atlantic over the past decade. It is important to note that these two studies used different methods for quantifying DOP concentrations; Case (2001) used the ash hydrolysis method of Solorzano and Sharp ({, 1980 #3455}), while the current study used the acid persulfate method. These two methods were continually checked for quantitative oxidative efficiency at the time the samples were analyzed. In addition, these two methods have been compared previously (e.g., {Monaghan, 1999 #6487}) and found, for all but two of the DOP compounds tested, to yield statistically similar oxidation efficiencies. So while concentrations changes over time may be due to methodological differences it is also possible that this is a real decrease in DOP.”

It is not clear if changes with time in SRPxs data are due to the (unlikely) changes in methodology between the two studies?

SRPxs data are all from the BATS core dataset so the methods have been consistent throughout the entire record. It is only the DOP data that arise from two different studies. This has been made more clear.

POC/PPhos ratio: Page 10150-10151: It makes complete sense that the arithmetic mean of the POC/PPhos ratio is substantially different (higher) than that determined from the linear regression. Closer examination of the linear regression data (Figure 7), however suggests that the relationship between the two datasets is not all that strong – a few points seem to drive a relationship that otherwise looks more like a “shotgun blast” – at least for the POC. No R² or p-value are provided for the data relationship given in Figure 7. Please provide and consider adding the 95% confidence limit to the Figure. I find it difficult to believe that the linear regression results in an only 8% error based on the data provided? Please clarify.

Yes, the relationship isn't as strong as one would like, perhaps due to temporal changes in species that have different C:P ratios. While the highest data are few in number, we

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have no reasonable reason to discount them. We agree with the reviewer that more information on the nature of the regression (R^2 , P-value, 95% CI) are needed and we have added them. The error on the regression was actually the STD ERR not the STD DEV, so given the 328 datapoints, the STD ERR was very low. This has been corrected with the values reported as STD DEV. It doesn't change the interpretation of the slope (as it is the STD ERR that is used in calculating significance). We thank the reviewer for catching this.

P Budget and P Export Fluxes: I am a big fan of mass balance models and applaud the authors for making the attempt at a mass balance budget for P in the Sargasso Sea. Errors are large, but the authors have done a very good job of at least starting to put constraints on the various input/export "arrows" when it comes to P cycling. I just have a few concerns/comments that I would like to see addressed.

First and foremost, looking at the arrow "directions", the authors have significantly more P flowing into the Sargasso Sea 150 m box than leaving it. In other words, you have a 135 mmol P/m²/y P demand (presumably based on the linear regression model, pg 10151 line 7, but this is not quite clear in the text), but a source of P of only 96 mmol P/m²/y. Within errors, this is pretty darn good.

Based upon the comments of another reviewer the summed source term has been reduced to 85 mmol P/m²/y. The reason for this is that the 96 mmolP/m²/y calculation assumes 100% bioavailability of the DOP pool. We have reduced that to 75% bioavailability based upon the data of Kolowitz and others that suggests ~75% of the DOP is P-esters and we assume they are completely bioavailable. That said recent work by Dyrman and others suggests that the remaining 25% of DOP that is phosphonates may be more bioavailable than generally assumed. So the 'real' value may lie between 85-96 mmolP/m²/y, but we have chosen to report the conservative estimate. This is based upon the linear regression in Figure 7. If indeed some of the phytoplankton have a particulate C:P that is higher than the linear regression value this will drive down the demand calculation thus further closing the gap, not making it worse. We have added

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text on this point as well.

What is a bit more interesting/alarming is that the export of P at 150 m is only 12.8 mmol P/m²/y. If P is advecting IN from the sides, eventually TOTAL P concentrations would have to increase OR there is loss that is not accounted for. In the time-series discussion, increases in SRP are balanced by DOP decreases, so apparently, no net change in total P standing stocks (dissolved or particulate) have occurred. So where does the P ultimately go? It cannot accumulate indefinitely - especially as it is hypothesized that even more DOP and SRP are advecting into the “Sargasso Sea” box from the South?

Related to this, are the export fluxes of particulate P. I find it amazing that so much of the P is lost to the trap solutions. Of course, this is likely due to such little fluxes of P containing material to the Sargasso Sea trap cups as much lower rates of P remineralization in trap cups have been reported (see Buesseler et al., 2007 and O'Neill et al., 2005). That having been said, it seems likely that the sediment trap samples may be underestimating P export from the system, either due to hydrodynamic effects, under collection associated with low export events, or due to other mechanisms of P transport to depth, i.e zooplankton migration (see recent paper of Hannides et al., 2009 for the N. Pacific). How would such an increase in particulate P fluxes impact the DOP utilization estimates??

The reviewer is absolutely correct, P cannot accumulate indefinitely. As far as where does the P go, we agree the PITS traps may underestimate flux and that zooplankton may serve as an active flux pathway. Fortunately there is sufficient data in the literature to speak to this, although it doesn't solve the problem. Steinberg et al. report DIC:DIP remineralization ratios for several copepods at depth at BATS, along with DIC flux rates. From this we calculate that vertically migrating zooplankton may contribute to P flux as much as 1 mmol P/m²/y (from DIP alone). The work of Hannides et al suggests that release of P by migrators below the euphotic zone is roughly 50:50 DIP and DOP, so a maximum contribution due to migrators would be an additional 2 mmol/m²/y. The

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PITS style traps used at BATS are known to have problems with hydrodynamic bias. Work by Stanley et al. comparing neutrally buoyant sediment traps to PITS style traps showed that the two had statistically similar P fluxes regardless of season (June vs. September) or depth (150m vs 300m). From this work it suggests that this bias is going to be small. So while these additions do raise the flux, closing the budget on P accumulation, it is not a complete answer. Perhaps other large vertical migrators (e.g., salps) are contributing more to flux than current calculations can account for as they are known to be important in other ocean regions. Increases in flux will likely have a minimum impact on DOP utilization estimates given that the utilization estimate is greater than the flux at present so increasing the flux will still result in a very high fraction of export production possibly supported by DOP. We have added a paragraph to the discussion on this mismatch.

On a side note, I was also interested in the rapid decrease in DOP concentrations with depth associated with the increase in SRP. This suggests rapid remineralization (most likely) or advective loss of DOP (less likely) with depth. Have you gone through the exercise to determine if mass balance is reached on annual time scales (or even just from 2004-2008)? A similar calculation could be done with the decrease in export fluxes with depth from 150 to 500 m. This would be a great addition to providing insight into the remineralization processes that occur beneath the euphotic zone, but yet ultimately influence the potential source of P to the euphotic zone.

We think that both degradation and advection is happening in the 200-500m range because in this range is the subtropical mode water (please see response to Reviewer #1) which appears to have lower DOP when it is formed at the surface than the DOP in the surface at BATS (paper by Torres-Valdes et al. 2009 showing two transect lines in the west Atlantic at 36oN and 24oN). The mass balance we present in Figure 7 is effectively an annual budget; we used the annual primary production to get annual P demand, we used the annualized P flux, etc. Further, it is an averaged annual budget for 2004-2008.

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This question is related to the above question, and really highlights that the discrepancy between the inputs and the outputs. As responded to above, we have added more text to discuss this and revise upward the export flux by including active transport by zooplankton. Even with a liberal revision upward that includes both active transport by zooplankton and additional gelatinous vertical migrators, export flux will only account for ~25-30% of the inputs. Unfortunately, we can't think of other defensible explanations to account for the 'missing' exported P.

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