

Author's response to the comments of Peter Kraal and Tom Jilbert on the manuscript:

First of all, we would like to thank both reviewers for the time they put into evaluating this manuscript and their constructive and valuable comments. Both reviewers underlined their interest in the combined approach of water column and sediment sampling for a benthic P budget in the Peruvian OMZ. We try to clarify all issues raised by the reviewers below.

In response to the comments of Peter Kraal, received and published 16 Nov 2015:

- 1 It would be nice if the pore water PO₄ profiles are referred to before the freeze-thaw experiments as background to the resulting calculated PO₄ fluxes.

Author's response: The benthic chamber TPO₄ fluxes from in situ measurements and the diffusive TPO₄ fluxes calculated from the PO₄³⁻ pore water profiles are addressed in section 4.2.1. before the freeze-thaw experiments in section 5.2.2. We will provide a clearer link to the pore water profiles shown in Fig. 7 in section 4.2.1 in a new version of the manuscript.

- 2 P56, L21. A few more words could be spent to clarify the statements regarding phosphorite formation.

Author's response: We will briefly extend the information on the indications for recent phosphorite formation found in the study area in the abstract. Anyhow, phosphorite formation is addressed in more detail in chapter 5.2.3.

- 3 P57, L21-22. Perhaps some nuance is needed here. Under certain conditions (such as nutrient-rich upwelling regions off Peru and Namibia), extensive (microbially-mediated) CFA authigenesis has been found. And during burial below the oxygen penetration depth, reductive release of P from metal (oxyhydr)oxides triggers apatite formation, often in disperse form at low concentrations (sensu Ruttenger, Slomp). These are two very different, anoxic mechanisms, where the latter may be more representative for non-upwelling oceanic settings.

Author's response: This is a very good aspect. We will address specifics on CFA authigenesis in the new manuscript as suggested by the reviewer.

- 4 P68, L7. "except slightly increasing ratios close to the seafloor" Clearly state that this refers to the difference between the deepest water column sample and the sediment surface (as there is a general decrease between the deepest water column sample and the one immediately above it).

Author's response: We will change the wording in a revised manuscript accordingly.

- 5 P68, L9. Description of the trend at Stat VIII deserved a little more detail. Truncated profile, cyclicity?

Author's response: We will describe the sediment profile for the POC/POP ratios of Sta. VIII in more detail in the results section and will provide more explanations for the profile shape in the discussion section 5.1. Obviously the POC/POP profile is truncated, but there are no indications for sedimentary events in the ²¹⁰Pb profiles shown by Dale et al., 2015. More likely, the sharp increase of POC/POP ratios below 2 cm of sediment depth is driven by authigenic formation of phosphorites.

- 6 P68, L23-24. Unclear what is meant here; I do not see any consistent strong changes in the deepest water column sample.

Author's response: It is meant that there is a drop between the deepest water column sample and the first sediment sample at station VIII. We will clarify this in the new version of the manuscript.

- 7 P70, L6. "that could be triggered by the TPP", rephrase and mention mechanism/process

Author's response: This will be modified in the manuscript.

The measured benthic TPO₄ fluxes exceed the phosphate fluxes that could be generated from TPP degradation by a factor of 6, but the potential TPO₄ fluxes are still higher (Table 4).

- 8 P73, L21. Here, phrasing could be more clear: enhanced POC preservation and/or enhanced P release could lead to higher C/P in anoxic sediments compared to oxic. Current phrasing is convoluted while an answer is not (and cannot) be provided regarding the main driver.

Author's response: The last sentence of the section will be rephrased according to the reviewers comment.

- 9 P75, L21-27. It seems from this that the authors assume that terrestrial P, i.e. P associated with riverine suspended particles, would not show up at all in the PIP fraction on the filters from the water column samples? If riverine particulate matter sinks through the water column (or do the authors assume all riverine input is lateral?), and consists at least in part of Ca-P and oxide-associated P, why would it not (partially) be part of the measured PIP on the filters? Even though it is a minor P source, the authors might want to elaborate slightly on why riverine P is treated as a completely separate P input.

Author's response: We were aiming to estimate the maximal effect of terrestrial P input to the sediments with this approach. Riverine transported material from the continent is likely underrepresented on our water column filter samples due to fast sinking speed of such particles and/or a laterally dominated transport. However, we do not exclude that a small fraction of the riverine transported material can be found on our filter samples. Anyhow, the results of the calculations show that terrestrial P input is of minor importance for the presented P budget.

- 10 P76, L12-18. Could sinking of fish debris through anoxic waters not provide a rapidly sinking source of both apatite and organic matter to the seafloor (biological fish remains, collagen etc. in fish bones)? Then, would fish debris necessarily leave a signature of very low C/P ratios? If these fish debris are indeed missed during water column sampling (or perhaps have a strong seasonal character), the associated OC would also be missed in the budgets, which would have an impact on the argument of the theoretically required low C/P ratio of incoming particles. Perhaps C/P ratios alone are insufficient to dismiss a potential role for fish debris as (additional) PO₄ source? The authors show nice links between PO₄ fluxes and sedimentary bacterial (biological) activity, which can be used to hypothesize on the likely source(s) of PO₄. Perhaps it would be better to focus on the evidence for the contribution of bacteria, to the point where other P sources are not necessarily required to close the budgets.

Author's response: We are convinced that an imprint of fish debris in the sediments which have not been sampled on the water column particle filters must lead to differences in the

POC/TPP ratios between the water column and sediment ratios. Since this difference is not observed it is likely that fish debris can be ruled out for closing the P budget during the sampling campaign.

However, if we only consider the bacterial P release as additional P source to the sediments, it is very likely that questions about the other mentioned sources arise. Hence, we want to make sure to discuss potential other sources briefly and show that the role of bacteria are key to the understanding of the P-budget.

- 11 78, L13-14. In fact, highest freeze-thaw P release was found in sediments with abundant foraminifera rather than microbial mats (Stat VIII). This deserves a bit more attention here, as it might put the potential role of bacteria in more context?

Author's response: This is a good point. However, the PO_4^{3-} concentrations after the freeze-thaw experiments of the stations V and IV, where sulfide-oxidizing bacteria are still abundant, are only slightly lower compared to station VIII. Hence, we assume that the occurring sulfide-oxidizing bacteria at station V and VI as well as the foraminifera observed at station VIII are contributing phosphate to the pore waters. However, it remains to be shown how these mechanisms play out in detail (e.g. nutrient concentration thresholds, time scales, P release from *Marithioploca*-related bacteria and foraminifera) and the impact on benthic P release in oxygen and nitrate deficient environments on longer time scales.

- 12 P80, L1-3. If foraminifera represent such an efficient sink of BW PO_4 , it would be good if the authors provide their preferred mechanism by which the internally-stored PO_4 makes it into authigenic apatite. Would this be a matter of release after death fueling apatite formation rather than uptake by living forams? What type of redox-dependent PO_4 uptake/release behavior do forams display?

Author's response: This is another interesting aspect, but unfortunately the mechanisms how the P release from foraminifera work in detail remains unknown and requires more detailed experimental work (e.g. are the foraminifera alive or dead releasing the P, redox-dependent P uptake and release?) and will be addressed in more planned experimental work in the study area in the near future. There are two expeditions planned to the Peruvian OMZ where detailed experiments will be carried out in order to answer this type of questions.

- 13 P80, L18-26. This is crucial information regarding potential PO_4 release mechanisms and should be included in the discussion. The conclusions should not contain such crucial new information, but rather should concisely synthesize the findings and interpretations already presented in the results and discussion.

Author's response: We will take this into account in the revised manuscript and suggest changes on P77, L13-17 and P80, L18-26.

All technical corrections will be considered in a revised version of the manuscript.

In response to the comments of Tom Jilbert, received and published: 22 Nov 2015:

Major:

- 1 One of the main challenges associated with the approach employed here is that the fluxes being measured are generally not in steady state, and a single sampling moment (i.e. one cruise) will struggle to tell the full story. The authors have acknowledged this and indeed conclude that their budget cannot be closed for this reason, but I agree with Peter Kraal's comment (re. P80 L18-26) that more specific contextual information about the variable redox regime of the study site should be included earlier in the paper. The authors refer to the studies of Guitierrez et al., 2008 and Schunk et al., 2013 in section 2 but perhaps it would be good to show in graphical form (e.g. incorporated into Fig. 1) how much the redox conditions can actually change at these sites, and how frequently. For example, can potential loading-unloading cycles for the bacterial P 'capacitor' the authors postulate be identified from past data?

Author's response: Due to the lack of time series data available for longer time scales and more water depth than presented in Gutiérrez et al. (2008), we decided to not duplicate any figure in this manuscript. However, we will provide more detailed information on where to find information for redox changes in the water column in the text of the revised manuscript (e.g. Noffke et al, 2012; Scholz et al., 2011).

- 2 I recommend that the authors present not only the various C/P ratios (e.g. Fig. 2) but also the raw C and P data in graphical form (these are currently given in table form and only in the supplement). This is important because in both the water column and sediments, trends in C and P concentrations may help to indicate transformations (e.g. breakdown of organic matter, precipitation of CFA), which are relevant for the interpretation of the data.

Author's response: We will add a new figure to the manuscript.

- 3 In the case of the water column data, I miss a conclusive statement from the authors about what they believe the PIP phase on their filters actually is.

Author's response: More detailed information will be added concerning this aspect. Nevertheless, a final conclusion on the composition of PIP cannot be made based on the available data set.

According to Labry et al. (2013) we expect the PIP phase to be comprised of inorganic P phases originating from abiotic particulate phosphorus as well as inorganic P phases from that are biogenic origin. Abiotic PIP comprises mineral associated P, e.g. from terrestrial sources. The inorganic phosphorus from biotic particulate phosphorus is composed of orthophosphates, pyrophosphates and polyphosphates incorporated into organic cells.

- 3.1. The authors refer to the paper of Sanudo-Wilhelmy et al. which describes P adsorbed on the surface of living *Trichodesmium* tissue, probably associated with hydrous Mn oxides. There are several questions which follow from this: How representative are the conclusions of that study in a high-productivity upwelling system such as this one, considering the different primary producer assemblages? And if there is indeed a major fraction of surface-adsorbed P associated with surface-water POC, is it realistic that P will be preserved in such a form as this material sinks through the water column?

Author's response: This is indeed a very interesting aspect. Sanudo-Wilhelmy et al. (2004) suspect that the finding of surface P-adsorption might be a general feature comprising all phytoplankton groups. To date, this statement has, unfortunately, neither been confirmed nor disproved by other studies. However, if it applies, there shouldn't be any general differences between low nutrient and upwelling areas. On the other hand, it doesn't seem likely that Mn-oxides play a major role off Peru. Mn-oxide concentrations were not measured on the filter samples, but SEM-analyses of the filter samples (data are not presented here) indicate that the overall concentrations are very low. In addition, Mn-oxides are not contained in surface sediments, indicating that they are continuously dissolved when sinking through the water column. The adsorbed P should be released during transport, but given the low concentrations the effect on our measured C/P ratios is likely negligible.

Generally, one should assume that remineralization in the water column leads to a decrease in the reactivity of the organic matter. However, our data do not reveal evidence that POP is transformed to PIP during transport. Statements about the quality of the organic matter or changes in reactivity would remain purely speculative.

- 4 The water column POC data from the offshore sites (Table S1) suggest export of ~5% of surface-water POC to the deep waters at Station VI (see POC at 10m vs. 240 m) and ~20% at Station VIII. What can the authors say about the quality of the exported POC, and what does this imply for the fate of any surface-adsorbed P? Furthermore, how would hydrous Mn-oxide bound P be expected to behave while sinking through the anoxic water column?

Author's response: The example the reviewer chose for estimating and comparing the POC export from the POC concentrations is biased. The POC concentration at 10 m water depth at station VI is by far the highest concentration compared to the other POC concentrations found at the same water depth (stations I, III and IV) and represents an outlier in our data set, which will explicitly be marked as such in a new version of the manuscript.

As outlined above (comment 3.1) we don't believe that Mn-oxide-bound P plays a major role in this context, because of the low concentrations. However, any Mn-oxide-bound P would be released in the anoxic water column due to the continuous dissolution of Mn-oxides.

- 5 It is indeed remarkable that POC/TPP is so close to Redfield throughout the water column. Could there be a role for conversion of POP to polyphosphates as suggested by Diaz et al. (Global Biogeochem. Cycles 26, 2012) or to CFA (Jilbert and Slomp, GCA 107, 2013), during the decay of organic matter in the water column? If P bearing molecules are preferentially broken down, and P is then stored in these forms, POC/TPP could stay quite constant as observed here. In summary, I think a discussion of these various options for the PIP phase is essential, including statements about the expected extraction behavior of the candidate phases (e.g. are polyphosphates expected to count as POP or PIP?).

Author's response: On the basis of our dataset, such a conversion can only be observed within the sediments, especially at station VIII and at some stations between the bottom water sample and the surface sediment sample (e.g. station I, IV, VI and VIII) as described in the manuscript. Here is likely a shift in the POP and PIP concentrations. The POP concentration drops while the PIP concentration increases, which could be a hint to such a process. Due to the fact, that we have not conducted sequential extraction it is not possible to follow up precisely which PIP phase (e.g. polyphosphates or CFA) is formed.

- 6 In the case of the sediment data, I would also like to see the raw plots of TPP, POP and PIP to see if there is evidence for transformations with depth, such as the precipitation of CFA as observed in many open ocean studies (Ruttenberg and Berner, GCA 57, 1993). As stated by Peter Kraal it is important to distinguish between different mechanisms of CFA formation and with all the data available here it is possible to say something more about this.

Author's response: According to comment 2 of the reviewer, we would like to include an additional figure similar to Fig. 2 that shows the water column and sediment raw concentrations of TPP, POP, PIP and POC. On the basis of that figure we will further explore on CFA formation mechanisms in section 5.2.3.

- 7 A further concern I have about the sediment data is the way in which the burial fluxes of P have been calculated. This has been done using average P concentrations in the top 10 cm and mass accumulation rates (Page 66). In the supplemental data it can be seen that TPP concentration decreases from the sediment surface downwards, so the ultimate burial flux is probably better calculated from the value at 10 cm rather than an average including the surface sediments. In fact the authors state that a previous related study (Dale et al., 2015) employed exactly this approach to determine carbon budgets. How would the P budget change if the same was done here?

Author's response: The numbers given in the manuscript were calculated from the average P concentration of the first 11 cm of sediment depth (11 cm is due to our sampling resolution). However, using the P concentration at 11 cm sediment depth would not lead to significant changes of the P burial fluxes. Only at the station V the burial flux would change slightly and the P deficit would deviate for less than 10% from the value given in the manuscript. Since there are no changes at any other station and only a change of less than 10 % for station V, we would like to stick to the calculation using the average P concentration of the first 11 cm of sediment depth which was also applied in Dale et al. (2015).

Minor/technical corrections: We thank the reviewer for his minor/technical corrections and will address these in the revised manuscript.

- 1 Page 61, Lines 16-20. What was the pH during analysis? The way this is phrased, it sounds like you carried out the analyses at neutral pH but normally this is not done. Please clarify.

Author's response: The analysis was carried out at low pH. The NaOH was added to the sample solutions to slightly raise the pH. It was done because the slope of the calibration curve was to flat for our low concentration measurements. However, due to the reagents added to the sample solution, the pH remained low.

- 2 Page 62, Line 25 onwards. Related to my earlier comment, it would be good to state somewhere which P phases are expected to dissolve in the 1M HCl (pre-combustion) extraction. Especially in this study where intracellular polyphosphate pools, and surface-adsorbed P, may be quantitatively important, the expected extraction behavior of different phases should be clarified.

Author's response: Please find the author's response related to that comment above (comment 3).

- 3 Page 73, Lines 10-20. Here I would state more clearly the role of Fe in sedimentary P cycling in oxic conditions i.e. the observation that POC/TPP in oxic sediments is typically 10-50 is primarily due to the association of P with Fe (oxy)hydroxides in surface sediments after release from decaying organic matter. Also check the reference given as Baturin (2007). In the reference list the only article with this first author is Baturin and Savenko, *Oceanologia* 37, 1997.

Author's response: We will clarify this in the revised manuscript and replace Baturin et al. (1997) with Baturin (2007).

- 4 Page 77, Lines 1-10. Again, add some more contextual statements about the expected role of Fe in P cycling in the OMZ environment. Iron availability in the surface sediments should vary greatly with water depth through the OMZ but this is not expressly discussed here.

Author's response: This is a good point. We will extent the information on Fe oxyhydroxides in the sediments in the revised manuscript accordingly.

Fe oxyhydroxides are expected to be important carriers for phosphorus from the water column to the sediments. Due to their dissolution in the sediments, the adsorbed P is released to the pore waters. However, in the Peruvian OMZ oxygen concentrations are already very low in the water column. In consequence, similar to Mn-oxides, a large part of the Fe oxyhydroxides is already dissolved in the water column and, as such, cannot be an important P source to the sediments (see P budget calculations).

- 5 Page 80, Lines 1-3. Once again I agree with Peter's comment, that the mechanism of the proposed foraminiferal P uptake should be discussed in more detail. If true this could be an exciting new process in sedimentary P cycling so it deserves more attention

Author's response: Please find the author's response in comment 12 of P. Kraal.

1 **Benthic phosphorus cycling in the Peruvian Oxygen**
2 **Minimum Zone**

3

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13

14 Abstract

15 Oxygen minimum zones (OMZs) that impinge on continental margins favor the release of
16 phosphorus (P) from the sediments to the water column, enhancing primary productivity and
17 the maintenance or expansion of low-oxygen waters. A comprehensive field program in the
18 Peruvian OMZ was undertaken to identify the sources of benthic P at six stations, including
19 the analysis of particles from the water column, surface sediments and pore fluids as well as
20 in situ benthic flux measurements. A major fraction of solid phase P was bound as particulate
21 inorganic P (PIP) both in the water column and in sediments. Sedimentary PIP increased with
22 depth in the sediment at the expense of particulate organic P (POP). The ratio of particulate
23 organic carbon (POC) to POP exceeded the Redfield ~~R_r~~ratio both in the water column ($202 \pm$
24 29) and in surface sediments (303 ± 77). However, the POC to total particulate P (TPP = POP
25 + PIP) ratio was close to Redfield in the water column (103 ± 9) and in sediment samples
26 (102 ± 15 This suggests that the relative burial efficiencies of POC and TPP are similar under
27 low oxygen conditions and that the sediments underlying the anoxic waters on the Peru
28 margin are not depleted in P compared to Redfield. ~~) taken from the core of the OMZ. This~~
29 ~~observation suggests that the burial efficiencies of POC and TPP are similar under the low~~
30 ~~oxygen conditions prevailing in the Peruvian OMZ.~~ Benthic fluxes of dissolved P were
31 extremely high (up to $1.04 \pm 0.31 \text{ mmol m}^{-2} \text{ d}^{-1}$), however, showing that a lack of oxygen
32 promotes the intensified release of dissolved P from sediments, whilst preserving the
33 POC/TPP burial ratio. Benthic dissolved P fluxes were always higher than the TPP rain rate to
34 the seabed, which is proposed to be caused by transient P release ~~) and exceeded the fluxes~~
35 ~~resulting from the degradation of particulate organic matter raining to the seabed. Most of the~~
36 ~~excess P may have been released by bacterial mats that had stored P during previous periods~~
37 ~~when bottom waters were less reducing. At one station located at the lower rim of the OMZ,~~
38 ~~dissolved P was taken up by the sediments indicating recent phosphorite formation. At one~~
39 ~~station located at the lower rim of the OMZ, dissolved P was taken up by the sediments~~
40 indicating ongoing phosphorite formation. This is further supported by decreasing porewater
41 phosphate concentrations with sediment depth, whereas solid phase P concentrations were
42 comparatively high. At this site, the POC/TPP and POC/PIP ratios dropped from average
43 water column values (close to Redfield for POC/TPP and POC/PIP ~250) to very low

44 sedimentary ratios of ~ 7 (POC/TPP and POC/PIP), indicative of intensive P enrichment in
45 the sediments.

46

47 **1 Introduction**

48 Phosphorus is an essential nutrient; it serves as an energy carrier for all living species and is a
49 limiting macronutrient for marine primary production on geological time scales [Ingall and
50 Jahnke, 1994; Föllmi, 1996; McManus et al., 1997; Filippelli, 2002; Paytan and McLaughlin,
51 2007; Tsandev et al., 2012; Ruttenberg, 2014][Filippelli, 2002; Föllmi, 1996; Ingall and
52 Jahnke, 1994; McManus et al., 1997; Paytan and McLaughlin, 2007; Tsandev et al., 2012].
53 Due to its impact on marine primary production, the oceanic phosphorus inventory modulates
54 the atmospheric CO₂ level and Earth's climate [Ganeshram et al., 2002; Wallmann, 2003;
55 Ingall, 2010][Ganeshram et al., 2002; Ingall, 2010; Wallmann, 2003]. Hence, it is crucial to
56 understand feedback mechanisms of the P cycle to make future predictions.

57 Particulate and dissolved phosphorus in the ocean originate from terrestrial chemical
58 weathering of the P containing mineral group of apatite ~~on land~~ [Filippelli, 2002]. Only
59 around 30% of the P discharged to the oceans is potentially bioavailable [Compton et al.,
60 2000] ~~including as~~ dissolved P ~~phases~~, inorganic P ~~phases~~ adsorbed ~~to the surface of clay~~
61 minerals or associated ~~with to Mn and Fe oxyhydroxides~~ ~~metal oxides as well as and~~ -P bound
62 within particulate organic matter. However, the largest fraction of the ~~delivered fluvial~~ P is
63 ~~immediately~~ trapped in estuaries or buried in continental margin sediments and thereby
64 removed from the P cycle before it reaches the open ocean [Compton et al., 2000]. The
65 delivery of P to the sediments in the open ocean is mainly composed of organic and inorganic
66 P ~~forms~~ associated with the export of ~~dead~~ organic ~~detritus matter~~ and other particles from the
67 photic zone. ~~Furthermore,~~ P adsorbed to minerals such as Mn and Fe (oxyhydr)oxides ~~or~~
68 ~~carbonate fluorapatites (CFA) is accumulated in the sediments~~ [Föllmi, 1996; Delany, 1998;
69 Faul et al., 2005][Delany, 1998; Faul et al., 2005; Föllmi, 1996] are further sources, as well as
70 ~~Additionally,~~ P input ~~to sediments by from~~ fish debris that is may be particularly important
71 in productive upwelling regions [Suess, 1981; Schenau and DeLange, 2001; Diaz-Ochoa et
72 al., 2009; Noffke, 2014][Diaz-Ochoa et al., 2009; Noffke, 2014; Schenau and DeLange, 2001;
73 Suess, 1981].

74 P cycling is strongly affected by redox-dependent processes. P can be scavenged by Fe
75 (oxyhydr)oxides in oxic sediment and released across the sediment-water interface due to the

76 reduction dissolution of Fe (oxyhydr)oxides in anoxic sediments [Sundby et al., 1986; Slomp
77 et al., 1998]. Furthermore, recent studies showed that sulfur bacteria found in surface
78 sediments of anoxic environments can internally store and release P under oscillating redox
79 conditions [Ingall and Jahnke, 1997 and references therein]. Therefore, these organisms are a
80 key player for the modulation of porewater P concentrations and benthic P release to the
81 water column.

82 Additionally, hypoxic or anoxic conditions favor the precipitation of P in the form of
83 authigenic carbonate fluorapatite (CFA) [Froelich et al., 1988; Suess and von Huene, 1988;
84 Goldhammer et al., 2010; Ingall, 2010; Schenau and De Lange, 2000]. For non-upwelling
85 areas, the required phosphate oversaturation in the porewaters has been attributed to the
86 reductive dissolution of P bearing Fe (oxyhydr)oxides [e.g. Ruttenger et al., 1993, Slomp et
87 al., 1996]. In contrast, the CFA formation in sediments of the Namibian upwelling area was
88 linked to microbial P release into the porewaters [Schulz and Schulz, 2005].

89 P cycling is strongly affected by redox dependent processes, due to the fact that P is typically
90 scavenged by Fe oxyhydroxides. Reduction of Fe oxyhydroxides during anoxic diagenesis
91 induces the release of phosphate across the sediment water interface [Slomp et al., 1998;
92 Sundby et al., 1986]. Additionally, hypoxic or anoxic conditions favor the precipitation of P
93 in the form of CFA [Froelich et al., 1988; Goldhammer et al., 2010; Ingall, 2010; Schenau
94 and De Lange, 2000; Suess and von Huene, 1988]. The resulting feedback on oceanic primary
95 production and atmospheric O₂ and CO₂ levels triggered by changes in benthic P release and
96 P burial from anoxic sediments sequestration is still unclear. Presently, there are three
97 opposing views in literature related to feedback mechanisms of the P cycling and its effect on
98 the oceanic and atmospheric processes have been raised: (1) Intensified phosphate release
99 from the sediments to the water column caused by an expansion of low oxygen waters [Ingall
100 and Jahnke, 1994; Stramma et al., 2008] could stimulate the primary production in the surface
101 waters [Wallmann, 2003]. This, in turn, may lead to a more intensified oxygen demand and a
102 positive feedback with benthic P release [Slomp and Van Cappellen, 2007; Wallmann, 2010;
103 Moffit et al., 2015; Moffit et al., 2015; Slomp and Van Cappellen, 2007; Wallmann, 2010]. (2)
104 A negative feedback on P release scenario has been postulated based on the
105 precipitation observations of CFA mineral precipitations found in the present-day oxygen
106 depleted upwelling areas [Schulz and Schulz, 2005; Arning et al., 2009a; Arning et al., 2009b;
107 Goldhammer et al., 2010; Cosmidis et al., 2013; Arning et al., 2009a; Arning et al., 2009b;

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108 ~~Cosmidis et al., 2013; Goldhammer et al., 2010; Schulz and Schulz, 2005]. Being a major~~
109 ~~sink CFA mineral formation is a major sink~~ for bioavailable P in marine environments
110 [Delaney, 1998; Ingall, 2010], ~~it has been argued that. Hence, it is thought that~~ the expansion
111 of OMZs may increase the ~~precipitation of CFA precipitation minerals~~ in the sediments and
112 ~~thus mitigate outbalance~~ the benthic phosphate release ~~from anoxic sediments~~ [Ganeshram et
113 al., 2002; Goldhammer et al., 2010; Ingall, 2010]. (3) A third scenario suggests that the
114 formation of CFA is in balance with enhanced P release from anoxic sediments, implying that
115 the dissolved oceanic P inventory is largely unaffected by oxygen concentrations [Delaney,
116 1988; Anderson et al., 2001; Roth et al., 2014 Anderson et al., 2001; Delaney, 1988; Roth et
117 al., 2014]. These conflicting scenarios show that there is further need to explore the benthic-
118 pelagic P cycling in oxygen deficient environments in order to enable improved predictions.

119 ~~In this study, we explore P cycling in. We address this topic using a comprehensive data set~~
120 ~~from t~~he Peruvian OMZ to identify ~~and quantify~~ P sources to the sediment ~~and the return of~~
121 ~~inorganic dissolved P back to the water column~~. Our data set comprises samples of particulate
122 matter from the water column as well as pore-water, ~~and~~ sediment samples ~~and samples of~~
123 ~~filamentous sulfur bacteria~~. We present in situ benthic phosphate fluxes, particulate matter
124 C/P ratios for water column particles and surface sediments and P burial fluxes, ~~and relative~~
125 ~~abundances of sulfur bacteria~~ for 6 stations along the depth transect across the Peruvian shelf
126 at 12°S. From ~~the data, we derive~~ a mass balance for P cycling ~~in the sediments, we conclude~~
127 ~~that the benthic P sources and sinks were, in general, imbalanced resolving the input of P, P~~
128 ~~burial and benthic P releases during our sampling campaign.e.~~

129

130 2 Study Area

131 The study area is located in the center of the Peruvian OMZ at 12°S covering the shallow
132 shelf from ~70 m water depth to mid-slope depths of about at ~400 m (Fig. 1). During our
133 sampling campaign in January 2013 neutral or slightly negative El Niño-Southern Oscillation
134 (ENSO) conditions dominated (<http://www.cpc.ncep.noaa.gov>) and the bottom water oxygen
135 concentrations were below detection limit ~~of the Winkler titration (5 μmol L⁻¹)~~ down to ~ 450
136 m water depth (Fig. 1, Table 1). Below the OMZ, oxygen concentrations ~~rise increased~~ to 19
137 and 53 μM at 770 m and 1025 m water depth, respectively. Nitrate concentrations were below
138 12 μM from 128 to 407 m water depth (Table 1). During the measuring period, the bottom

139 | water at station I (74 m) was sulfidic and depleted in nitrate (Table 1; Sommer et al., [in](#)
140 | [reviewsubmitted](#)).

141 | The oxygen deficient waters off Peru belong to one of the world's most prominent OMZs.
142 | Southeasterly trade winds that are driven by the Pacific Subtropical Anticyclone engender
143 | offshore transport of surface waters and upwelling of subsurface waters from the poleward
144 | propagating Peru undercurrent (PUC) [Strub et al., 1998]. These water masses are oxygen
145 | depleted and rich in nutrients, favoring primary production of up to $3.6 \text{ g C m}^{-2} \text{ d}^{-1}$ in surface
146 | waters [Pennington et al., 2006]. As a consequence, the intense oxygen consumption induced
147 | by the degradation of sinking particulate organic matter and a sluggish ventilation induce the
148 | development of a strong OMZ. Based on the definition that the oxycline of an OMZ is at ~ 22
149 | μM [Fuenzalida et al., 2009], the Peruvian OMZ extends from approximately 50 – 700 m
150 | water depth. The greatest upwelling strength is reached during austral winter and spring
151 | between 5 and 15°S [Strub et al., 1998]. The phases of strong upwelling are followed by high
152 | [rates of primary production](#)~~onvity rates~~ in austral summer. The coastal area off Peru ~~is-displays~~ a
153 | highly variable [hydrographic](#) regime ~~underlying the ENSO~~. Especially during positive ENSO
154 | periods coastal trapped waves emerging from equatorial Kelvin waves in the equatorial East
155 | Pacific occur frequently [Gutiérrez et al., 2009 and references therein; [Mosch et al., 2012](#)].
156 | Consequently, the thermocline and the oxycline shift [downwards by ca. for](#) 100 m and [bottom](#)
157 | [watermore downwards and](#) oxygen concentrations [can increase from practically zero to](#)
158 | [around variations from 0 to](#) 100 μM [can occur in the timespan of in](#) days to weeks [Gutiérrez
159 | [et al., 2008; Schunck et al., 2013; Graco et al., 2016Gutiérrez et al., 2008; Schunck et al.,](#)
160 | [2013](#)]. [Seasonally, bottom waters of the shelf \(75 m\) can transition from oxic or hypoxic](#)
161 | [between austral winter/spring \(low primary production\) to anoxic throughout the rest of the](#)
162 | [year \[Noffke et al., 2012\]. Furthermore, porewater uranium \(U\) profiles at 11°S indicate](#)
163 | [variable redox conditions at the upper rim of the OMZ \[Scholz et al., 2011\]. The shelf area](#)
164 | above 200m water depth is therefore characterized by non-steady state conditions, whereas
165 | the oxygen concentrations in the core OMZ ($\sim 200\text{-}400$ m water depth) are predominantly
166 | below ~~the~~ detection limit of $5 \mu\text{M}$ throughout the year.

167 | The sediments of the Peruvian OMZ have POC contents ranging from 15-20 wt. % within the
168 | OMZ and > 5 wt. % [below the OMZ and](#) on the shelf ~~and below~~ [Dale et al., 2015]. The fine-
169 | grained, diatomaceous mud lens between 11°S and 15°S accumulates under low PUC bottom
170 | water velocities in 50 to 500 m water depth [Krissek et al., 1980]. This favors high

Kommentar [LU2]: T. Jilbert comment
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171 sedimentation rates, carbon preservation and burial [Suess et al., 1987; Dale et al., 2015].
172 Further down, at mid-slope depth, a high energy regime favoring erosive settings leads to the
173 formation of phosphorites [Reimers and Suess, 1983; Glenn and Arthur, 1988; Arning et al.,
174 2009b; Mosch et al., 2012][Glenn and Arthur, 1988; Arning et al., 2009b; Reimers and Suess,
175 1983]. Another interesting observation between 70 and ~ 300 m of water depth is the
176 occurrence of mat-forming filamentous sulfur bacteria [Mosch et al., 2012]. Bacterial mats are
177 not conspicuous below below 300 to 400 m water depth, and instead foraminiferal sands are
178 more common.

179

180 3 Methods

181 Sampling of water column particulate matter and sediment cores as well as the deployment of
182 the benthic landers BIGO I and II (Biogeochemical Observatories) was conducted along the
183 12°S depth transect during the RV *Meteor* cruise M92 in January 2013. The geographical
184 position and water column properties for the main stations are reported in Table 1. The
185 ~~dataset~~data set on in situ phosphate fluxes comprised 10 stations from 74 to 989 m water
186 depth. The water column particle sampling was performed at 6 stations from 74 to 407 m
187 water depth. These stations are considered as main stations and for consistency the stations
188 are numbered according to the data set published in Dale et al. (2015). Hydrographic
189 parameters and oxygen concentrations were obtained by deploying a CTD/rosette equipped
190 with a Seabird oxygen sensor (detection limit is 5 µM) calibrated by Winkler titration.

191 3.1 Water column particles

192 Particulate matter was filtered using water from Niskin bottles from the CTD/rosette and
193 analyzed for total particulate phosphorus (TPP), particulate inorganic phosphorus (PIP) and
194 particulate organic carbon (POC) concentrations. Following Labry et al. (2013), we expect the
195 PIP phase to be comprised of inorganic P phases originating from abiotic particulate P as well
196 as inorganic P from biogenic particulate P. Abiotic PIP comprises detrital P associated to
197 minerals from terrigenous sources. Biotic PIP is composed of orthophosphates,
198 pyrophosphates and polyphosphates within eukaryotic and prokaryotic cells.

199 Between three and six water depths were sampled per station. The water was filled into 10 ~~HL~~
200 ~~eans~~PE containers rinsed beforehand with ultrapure water (MilliQ)~~before~~. The ~~eans~~

Kommentar [LU3]: T. Jilbert comment
3

201 containers were shaken before filtration which was performed within 24 h after sample
202 retrieval. Approximately 2 to 4 L of sea-water were filtered through pre-weighed and
203 combusted (450°C, 5h) 0.7 µM Whatman GF/F filter using a sea-water vacuum pump and
204 Duran bottle top filters. After filtration, all filters were immediately frozen at -20°C. At the
205 shore-based laboratory the GF/F filters were dried over night at 45°C, and divided into 3
206 equally sized pieces using a scalpel. The total filtered water volume was divided by three to
207 calculate elemental concentrations on each filter section assuming homogenous coverage of
208 particles on the filters.

209 **3.1.1 Total particulate phosphorus (TPP), particulate inorganic phosphorus** 210 **(PIP) and particulate organic phosphorus (POP)**

211 The determination of TPP and PIP concentrations by combustion and colorimetric methods
212 has been described by Asahi et al. (2014), Aspila et al. (1976), Loh and Bauer (2000) and
213 others.- However, the combustion and acid dissolution (HTC/hydrolysis) that has been applied
214 for PIP-determination is limited by the fact that polyphosphates are only partly hydrolysed,
215 but provides the best compromise compared to other methods (Labry et al., 2013). Although
216 polyphosphates are underestimated, it includes intracellular P that is often dominant in
217 plankton and only small amounts of organic P. In the case of TPP we used the Aspila (1976)
218 method without an oxidant (e.g. MgSO₄) during combustion, which underestimates the TPP
219 concentration in water column particles. However, for the sediments, the results following of
220 the Aspila (1976) method were compared total digestions showing an average recovery of the
221 Aspila method of approximately 102%. In two samples we found an overestimation in total
222 digestion of more than 100% and in one sample an underestimation of 32%, possibly due to
223 heterogeneity of the samples caused by very small phosphorite granules.

224 Filter segments for TPP concentration were combusted at 550°C for 90 min and afterwards
225 soaked with 20 ml 1 N hydrochloric acid (HCl) and shaken for 24 h at room temperature.
226 Then, the solution was filtered and 0.35 ml triple reagent (40 ml 9.8 N sulfuric acid, 12 ml
227 ammonium molybdate and 4 ml potassium antimonyl tartrate solution) and 0.175 ml ascorbic
228 acid and 3 ml 1 N HCl were added to 3.75 ml of the sample solution. Then, 0.3 ml of 12.5 N
229 sodium hydroxide (NaOH) was added to the solution before colorimetric measurement of
230 phosphate at 880 nm using a Hitachi U-2001 photospectrometer. This was done because test
231 runs with the standard series revealed that the slope of the calibration curve was not steep

232 enough to measure the low phosphate concentrations expected. To resolve this issue, the pH
 233 of the solution was slightly increased usingg NaOH. Measurements were accompanied using
 234 a standard series consisting of 8 standards ranging from 5 to 100 $\mu\text{M PO}_4^{3-}$, prepared from a
 235 Merck phosphate stock solution. We used 0.75 ml of each standard for the standard series and
 236 treated each of them in the same manner as described above. ~~Before colorimetric~~
 237 ~~measurement of phosphate at 880nm using a Hitachi U 2001 photospectrometer the solution~~
 238 ~~was neutralized for the HCl by 0.3 ml 12.5 N sodium hydroxide (NaOH) in order to adjust the~~
 239 ~~pH. Measurements were u ranging from 5 to 100 μM .~~ The samples were measured undiluted
 240 due to low concentrations and the technical detection limit of a 1 cm cuvette. Hence, we used
 241 3.75 ml of the filtered sample solution, added the reagents mentioned above and divided the
 242 concentrations by a factor of 5 to adjust the ~~measurements results to the those ones~~ of the
 243 standard series. A factor of 0.02 was used to transform the concentration unit to $\mu\text{mol L}^{-1}$. The
 244 amount of filtered water (f) refers to 1/3 of the total filtered water volume (f is different for
 245 each sample):

$$\text{TPP or PIP } [\mu\text{mol L}^{-1}] = \frac{[\text{PO}_4^{3-}] \cdot 0.02}{5 \cdot f}$$

246 ~~$\text{TPP} / \text{PIP} [\mu\text{mol L}^{-1}] = (\text{measured concentration} / 5 * 0.02) / (1/3 \text{ of the amount of filtered}$~~
 247 ~~$\text{water})$~~

248 The same procedure was performed for PIP without the combustion step. The POP
 249 concentration was calculated by the difference of the measured (as phosphate) TPP and PIP
 250 concentrations.

251 3.1.2 Organic carbon ~~concentration~~ concentration

252 The filter sections for the analysis of POC ~~concentration~~ concentration were fumed with 37 %
 253 HCl overnight to remove inorganic carbon, dried and wrapped into tin caps. Samples were
 254 measured by flash combustion with a Carlo Erba elemental analyzer (NA1500). The
 255 analytical precision and detection limit ~~amounted to were~~ 0.04 dry ~~weight percent~~ wt. %
 256 ~~(%).~~ The water column POC concentrations are given in $\mu\text{mol L}^{-1}$.

Kommentar [LU4]: T. Jilbert comment
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Kommentar [LU5]: P. Kraal comment
20

Kommentar [LU6]: P. Kraals comment
21

257 3.2 Pore-water and solid phase analysis

258 Sediment cores were recovered using video-guided multiple corers (MUC) equipped with
259 PVC liners with an inner diameter of 10 cm. The pore-water and solid phase sub-sampling
260 was performed immediately after recovery in an argon-filled glove bag at in situ sea-floor
261 temperature. The bottom water was siphoned with a plastic tube and filtered through cellulose
262 acetate filters. Afterwards, the cores were sectioned into 0.5 cm intervals from 0-5 cm
263 sediment depth and 1 cm intervals afterwards. The sediment samples were filled into
264 centrifuge tubes and the pore-water was separated from the sediments by centrifuging for 20
265 min at 4500 rpm. The supernatant pore-water was filtered through cellulose acetate filters
266 inside the glove bag. Samples were immediately analyzed for total dissolved phosphate
267 (TPO₄) and dissolved ferrous iron (Fe²⁺) after pore water extraction using a Hitachi U-2001
268 spectrophotometer. The analyses were performed according to the standard techniques
269 described in Grasshoff et al. (1999). A sediment subsample was taken from each sediment
270 depth and stored refrigerated in pre-weighed air-tight plastic cups to determine the water
271 content, porosity and total organic carbon (TOC) content. The residual sediments were stored
272 frozen at -20°C (sediment and filter samples) and the pore water samples were ~~or~~ refrigerated
273 at 4°C for land-based analytics.

Kommentar [LU7]: clarified after P.
Kraals comment 22

274 The TOC ~~content~~ concentration (in $\mu\text{mol mg}^{-1}$) of freeze-dried and ground sediment samples
275 was determined by flash combustion in a Carlo Erba Elemental Analyzer (NA 1500). For
276 POC determination, samples were decalcified with 2.5 N HCl prior to the measurement. Solid
277 phase TPP and PIP concentrations were measured according to the method of Aspila et al.
278 (1976) in a similar manner as described before for the water column particles. 50 mg of
279 freeze-dried and ground sediment were digested in 1N HCl for a minimum of 24 hours to
280 dissolve the sedimentary PIP phase. Sediment portions analyzed for TPP were combusted at
281 550°C for 90 min before adding 1 N HCl. The solutions were filtered and the reagents
282 mentioned ~~before~~ ~~above~~ were added ~~prior to~~ ~~before~~ measurement. We used the sedimentary
283 reference standards SDO-1 (Devonian Ohio Shale, USGS; Govindaraju, 1994) and MESS-3
284 (Marine Sediment Reference Material, Canadian Research Council) and replicate
285 measurements of samples to ensure measurement accuracy. The standard series applied to the
286 measurements covered a concentration range from 5 to 100 μM .

Kommentar [LU8]: P. Kraals comment
23

287 To determine the terrigenous P input flux to the sediments, and to calculate the TPP burial
288 flux (for calculation see section 3.6 and Table 2), sediments were analyzed using total
289 digestion. About 100 mg of freeze dried and ground sediment was digested in hydrofluoric
290 acid (40%, supra pure), nitric acid (65%, supra pure) and perchloric acid (60%, supra pure).
291 For measurement accuracy the reference standards SDO-1 and MESS-3 as well as
292 methodological blanks were included in the analysis. The aluminum concentration in the
293 digestion solutions wasere measured using an inductively coupled plasma optical emission
294 spectrometer (ICP-OES, Varian 720 ES). The relative standard deviation (RSD) for [Al] was
295 found to be < 1%.

Kommentar [LU9]: changed after P.
Kraals comments 24 & 25

296 The XRD data of core 107MUC23 from 407 m water depth were obtained from
297 approximately 1 g of freeze dried and ground sediment in the lab of the University of Bremen.

298 3.3 POC in relation to various fractions of P (POC/xP ratios)

299 The molar POC/xP ratios (where xP = TPP, PIP and-or POP) of the water column particles at
300 stations I, IV and V were calculated from two independent sample measurements on two filter
301 samples per water depth. For these samples a minimum and maximum value was calculated.
302 For the other stations III, VI and VIII, it was only one sample per water depth was available.
303 Here, we assumed an average error-neutral variability calculated from the duplicate
304 measurements of stations I, IV and V for each P species (supplementary material). For
305 sediment samples we calculated a standard deviation for each station (supplementary
306 material). For sediment samples we calculated a standard deviation from repeated
307 measurements of the sediment standards MESS-3 and SDO-1 (supplementary material).

Kommentar [LU10]: P. Kraal comment
26

308 3.4 Benthic lander fluxes

309 Benthic lander deployments were performed at 10 stations along the 12°S transect (I to X
310 according to Dale et al., 2015). In situ benthic fluxes were obtained using the two BIGOs I
311 and II (BIGO: Biogeochemical Observatory). They were equipped with two circular flux
312 chambers (internal diameter 28.8 cm, area 651.4 cm²) [Sommer et al., 2009]. An online video-
313 controlled launch system allowed precise placement of the chambers-BIGO at the seafloor
314 directly located beneath the particle sampling stations in the water column and in proximity to
315 the multi-corer stations. After a 2-4 hour rest period at the seafloor during which surrounding

316 bottom water was periodically flushed into the chamber, the chambers were slowly driven
317 into the sediment. The BIGOs stayed for 28 hours at the seafloor, while 8 water samples per
318 chamber were taken via glass syringes. In order to obtain bottom water background
319 information, additional samples were taken every 8 hours from the ambient bottom water.
320 Phosphate concentrations in the syringe samples were measured on board using an auto
321 analyzer. The standard series covered a concentration range from 0.05 to 3.5 μM . The fluxes
322 were calculated from the slope of linear regression of all 8 data points versus the sampling
323 time (supplementary material) and corrected for the water volume in the chamber and the
324 dead volume of the 1 m long Vygon tubes connecting the syringes with the flux chambers.
325 The error caused by the dilution from the dead volume of these tubes was calculated from the
326 chloride concentration measured in the syringe samples. Benthic lander TPO_4 fluxes for most
327 sites are based on two replicate chamber measurements. The uncertainty given for the TPO_4
328 fluxes is the difference between the minimum and maximum fluxes from the average of the
329 two benthic chambers. At two stations (IV and V), it was only possible to calculate the flux
330 from one chamber. For further details on the benthic flux measurements during the M92
331 cruise see Dale et al. (2015).

332 3.5 Diffusive flux calculations

333 The diffusive fluxes of TPO_4 and Fe^{2+} from the sediment to the bottom water were calculated
334 by applying Fick's First Law of diffusion:

$$335 F_{\text{TPO}_4/\text{Fe}^{2+}} = -\phi D_{\text{SED}} \left(\frac{d[C]}{dx} \right) \quad (1)$$

336 where the term $d[C]/dx$ describes the concentration gradient between the bottom water and the
337 first pore-water sample of the surface sediment divided by the corresponding sediment depth
338 (0.25 cm or 0.5 cm) and ϕ is the porosity of the surface sediment. The diffusion coefficient,
339 D_{SED} , for sediments was calculated according:

$$340 D_{\text{SED}} = D_{\text{SW}} / \theta^2 \quad (2)$$

341 The diffusion coefficients for TPO_4 and Fe^{2+} under standard conditions (D_{SW} under standard
342 conditions (298.15 K and 1 bar) were taken from Li and Gregory (1974) and corrected for
343 the in situ temperature and pressure using the Stokes-Einstein equation. The tortuosity (θ^2)

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344 was derived from the sediments porosity according to [the modified Weissberg formulation](#)
345 [\[Boudreau, \(1996\)\]](#):

$$346 \theta^2 = 1 - \ln(\phi^2) \quad (3)$$

347 [Uncertainty in the diffusive flux was calculated at St. I as the difference between the fluxes](#)
348 [calculated from two separate sediment cores. For the other stations, only one core was](#)
349 [available to calculate the flux.](#)

350 3.6 Mass balance of benthic phosphorus cycling

351 To investigate benthic P cycling quantitatively, a mass balance was developed considering P
352 input, P burial, and P release. The equations for the P mass balance calculations are shown in
353 Table 2. Under steady state conditions, the total P rain rate should balance the P buried in the
354 sediments and the benthic TPO₄ flux ([Eq. 4 in Table 2, Eq. 4](#)). The rain rates of particulate P
355 delivered to the sediments are differentiated in inorganic P (RR_{PIP}) ([Eq. 5 in Table 2, Eq. 5](#))
356 and organic P (RR_{POP}) ([Eq. 6 in Table 2, Eq. 6](#)). The rates were calculated using the POC/xP
357 ratio of the water column particles that were taken as close as possible to the sea-floor at each
358 station (2-5 m above [ground](#)) and the POC rain rate (RR_{POC}) (Table 4 and supplementary
359 material). RR_{POC} for the same stations along the 12°S transect were previously calculated by
360 Dale et al. (2015) as the sum of the measured benthic DIC flux and the POC accumulation
361 [rate at 10 cm sediment depth](#). The terrigenous P input (RR_{Pterr}) ([Eq. 7 in Table 2, Eq. 7](#)) can be
362 estimated by multiplying the solid phase [aluminum-Al](#) concentration of the first sediment
363 [centimeter sample by](#) with the mass accumulation rate [Dale et al., 2015] and a P/Al ratio of
364 0.02 that characterizes the P/Al ratio of riverine [transported](#) particles originating from the
365 continents [Viers et al., 2009].

366 The P burial flux (F_{Pbur}) ([Eq. 8 in Table 2, Eq. 8](#)) was calculated by multiplying the mass
367 accumulation rate ([MAR](#)) and the average solid phase P concentration of the first [10](#)
368 [centimeter centimeters \(P₁₁\) \(11 cm is due to our sampling resolution\)](#). [This](#)
369 [approach was chosen according to Dale et al. \(2015\) who also calculated POC accumulation](#)
370 [rate for the OMZ stations \(i.e. not on the shelf or below the OMZ\) using the elemental](#)
371 [average concentration of the first 10 cm of sediment. The sediment mass accumulation rate](#)
372 [\(MAR\)](#) ([Eq. 9 in Table 2, Eq. 9](#)) was calculated from the sedimentation rate ([ω_{acc} in cm y⁻¹ SR](#)
373 [in cm ky⁻¹](#)), dry bulk density (ρ_{dry}; in g cm⁻³) and the average porosity of the sediments at the

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374 | lower core end (ϕ_{∞}). Sedimentation [accumulation](#) rates were determined from particle-bound
375 | $^{210}\text{Pb}_{\text{xs}}$ measurements using a modeling approach. A detailed method description and the
376 | values used for this work are published in Dale et al. (2015). The error derived from modeling
377 | the sedimentation rate was given as 20 % and propagates to all subsequent calculations where
378 | it was used.

379 | **3.7 Freeze/thaw experiments**

380 | In order to determine the amount of polyphosphate stored in sulfide-oxidizing bacteria,
381 | foraminifera and other bacteria we conducted additional sediment experiments at all transect
382 | stations, except station IV. Sediments from MUC corers were sliced into 1 cm thick slices
383 | from the surface sediment to 10 cm sediment depth. Before phosphate analysis, sediments
384 | slices were repeatedly frozen at -80°C and defrosted in order to burst microbial cells and
385 | release the internally stored P to the pore-water.

386 | **3.8 Molecular quantification of filamentous bacteria**

387 | In order to quantify the abundance of filamentous microbes at the benthic boundary layer, we
388 | used a molecular approach. Nucleic acid purification was performed on 0.5 g sediment
389 | following established protocols [Bertics et al., 2013]. DNA was quality checked on an agarose
390 | gel and quantified using a Nanodrop spectrophotometer (Peqlab, Erlangen, Germany). ~~A-16S~~
391 | ~~rDNA PCR was performed with universal primers 27F and 1492R and obtained fragments~~
392 | ~~were Topo TA cloned using the Topo TA cloning Kit (Invitrogen, Carlsbad, USA) and Sanger~~
393 | ~~sequenced as previously described [e.g. Löscher et al., 2012]. fragments were taken from a~~
394 | ~~previously generated metagenome from this region (GenBank Bioproject PRJNA280940) and~~
395 | ~~the respective sequence counting's were deposited at GenBank (ID KU312264-KU312267).~~
396 | Sequencing was carried out in the Institute of Clinical Molecular Biology at Kiel
397 | University. Sequences were analyzed using a Clustal W alignment tool on Mega 6 [Tamura et
398 | al., 2013] ~~and deposited on GenBank (submitted)~~. A qPCR primer and probe set was
399 | established using the Primer Express software (Life Technologies, Carlsbad, USA) with the
400 | forward primer 5' AGAAGCACCGGCTAACTCTG-3' , the reverse primer, ~~5'~~
401 | ~~TCGAATTAACCACA-3'~~

Kommentar [LU11]: P. Kraals
comment 26

402 5' -CCAGGTAAGGTTCTTCGCGT-3' and the probe 829-Thioploca 5'-
403 GGATTAATTTCCCCAACAT-3' [Teske et al., 1995]. Primers and probes were tested *in*
404 *silico* on the Silva database and cross amplification was excluded on a variety of 16S rDNA
405 clones. The qPCRs were performed in technical duplicates on a ViiA7 system (Life
406 Technologies, Carlsbad, USA) as previously described [Löscher et al., 2014] using 1x
407 TaqMan PCR buffer (Life Technologies, Carlsbad, USA), ~~100 nM~~ 2.5 pmol μL^{-1} TaqMan
408 probe, 5 pmol μL^{-1} of each primer, 400 ng μL^{-1} bovine serum albumin (to avoid PCR inhibition
409 without affecting standard curves or detection limits), 3 μL PCR water, and 5 μL of either
410 standard DNA or environmental sample. A plasmid containing the target sequence was used
411 to generate a standard dilution series for absolute quantification. The melting temperature was
412 set to 50°C. A theoretical detection limit of 4 copies per PCR reaction was calculated. The
413 results of the analysis are given in copies g^{-1} of 16S rDNA sequences of sulfur bacteria that
414 are related to Marithioploca.
415 PCR reaction has been calculated. The results of the analysis are given in copies g^{-1} whereas a
416 copy of the target 16S gene is equal to a single organism of Thioploca spp.

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418 4 Results

419 4.1 P composition of water column particulate matter and surface sediments

420 4.1.1 TPP, PIP, POP and POC concentrations

421 The TPP concentrations ranged from 0.02 to 0.2 $\mu\text{mol L}^{-1}$ in the water column particles and
422 from 0.04 to 2.37 $\mu\text{mol mg}^{-1}$ in the surface sediments (supplementary material). Overall, the
423 profiles along the transect show no significant trends through the water column (Fig. 2A). The
424 highest concentrations occurred in the surface waters around 10 m of water depth. At stations
425 I, V and VIII (74, 195 and 407 m) the TPP concentrations slightly increased close to the
426 seafloor, whereas at the other stations no such trend was observed (Fig. 2A and
427 supplementary material). In the sediments the TPP concentrations slightly decreased with
428 sediment depth, except at station VIII (407 m). Here, the highest sedimentary TPP
429 concentrations across the transect were found at 2.25 cm sediment depth (17 $\mu\text{mol mg}^{-1}$).
430 Below that depth the concentrations decreased, but remained high compared to the other
431 stations.

432 The PIP and POP concentrations (water column and sediments) generally followed the trends
433 of the TPP profiles and contributed roughly equally to TPP. The PIP fraction accounted for 21
434 to 74 % of TPP in the water column particles (Fig. 3), similar as reported in previous studies
435 [Paytan et al., 2003; Faul et al., 2005; Benitez-Nelson et al., 2007; Lyons et al., 2011; Sekula-
436 Wood et al., 2012]. At stations I, VI and VIII (74, 244 and 407 m), the PIP concentrations
437 were larger than POP. The opposite occurred at station V (195 m) where the POP fraction was
438 clearly larger than the PIP fraction throughout the entire water column. In comparison to the
439 water column particles, the PIP fraction was larger than POP in most samples reaching
440 between 48 to 98% of TPP. However, the strongest deviation between PIP and POP
441 concentrations was found in the sediments of station VIII (407 m) where the PIP
442 concentration was up to a factor of ~ 50 larger than the POP concentration and comprised up
443 to 98% of TPP. XRD data from that station revealed that 7 to 16 wt.% of the sediments
444 consisted of apatite and other particulate phosphates (data not shown).

445 The particulate organic carbon concentrations ranged from 2.2 to 17.6 $\mu\text{mol L}^{-1}$ in the water
446 column particles and from 2.8 to 13.4 $\mu\text{mol mg}^{-1}$ in the surface sediments. Within the water
447 column the highest concentrations occurred in the surface water samples, while the
448 concentration measured at station VI (244 m) is about 5 times higher than compared to other
449 samples from the same water depth. Below the surface water concentration peak, the
450 concentrations were on average 7 $\mu\text{mol L}^{-1}$ with distinct depth trends. The sedimentary POC
451 concentrations were on average 7.7 $\mu\text{mol mg}^{-1}$ for the whole transect. Overall, the POC
452 concentrations showed little variability with sediment depth. At station III, VI and VIII (128,
453 244 and 407 m) the concentrations increased slightly with sediment depth. At station I (74 m)
454 the concentration decreased slightly with sediment depth.

455 **PIP and POP fractions of TPP**

456 The PIP fraction made up a large portion (21 to 74%) of TPP in the water column particles
457 (Fig. 3), as observed in previous studies [Benitez-Nelson et al., 2007; Faul et al., 2005; Lyons
458 et al., 2011; Paytan et al., 2003; Sekula-Wood et al., 2012]. The PIP fraction in the sediments
459 reached 48 to 98%. In comparison to the water column particles, the average sedimentary PIP
460 fraction of TPP increased at each station, except at station VI. However, the strongest effect
461 occurred at station VIII where the sedimentary PIP fraction comprised 98 % of TPP. XRD

462 ~~data from that station revealed that 7–16 wt. % of the sediments consisted of apatite and other~~
463 ~~phosphates (data not shown).~~

464 4.2 Particulate organic carbon to phosphorus (POP, PIP, TPP) ratios

465 *POC/POP ratios*

466 The molar POC/POP ratios of the water column particles and of the surface sediments were
467 consistently higher than the Redfield ratio at all stations (Fig. 2B). The average POC/POP
468 ratio of the water column particles was 202 ± 29 . There was no clear trend through the water
469 column, except slightly increasing ratios ~~close to the seafloor~~ between the deepest water
470 column samples and the surface sediment samples. In the surface sediments, the ratios
471 increased within the ~~upper~~ analyzed 0 to 6 cm of sediment depth, except at station VIII, with
472 an average POC/POP ratio of 303 ± 77 . Station VIII (407 m) is an exception, and here the
473 ratio decreased to 81 within the first ~ 2 cm of sediment and then strongly increased to ≥ 600 .

Kommentar [LU12]: modified after P.
Kraals comment (4)

Kommentar [LU13]: modified after P.
Kraals comment (5)

474 *POC/PIP ratios*

475 The average POC/PIP ratio of the water column particles was 248 ± 34 . Similar to the
476 POC/POP ratios, there was no significant trend through the water column. At the majority of
477 the stations, the ratios decreased close to the seabed. The average POC/PIP ratio of the
478 surface sediments was 184 ± 34 and almost ~~constant-invariable with water~~ over depth. In the
479 sediments, the ratios showed no significant down-core trend. At station VIII (407 m) the ratio
480 in the sediments showed a dramatic decrease compared to the water column, with drastically
481 decreased to a an average of 7, similar to the POC/TPP ratios (below).

482 *POC/TPP ratios*

483 The POC/TPP ratios of the water column particles and surface sediments consistently ~~ranged~~
484 varied around the Redfield ratio. ~~The exceptions are, with the exception of the sedimentary~~
485 ratios at the shallowest (Station I; (74 m)) and the deepest stations (Sta. VIII, 407 m). At
486 station I, the sediments ~~showed measurements indicated~~ significantly lower ~~ratios~~
487 Redfield ratios with an average of 69 in the surface sediments. The average POC/TPP ratio of
488 the surface sediments at station VIII (407 m) was 7. Between the deepest water column
489 sample and the first sediment sample, the POC/TPP ratios were rather constant without a

490 consistent trend, again with the exception of station VIII (407 m) where the ratios decreased
491 sharply.

Kommentar [LU14]: modified after P. Kraals comment (6)

492 ~~Close to the seabed, the POC/TPP ratios were stable or slightly increasing, with exception of~~
493 ~~station VIII where the ratios decreased sharply.~~

494 ~~4.1.11.1.1~~ **PIP and POP fractions of TPP**

495 ~~The PIP fraction made up a large portion (21 to 74%) of TPP in the water column particles~~
496 ~~(Fig. 3), as observed in previous studies [Benitez-Nelson et al., 2007; Faul et al., 2005; Lyons~~
497 ~~et al., 2011; Paytan et al., 2003; Sekula-Wood et al., 2012]. The PIP fraction in the sediments~~
498 ~~reached 48 to 98%. In comparison to the water column particles, the average sedimentary PIP~~
499 ~~fraction of TPP increased at each station, except at station VI. However, the strongest effect~~
500 ~~occurred at station VIII where the sedimentary PIP fraction comprised 98 % of TPP. XRD~~
501 ~~data from that station revealed that 7-16 wt. % of the sediments consisted of apatite and other~~
502 ~~phosphates (data not shown).~~

503 **4.24.3 In situ benthic chamber fluxes**

504 The benthic lander TPO_4 fluxes (F_{TPO_4}) are presented in Table 3 and Fig. 4A. Positive fluxes
505 are defined as directed from the sediments into the water column. The highest TPO_4 flux
506 along the depth transect of ~~about~~ $1.04 \pm 0.31 \text{ mmol m}^{-2} \text{ d}^{-1}$ occurred at station I ~~at 74 m water~~
507 ~~depth(74 m)~~. Below 74 m water depth, fluxes decreased ~~at least~~ by ~~at least~~ a factor of 3 ~~from~~
508 ~~100 to 144 m water~~ to $0.2 - 0.3 \text{ mmol m}^{-2} \text{ d}^{-1}$ ~~at 144 m water depth~~. Measurements at ~~station~~
509 ~~V (195 m)198 m water depth~~ showed a slightly increased TPO_4 flux of $0.44 \pm 0.07 \text{ mmol m}^{-2}$
510 d^{-1} , while the fluxes measured at 244 m (St. VI) and 306 m (St. VII) ~~water depth~~ decreased
511 to the before mentioned levels. At 407 m water depth (St. VIII) ~~the TPO_4 fluxes became was~~
512 negative, indicating a phosphate uptake by the sediment. ~~At the stations b~~Below the OMZ
513 (Sta. IX, 756 m and Sta. X, 989 m ~~water depth~~), the fluxes increased to slightly positive
514 values, but remained ~~ed~~ low at 0.06 and $0.02 \pm 0.02 \text{ mmol m}^{-2} \text{ d}^{-1}$.

515 ~~4.2.14.3.1~~ **Comparison of benthic chamber TPO_4 fluxes and diffusive TPO_4** 516 **fluxes**

517 The measured benthic chamber TPO_4 fluxes and the calculated diffusive TPO_4 fluxes showed
518 large discrepancies. ~~The calculated diffusive~~ fluxes ~~we~~are consistently higher than the benthic

Kommentar [LU15]: P. Kraals comment 27

519 | fluxes (Table 4, Fig. 4B). In contrast to the in situ measured benthic chamber TPO₄ release
520 | rates, the calculation of diffusive TPO₄ fluxes relies on bottom water and pore water PO₄³⁻
521 | concentrations. A subsurface PO₄³⁻ peak occurs at all stations in the uppermost depth
522 | interval at 0-0.25 cm causing a large concentration gradient between the bottom water and the
523 | pore water PO₄³⁻ concentrations (Fig. 7). Even though the measured benthic TPO₄ fluxes
524 | exceeded the fluxes that could be triggered-generated by TPP degradation by a factor by the
525 | TPP by a factor of approximately 6, but the potential diffusive TPO₄ fluxes were still higher
526 | (Table 4). Hence, the diffusive TPO₄ flux will be referred to as potential TPO₄ flux in the
527 | following.

Kommentar [LU16]: modified according P Kraal's comment (7)

528 | **4.34.4 TPP burial fluxes and TPP burial efficiency**

529 | The P burial fluxes reported in Table 4 decrease-decreased with increasing water depth (Table
530 | 4). Station I (74 m) has showed by far the highest P burial flux with at 10 cm sediment depth
531 | with 0.23 mmol m⁻² d⁻¹. In contrast the P burial efficiency at this station (Eq. 10) was
532 | comparatively low reaching only approximately 26 %. At Station VIII (407 m), the TPP
533 | burial flux was 0.103 mmol m⁻² d⁻¹ and the P burial efficiency exceeded 100 % exceeds 100
534 | % due to the uptake of dissolved P from ambient bottom waters.

535 | **4.44.5 Molecular analysis and relative abundance of filamentous sulfur** 536 | **bacteriamethods**

537 | Molecular analysis indicated the presence of Marithioploca-related bacteria [Salman et al.,
538 | 2011] in the surface sediments (0-5 cm). Gene sequencing revealed that the filamentous sulfur
539 | bacteria in the surface sediments (0-5 cm) were Thioploca ingrica. By now, Thioploca was
540 | described to have one single 16S rDNA gene. Hence, the number of copies of this gene per g
541 | sediment can be directly translated into the abundance. Our analysis may, however,
542 | underestimate the absolute abundance of these organisms due to a self-splicing mechanism of
543 | the 16S rDNA gene (Salman et al., 2012) and is therefore only indicative for their relative
544 | abundance.

545 |
546 | Their relative abundance of Marithioploca-related bacteria decreased with increasing water
547 | depth (Table 4). Its highest relative abundance with more than 4000 copies g⁻¹ sediment was

548 found at station I (74 m), decreasing by more than a factor of 20 to 190 copies g⁻¹ sediment at
549 station VIII (407 m).

550

551 **5 Discussion**

552 **5.1 POC/xP ratios in water column particles and sediments**

553 In order to characterize the fate of P in oxygen deficient waters and ~~anoxic~~ sediments we
554 determined POC/xP ratios from both environments. Previous studies ~~were~~ focused either on
555 the water column or on the sediments [Anderson et al., 2001 and references therein; Benitez-
556 Nelson et al., 2004; Faul et al., 2005; Jilbert et al., 2011; Lyons et al., 2011; Sekula-Wood et
557 al., 2012]. The present data set provides a more complete insight into of P compositional
558 changes ~~between the water column and surface sediment. Furthermore, it~~ and allows us to
559 more rigorously constrain the sedimentary P mass balance compared to earlier studies [Ingall
560 and Jahnke, 1994; Mort et al., 2010; Kraal et al., 2012; Noffke, 2014]. ~~Ingall and Jahnke,~~
561 ~~1994; Kraal et al., 2012; Mort et al., 2010; Noffke, 2014~~].

562 Both water column particles and the surface sediments from the Peruvian OMZ displayed
563 POC/POP ratios above Redfield, indicating depletion of organic P relative to organic C.
564 Similar observations have been reported before from this and other regions of the ocean [Loh
565 and Bauer, 2000; Benitez-Nelson et al., 2004; Faul et al., 2005; Franz et al., 2012 and others].
566 Preferential remineralization of P phases from sinking particles should lead to increasing
567 POC/POP ratios with increasing water depth, as observed in oxygenated areas of the ocean
568 [reviewed by Ruttenberg, 2014]. However, in the anoxic Cariaco Basin, no such preferential P
569 mineralization was noted [Benitez-Nelson et al., 2004]. Our results also showed no clear
570 decrease in the POC/POP ratio in the water column, with the possible exception of St. I and
571 VIII. Higher than Redfield POC/POP ratios were observed at Peru on a previous occasion,
572 and may instead be driven by the C-to-P composition of the diatomaceous phytoplankton
573 communities [Franz et al., 2012] rather than preferential P dissolution or other controls such
574 as the input of terrestrial plant material with high POC/POP ratios.

575 Preferential POP over POC remineralization in anoxic sediments remains controversial [Ingall
576 and Van Cappellen, 1990; Ingall and Jahnke, 1994; Colman et al., 1997; Anderson et al, 2001;

Kommentar [LU17]: P. Kraals
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577 McManus et al. 1997; Ruttenberg, 2003; Jilbert et al. 2011]. Our results, however, also
578 showed no clear trend across all stations. At station I, IV and VI (74, 141 and 244m) the
579 POC/POP increased with sediment depth indicating preferential POP over POC
580 remineralization. At station III (128 m) this trend occurred only in the upper cm and at station
581 V (195 m) no preferential POP over POC remineralization was found. POC/POP ratios at
582 station VIII (407 m) showed a POP enrichment over the upper 2 cm of the sediment. Below
583 this depth, there was a sudden increase in POC/POP ratios, which is likely due to intense POP
584 remineralization and subsequent authigenic formation of phosphorites (sink-switching, see
585 section 5.2.3).

586 Another interesting finding pointing to sink-switching can be found in the POC/POP and
587 POC/PIP ratios of the deepest water column particle sample and the first sediment sample at
588 stations I, IV, VI and VIII (74, 141 and 407 m). Increasing POC/POP and decreasing
589 POC/PIP ratios indicate that POP is converted into PIP while the TPP content of the sediment
590 is conserved (Fig. 2A and B). In agreement with similar findings in anoxic sediments
591 [Ruttenberg and Berner, 1993; Faul et al., 2005 and others] we assume that the observed POP
592 to PIP transformation is due to the formation of CFAs. However, our results emphasize that
593 sink-switching is obviously occurring at the interface between bottom waters and sediments.

594 Interestingly, the water column POC/TPP ratios were close to Redfield ratio. This could be an
595 effect of surface adsorption of P on phytoplankton as previously described by Sanudo-
596 Wilhelmy et al. (2004). Those authors investigated different species of *Trichodesmium* from
597 the Atlantic Ocean and found that the intracellular P pool was strongly depleted relative to C,
598 whereas the combination of the intracellular plus the surface adsorbed P was close to the
599 Redfield ratio. Although we did not exactly differentiate between internal and external P
600 pools, and considering that additional P sources like terrigenous P are negligible (see section
601 5.2.1), our results generally support the findings of Sanudo-Wilhelmy et al. (2004). However,
602 future studies are required to substantiate this hypothesis.

603 Sedimentary POC/TPP ratios were also close to Redfield, except at station I and VIII (74 and
604 407 m). Thus, on the one hand, the sink switching mechanism operates efficiently under low
605 oxygen conditions and on the other hand, the relative degradation of TPP and POC are not
606 changing from the water column to the sediments (Fig. 2B). This is an important finding
607 because at first sight this observation seems to be inconsistent with the long-standing

608 paradigm that low oxygen conditions promote the enhanced release of dissolved P from
609 sediments [Van Cappellen and Ingall, 1996]. However, it should be noted that marine
610 sediments covered by oxygenated bottom waters display molar POC/TPP ratios ranging from
611 about 10 to 50 [Baturin 2007]. These ratios are much lower than Redfield because P is
612 retained in sediments via adsorption, authigenic mineral precipitation such as Fe
613 (oxyhydr)oxides and microbial P sequestration [Ingall and Jahnke, 1994], and because POC is
614 more efficiently degraded under aerobic conditions [Hedges et al., 1999, Wallmann, 2010]. In
615 contrast, our data set implies that oxygen deficiency causes a shift of POC/TPP ratios to
616 values closer to Redfield compared to oxygenated regions, which is due to both, the enhanced
617 preservation of POC (Dale et al., 2015) and release of dissolved phosphate under low oxygen
618 conditions. It remains puzzling why the extreme P depletion observed in some black shale
619 sequences (e.g. POC/TPP > 3000, Ingall and Jahnke, 1994) are not found in modern anoxic
620 sediments such as those on the Peru margin.

621 **5.2 P mass balance**

622 P release rates from sediments underlying oxygen deficient waters are strongly enhanced
623 compared to oxygenated marine settings, especially in the Peruvian OMZ [Noffke et al., 2012
624 and 2016]. Nonetheless, the sources for the enhanced P release are still not completely
625 identified. The widely held view is that POP raining from the water column to the sediments
626 represents the main source for sedimentary P in high productive areas like the Peru upwelling
627 system [Delaney, 1998; Filippelli, 2008]. Mass balance approaches that resolve the P
628 regeneration versus burial in oxygen deficient environments by combining sedimentary data
629 and benthic P fluxes are rare [Ingall and Jahnke, 1994; Ingall et al., 2005; Mort et al., 2010;
630 Kraal et al., 2012; Noffke, 2014Ingall and Jahnke, 1994; Kraal et al., 2012; Mort et al., 2010;
631 Noffke, 2014]. These studies are all based on sediment data only, that is, the external P input
632 to the sediments is estimated or ignored. Furthermore, the study areas were often not covered
633 by fully anoxic bottom waters. Noffke (2014) presented an approach that combines
634 measurements of solid phase P speciation, sediment burial fluxes and benthic chamber flux
635 measurements for a mass balance on benthic P cycling in the Peruvian OMZ. Interestingly,
636 the measurements on the solid phase P speciation revealed that organic P accounted for only
637 18-37% of the total sedimentary P on the shelf and upper slope [Noffke, 2014]. Furthermore,
638 it was found that P bound to Fe (oxyhydr)oxides and ~~detrital-terrigenous~~ P was of minor
639 importance for the total sedimentary P inventory. However, authigenic Ca-P with a high

640 amount of fish-P accounted for up to 47% of the total P in sediments down to 300 m water
641 depth and for up to 70% in sediments below 300 m water depth. Consequently, Noffke (2014)
642 suggested that authigenic Ca-P phases are an additional major P source besides organic P for
643 benthic P release in the Peruvian OMZ.

644 Their mass balance approach was solely based on benthic work and has large uncertainties
645 regarding the particulate P input from the water column. Our approach includes the particulate
646 organic and inorganic P input from the water column, benthic P flux measurements and the P
647 burial fluxes and is based on the steady state assumption that the P input has to be sufficient to
648 maintain the benthic P flux and P burial flux. The P mass balance calculations (Table 4)
649 illustrate the variability in TPO₄ release and burial as well as in the magnitude of particulate
650 organic (Fig. 5A) and particulate inorganic P input (Fig. 5B) across the transect. Following
651 the general assumption that POP is the major P phase delivered to the sediments [Delaney,
652 1998; Filippelli, 2008], we first calculated whether the rain rate of POP (RR_{POP}) to the
653 seafloor can account for the measured benthic P fluxes (F_{TPO₄}) and P burial fluxes (F_{P_{bur}}) (Fig.
654 5A, Table 4). However, as already suggested ~~in the first order estimate~~ by Noffke et al.
655 (2012 and 2014), ~~and in Noffke (2014)~~, the POP fraction is ~~by~~ far too small to balance the
656 measured benthic fluxes in the Peruvian OMZ. The POP rain rates calculated along the
657 transect can account for only 24% to 48% of the measured TPO₄ fluxes (Fig. 5A), suggesting
658 the likely presence of an additional inorganic source of dissolved ~~source of inorganic P~~
659 ~~phosphate~~ [Noffke, 2014]. Similar to previous studies [Paytan et al., 2003; Faul et al., 2005;
660 Benitez-Nelson et al., 2007; Lyons et al., 2011; Sekula-Wood et al., 2012; Benitez-Nelson et
661 al., 2007; Faul et al., 2005; Lyons et al., 2011; Paytan et al., 2003; Sekula-Wood et al., 2012],
662 we found that the PIP fraction in water column particles ranging from 75 to 407 m water
663 depth comprises between 21-74% of TPP (Fig. 3). In the sediments, the average PIP fraction
664 rises to 48-98% of TPP (Fig. 3). Furthermore, POC and PIP were correlated ($r^2=0.74$) in the
665 water column particles indicating highly reactive material.

666 ~~The~~ The mass balance approach including the ~~particulate inorganic phosphorus~~ PIP rain rate to
667 the seafloor (Fig. 5B) allows the depth transect to be divided into two sections. The ~~first~~
668 ~~transect section I~~ (station I, 74 m and III, 128 m) is characterized by high P input and release
669 rates. The calculations on the P budget show a balance between the particulate P input, the
670 benthic P fluxes and the P burial fluxes within the error margin ($\pm 20\%$). In transect section
671 ~~two~~ II (stations IV, 141 m, V, 195 m and VI, 244 m), the P input decreases drastically (Fig.

Kommentar [LU18]: P. Kraals
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672 5B, Table 4) whereas the benthic P fluxes are still comparatively high. The distinct mismatch
673 in P input and P output prevails as the particulate P rain rates ~~only supported~~ only 377 to 6534
674 % of the measured TPO₄ fluxes and calculated burial fluxes. This leads to the question: What
675 drives the excess TPO₄ release in the core of the Peruvian OMZ?

676 **5.2.1 Additional P input**

677 Besides the particulate matter raining to the sediments, other potential other P sources can be
678 considered. Firstly, riverine transported material from the continent may be an additional
679 source of P to the sediments. Due to fast sinking speed and laterally dominated transport it is
680 possible that this P fraction is at least underrepresented on the filter samples. In order to
681 provide a maximum estimate for the contribution of the terrigenous P input to the sediments,
682 this fraction was calculated using the mass accumulation rate of Al in the first centimeter of
683 sediment and an average molar P/Al-ratio (Table 2) of 0.02 for riverine suspended particles
684 [Viers et al., 2009]. The resulting terrigenous P flux accounted for 5-19 % of the total P input,
685 which is insufficient to explain the observed discrepancies in the P budget of transect section
686 II (Table 4, Fig. 4C, 5B).

687 Laterally transported particles enriched in P from the very shallow shelf could be an
688 additional P source [e.g. Jahnke, 1990]. However, the particles would ~~have-need~~ to be
689 strongly enriched in P, which is not the case. In addition, this would have to be reflected in
690 the POC/TPP ratios of the surface sediments in transect section II (Fig. 2B). The ratios are
691 not, or only slightly, enriched in TPP compared to the water column particles, which leads
692 leading to the conclusion that lateral transport of P-enriched particles to the sediments is an
693 unlikely candidate for the missing P source.

694 Another ~~alternative, alternative~~ is the existence of an additional PIP phase supplied by fast
695 sinking material (e.g. P containing fish scales; Suess, 1981) that was not sampled during CTD
696 casts, and hence ~~is not underrepresented~~ on our filter samples. Díaz-Ochoa et al. (2009)
697 showed that fish P can make up to 20% of the total sedimentary P inventory in the shelf
698 sediments of the Peruvian OMZ. ~~Hence, the fish P input should be depicted in~~ strongly
699 depleted low sedimentary POC/TPP ratios compared to the water column particles. Since this
700 difference is not observed it is likely that fish debris can be ruled out for closing the P budget
701 during the sampling campaign, which are not found, as described above. ~~Theoretically,~~
702 sediments need to be composed of particles having POC/TPP ratios between 11 ± 1 and $25 \pm$

Kommentar [LU19]: P. Kraals
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703 12 (Table 4) to maintain the measured P release rates in transect section II. It seems unlikely
704 that the mismatch in the P mass balance is caused by additional particles deposited at the
705 seabed since their POC/TPP ratio would need to be much lower than any value observed in
706 our data set.

707 5.2.2 Non steady state scenarios – internal sedimentary P pools

708 Besides an additional P input to the sediments from the water column, episodic regeneration
709 dissolution of particulate P within the sediment could contribute to the excess P release
710 [Noffke et al., 2012]. This could include P solubilized released from the dissolution of Fe
711 (oxyhydr)oxides or the degradation of internally stored polyphosphates by within sulfide-
712 oxidizing bacteria. Such Driving factors could include the temporal variability in bottom
713 water oxygen and nutrient concentrations induced by the passage of internal Kelvin waves
714 and/or interannual variability related to El Niño and La Niña non steady state scenarios can be
715 induced by repeatedly occurring short term changes in the bottom water geochemistry.
716 Annual changes like El Niño and La Niña events as well as internally occurring Kelvin waves
717 cause oxygenation events and influence nutrient concentrations [Guitérrez et al., 2008].

718 It is well known-recognized that the sedimentary cycles of Fe and P are strongly linked [e.g.
719 Sundby et al., 1986Kraal et al., 2015]. -Fe (oxyhydr)oxides are expected to be important
720 carriers for phosphorus from the water column to the sediments. Following dissolution of
721 solid Fe minerals in the sediments, the adsorbed P is released to the porewaters. However, in
722 the Peruvian OMZ, oxygen concentrations in the water column are generally below detection
723 limit. Consequently, Fe (oxyhydr)oxides are likely already dissolved in the water column and
724 not such an important P source to the sediments, and the reductive dissolution of Fe
725 oxyhydroxides leads to an enhanced PO₄³⁻ accumulation in the pore waters of anoxic
726 sediments. -An minimum estimate of TPO₄-phosphate released during the reduction of Fe
727 (oxyhydr)oxides can be calculated from the diffusive Fe²⁺ fluxes and the molar Fe/P ratio that
728 is typically found in Fe (oxyhydr)oxides. The diffusive Fe²⁺ fluxes were in the range of 0.03-0
729 to 0.03-0 mmol m⁻² d⁻¹ during the M92 cruise (Table 4)- and -The molar Fe/P ratio of Fe
730 (oxyhydr)oxides in sediment is about round 10 [Slomp et al., 1996]. The calculation of the
731 minimum-TPO₄ release rates from Fe (oxyhydr)oxides (Eq. 14 in Table 2) results in a
732 maximum flux of 0.003 mmol PO₄³⁻ m⁻² d⁻¹ (Table 4, Fig. 4C and 5B), which is equivalent to
733 less than 5% of the benthic P flux and burial flux.

Kommentar [LU20]: T. Jilbert
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734 ~~Another~~ An additional internally activated P pool is phosphate released from large sulfur-
735 oxidizing bacteria, e.g. *Beggiatoa* [Sannigrahi and Ingall, 2005; Brock and Schulz-Vogt,
736 2011; Brock and Schulz-Vogt, 2011; Sannigrahi and Ingall, 2005]. These microorganisms store
737 P in the form of intracellular polyphosphate granules when terminal electron acceptors for
738 sulfide oxidation are available (oxic conditions) and release dissolved P during periods when
739 these oxidants are scarce (anoxic conditions). Hence, it is generally assumed that they
740 strongly affect benthic TPO₄ fluxes in a system with frequently changing bottom water redox
741 conditions [Ingall and Jahnke, 1994; Sannigrahi and Ingall, 2005; Schulz and Jørgensen,
742 2005; Brock and Schulz-Vogt, 2011; Dale et al., 2013; Brock and Schulz-Vogt, 2011; Dale et
743 al., 2013; Ingall and Jahnke, 1994; Sannigrahi and Ingall, 2005; Schulz and Jørgensen, 2005].
744 ~~Hence,~~ Polyphosphates have been shown to be an important P pool in the sediments of
745 highly productive upwelling areas [Kraal et al., 2015]. Along the depth transect at Peru, dense
746 mats of sulfur bacteria related to *Marit* Thioploca *ingrica* were observed on the sediments
747 during video-launched MUC and benthic lander deployments down to 300 m water depth
748 [Dale et al., 2015]. ~~This was also~~ Similar findings extended distributions of microbial mats
749 along a latitudinal transect at 11°S off were also previously described by Mosch et al. (2012)
750 and Gutiérrez et al. (2008) previously described by Mosch et al. (2012) and references therein.
751 Although, ~~it is not confirmed that~~ *Thioploca* spp. these organisms are not known to store
752 polyphosphates like has a mechanism to store and degrade polyphosphates similar like its
753 their close relatives, ~~the sulfur bacteria~~ *Beggiatoa* spp. and *Thiomargarita* spp. [Høgslund et
754 al., 2009; Holmkvist et al., 2010; Holmkvist et al., 2010; Høgslund et al., 2009], our findings
755 provide circumstantial indications for P uptake and release by that this is also applicable to
756 *Thioploca* spp. *Marit* Thioploca-related bacteria.

757 Firstly, we found that the relative abundance of copies of *Marit* Thioploca-related bacteria per
758 g⁻¹ sediment and the measured benthic TPO₄ release rates have a correlate linearly
759 relationship with a correlation factor of (r²=0.92) (Fig. 6). This finding may support the
760 suggestion that bacteria have exert an important systematic control on benthic P fluxes.
761 Secondly, a comparison of the in situ measured benthic P fluxes and the diffusive P fluxes
762 calculated from the difference of the TPO₄ bottom water concentration and the TPO₄ pore
763 water concentration of the surface sediments revealed great large differences (Fig. 4B). Such a
764 difference could be explained by the lysis of bacterial cells during sample retrieval followed
765 by the release of the internally stored polyphosphate pool into the pore-water. Following this

Kommentar [LU21]: P. Kraal comment
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Kommentar [LU22]: T. Jilbert
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766 argument, the diffusive P fluxes cannot be taken as real fluxes, but as a measure for potential
767 maximum release rates of P by MariTthioploca-related bacteria. ~~Moreover~~It should be noted
768 that, the potential fluxes are ~~by far~~more than sufficient to compensate for the missing P
769 fraction in transect section II (ranging from 0.956 ± 0.02 to $0.3 \pm 0.041_6$ mmol m⁻² d⁻¹; Table
770 4, Fig. 4CB).

771 ~~In a~~Additionally to the established pore-water extraction procedure, we carried out
772 freeze/thaw experiments to quantify the amount of P stored in sulfide-oxidizing bacteria (see
773 method section 3.7). ~~However using this method, it cannot be excluded that the P released~~
774 ~~during the procedure originates also from other bacteria and foraminifera in the sediments.~~
775 The released polyphosphates from the microbial cells after repeated freeze/thaw cycles are
776 rapidly hydrolyzed to orthophosphate under acidic conditions [Jager and Heyns, 1998].
777 Hence, the standard method to determine phosphate in the pore-waters using acidic reagents
778 will ~~likely support~~favor the hydrolysis of polyphosphates enabling us the measure its
779 concentration in the pore-waters after conducting the experiments. ~~However, this method~~
780 ~~cannot exclude P release from other bacteria and, possibly, foraminifera in the sediments.~~ A
781 comparison of the pore-water phosphate concentrations and the experiment results shows that
782 the amount of the internal additionally released P reservoir is as twice as high as the pore
783 water P concentration in transect section I and more than ~~10~~ten times ~~higher~~larger in section
784 II (Fig. 7). These results are coincident with the findings from the mass balance approach,
785 where the largest discrepancies occur in transect section II and are another indication for the
786 bacterial impact on the benthic P release. Interestingly, the highest phosphate concentrations
787 after the freeze/thaw experiments were found at station VIII (407 m) with abundant
788 foraminifera rather than sulfide-oxidizing bacteria. Those results are coincident with the
789 finding from the mass balance approach, where the largest discrepancies occur in transect
790 section II and are another indication for the bacterial impact on the benthic P release. Hence,
791 we assume that the sulfide-oxidizing bacteria at station IV, V and VI (141, 194 and 244 m)
792 and, potentially, the foraminifera observed at station VIII (407 m) are contributing phosphate
793 to the porewaters. To our knowledge, P storage by foraminifera has not been demonstrated
794 previously and awaits further study.

795 It remains to be shown how these mechanisms play out in detail (e.g. nutrient concentration
796 thresholds, ~~time scales~~, P uptake and release time scales ~~from~~by MariTthioploca-related
797 bacteria) and how they impact ~~on~~benthic P release in oxygen and nitrate deficient

Kommentar [LU23]: P. Kraal comment
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798 environments on longer time scales. Summarizing the results of the mass balance, it should be
799 noted, that, even with ~~the relevant data on determining the~~ particulate P rain rates ~~from the~~
800 ~~water column to the sediments~~, the benthic P mass balance for the core of the Peruvian OMZ
801 is imbalanced and requires an additional P source to maintain the benthic TPO₄ fluxes. We
802 suggest that and P burial fluxes sulfur bacteria make an important contribution to this missing
803 P sources.

804 5.2.3 Indications for active phosphorite formation

805 In contrast to the stations between 74 and 244 m water depth characterized by P release, data
806 ~~from~~ station VIII at 407 m water depth indicate the uptake of phosphate from the bottom
807 water. To our best knowledge, this is the first time that a downward flux of dissolved
808 phosphate from bottom waters into phosphorite-bearing surface sediments has been
809 documented by in situ benthic flux measurements. Furthermore, the PIP concentrations in the
810 surface sediments of station VIII (Fig. 2a) were 10 to 60 times higher compared to the
811 shallower stations where P was released from the sediments. Taken together, these
812 observations indicate that a PIP phase, likely phosphorite, is precipitating from the porewater
813 phosphate at the time of sampling. This is also reflected in decreasing porewater phosphate
814 concentrations (Fig. 7).

815 Arning et al. (2008) presented investigations on phosphorites ~~that were~~ recovered from the
816 Peruvian OMZ including a station at 12°S from the same water depth (~ 400 m) ~~and in~~ close
817 ~~vicinity~~ to sampling station VIII. The suboxic bottom waters and low sedimentation rates in
818 that area seem to be favorable for phosphorite formation close to the sediment-water interface
819 [Arning et al., 2009b]. Cosmidis et al. (2013) suggested three mechanisms how high pore
820 water phosphate concentrations that are essential for the phosphogenesis can be generated in
821 the sediments: (1) remineralization of organic matter mainly through bacterial sulfate
822 reduction releasing phosphate to the pore-waters, (2) reductive dissolution of Fe
823 (oxyhydr)oxides and the release of adsorbed P and (3) ~~use~~ synthesis of internally stored
824 polyphosphates by large sulfide-oxidizing bacteria. Using the same mass balance approach as
825 presented before, we calculate a P accumulation rate of $33 \pm 4 \text{ mmol m}^{-2} \text{ yr}^{-1}$ at station VII
826 where most of the P is derived from ambient bottom waters ($26 \text{ mmol m}^{-2} \text{ yr}^{-1}$). Hence, our
827 data suggest that the phosphorite nodules at this station contain phosphate that originates
828 predominantly from ambient bottom waters. Additionally, as already mentioned, S sediments

Kommentar [LU24]: T. Jilbert
comment 6

829 at station VIII were covered by benthic foraminifera instead of mat-forming sulfur bacteria.
830 The release of phosphate from ~~frosted and defrosted~~frozen samples from this site may
831 indicate that these foraminifera are ~~storing a source for large quantities of~~ polyphosphates ~~in~~
832 ~~their cells~~ (see section 3.7 and Fig. 7). ~~Contrary to the findings of Goldhammer et al. (2010)~~
833 ~~and Schulz and Schulz (2005), o~~Our observations suggest that ~~polyphosphate storing~~ benthic
834 foraminifera rather than bacterial mats might facilitate the uptake of bottom water phosphate
835 and the formation of phosphorites at ~~this station VIII~~. ~~However, this remains an open question~~
836 ~~and should be addressed in future field campaigns.~~

837 The P uptake rate ~~of~~ $\sim 26 \text{ mmol P m}^{-2} \text{ yr}^{-1}$ derived from our lander measurements may be
838 compared to previous estimates on phosphorite growth rates in the area. ~~However, the latter~~
839 ~~approach is based on the d~~Dating of phosphoric laminites ~~and~~ yields a P uptake rate of only 3
840 $\text{mmol P m}^{-2} \text{ yr}^{-1}$ for a ca. 1 Ma old nodule [Arning et al., 2009a]. ~~These is~~ ~~different~~ fluxes
841 may be at least partly explained by the methodological difference (present flux measurement
842 vs. long-term average). ~~H~~However, growth rates determined on modern nodules are broadly
843 consistent with our flux measurements [Burnett et al., 1982].

844

845 6 Conclusions

846 This study aimed to identify the P sources of benthic P release in the Peruvian OMZ. We
847 determined the rain rates of ~~organic~~ particulate organic phosphorus and ~~inorganic~~ particulate
848 inorganic phosphorus ~~and determined as well as~~ benthic P release rates and P burial fluxes.

849 Our calculations revealed that ~~in nearly all cases rain rates within the core OMZ particulate~~
850 phosphorus rain rates cannot ~~account for~~ compensate measured benthic P fluxes and burial
851 fluxes. ~~From S~~Systematic analysis of potential P sources, ~~we conclude~~ ~~revealed~~ that periodic
852 most likely P release ~~from sulfide~~ sulfur oxidizing bacteria ~~that store and release P under~~
853 oscillation redox conditions could strongly modulate ~~is (periodically) increasing~~ benthic P
854 fluxes, and hence ~~compensation~~ explain for ~~the~~ missing P source. ~~These bacteria store P~~
855 ~~when terminal electron acceptors for sulfide oxidation are available and release dissolved P~~
856 ~~during periods when these oxidants are scarce.~~ We visited the area during austral summer
857 when oxygen and nitrate levels were depleted by high export production and respiration. It is
858 possible that the Peruvian OMZ was less reducing prior to our sampling period due to lower

Kommentar [LU25]: P. Kraals
comment 32

Kommentar [LU26]: P. Kraals
comment 13

859 respiration rates and/or better ventilation. Thus, we propose that the bacterial mats on the
860 Peruvian margin act as ~~a-phosphorus~~ capacitors being ~~unloaded-discharged~~ during austral
861 summer and recharged during other periods of the year when bottom waters are less reducing,
862 ~~as-which-was~~ previously proposed in Dale et al. (2013). This hypothesis could be tested
863 ~~verified/falsified~~ by ~~a-systematic-study~~ ing-of the seasonality of benthic fluxes in the Peruvian
864 up-welling system and P dynamics within the bacterial community.

865 In addition, measurements at ~~the phosphorite~~ station ~~VIII (407 m water depth)~~ showed
866 clear indications for the uptake of dissolved phosphate by the sediments facilitating
867 phosphorite formation. Our data imply that most of the P accumulating in these authigenic
868 minerals originates from ambient bottom waters. Since this site was marked by a high
869 abundance of P-bearing benthic foraminifera, we speculate that phosphate uptake and
870 phosphorite formation may be ~~supported-by~~ linked to the presence of these organisms. This
871 requires further study.

872 There was no clear preferential mineralization of POP relative to POC with depth in the water
873 column. POC/TPP ratios in both water column particles and sediments were close to Redfield
874 at most sites in the Peruvian OMZ. This observation strongly suggests that the relative burial
875 efficiencies of POC and TPP are similar under low oxygen conditions. Importantly, it further
876 shows that the sediments underlying the anoxic waters on the Peru margin are not depleted in
877 P compared to Redfield. Rather, they are depleted relative to sediments underlying oxic
878 waters, which show POC/TPP ratios well below Redfield (Wallmann, 2010). Thus, at Peru, a
879 lack of oxygen promotes the intensified release of dissolved P from sediments, whilst
880 preserving a POC/TPP burial ratio that is-whereas TPP is better conserved than POC in the
881 presence of oxygen-similar to Redfield.

882 ~~[Wallmann, 2010]. Thus, a lack of oxygen promotes the release of dissolved P from~~
883 ~~sediments and the preservation of POC (Dale et al. 2015) until both phases are buried at a~~
884 ~~ratio similar to Redfield.~~

885 Our data support the hypothesis that benthic P release ~~triggers-is linked via~~ a positive
886 feedback loop ~~leading~~ to intensified primary production in the surface water and ~~enhanced~~
887 oxygen demand ~~in the water column specifically~~ during periods where ~~a-lack-of-terminal~~
888 ~~electron acceptors in ambient~~ bottom water redox conditions promotes the release of P from
889 ~~bacterial mats~~ the sediments. However, this positive feedback is limited by the formation of

890 | authigenic inorganic P phases that maintains the long-term average POC/TPP burial ratio
891 | close to Redfield.

892

893 **Author contribution**

894 | UL, AD and SS supported the shipboard work, geochemical analysis and contributed to the
895 | manuscript preparations. CH, KW and AN helped with fruitful discussions related to the
896 | manuscript and helped with the manuscript preparation. CL carried out the molecular analysis
897 | and contributed to the manuscript.

898

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908

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1190 **Tables**

1191 **Table 1:** Station list for the sites of the benthic lander (BIGO), multi-corer (MUC) and CTD deployments including. ~~Also shown are the~~
 1192 bottom water concentrations of oxygen (O₂), nitrate (NO₃⁻) and sulfide (H₂S) in μM. The station numbers were ~~chosen according for~~
 1193 comparability according to Dale et al., 2015. bdl=below detection limit (5 μM)

Nr.	Station	Gear	Date (2013)	Longitude (°W)	Latitude (°S)	Water depth (m)	BW O ₂ (μM)	BW NO ₃ ⁻ (μM)	BW H ₂ S (μM)
	98	CTD26	14.01.	12°13.504'	77°10.799'	75			
I	220	MUC39	25.01.	12°13.531'	77°10.061'	72	bdl	-	33.22
	110	BIGO1-2	15.01.	12°13.506 [±]	77°10.793 [±]	74			
	269	CTD79	29.01.	12°16.690'	77°14.999'	128			
III	248	MUC46	27.01.	12°16.697'	77°15.001'	129	bdl	0.02	-
	165	BIGO2-4	20.01.	12°16.690 [±]	77°14.995 [±]	128			
	111	CTD29	15.01.	12°18.729'	77°17.757'	145			
IV	36	MUC10	09.01.	12°18.708'	77°17.794	145	bdl	7.1	
	57	BIGO1-1	11.01.	12°18.711 [±]	77°17.803 [±]	141			
	279	CTD81	30.01.	12°21.490'	77°21.713'	195			
V	247	MUC45	27.01.	12°21.491'	77°21.702'	195	bdl	6.3	-
	201	BIGO1-4	23.01.	12°21.502 [±]	77°21.712 [±]	195			
	92	CTD24	13.01.	12°23.300'	77°24.200'	244			
VI	198	MUC34	23.01.	12°23.300'	77°24.228'	244	bdl	11.9	-
	74	BIGO2-2	12.01.	12°23.300 [±]	77°24.186 [±]	244			

	66	CTD16	12.01.	12°27.535'	77°29.593	414			
VIII	107	MUC23	15.01.	12°27.198'	77°29.497'	407	bdl	12.1	-
	207	BIGO2-5	24.01.	12°27.207'	77°29.517'	409			

1194

1195 **Table 2:** Equations for the P mass balance calculations. Results are shown in Table 4.

Equations for P mass balance calculations	
P Input to the sediments (mmol m⁻² d⁻¹)	
(4) Total particulate phosphorus rain rate	$RR_{TPP} = RR_{PIP} + RR_{POP} = F_{TPO4} + F_{Pbur}$
(5) Particulate inorganic phosphorus rain rate	$RR_{PIP} = RR_{POC} / \left(\frac{POC}{PIP} \right)$
(6) Particulate organic phosphorus rain rate	$RR_{POP} = RR_{POC} / \left(\frac{POC}{POP} \right)$
(7) Terrigenous P input ($P/Al = 0.02$, Vier et al., 2009)	$RR_{Pterr} = Al_{(0-1)} * MAR * 0.02 \frac{P}{Al}$
P Burial in the sediments (mmol m⁻² d⁻¹ and g m⁻² d⁻¹) at 11 cm	
(8) Phosphorus burial flux	$F_{Pbur} = MAR * P_{101}$
(9) Mass accumulation rate	$MAR = \rho_{dry} * (1 - \phi_{\infty}) * SR$
(10) TPP burial efficiency	$PBE = MAR * \left(\frac{P_{101}}{RR_{TPP}} \right) * 100 \%$
P release from the sediments (mmol m⁻² d⁻¹)	
Benthic P fluxes (F_{TPO4}) and the potential diffusive P fluxes were determined as described in the methods above	
(11) P release from POP degradation according to Redfield (C/P = 106)	$F_{P(Red)} = F_{DIC} / 106 PBE$ $= MAR * \left(\frac{P_{101}}{RR_{TPP}} \right) * 100$
(12) True P release from POP	$F_{P(POP)} = F_{DIC} / \left(\frac{POC}{POP} \right) F_{P(POP)} = F_{DIC} / 106$
(13) P release from total particulate phosphorus	$F_{P(TPP)} = F_{DIC} / \left(\frac{POC}{TPP} \right)$
(14) P release from the dissolution of Fe (oxyhydr)oxides (Fe/P = 10, Slomp et al., 1996)	$F_{P(Fe)} = F_{Fe2+} / \left(\frac{Fe}{P} \right)$
(15) P deficit to outbalance the P budget	$F_{P(deficit)} = RR_{TPP} + RR_{terr} + F_{P(Fe)}$ $- (F_{TPO4} + F_{Pbur})$ $- RR_{PIP} + RR_{terr} + F_{P(Fe)}$

1196

1197

1198 **Table 3:** In situ benthic chamber TPO₄ fluxes in mmol m⁻² d⁻¹ along the 12°S transect. The
 1199 numbers are shown as an average calculated from the minimum and maximum flux
 1200 determined from two benthic chambers. In the cases where only a single number is displayed,
 1201 the benthic flux was determined from only one benthic chamber. ~~The averages are given~~
 1202 ~~where both benthic chambers were completely recovered and the uncertainty corresponds to~~
 1203 ~~the mean difference between the minimum and maximum fluxes from the two benthic~~
 1204 ~~chambers.~~

Station	Water depth (m)	F _{TPO4} (mmol m ⁻² d ⁻¹)	
I	BIGO1_2	74	1.04 ± 0.31
II	BIGO1_5	101	0.35 ± 0.01
III	BIGO2_4	128	0.30 ± 0.05
IV	BIGO1_1	141	0.23 ^a
V	BIGO1_4	195	0.12 ^a
VI	BIGO2_2	243	0.44 ± 0.07
VII	BIGO2_1	306	0.26 ± 0.04
VIII	BIGO2_5	409	-0.07 ^a
IX	BIGO2_3	756	0.06 ^a
X	BIGO1_3	989	0.02 ± 0.02

1205 ^a only one benthic flux was measured

1206 **Table 4:** Measured and calculated parameters for the P mass balance along the 12°S transect. The numbers in front of key parameters
 1207 correspond to equations in Table 2.

12°S	Transect section I		Transect section II			Phosphorite formation
	Station I 74 m	Station III 128 m	Station IV 141 m	Station V 195 m	Station VI 244 m	Station VIII 407 m
Benthic chamber TPO₄ flux (F_{TPO4})* mmol m ⁻² d ⁻¹	1.04 ± 0.31	0.3 ± 0.05	0.23 -	0.12 -	0.44 ± 0.07	-0.07 -
Potential (diffusive) TPO₄ flux (pot. F_{TPO3}) mmol m ⁻² d ⁻¹	1.07 ± 0.23	2.0 -	0.5 -	1.6	1.5 -	
Relative abundance of Marithioploca-related bacteria* copies g ⁻¹ (0-5 cm sediment depth)	4159		1687	3072		190
Benthic chamber DIC flux (F_{DIC})** mmol m ⁻² d ⁻¹	65.9 ± 21	20.4 ± 7	8 ± 0.4	3.2 ± 1	4.7 ± 1	2.2 ± 0.3
POC rain rate (RR_{POC})** mmol m ⁻² d ⁻¹	79.5 ± 33	28.2 ± 12	10.5 ± 3	12.5 ± 6	10.6 ± 4	2.7 ± 1
Sediment accumulation rate (ω_{acc})** cm yr ⁻¹	0.45 ± 0.09	0.2 ± 0.04	0.04 ± 0.008	0.1 ± 0.02	0.07 ± 0.014	0.01 ± 0.002
Mass accumulation rate (MAR)** g m ⁻² yr ⁻¹	1800 ± 360	600 ± 120	128 ± 26	320 ± 64	182 ± 37	44 ± 9
Rratios for particulate matter from the water column (2 to 5 m above the sea floor):						
POC₂/TPP*	76 ± 4	68 ± 9	94 ± 10	132 ± 36	62 ± 9	96 ± 9
POC₂/PIP*	197 ± 17	125 ± 34	291 ± 79	385 ± 7	217 ± 34	209 ± 34
POC₂/POP*	126 ± 17	149 ± 29	142 ± 3	214 ± 87	87 ± 29	178 ± 29
(4) TPP rain rate (RR_{TPP})	1.00 ± 0.31	0.40 ± 0.09	0.11 ± 0.02	0.09 ± 0.02	0.17 ± 0.02	0.03 ± 0.01

mmol m ⁻² d ⁻¹							
(5) PIP rain rate (RR _{PIP})	0.39 ± 0.14	0.22 ± 0.04	0.04 ± 0	0.03 ± 0.02	0.05 ± 0.01	0.01 ± 0.01	
mmol m ⁻² d ⁻¹							
(6) POP rain rate (RR _{POP})	0.61 ± 0.18	0.18 ± 0.05	0.07 ± 0.02	0.06 ± 0.01	0.12 ± 0.01	0.01 ± 0.01	
mmol m ⁻² d ⁻¹							
(7) Terrigenous P input (RR _{Pterr})	0.10 -	0.02 -	0.01 -	0.02 -	0.01 -	0.00 -	
(8) Burial flux (F _{Pbur}) in 10 cm sediment depth	0.23 -	0.089 -	0.052 -	0.058 -	0.04 -	0.103 -	
mmol m ⁻² d ⁻¹							
Avg. Al conc. of 0-1 cm sediment depth (Al ₀₋₁)*	0.99 -	0.70 -	1.10 -	0.97 -	0.72 -	0.66 -	
mmol g ⁻¹							
Avg. P conc. of first 10 cm sediment depth (P ₁₀)*	0.05 -	0.05 -	0.4407 -	0.096 -	0.087 -	1.0502 -	
mmol g ⁻¹							
(10) P burial efficiency (PBE) at 10 cm sediment depth	26 ± 8	203 ± 4	2347 ± 58	6192 ± 1204	213 ± 32	490406 ± 10023	
%							
(11) P release from POP degradation according to Redfield (F _{P(Red)})	0.62 ± 0.2	0.19 ± 0.06	0.08 ± 0.01	0.03 ± 0.01	0.04 ± 0.02	0.02 ± 0	
mmol m ⁻² d ⁻¹							
(12) P release from POP degradation (F _{P(POP)})	0.52 ± 0.16	0.14 ± 0.05	0.06 ± 0.01	0.02 ± 0.01	0.05 ± 0.02	0.01 ± 0	
mmol m ⁻² d ⁻¹							
(13) P release from TPP degradation (F _{P(TPP)})	0.87 ± 0.17	0.3 ± 0.1	0.09 ± 0.01	0.02 ± 0.01	0.08 ± 0.02	0.02 ± 0.01	
mmol m ⁻² d ⁻¹							
Benthic diffusive TPO ₄ flux (potential P flux)*	1.08 ± 0.23	2.0 -	0.5 -	1.6 -	1.5 -	- -	

	Diffusive Fe²⁺ flux (F_{Fe2+})*	0.04	± 0.02	0.01		0.02	0.0	0.03		0.0	
	(14) P released from Fe (oxyhydr)oxides (F_{P(Fe)})	0.004	± 0.002	0.001		0.002	0.0	0.003		0.0	
	(15) P deficit to outbalance the P budget Potential bacterial P-release (F_{P(bacterial deficit)})	-		-		0.150.12	±0.02	0.069	±0.02	0.3	±0.04

1208 * measured this study

1209 **published data from Dale et al. (2015)

1210 **Figure captions**

1211 **Figure 1:** Study area, sampling stations and O₂ concentration in μM along the 12°S transect.

1212 **Figure 2A:** Concentration profiles of TPP, PIP, POP and POC of the water column particles
1213 and the surface sediments along the 12°S transect. Water column particle concentrations
1214 (upper panel) are given in $\mu\text{mol L}^{-1}$ and surface sediment concentrations (lower panel) are
1215 shown in $\mu\text{mol mg}^{-1}$. Note that the water column particle concentrations shown for station VI
1216 (244 m) at 10 m water depth are ~ 5 times higher than at the other stations.

1217 **Figure 2B:** Ratios of POC to TPP, PIP and POP (POC/xP) along the 12°S depth transect
1218 off from water column particles and surface sediments from (0 – 5.5 cm sediment depth) of
1219 station I to VIII (74 to 407 m).

1220 **Figure 3:** Average distribution of POP and PIP (%) per station in the water column particles
1221 and in the top 5.5 cm of the sediments.

1222 **Figure 4A:** Measured benthic TPO₄ fluxes ($\text{mmol m}^{-2} \text{d}^{-1}$) at 12°S. The black line shows the
1223 theoretical TPO₄ flux generated from organic matter degradation remineralization with a
1224 Redfield POC/POP ratio of 106.

1225 **Figure 4B:** Potential TPO₄ fluxes ($\text{mmol m}^{-2} \text{d}^{-1}$) calculated from porewater profiles ~~diffusive~~
1226 ~~flux calculations~~ compared to the measured benthic TPO₄ fluxes ($\text{mmol m}^{-2} \text{d}^{-1}$) of the
1227 stations I to VIII (74 to 407 m). The black line with triangles depicts the TPO₄ flux that could
1228 be generated from during degradation of the total particulate phosphorus by organic matter
1229 remineralization.

1230
1231 **Figure 4C:** ~~The bar chart illustrates the~~ P percentages of the different P input-sources and the
1232 missing P that is needed to maintain the measured TPO₄ release rates and P burial fluxes for
1233 stations IV, V and VI (141, 195 and 244 m) of transect section II. The missing P is assumed to
1234 be supplied by sulfide-oxidizing Marithioploca-related bacteria- (see Discussion) *Thioploca*
1235 *ingrica*.

1236 **Figure 5:** Mass balance calculations and measured benthic TPO₄ fluxes [$\text{mmol m}^{-2} \text{d}^{-1}$] for
1237 stations I to VIII (74 to 407 m). All fluxes are in $\text{mmol m}^{-2} \text{d}^{-1}$

1238 **Figure 5A:** POP rain rates, TPO₄ fluxes and P burial rates only. The number in percent
1239 ~~depicts~~ denotes missing P needed to sustain the benthic TPO₄ fluxes.

1240 **Figure 5B:** Mass balance calculations including the POP and PIP rain rates, the terrigenous P
1241 input, P release from the reductive dissolution of Fe (oxyhydr)oxides and the benthic TPO₄
1242 fluxes into the bottom waters as well as the P burial rates.

1243 **Figure 6:** Measured TPO₄ fluxes versus relative Abundance of *MariF*thioploca in cells g⁻¹ in
1244 the first upper 5 centimeter of the sediment. ~~in correlation to the measured benthic TPO₄~~
1245 fluxes. Highest abundance and TPO₄ flux was found at station I. The other data points are for
1246 the stations IV, VI and VIII (with decreasing abundance and TPO₄ flux).

1247 **Figure 7:** Comparison of pore water PO₄³⁻ concentrations before (circlesblue) and after
1248 (triangles) the freeze/thawing experiments (red) in μmol L⁻¹.

1 **Benthic phosphorus cycling in the Peruvian Oxygen**
2 **Minimum Zone**

3

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12

13 **Abstract**

14 Oxygen minimum zones (OMZs) that impinge on continental margins favor the release of
15 phosphorus (P) from the sediments to the water column, enhancing primary productivity and
16 the maintenance or expansion of low-oxygen waters. A comprehensive field program in the
17 Peruvian OMZ was undertaken to identify the sources of benthic P at six stations, including
18 the analysis of particles from the water column, surface sediments and pore fluids as well as
19 in situ benthic flux measurements. A major fraction of solid phase P was bound as particulate
20 inorganic P (PIP) both in the water column and in sediments. Sedimentary PIP increased with
21 depth in the sediment at the expense of particulate organic P (POP). The ratio of particulate
22 organic carbon (POC) to POP exceeded the Redfield ratio both in the water column ($202 \pm$
23 29) and in surface sediments (303 ± 77). However, the POC to total particulate P (TPP = POP
24 + PIP) ratio was close to Redfield in the water column (103 ± 9) and in sediment samples
25 (102 ± 15). This suggests that the relative burial efficiencies of POC and TPP are similar
26 under low oxygen conditions and that the sediments underlying the anoxic waters on the Peru
27 margin are not depleted in P compared to Redfield. Benthic fluxes of dissolved P were
28 extremely high (up to $1.04 \pm 0.31 \text{ mmol m}^{-2} \text{ d}^{-1}$), however, showing that a lack of oxygen
29 promotes the intensified release of dissolved P from sediments, whilst preserving the
30 POC/TPP burial ratio. Benthic dissolved P fluxes were always higher than the TPP rain rate to
31 the seabed, which is proposed to be caused by transient P release by bacterial mats that had
32 stored P during previous periods when bottom waters were less reducing. At one station
33 located at the lower rim of the OMZ, dissolved P was taken up by the sediments indicating
34 ongoing phosphorite formation. This is further supported by decreasing porewater phosphate
35 concentrations with sediment depth, whereas solid phase P concentrations were comparatively
36 high. At this site, the POC/TPP and POC/PIP ratios dropped from average water column
37 values (close to Redfield for POC/TPP and POC/PIP ~ 250) to very low sedimentary ratios of
38 ~ 7 (POC/TPP and POC/PIP), indicative of intensive P enrichment in the sediments.

39 **1 Introduction**

40 Phosphorus is an essential nutrient; it serves as an energy carrier for all living species and is a
41 limiting macronutrient for marine primary production on geological time scales [Ingall and
42 Jahnke, 1994; Föllmi, 1996; McManus et al., 1997; Filippelli, 2002; Paytan and McLaughlin,
43 2007; Tsandev et al., 2012; Ruttenberg, 2014]. Due to its impact on marine primary

44 production, the oceanic phosphorus inventory modulates the atmospheric CO₂ level and
45 Earth's climate [Ganeshram et al., 2002; Wallmann, 2003; Ingall, 2010]. Hence, it is crucial
46 to understand feedback mechanisms of the P cycle to make future predictions.

47 Particulate and dissolved phosphorus in the ocean originate from terrestrial chemical
48 weathering of the P containing mineral group of apatite [Filippelli, 2002]. Only around 30%
49 of the P discharged to the oceans is potentially bioavailable [Compton et al., 2000] as
50 dissolved P, inorganic P adsorbed to minerals or associated with metal oxides and P bound
51 within particulate organic matter. However, the largest fraction of the fluvial P is trapped in
52 estuaries or buried in continental margin sediments and thereby removed from the P cycle
53 before it reaches the open ocean [Compton et al., 2000]. The delivery of P to the sediments in
54 the open ocean is mainly composed of organic and inorganic P associated with the export of
55 organic detritus and other particles from the photic zone. P adsorbed to minerals such as Mn
56 and Fe (oxyhydr)oxides [Föllmi, 1996; Delany, 1998; Faul et al., 2005] are further sources, as
57 well as P input from fish debris that is may be particularly important in productive upwelling
58 regions [Suess, 1981; Schenau and DeLange, 2001; Diaz-Ochoa et al., 2009; Noffke, 2014].

59 P cycling is strongly affected by redox-dependent processes. P can be scavenged by Fe
60 (oxyhydr)oxides in oxic sediment and released across the sediment-water interface due to the
61 reduction dissolution of Fe (oxyhydr)oxides in anoxic sediments [Sundby et al., 1986; Slomp
62 et al., 1998]. Furthermore, recent studies showed that sulfur bacteria found in surface
63 sediments of anoxic environments can internally store and release P under oscillating redox
64 conditions [Ingall and Jahnke, 1997 and references therein]. Therefore, these organisms are a
65 key player for the modulation of porewater P concentrations and benthic P release to the
66 water column.

67 Additionally, hypoxic or anoxic conditions favor the precipitation of P in the form of
68 authigenic carbonate fluorapatite (CFA) [Froelich et al., 1988; Suess and von Huene, 1988;
69 Goldhammer et al., 2010; Ingall, 2010; Schenau and De Lange, 2000]. For non-upwelling
70 areas, the required phosphate oversaturation in the porewaters has been attributed to the
71 reductive dissolution of P bearing Fe (oxyhydr)oxides [e.g. Ruttenger et al, 1993, Slomp et
72 al., 1996]. In contrast, the CFA formation in sediments of the Namibian upwelling area was
73 linked to microbial P release into the porewaters [Schulz and Schulz, 2005].

74 The resulting feedback on oceanic primary production and atmospheric O₂ and CO₂ levels
75 triggered by changes in benthic P sequestration is still unclear. Presently, three opposing

76 views have been raised: (1) Intensified phosphate release from the sediments to the water
77 column caused by an expansion of low oxygen waters [Ingall and Jahnke, 1994; Stramma et
78 al., 2008] could stimulate the primary production in the surface waters [Wallmann, 2003].
79 This, in turn, may lead to a more intensified oxygen demand and a positive feedback with
80 benthic P release [Slomp and Van Cappellen, 2007; Wallmann, 2010; Moffit et al., 2015]. (2)
81 A negative feedback on P release has been postulated based on observations of CFA mineral
82 precipitation in the present-day oxygen depleted upwelling areas [Schulz and Schulz, 2005;
83 Arning et al., 2009a; Arning et al., 2009b; Goldhammer et al., 2010; Cosmidis et al., 2013].
84 Being a major sink for bioavailable P [Delaney, 1998; Ingall, 2010], it has been argued that
85 the expansion of OMZs may increase the CFA precipitation in the sediments and thus
86 mitigate benthic phosphate release [Ganeshram et al., 2002; Goldhammer et al., 2010; Ingall,
87 2010]. (3) A third scenario suggests that the formation of CFA is in balance with enhanced P
88 release from anoxic sediments, implying that the dissolved oceanic P inventory is largely
89 unaffected by oxygen concentrations [Delaney, 1988; Anderson et al., 2001; Roth et al.,
90 2014]. These conflicting scenarios show that there is further need to explore the benthic-
91 pelagic P cycling in oxygen deficient environments in order to enable improved predictions.

92 In this study, we explore P cycling in the Peruvian OMZ to identify and quantify P sources to
93 the sediment and the return of inorganic dissolved P back to the water column. Our data set
94 comprises samples of particulate matter from the water column as well as porewater, sediment
95 and samples of filamentous sulfur bacteria. We present in situ benthic phosphate fluxes,
96 particulate matter C/P ratios for water column particles and surface sediments, P burial fluxes
97 and relative abundances of sulfur bacteria for 6 stations along the depth transect across the
98 Peruvian shelf at 12°S. From a mass balance for P cycling in the sediments, we conclude that
99 the benthic P sources and sinks were, in general, imbalanced during our sampling campaign.

100

101 2 Study Area

102 The study area is located in the center of the Peruvian OMZ at 12°S covering the shallow
103 shelf from ~70 m water depth to mid-slope depths of about at ~400 m (Fig. 1). During our
104 sampling campaign in January 2013 neutral or slightly negative El Niño-Southern Oscillation
105 (ENSO) conditions dominated (<http://www.cpc.ncep.noaa.gov>) and the bottom water oxygen
106 concentrations were below detection limit of the Winkler titration ($5 \mu\text{mol L}^{-2}$) down to ~ 450

107 m water depth (Fig. 1, Table 1). Below the OMZ, oxygen concentrations increased to 19 and
108 53 μ M at 770 m and 1025 m water depth, respectively. Nitrate concentrations were below 12
109 μ M from 128 to 407 m water depth (Table 1). During the measuring period, the bottom water
110 at station I (74 m) was sulfidic and depleted in nitrate (Table 1; Sommer et al., in review).

111 The oxygen deficient waters off Peru belong to one of the world's most prominent OMZ.
112 Southeasterly trade winds that are driven by the Pacific Subtropical Anticyclone engender
113 offshore transport of surface waters and upwelling of subsurface waters from the poleward
114 propagating Peru undercurrent (PUC) [Strub et al., 1998]. These water masses are oxygen
115 depleted and rich in nutrients, favoring primary production of up to 3.6 g C m⁻² d⁻¹ in surface
116 waters [Pennington et al., 2006]. As a consequence, the intense oxygen consumption induced
117 by the degradation of sinking particulate organic matter and a sluggish ventilation induce the
118 development of a strong OMZ. Based on the definition that the oxycline of an OMZ is at ~22
119 μ M [Fuenzalida et al., 2009], the Peruvian OMZ extends from approximately 50 – 700 m
120 water depth. The greatest upwelling strength is reached during austral winter and spring
121 between 5 and 15°S [Strub et al., 1998]. The phases of strong upwelling are followed by high
122 rates of primary production in austral summer. The coastal area off Peru displays a highly
123 variable hydrographic regime. Especially during positive ENSO periods coastal trapped
124 waves emerging from equatorial Kelvin waves in the equatorial East Pacific occur frequently
125 [Gutiérrez et al., 2009 and references therein; Mosch et al., 2012]. Consequently, the
126 thermocline and the oxycline shift downwards by ca. 100 m and bottom water oxygen
127 concentrations can increase from practically zero to around 100 μ M in days to weeks
128 [Gutiérrez et al., 2008; Schunck et al., 2013; Graco et al., 2016]. Seasonally, bottom waters of
129 the shelf (75 m) can transition from oxic or hypoxic between austral winter/spring (low
130 primary production) to anoxic throughout the rest of the year [Noffke et al., 2012].
131 Furthermore, porewater uranium (U) profiles at 11°S indicate variable redox conditions at the
132 upper rim of the OMZ possibly related to ENSO [Scholz et al., 2011]. The shelf area above
133 200m water depth is therefore characterized by non-steady state conditions, whereas the
134 oxygen concentrations in the core OMZ (~200-400 m water depth) are predominantly below
135 detection limit throughout the year.

136 The sediments of the Peruvian OMZ have POC contents ranging from 15-20 wt. % within the
137 OMZ and > 5 wt. % below the OMZ and on the shelf [Dale et al., 2015]. The fine-grained,
138 diatomaceous mud lens between 11°S and 15°S accumulates under low PUC bottom water

139 velocities in 50 to 500 m water depth [Krissek et al., 1980]. This favors high sedimentation
140 rates, carbon preservation and burial [Suess et al., 1987; Dale et al., 2015]. Further down, at
141 mid-slope depth, a high energy regime favoring erosive settings leads to the formation of
142 phosphorites [Reimers and Suess, 1983; Glenn and Arthur, 1988; Arning et al., 2009b; Mosch
143 et al., 2012]. Another interesting observation between 70 and ~ 300 m of water depth is the
144 occurrence of mat-forming filamentous sulfur bacteria [Mosch et al., 2012]. Bacterial mats
145 not conspicuous below 300 to 400 m water depth, and instead foraminiferal sands are more
146 common.

147

148 **3 Methods**

149 Sampling of water column particulate matter and sediment cores as well as the deployment of
150 the benthic landers BIGO I and II (Biogeochemical Observatories) was conducted along the
151 12°S depth transect during the RV *Meteor* cruise M92 in January 2013. The geographical
152 position and water column properties for the main stations are reported in Table 1. The **data**
153 **set** on in situ phosphate fluxes comprised 10 stations from 74 to 989 m water depth. The water
154 column particle sampling was performed at 6 stations from 74 to 407 m water depth. These
155 stations are considered as main stations and for consistency the stations are numbered
156 according to the data set published in Dale et al. (2015). Hydrographic parameters and oxygen
157 concentrations were obtained by deploying a CTD/rosette equipped with a Seabird oxygen
158 sensor (detection limit is 5 μ M) calibrated by Winkler titration.

159 **3.1 Water column particles**

160 Particulate matter was filtered using water from Niskin bottles from the CTD/rosette and
161 analyzed for total particulate phosphorus (TPP), particulate inorganic phosphorus (PIP) and
162 particulate organic carbon (POC) concentrations. Following Labry et al. (2013), we expect the
163 PIP phase to be comprised of inorganic P phases originating from abiotic particulate P as well
164 as inorganic P from biogenic particulate P. Abiotic PIP comprises detrital P associated to
165 minerals from terrigenous sources. Biotic PIP is composed of orthophosphates,
166 pyrophosphates and polyphosphates within eukaryotic and prokaryotic cells.

167 Between three and six water depths were sampled per station. The water was filled into 10 L
168 PE containers rinsed beforehand with ultrapure water (MilliQ). The containers were shaken
169 before filtration which was performed within 24 h after sample retrieval. Approximately 2 to
170 4 L of seawater were filtered through pre-weighed and combusted (450°C, 5h) 0.7 µM
171 Whatman GF/F filter using a seawater vacuum pump and Duran bottle top filters. After
172 filtration, all filters were immediately frozen at -20°C. At the shore-based laboratory the GF/F
173 filters were dried over night at 45°C, and divided into 3 equally sized pieces using a scalpel.
174 The total filtered water volume was divided by three to calculate elemental concentrations on
175 each filter section assuming homogenous coverage of particles on the filters.

176 3.1.1 Total particulate phosphorus (TPP), particulate inorganic phosphorus 177 (PIP) and particulate organic phosphorus (POP)

178 The determination of TPP and PIP concentrations by combustion and colorimetric methods
179 has been described by Asahi et al. (2014), Aspila et al. (1976), Loh and Bauer (2000) and
180 others. However, the combustion and acid dissolution (HTC/hydrolysis) that has been applied
181 for PIP-determination is limited by the fact that polyphosphates are only partly hydrolysed,
182 but provides the best compromise compared to other methods (Labry et al., 2013). Although
183 polyphosphates are underestimated, it includes intracellular P that is often dominant in
184 plankton and only small amounts of organic P. In the case of TPP we used the Aspila (1976)
185 method without an oxidant (e.g. MgSO₄) during combustion, which underestimates the TPP
186 concentration in water column particles. However, for the sediments, the results following the
187 Aspila (1976) method were compared to total digestions, showing an average recovery of the
188 Aspila method of approximately 102%. In two samples we found an overestimation in total
189 digestion of more than 100% and in one sample an underestimation of 32%, possibly due to
190 heterogeneity of the samples caused by very small phosphorite granules.

191 Filter segments for TPP concentration were combusted at 550°C for 90 min and afterwards
192 soaked with 20 ml 1 N hydrochloric acid (HCl) and shaken for 24 h at room temperature.
193 Then, the solution was filtered and 0.35 ml triple reagent (40 ml 9.8 N sulfuric acid, 12 ml
194 ammonium molybdate and 4 ml potassium antimonyl tartrate solution) and 0.175 ml ascorbic
195 acid and 3 ml 1 N HCl were added to 3.75 ml of the sample solution. Then, 0.3 ml of 12.5 N
196 sodium hydroxide (NaOH) was added to the solution before colorimetric measurement of
197 phosphate at 880 nm using a Hitachi U-2001 photospectrometer. This was done because test

198 runs with the standard series revealed that the slope of the calibration curve was not steep
199 enough to measure the low phosphate concentrations expected. To resolve this issue, the pH
200 of the solution was slightly increased using NaOH. Measurements were accompanied using a
201 standard series consisting of 8 standards ranging from 5 to 100 $\mu\text{M PO}_4^{3-}$, prepared from a
202 Merck phosphate stock solution. We used 0.75 ml of each standard for the standard series and
203 treated each of them in the same manner as described above. The samples were measured
204 undiluted due to low concentrations and the technical detection limit of a 1 cm cuvette.
205 Hence, we used 3.75 ml of the filtered sample solution, added the reagents mentioned above
206 and divided the concentrations by a factor of 5 to adjust the results to those of the standard
207 series. A factor of 0.02 was used to transform the concentration unit to $\mu\text{mol L}^{-1}$. The amount
208 of filtered water (f) refers to 1/3 of the total filtered water volume (f is different for each
209 sample):

$$\text{TPP or PIP } [\mu\text{mol L}^{-1}] = \frac{[\text{PO}_4^{3-}] \cdot 0.02}{5 \cdot f}$$

210 The same procedure was performed for PIP without the combustion step. The POP
211 concentration was calculated by the difference of the measured (as phosphate) TPP and PIP
212 concentrations.

213 3.1.2 Organic carbon concentration

214 The filter sections for the analysis of POC concentration were fumed with 37 % HCl
215 overnight to remove inorganic carbon, dried and wrapped into tin caps. Samples were
216 measured by flash combustion with a Carlo Erba elemental analyzer (NA1500). The
217 analytical precision and detection limit were 0.04 dry wt. %. The water column POC
218 concentrations are given in $\mu\text{mol L}^{-1}$.

219 3.2 Porewater and solid phase analysis

220 Sediment cores were recovered using video-guided multiple corers (MUC) equipped with
221 PVC liners with an inner diameter of 10 cm. The porewater and solid phase sub-sampling was
222 performed immediately after recovery in an argon-filled glove bag at in situ seafloor
223 temperature. The bottom water was siphoned with a plastic tube and filtered through cellulose
224 acetate filters. Afterwards, the cores were sectioned into 0.5 cm intervals from 0-5 cm

225 sediment depth and 1 cm intervals afterwards. The sediment samples were filled into
226 centrifuge tubes and the porewater was separated from the sediments by centrifuging for 20
227 min at 4500 rpm. The supernatant porewater was filtered through cellulose acetate filters
228 inside the glove bag. Samples were immediately analyzed for total dissolved phosphate
229 (TPO_4) and dissolved ferrous iron (Fe^{2+}) after porewater extraction using a Hitachi U-2001
230 spectrophotometer. The analyses were performed according to the standard techniques
231 described in Grasshoff et al. (1999). A sediment subsample was taken from each sediment
232 depth and stored refrigerated in pre-weighed air-tight plastic cups to determine the water
233 content, porosity and total organic carbon (TOC) content. The residual sediments were stored
234 frozen at -20°C (sediment and filter samples) and the porewater samples were refrigerated at
235 4°C for land-based analytics.

236 The TOC concentration (in $\mu\text{mol mg}^{-1}$) of freeze-dried and ground sediment samples was
237 determined by flash combustion in a Carlo Erba Elemental Analyzer (NA 1500). For POC
238 determination, samples were decalcified with 2.5 N HCl prior to the measurement. Solid
239 phase TPP and PIP concentrations were measured according to the method of Aspila et al.
240 (1976) in a similar manner as described before for the water column particles. 50 mg of
241 freeze-dried and ground sediment were digested in 1N HCl for a minimum of 24 hours to
242 dissolve the sedimentary PIP phase. Sediment portions analyzed for TPP were combusted at
243 550°C for 90 min before adding 1 N HCl. The solutions were filtered and the reagents
244 mentioned above were added prior to measurement. We used the sedimentary reference
245 standards SDO-1 (Devonian Ohio Shale, USGS; Govindaraju, 1994) and MESS-3 (Marine
246 Sediment Reference Material, Canadian Research Council) and replicate measurements of
247 samples to ensure measurement accuracy. The standard series applied to the measurements
248 covered a concentration range from 5 to 100 μM .

249 To determine the terrigenous P input to the sediments, and to calculate the TPP burial flux
250 (for calculation see section 3.6 and Table 2), sediments were analyzed using total digestion.
251 About 100 mg of freeze dried and ground sediment was digested in hydrofluoric acid (40%,
252 supra pure), nitric acid (65%, supra pure) and perchloric acid (60%, supra pure). For
253 measurement accuracy the reference standards SDO-1 and MESS-3 as well as methodological
254 blanks were included in the analysis. The aluminum concentration in the digestion solutions
255 was measured using an inductively coupled plasma optical emission spectrometer (ICP-OES,
256 Varian 720 ES). The relative standard deviation (RSD) for [Al] was found to be $< 1\%$.

257 The XRD data of core 107MUC23 from 407 m water depth were obtained from
258 approximately 1 g of freeze dried and ground sediment in the lab of the University of Bremen.

259 **3.3 POC in relation to various fractions of P (POC/xP ratios)**

260 The molar POC/xP ratios (where xP = TPP, PIP or POP) of the water column particles at
261 stations I, IV and V were calculated from measurements on two filter samples per water
262 depth. For these samples a minimum and maximum value was calculated. For the other
263 stations III, VI and VIII, only one filter sample per water depth was available. Here, we
264 assumed an average natural variability calculated from the duplicate measurements of stations
265 I, IV and V for each P species (supplementary material). For sediment samples we calculated
266 a standard deviation from repeated measurements of the sediment standards MESS-3 and
267 SDO-1 (supplementary material).

268 **3.4 Benthic lander fluxes**

269 Benthic lander deployments were performed at 10 stations along the 12°S transect (I to X
270 according to Dale et al., 2015). In situ benthic fluxes were obtained using the two BIGOs I
271 and II (BIGO: Biogeochemical Observatory). They were equipped with two circular flux
272 chambers (internal diameter 28.8 cm, area 651.4 cm²) [Sommer et al., 2009]. An online video-
273 controlled launch system allowed precise placement of the BIGO at the seafloor directly
274 located beneath the particle sampling stations in the water column and in proximity to the
275 multi-corer stations. After a 4 hour rest period at the seafloor during which surrounding
276 bottom water was periodically flushed into the chamber, the chambers were slowly driven
277 into the sediment. The BIGOs stayed for 28 hours at the seafloor, while 8 water samples per
278 chamber were taken via glass syringes. In order to obtain bottom water background
279 information, additional samples were taken every 8 hours from the ambient bottom water.
280 Phosphate concentrations in the syringe samples were measured on board using an auto
281 analyzer. The standard series covered a concentration range from 0.05 to 3.5 μM. The fluxes
282 were calculated from the slope of linear regression of all 8 data points versus the sampling
283 time (supplementary material) and corrected for the water volume in the chamber and the
284 dead volume of the 1 m long Vygon tubes connecting the syringes with the flux chambers.
285 The error caused by the dilution from the dead volume of these tubes was calculated from the
286 chloride concentration measured in the syringe samples. Benthic lander TPO₄ fluxes for most

287 sites are based on two replicate chamber measurements. The uncertainty given for the TPO₄
288 fluxes is the difference between the minimum and maximum fluxes from the average of the
289 two benthic chambers. At two stations (IV and V), it was only possible to calculate the flux
290 from one chamber. For further details on the benthic flux measurements during the M92
291 cruise see Dale et al. (2015).

292 3.5 Diffusive flux calculations

293 The diffusive fluxes of TPO₄ and Fe²⁺ from the sediment to the bottom water were calculated
294 by applying Fick's First Law of diffusion:

$$295 F_{TPO_4/Fe^{2+}} = -\phi D_{SED} (d[C]/dx) \quad (1)$$

296 where the term $d[C]/dx$ describes the concentration gradient between the bottom water and the
297 first porewater sample of the surface sediment divided by the corresponding sediment depth
298 (0.25 cm or 0.5 cm) and ϕ is the porosity of the surface sediment. The diffusion coefficient,
299 D_{SED} , for sediments was calculated according:

$$300 D_{SED} = D_{SW}/\theta^2 \quad (2)$$

301 The diffusion coefficients for TPO₄ and Fe²⁺ (D_{SW}) under standard conditions (298.15 K and 1
302 bar) were taken from Li and Gregory (1974) and corrected for the in situ temperature and
303 pressure using the Stokes-Einstein equation. The tortuosity (θ^2) was derived from the
304 sediments porosity according to Boudreau (1996):

$$305 \theta^2 = 1 - \ln(\phi^2) \quad (3)$$

306 Uncertainty in the diffusive flux was calculated at St. I as the difference between the fluxes
307 calculated from two separate sediment cores. For the other stations, only one core was
308 available to calculate the flux.

309 3.6 Mass balance of benthic phosphorus cycling

310 To investigate benthic P cycling quantitatively, a mass balance was developed considering P
311 input, P burial, and P release. The equations for the P mass balance calculations are shown in
312 Table 2. Under steady state conditions, the total P rain rate should balance the P buried in the
313 sediments and the benthic TPO₄ flux (Eq. 4 in Table 2). The rain rates of particulate P

314 delivered to the sediments are differentiated in inorganic P (RR_{PIP}) (Eq. 5 in Table 2) and
315 organic P (RR_{POP}) (Eq. 6 in Table 2). The rates were calculated using the POC/xP ratio of the
316 water column particles that were taken as close as possible to the seafloor at each station (2-5
317 m above ground) and the POC rain rate (RR_{POC}) (Table 4 and supplementary material). RR_{POC}
318 for the same stations along the 12°S transect were previously calculated by Dale et al. (2015)
319 as the sum of the measured benthic DIC flux and the POC accumulation rate. The terrigenous
320 P input (RR_{Pterr}) (Eq. 7 in Table 2) can be estimated by multiplying the solid phase Al
321 concentration of the first sediment sample by the mass accumulation rate (MAR) [Dale et al.,
322 2015] and a P/Al ratio of 0.02 that characterizes the P/Al ratio of riverine particles originating
323 from the continent [Viers et al., 2009].

324 The P burial flux (F_{Pbur}) (Eq. 8 in Table 2) was calculated by multiplying the mass
325 accumulation rate (MAR) and the average solid phase P concentration of the first 11 sediment
326 centimeters (P_{11}) (11 cm is due to our sampling resolution). This approach was chosen
327 according to Dale et al. (2015) who also calculated POC accumulation rate for the OMZ
328 stations (i.e. not on the shelf or below the OMZ) using the elemental average concentration of
329 the first 10 cm of sediment. MAR (Eq. 9 in Table 2) was calculated from the sedimentation
330 accumulation rate (ω_{acc} in $cm\ y^{-1}$), dry bulk density (ρ_{dry} ; in $g\ cm^{-3}$) and the average porosity
331 of the sediments at the lower core end (ϕ_{∞}). Sedimentation accumulation rates were
332 determined from particle-bound $^{210}Pb_{xs}$ measurements using a modeling approach. A detailed
333 method description and the values used for this work are published in Dale et al. (2015). The
334 error derived from modeling the sedimentation rate was given as 20 % and propagates to all
335 subsequent calculations where it was used.

336 3.7 Freeze/thaw experiments

337 In order to determine the amount of polyphosphate stored in sulfide-oxidizing bacteria,
338 foraminifera and other bacteria we conducted additional sediment experiments at all transect
339 stations, except station IV. Sediments from MUC corers were sliced into 1 cm thick slices
340 from the surface sediment to 10 cm sediment depth. Before phosphate analysis, sediment
341 slices were repeatedly frozen at -80°C and defrosted in order to burst microbial cells and
342 release the internally stored P to the porewater.

343 3.8 Molecular quantification of filamentous bacteria

344 In order to quantify the abundance of filamentous microbes at the benthic boundary layer, we
345 used a molecular approach. Nucleic acid purification was performed on 0.5 g sediment
346 following established protocols [Bertics et al., 2013]. DNA was quality checked on an agarose
347 gel and quantified using a Nanodrop spectrophotometer (Peqlab, Erlangen, Germany). 16S
348 rDNA fragments were taken from a previously generated metagenome from this region
349 (GenBank Bioproject PRJNA280940) and the respective sequence counting's were deposited
350 at GenBank (ID KU312264-KU312267). Sequencing was carried out in the Institute of
351 Clinical Molecular Biology at Kiel University. Sequences were analyzed using a Clustal W
352 alignment tool on Mega 6 [Tamura et al., 2013]. A qPCR primer and probe set was
353 established using the Primer Express software (Life Technologies, Carlsbad, USA) with the
354 forward primer 5' AGAAGCACCGGCTAACTCTG-3' , the reverse primer, 5' -
355 CCAGGTAAGGTTCTTCGCGT-3' and the probe 829-Thioploca 5'-
356 GGATTAATTTCCCCAACAT-3' [Teske et al., 1995]. Primers and probes were tested *in*
357 *silico* on the Silva database and cross amplification was excluded on a variety of 16S rDNA
358 clones. The qPCRs were performed in technical duplicates on a ViiA7 system (Life
359 Technologies, Carlsbad, USA) as previously described [Löscher et al., 2014] using 1x
360 TaqMan PCR buffer (Life Technologies, Carlsbad, USA), 2.5 pmol μL^{-1} TaqMan probe, 5
361 pmol μL^{-1} of each primer, 400 ng μL^{-1} bovine serum albumin (to avoid PCR inhibition without
362 affecting standard curves or detection limits), 3 μl PCR water, and 5 μl of either standard
363 DNA or environmental sample. A plasmid containing the target sequence was used to
364 generate a standard dilution series for absolute quantification. The melting temperature was
365 set to 50°C. A theoretical detection limit of 4 copies per PCR reaction was calculated. The
366 results of the analysis are given in copies g^{-1} of 16S rDNA sequences of sulfur bacteria that
367 are related to Marithioploca.

368

369 4 Results

370 4.1 P composition of water column particulate matter and surface sediments

371 4.1.1 TPP, PIP, POP and POC concentrations

372 The TPP concentrations ranged from 0.02 to 0.2 $\mu\text{mol L}^{-1}$ in the water column particles and
373 from 0.04 to 2.37 $\mu\text{mol mg}^{-1}$ in the surface sediments (supplementary material). Overall, the
374 profiles along the transect show no significant trends through the water column (Fig. 2A). The
375 highest concentrations occurred in the surface waters around 10 m of water depth. At stations
376 I, V and VIII (74, 195 and 407 m) the TPP concentrations slightly increased close to the
377 seafloor, whereas at the other stations no such trend was observed (Fig. 2A and
378 supplementary material). In the sediments the TPP concentrations slightly decreased with
379 sediment depth, except at station VIII (407 m). Here, the highest sedimentary TPP
380 concentrations across the transect were found at 2.25 cm sediment depth (17 $\mu\text{mol mg}^{-1}$).
381 Below that depth the concentrations decreased, but remained high compared to the other
382 stations.

383 The PIP and POP concentrations (water column and sediments) generally followed the trends
384 of the TPP profiles and contributed roughly equally to TPP. The PIP fraction accounted for 21
385 to 74 % of TPP in the water column particles (Fig. 3), similar as reported in previous studies
386 [Paytan et al., 2003; Faul et al., 2005; Benitez-Nelson et al., 2007; Lyons et al., 2011; Sekula-
387 Wood et al., 2012]. At stations I, VI and VIII (74, 244 and 407 m), the PIP concentrations
388 were larger than POP. The opposite occurred at station V (195 m) where the POP fraction was
389 clearly larger than the PIP fraction throughout the entire water column. In comparison to the
390 water column particles, the PIP fraction was larger than POP in most samples reaching
391 between 48 to 98% of TPP. However, the strongest deviation between PIP and POP
392 concentrations was found in the sediments of station VIII (407 m) where the PIP
393 concentration was up to a factor of ~ 50 larger than the POP concentration and comprised up
394 to 98% of TPP. XRD data from that station revealed that 7 to 16 wt.% of the sediments
395 consisted of apatite and other particulate P (data not shown).

396 The particulate organic carbon concentrations ranged from 2.2 to 17.6 $\mu\text{mol L}^{-1}$ in the water
397 column particles and from 2.8 to 13.4 $\mu\text{mol mg}^{-1}$ in the surface sediments. Within the water
398 column the highest concentrations occurred in the surface water samples, while the

399 concentration measured at station VI (244 m) is about 5 times higher than compared to other
400 samples from the same water depth. Below the surface water concentration peak, the
401 concentrations were on average $7 \mu\text{mol L}^{-1}$ with distinct depth trends. The sedimentary POC
402 concentrations were on average $7.7 \mu\text{mol mg}^{-1}$ for the whole transect. Overall, the POC
403 concentrations showed little variability with sediment depth. At station III, VI and VIII (128,
404 244 and 407 m) the concentrations increased slightly with sediment depth. At station I (74 m)
405 the concentration decreased slightly with sediment depth.

406 **4.2 Particulate organic carbon to phosphorus (POP, PIP, TPP) ratios**

407 *POC/POP ratios*

408 The molar POC/POP ratios of the water column particles and of the surface sediments were
409 consistently higher than the Redfield ratio at all stations (Fig. 2B). The average POC/POP
410 ratio of the water column particles was 202 ± 29 . There was no clear trend through the water
411 column, except slightly increasing ratios between the deepest water column samples and the
412 surface sediment samples. In the surface sediments, the ratios increased within the upper 6 cm
413 with an average POC/POP ratio of 303 ± 77 . Station VIII (407 m) is an exception and here the
414 ratio decreased to 81 within the first ~ 2 cm of sediment and then strongly increased to ≥ 600 .

415 *POC/PIP ratios*

416 The average POC/PIP ratio of the water column particles was 248 ± 34 . Similar to the
417 POC/POP ratios, there was no significant trend through the water column. At the majority of
418 the stations, the ratios decreased close to the seabed. The average POC/PIP ratio of the
419 surface sediments was 184 ± 34 and almost invariable with water depth. In the sediments, the
420 ratios showed no significant down-core trend. At station VIII (407 m) the ratio in the
421 sediment showed a dramatic decreased compared to the water column, with an average of 7,
422 similar to the POC/TPP ratios (below).

423 *POC/TPP ratios*

424 The POC/TPP ratios of the water column particles and surface sediments consistently varied
425 around the Redfield ratio. The exceptions are station I (74 m) and the deepest station (Sta.
426 VIII, 407 m). At station I, the sediments showed significantly lower than Redfield ratios with
427 an average of 69 in the surface sediments. The average POC/TPP ratio of the surface

428 sediments at station VIII (407 m) was 7. Between the deepest water column sample and the
429 first sediment sample, the POC/TPP ratios were rather constant without a consistent trend,
430 again with the exception of station VIII (407 m) where the ratios decreased sharply.

431 4.3 In situ benthic chamber fluxes

432 The benthic lander TPO_4 fluxes (F_{TPO_4}) are presented in Table 3 and Fig. 4A. Positive fluxes
433 are defined as directed from the sediments into the water column. The highest TPO_4 flux
434 along the depth transect of $1.04 \pm 0.31 \text{ mmol m}^{-2} \text{ d}^{-1}$ occurred at station I (74 m). Below 74 m
435 water depth, fluxes decreased by at least a factor of 3 to $0.2 - 0.3 \text{ mmol m}^{-2} \text{ d}^{-1}$ at 144 m water
436 depth. Measurements at station V (198 m) showed a slightly increased TPO_4 flux of $0.44 \pm$
437 $0.07 \text{ mmol m}^{-2} \text{ d}^{-1}$, while the fluxes measured at 244 m (St. VI) and 306 m (St. VII) decreased
438 to the before mentioned levels. At 407 m water depth (St. VIII) the TPO_4 flux was negative,
439 indicating a phosphate uptake by the sediment. Below the OMZ, the fluxes increased to
440 slightly positive values, but remained low at 0.06 and $0.02 \pm 0.02 \text{ mmol m}^{-2} \text{ d}^{-1}$.

441 4.3.1 Comparison of benthic chamber TPO_4 fluxes and diffusive TPO_4 fluxes

442 The measured benthic chamber TPO_4 fluxes and the calculated diffusive TPO_4 fluxes showed
443 large discrepancies. The calculated diffusive fluxes were consistently higher than the benthic
444 fluxes (Table 4, Fig. 4B). In contrast to the in situ measured benthic chamber TPO_4 release
445 rates, the calculation of diffusive TPO_4 fluxes relies on bottom water and porewater PO_4^{3-}
446 concentrations. A subsurface PO_4^{3-} peak occurred at all stations in the uppermost depth
447 interval at 0-0.25 cm causing a large concentration gradient between the bottom water and the
448 porewater PO_4^{3-} concentrations (Fig. 7). Even though the measured benthic TPO_4 fluxes
449 exceeded the fluxes that could be generated by TPP degradation by a factor of approximately
450 6, the diffusive TPO_4 fluxes were still higher (Table 4). Hence, the diffusive TPO_4 flux will
451 be referred to as potential TPO_4 flux in the following.

452 4.4 TPP burial fluxes and TPP burial efficiency

453 The P burial fluxes decreased with increasing water depth (Table 4). Station I (74 m) showed
454 by far the highest P burial flux with $0.23 \text{ mmol m}^{-2} \text{ d}^{-1}$. In contrast the P burial efficiency at
455 this station (Eq. 10) was comparatively low reaching only 26 %. At Station VIII (407 m), the

456 TPP burial flux was $0.03 \text{ mmol m}^{-2} \text{ d}^{-1}$ and the P burial efficiency exceeded 100 % due to the
457 uptake of dissolved P from ambient bottom waters.

458 **4.5 Molecular analysis and relative abundance of filamentous sulfur bacteria**

459 Molecular analysis indicated the presence of Marithioploca-related bacteria in the surface
460 sediments (0-5 cm) [Salman et al., 2011]. Our analysis may, however, underestimate the
461 absolute abundance of these organisms due to a self-splicing mechanism of the 16S rDNA
462 gene (Salman et al., 2012) and is therefore only indicative of their relative abundance.

463 The relative abundance of Marithioploca-related bacteria decreased with increasing water
464 depth (Table 4). Highest relative abundance with more than 4000 copies g^{-1} sediment was
465 found at station I (74 m), decreasing by more than a factor of 20 to 190 copies g^{-1} sediment at
466 station VIII (407 m).

467

468 **5 Discussion**

469 **5.1 POC/xP ratios in water column particles and sediments**

470 In order to characterize the fate of P in oxygen deficient waters and sediments we determined
471 POC/xP ratios from both environments. Previous studies focused either on the water column
472 or on the sediments [Anderson et al., 2001 and references therein; Benitez-Nelson et al., 2004;
473 Faul et al., 2005; Jilbert et al., 2011; Lyons et al., 2011; Sekula-Wood et al., 2012]. The
474 present data set provides a more complete insight into compositional changes and allows us to
475 more rigorously constrain the sedimentary P mass balance compared to earlier studies [Ingall
476 and Jahnke, 1994; Mort et al., 2010; Kraal et al., 2012; Noffke, 2014].

477 Both water column particles and the surface sediments from the Peruvian OMZ displayed
478 POC/POP ratios above Redfield, indicating depletion of organic P relative to organic C.
479 Similar observations have been reported before from this and other regions of the ocean [Loh
480 and Bauer, 2000; Benitez-Nelson et al., 2004; Faul et al., 2005; Franz et al., 2012 and others].
481 Preferential remineralization of P phases from sinking particles should lead to increasing
482 POC/POP ratios with increasing water depth, as observed in oxygenated areas of the ocean
483 [reviewed by Ruttenberg, 2014]. However, in the anoxic Cariaco Basin, no such preferential P

484 mineralization was noted [Benitez-Nelson et al., 2004]. Our results also showed no clear
485 decrease in the POC/POP ratio in the water column, with the possible exception of St. I and
486 VIII. Higher than Redfield POC/POP ratios were observed at Peru on a previous occasion,
487 and may instead be driven by the C-to-P composition of the diatomaceous phytoplankton
488 communities [Franz et al., 2012] rather than preferential P dissolution or other controls such
489 as the input of terrestrial plant material with high POC/POP ratios.

490 Preferential POP over POC remineralization in anoxic sediments remains controversial [Ingall
491 and Van Cappellen, 1990; Ingall and Jahnke, 1994; Colman et al., 1997; Anderson et al, 2001;
492 McManus et al, 1997; Ruttenberg, 2003; Jilbert et al, 2011]. Our results, however, also
493 showed no clear trend across all stations. At station I, IV and VI (74, 141 and 244m) the
494 POC/POP increased with sediment depth indicating preferential POP over POC
495 remineralization. At station III (128 m) this trend occurred only in the upper cm and at station
496 V (195 m) no preferential POP over POC remineralization was found. POC/POP ratios at
497 station VIII (407 m) showed a POP enrichment over the upper 2 cm of the sediment. Below
498 this depth, there was a sudden increase in POC/POP ratios, which is likely due to intense POP
499 remineralization and subsequent authigenic formation of phosphorites (sink-switching, see
500 section 5.2.3).

501 Another interesting finding pointing to sink-switching can be found in the POC/POP and
502 POC/PIP ratios of the deepest water column particle sample and the first sediment sample at
503 stations I, IV, VI and VIII (74, 141 and 407 m). Increasing POC/POP and decreasing
504 POC/PIP ratios indicate that POP is converted into PIP while the TPP content of the sediment
505 is conserved (Fig. 2A and B). In agreement with similar findings in anoxic sediments
506 [Ruttenberg and Berner, 1993; Faul et al., 2005 and others] we assume that the observed POP
507 to PIP transformation is due to the formation of CFAs. However, our results emphasize that
508 sink-switching is obviously occurring at the interface between bottom waters and sediments.

509 Interestingly, the water column POC/TPP ratios were close to Redfield ratio. This could be an
510 effect of surface adsorption of P on phytoplankton as previously described by Sanudo-
511 Wilhelmy et al. (2004). Those authors investigated different species of *Trichodesmium* from
512 the Atlantic Ocean and found that the intracellular P pool was strongly depleted relative to C,
513 whereas the combination of the intracellular plus the surface adsorbed P was close to the
514 Redfield ratio. Although we did not exactly differentiate between internal and external P

515 pools, and considering that additional P sources like terrigenous P are less important (see
516 section 5.2.1), our results generally support the findings of Sanudo-Wilhelmy et al. (2004).
517 However, future studies are required to substantiate this hypothesis.

518 Sedimentary POC/TPP ratios were also close to Redfield, except at station I and VIII (74 and
519 407 m). Thus, on the one hand, the sink switching mechanism operates efficiently under low
520 oxygen conditions and on the other hand, the relative degradation of TPP and POC are not
521 changing from the water column to the sediments (Fig. 2B). This is an important finding
522 because at first sight this observation seems to be inconsistent with the long-standing
523 paradigm that low oxygen conditions promote the enhanced release of dissolved P from
524 sediments [Van Cappellen and Ingall, 1996]. However, it should be noted that marine
525 sediments covered by oxygenated bottom waters display molar POC/TPP ratios ranging from
526 about 10 to 50 [Baturin 2007]. These ratios are much lower than Redfield because P is
527 retained in sediments via adsorption, authigenic mineral precipitation such as Fe
528 (oxyhydr)oxides and microbial P sequestration [Ingall and Jahnke, 1994], and because POC is
529 more efficiently degraded under aerobic conditions [Hedges et al., 1999, Wallmann, 2010]. In
530 contrast, our data set implies that oxygen deficiency causes a shift of POC/TPP ratios to
531 values closer to Redfield compared to oxygenated regions, which is due to both, the enhanced
532 preservation of POC (Dale et al., 2015) and release of dissolved phosphate under low oxygen
533 conditions. It remains puzzling why the extreme P depletion observed in some black shale
534 sequences (e.g. POC/TPP > 3000, Ingall and Jahnke, 1994) are not found in modern anoxic
535 sediments such as those on the Peru margin.

536 **5.2 P mass balance**

537 P release rates from sediments underlying oxygen deficient waters are strongly enhanced
538 compared to oxygenated marine settings, especially in the Peruvian OMZ [Noffke et al., 2012
539 and 2016]. Nonetheless, the sources for the enhanced P release are still not completely
540 identified. The widely held view is that POP raining from the water column to the sediments
541 represents the main source for sedimentary P in high productive areas like the Peru upwelling
542 system [Delaney, 1998; Filippelli, 2008]. Mass balance approaches that resolve the P
543 regeneration versus burial in oxygen deficient environments by combining sedimentary data
544 and benthic P fluxes are rare [Ingall and Jahnke, 1994; Ingall et al., 2005; Mort et al., 2010;
545 Kraal et al., 2012; Noffke, 2014]. These studies are all based on sediment data only, that is,

546 the external P input to the sediments is estimated or ignored. Furthermore, the study areas
547 were often not covered by fully anoxic bottom waters. Noffke (2014) presented an approach
548 that combines measurements of solid phase P speciation, sediment burial fluxes and benthic
549 chamber flux measurements for a mass balance on benthic P cycling in the Peruvian OMZ.
550 Interestingly, the measurements on the solid phase P speciation revealed that organic P
551 accounted for only 18-37% of the total sedimentary P on the shelf and upper slope [Noffke,
552 2014]. Furthermore, it was found that P bound to Fe (oxyhydr)oxides and terrigenous P was
553 of minor importance for the total sedimentary P inventory. However, authigenic Ca-P with a
554 high amount of fish-P accounted for up to 47% of the total P in sediments down to 300 m
555 water depth and for up to 70% in sediments below 300 m water depth. Consequently, Noffke
556 (2014) suggested that authigenic Ca-P phases are an additional major P source besides
557 organic P for benthic P release in the Peruvian OMZ.

558 Their mass balance approach was solely based on benthic work and has large uncertainties
559 regarding the particulate P input from the water column. Our approach includes the particulate
560 organic and inorganic P input from the water column, benthic P flux measurements and the P
561 burial fluxes and is based on the steady state assumption that the P input has to be sufficient to
562 maintain the benthic P flux and P burial flux. The P mass balance calculations (Table 4)
563 illustrate the variability in TPO₄ release and burial as well as in the magnitude of particulate
564 organic (Fig. 5A) and particulate inorganic P input (Fig. 5B) across the transect. Following
565 the general assumption that POP is the major P phase delivered to the sediments [Delaney,
566 1998; Filippelli, 2008], we first calculated whether the rain rate of POP (RR_{POP}) to the
567 seafloor can account for the measured benthic P fluxes (F_{TPO₄}) and P burial fluxes (F_{P_{bur}}) (Fig.
568 5A, Table 4). However, as already suggested by Noffke et al. (2012 and 2014), the POP
569 fraction is far too small to balance the measured benthic fluxes in the Peruvian OMZ. The
570 POP rain rates calculated along the transect can account for only 25 to 48% of the measured
571 TPO₄ fluxes (Fig. 5A), suggesting likely the presence of an additional inorganic source of
572 dissolved phosphate [Noffke, 2014]. Similar to previous studies [Paytan et al., 2003; Faul et
573 al., 2005; Benitez-Nelson et al., 2007; Lyons et al., 2011; Sekula-Wood et al., 2012], we
574 found that the PIP fraction in water column particles ranging from 75 to 407 m water depth
575 comprises between 21-74% of TPP (Fig. 3). In the sediments, the average PIP fraction rises to
576 48-98% of TPP (Fig. 3). Furthermore, POC and PIP were correlated ($r^2=0.74$) in the water
577 column particles indicating highly reactive material.

578 **The** mass balance approach including the PIP rain rate to the seafloor (Fig. 5B) allows the
579 depth transect to be divided into two sections. The **transect section I** (station I, 74 m and III,
580 128 m) is characterized by high P input and release rates. The calculations on the P budget
581 show a balance between the particulate P input, the benthic P fluxes and the P burial fluxes
582 within the error margin ($\pm 20\%$). In transect section **II** (stations IV, 141 m, **V, 195 m** and VI,
583 244 m), the P input decreases drastically (Fig. 5B, Table 4) whereas the benthic P fluxes are
584 still comparatively high. The distinct mismatch in P input and P output prevails as the
585 particulate P rain **rates supported only 37 to 53 %** of the measured TPO₄ fluxes and calculated
586 burial fluxes. This leads to the question: What drives the excess TPO₄ release in the core of
587 the Peruvian OMZ?

588 **5.2.1 Additional P input**

589 **Besides the particulate matter raining to the sediments, other potential other P sources can be**
590 **considered. Firstly,** riverine transported material from the **continent may be an additional**
591 **source of P to the sediments. Due to fast sinking speed and laterally dominated transport it is**
592 **possible that this P fraction is at least underrepresented on the filter samples. In order to**
593 **provide a maximum estimate for the contribution of the terrigenous P input to the sediments,**
594 **this fraction was calculated using the mass accumulation rate of Al in the first centimeter of**
595 **sediment and an average molar P/Al-ratio (Table 2) of 0.02 for riverine suspended particles**
596 **[Viers et al., 2009]. The resulting terrigenous P flux accounted for 5-19 % of the total P input,**
597 **which is insufficient to explain the observed discrepancies in the P budget of transect section**
598 **II (Table 4, Fig. 4C, 5B).**

599 Laterally transported particles enriched in P from the very shallow shelf could be an
600 additional P source [e.g. Jahnke, 1990]. However, the particles would **need** to be strongly
601 enriched in P, which is not the case. In addition, this would have to be reflected in the
602 POC/TPP ratios of the surface sediments in transect section II (Fig. 2B). The ratios are **not,** or
603 only **slightly,** enriched in TPP compared to the water column **particles, which leads** to the
604 conclusion that lateral transport of P-enriched particles to the sediments is an unlikely
605 candidate for the missing P source.

606 **Another alternative** is the existence of an additional PIP phase supplied by fast sinking
607 material (e.g. P containing fish scales; **Suess, 1981**) that was not sampled during CTD **casts**
608 and hence **underrepresented** on our filter samples. Díaz-Ochoa et al. (2009) showed that fish P

609 can make up to 20% of the total sedimentary P inventory in the shelf sediments of the
610 Peruvian OMZ. Fish P input should be depicted in low sedimentary POC/TPP ratios
611 compared to the water column particles. Since this difference is not observed it is likely that
612 fish debris can be ruled out for closing the P budget during the sampling campaign.
613 Theoretically, sediments need to be composed of particles having POC/TPP ratios between 11
614 ± 1 and 25 ± 12 (Table 4) to maintain the measured P release rates in transect section II. It
615 seems unlikely that the mismatch in the P mass balance is caused by additional particles
616 deposited at the seabed since their POC/TPP ratio would need to be much lower than any
617 value observed in our data set.

618 5.2.2 Non steady state scenarios – internal sedimentary P pools

619 Besides an additional P input to the sediments from the water column, episodic dissolution of
620 particulate P within the sediment could contribute to the excess P release [Noffke et al.,
621 2012]. This could include P solubilized from Fe (oxyhydr)oxides or the degradation of
622 internally stored polyphosphates within sulfide-oxidizing bacteria. Driving factors could
623 include the temporal variability in bottom water oxygen and nutrient concentrations induced
624 by the passage of internal Kelvin waves and/or interannual variability related to El Niño and
625 La Niña [Gutiérrez et al., 2008].

626 It is well recognized that the sedimentary cycles of Fe and P are strongly linked [e.g. Sundby
627 et al., 1986]. Fe (oxyhydr)oxides are expected to be important carriers for phosphorus from
628 the water column to the sediments. Following dissolution of solid Fe minerals in the
629 sediments, the adsorbed P is released to the porewaters. However, in the Peruvian OMZ,
630 oxygen concentrations in the water column are generally below detection limit. Consequently,
631 Fe (oxyhydr)oxides are likely already dissolved in the water column and not such an
632 important P source to the sediments. An estimate of phosphate released during the reduction
633 of Fe (oxyhydr)oxides can be calculated from the diffusive Fe^{2+} fluxes and the molar Fe/P
634 ratio typically found in Fe (oxyhydr)oxides. The diffusive Fe^{2+} fluxes were in the range of 0
635 to $0.03 \text{ mmol m}^{-2} \text{ d}^{-1}$ during the M92 cruise (Table 4) and the molar Fe/P ratio of Fe
636 (oxyhydr)oxides in the sediments is around 10 [Slomp et al., 1996]. The calculation of the
637 TPO_4 release rates from Fe (oxyhydr)oxides (Eq. 14 in Table 2) results in a flux of 0.003
638 $\text{mmol PO}_4^{3-} \text{ m}^{-2} \text{ d}^{-1}$ (Table 4, Fig. 4C and 5B), which is equivalent to less than 5% of the
639 benthic P flux and burial flux.

640 An additional internally activated P pool is phosphate released from large sulfur-oxidizing
641 bacteria, e.g. *Beggiatoa* [Sannigrahi and Ingall, 2005; Brock and Schulz-Vogt, 2011]. These
642 microorganisms store P in the form of intracellular polyphosphate granules when terminal
643 electron acceptors for sulfide oxidation are available (oxic conditions) and release dissolved P
644 during periods when these oxidants are scarce (anoxic conditions). Hence, it is generally
645 assumed that they strongly affect benthic TPO₄ fluxes in a system with frequently changing
646 bottom water redox conditions [Ingall and Jahnke, 1994; Sannigrahi and Ingall, 2005; Schulz
647 and Jørgensen, 2005; Brock and Schulz-Vogt, 2011; Dale et al., 2013]. Polyphosphates have
648 been shown to be an important P pool in the sediments of highly productive upwelling areas
649 [Kraal et al., 2015]. Along the depth transect at Peru, dense mats of sulfur bacteria related to
650 *Marithioploca* were observed on the sediments during video-launched MUC and benthic
651 lander deployments down to 300 m water depth [Dale et al., 2015]. Similar findings extended
652 distributions of microbial mats along a latitudinal transect at 11°S off were also previously
653 described by Mosch et al. (2012) and Gutiérrez et al. (2008). Although, these organisms are
654 not known to store polyphosphates like their close relatives, *Beggiatoa* spp. and
655 *Thiomargarita* spp. [Høgslund et al., 2009; Holmkvist et al., 2010], our findings provide
656 circumstantial indications for P uptake and release by *Marithioploca*-related bacteria.

657 Firstly, we found that the relative abundance of copies of *Marithioploca*-related bacteria per g⁻¹
658 sediment and the measured benthic TPO₄ release rates correlate linearly ($r^2=0.92$, Fig. 6).
659 This finding supports the suggestion that bacteria exert an important control on benthic P
660 fluxes. Secondly, a comparison of the in situ measured benthic P fluxes and the diffusive P
661 fluxes calculated from the difference of the TPO₄ bottom water concentration and the TPO₄
662 porewater concentration of the surface sediments revealed large differences (Fig. 4B). Such a
663 difference could be explained by the lysis of bacterial cells during sample retrieval followed
664 by the release of the internally stored polyphosphate pool into the porewater. Following this
665 argument, the diffusive P fluxes cannot be taken as real fluxes, but as a measure for potential
666 maximum release rates of P by *Marithioploca*-related bacteria. It should be noted that, the
667 potential fluxes are more than sufficient to compensate for the missing P fraction in transect
668 section II (ranging from 0.5 to 1.6 mmol m⁻² d⁻¹; Table 4, Fig. 4B).

669 In addition to the established porewater extraction procedure, we carried out freeze/thaw
670 experiments to quantify the amount of P stored in sulfide-oxidizing bacteria (see method
671 section 3.7). The released polyphosphates from the microbial cells after repeated freeze/thaw

672 cycles are rapidly hydrolyzed to orthophosphate under acidic conditions [Jager and Heyns,
673 1998]. Hence, the standard method to determine phosphate in the porewaters using acidic
674 reagents will favor the hydrolysis of polyphosphates enabling us to measure its concentration
675 in the porewaters after conducting the experiments. However, this method cannot exclude P
676 release from other bacteria and, possibly, foraminifera in the sediments. A comparison of the
677 porewater phosphate concentrations and the experiment results shows that the internal P
678 reservoir is as twice as high as the porewater P concentration in transect section I and more
679 than ten times larger in section II (Fig. 7). These results are coincident with the findings from
680 the mass balance approach, where the largest discrepancies occur in transect section II and are
681 another indication for the bacterial impact on the benthic P release. Interestingly, the highest
682 phosphate concentrations after the freeze/thaw experiments were found at station VIII (407
683 m) with abundant foraminifera rather than sulfide-oxidizing bacteria. Hence, we assume that
684 the sulfide-oxidizing bacteria at station IV, V and VI (141, 194 and 244 m) and, potentially,
685 the foraminifera observed at station VIII (407 m) are contributing phosphate to the
686 porewaters. To our knowledge, P storage by foraminifera has not been demonstrated
687 previously and awaits further study.

688 It remains to be shown how these mechanisms play out in detail (e.g. nutrient concentration
689 thresholds, P uptake and release time scales by *Marithioploca*-related bacteria) and how they
690 impact benthic P release in oxygen and nitrate deficient environments on longer time scales.
691 Summarizing the results of the mass balance, it should be noted, that, even with the relevant
692 data on particulate P rain rates, the benthic P mass balance for the core of the Peruvian OMZ
693 is imbalanced and requires an additional P source to maintain the benthic TPO_4 fluxes. We
694 suggest that sulfur bacteria make important contribution to this missing P source.

695 5.2.3 Indications for active phosphorite formation

696 In contrast to the stations between 74 and 244 m water depth characterized by P release, data
697 from station VIII at 407 m water depth indicate the uptake of phosphate from the bottom
698 water. To our best knowledge, this is the first time that a downward flux of dissolved
699 phosphate from bottom waters into phosphorite-bearing surface sediments has been
700 documented by in situ benthic flux measurements. Furthermore, the PIP concentrations in the
701 surface sediments of station VIII (Fig. 2A) were 10 to 60 times higher compared to the
702 shallower stations where P was released from the sediments. Taken together, these

703 observations indicate that a PIP phase, likely phosphorite, was precipitating from the
704 porewater phosphate at the time of sampling. This is also reflected in decreasing porewater
705 phosphate concentrations (Fig. 7).

706 Arning et al. (2008) presented investigations on phosphorites recovered from the Peruvian
707 OMZ including a station at 12°S from the same water depth (~ 400 m) close to sampling
708 station VIII. The suboxic bottom waters and low sedimentation rates in that area seem to be
709 favorable for phosphorite formation close to the sediment-water interface [Arning et al.,
710 2009b]. Cosmidis et al. (2013) suggested three mechanisms how high porewater phosphate
711 concentrations that are essential for the phosphogenesis can be generated in the sediments: (1)
712 remineralization of organic matter mainly through bacterial sulfate reduction releasing
713 phosphate to the porewaters, (2) reductive dissolution of Fe (oxyhydr)oxides and the release
714 of adsorbed P and (3) synthesis of internally stored polyphosphates by large sulfide-oxidizing
715 bacteria. Using the same mass balance approach as presented before, we calculated a P
716 accumulation rate of $33 \pm 4 \text{ mmol m}^{-2} \text{ yr}^{-1}$ at station VIII where most of the P is derived from
717 ambient bottom waters ($26 \text{ mmol m}^{-2} \text{ yr}^{-1}$). Hence, our data suggest that the phosphorite
718 nodules at this station contain phosphate that originates predominantly from ambient bottom
719 waters. Additionally, as already mentioned, sediments at station VIII were covered by benthic
720 foraminifera instead of mat-forming sulfur bacteria. The release of phosphate from frozen
721 samples from this site may indicate that these foraminifera are a source for polyphosphates
722 (see section 3.7 and Fig. 7). Our observations suggest that benthic foraminifera rather than
723 bacterial mats might facilitate the uptake of bottom water phosphate and the formation of
724 phosphorites at this station. However, this remains an open question and should be addressed
725 in future field campaigns.

726 The P uptake rate of $\sim 26 \text{ mmol P m}^{-2} \text{ yr}^{-1}$ derived from our lander measurements may be
727 compared to previous estimates on phosphorite growth rates in the area. Dating of phosphoric
728 laminites yields a P uptake rate of only $3 \text{ mmol P m}^{-2} \text{ yr}^{-1}$ for a ca. 1 Ma old nodule [Arning et
729 al., 2009a]. These different fluxes may be at least partly explained by the methodological
730 difference (present flux measurement vs. long-term average). However, growth rates
731 determined on modern nodules are broadly consistent with our flux measurements [Burnett et
732 al., 1982].

733

734 6 Conclusions

735 This study aimed to identify the P sources of benthic P release in the Peruvian OMZ. We
736 determined the rain rates of particulate organic phosphorus and particulate inorganic
737 phosphorus as well as benthic P release rates and P burial fluxes.

738 Our calculations revealed that within the core OMZ particulate phosphorus rain rates cannot
739 account for measured benthic P fluxes and burial fluxes. From systematic analysis of potential
740 P sources, we conclude that periodic P release from sulfur bacteria that store and release P
741 under oscillating redox conditions could strongly modulate benthic P fluxes, and hence
742 explain the missing P source. We visited the area during austral summer when oxygen and
743 nitrate levels were depleted by high export production and respiration. It is possible that the
744 Peruvian OMZ was less reducing prior to our sampling period due to lower respiration rates
745 and/or better ventilation. Thus, we propose that the bacterial mats on the Peru margin act as
746 phosphorus capacitors, being discharged during austral summer and recharged during other
747 periods of the year when bottom waters are less reducing, as previously proposed in Dale et
748 al. (2013). This hypothesis could be tested by studying of the seasonality of benthic fluxes in
749 the Peruvian up-welling system and P dynamics within the bacterial community.

750 In addition, measurements at one station (407 m water depth) showed clear indications for the
751 uptake of dissolved phosphate by the sediments facilitating phosphorite formation. Our data
752 imply that most of the P accumulating in these authigenic minerals originates from ambient
753 bottom waters. Since this site was marked by a high abundance of P-bearing benthic
754 foraminifera, we speculate that phosphate uptake and phosphorite formation may be linked to
755 the presence of these organisms. This requires further study.

756 There was no clear preferential mineralization of POP relative to POC with depth in the water
757 column. POC/TPP ratios in both water column particles and sediments were close to Redfield
758 at most sites in the Peruvian OMZ. This observation strongly suggests that the relative burial
759 efficiencies of POC and TPP are similar under low oxygen conditions. Importantly, it further
760 shows that the sediments underlying the anoxic waters on the Peru margin are not depleted in
761 P compared to Redfield. Rather, they are depleted relative to sediments underlying oxic
762 waters, which show POC/TPP ratios well below Redfield (Wallmann, 2010). Thus, at Peru, a
763 lack of oxygen promotes the intensified release of dissolved P from sediments, whilst
764 preserving a POC/TPP burial ratio that is similar to Redfield.

765 Our data support the hypothesis that benthic P release is linked via a positive feedback loop to
766 intensified primary production in the surface water and oxygen demand in the water column
767 during periods where bottom waters redox conditions promote the release of P from the
768 sediments. However, this positive feedback is limited by the formation of authigenic
769 inorganic P phases that maintains the long-term average POC/TPP burial ratio close to
770 Redfield.

771

772 **Author contribution**

773 UL, AD and SS supported the shipboard work, geochemical analysis and contributed to the
774 manuscript. CH, KW and AN helped with fruitful discussions related to the manuscript and
775 with the manuscript preparation. CL carried out the molecular analysis and contributed to the
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777

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787

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1065 **Tables**

1066 **Table 1:** Station list for the sites of the benthic lander (BIGO), multi-corer (MUC) and CTD deployments including the bottom water
 1067 concentrations of oxygen (O₂), nitrate (NO₃⁻) and sulfide (H₂S) in μM. The station numbers were according to Dale et al., 2015. bdl=below
 1068 detection limit (5 μM)

Nr.	Station	Gear	Date (2013)	Longitude (°W)	Latitude (°S)	Water depth (m)	BW O ₂ (μM)	BW NO ₃ ⁻ (μM)	BW H ₂ S (μM)
	98	CTD26	14.01.	12°13.504'	77°10.799'	75			
I	220	MUC39	25.01.	12°13.531'	77°10.061'	72	bdl	-	33.22
	110	BIGO1-2	15.01.	12°13.506'	77°10.793'	74			
	269	CTD79	29.01.	12°16.690'	77°14.999'	128			
III	248	MUC46	27.01.	12°16.697'	77°15.001'	129	bld	0.02	-
	165	BIGO2-4	20.01.	12°16.690'	77°14.995'	128			
	111	CTD29	15.01.	12°18.729'	77°17.757'	145			
IV	36	MUC10	09.01.	12°18.708'	77°17.794'	145	bdl	7.1	
	57	BIGO1-1	11.01.	12°18.711'	77°17.803'	141			
	279	CTD81	30.01.	12°21.490'	77°21.713'	195			
V	247	MUC45	27.01.	12°21.491'	77°21.702'	195	bdl	6.3	-
	201	BIGO1-4	23.01.	12°21.502'	77°21.712'	195			
	92	CTD24	13.01.	12°23.300'	77°24.200'	244			
VI	198	MUC34	23.01.	12°23.300'	77°24.228'	244	bdl	11.9	-
	74	BIGO2-2	12.01.	12°23.300'	77°24.186'	244			

	66	CTD16	12.01.	12°27.535'	77°29.593	414			
VIII	107	MUC23	15.01.	12°27.198'	77°29.497'	407	bdl	12.1	-
	207	BIGO2-5	24.01.	12°27.207'	77°29.517'	409			

1069

1070 **Table 2:** Equations for the P mass balance calculations. Results are shown in Table 4.

Equations for P mass balance calculations

P Input to the sediments ($\text{mmol m}^{-2} \text{d}^{-1}$)

- (4) Total particulate phosphorus rain rate $RR_{TPP} = RR_{PIP} + RR_{POP} = F_{TPO4} + F_{Pbur}$
- (5) Particulate inorganic phosphorus rain rate $RR_{PIP} = RR_{POC} / \left(\frac{POC}{PIP} \right)$
- (6) Particulate organic phosphorus rain rate $RR_{POP} = RR_{POC} / \left(\frac{POC}{POP} \right)$
- (7) Terrigenous P input ($P/Al = 0.02$, Vier et al., 2009) $RR_{Pterr} = Al_{(0-1)} * MAR * \frac{P}{Al}$

P Burial in the sediments ($\text{mmol m}^{-2} \text{d}^{-1}$ and $\text{g m}^{-2} \text{d}^{-1}$) at 11 cm

- (8) Phosphorus burial flux $F_{Pbur} = MAR * P_{11}$
- (9) Mass accumulation rate $MAR = \rho_{dry} * (1 - \Phi_{\infty}) * SR$
- (10) TPP burial efficiency $PBE = MAR * \left(\frac{P_{11}}{RR_{TPP}} \right) * 100 \%$

P release from the sediments ($\text{mmol m}^{-2} \text{d}^{-1}$)

Benthic P fluxes (F_{TPO4}) and the potential diffusive P fluxes were determined as described in the methods

- (11) P release from POP degradation according to Redfield ($C/P = 106$) $F_{P(Red)} = F_{DIC}/106$
- (12) True P release from POP $F_{P(POP)} = F_{DIC} / \left(\frac{POC}{POP} \right)$
- (13) P release from total particulate phosphorus $F_{P(TPP)} = F_{DIC} / \left(\frac{POC}{TPP} \right)$
- (14) P release from the dissolution of Fe (oxyhydr)oxides ($Fe/P = 10$, Slomp et al., 1996) $F_{P(Fe)} = F_{Fe2+} / \left(\frac{Fe}{P} \right)$
- (15) P deficit to outbalance the P budget $F_{P(deficit)} = RR_{TPP} + RR_{terr} + F_{P(Fe)} - (F_{TPO4} + F_{Pbur})$
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1073 **Table 3:** In situ benthic chamber TPO₄ fluxes in mmol m⁻² d⁻¹ along the 12°S transect. The
 1074 numbers are shown as an average calculated from the minimum and maximum flux
 1075 determined from two benthic chambers.

Station		Water depth (m)	F _{TPO4} (mmol m ⁻² d ⁻¹)
I	BIGO1_2	74	1.04 ± 0.31
II	BIGO1_5	101	0.35 ± 0.01
III	BIGO2_4	128	0.30 ± 0.05
IV	BIGO1_1	141	0.23 ^a
V	BIGO1_4	195	0.12 ^a
VI	BIGO2_2	243	0.44 ± 0.07
VII	BIGO2_1	306	0.26 ± 0.04
VIII	BIGO2_5	409	-0.07 ^a
IX	BIGO2_3	756	0.06 ^a
X	BIGO1_3	989	0.02 ± 0.02

1076 ^a only one benthic flux was measured

1077 **Table 4:** Measured and calculated parameters for the P mass balance along the 12°S transect. The numbers in front of key parameters
 1078 correspond to equations in Table 2.

12°S	Transect section I		Transect section II			Phosphorite formation	
	Station I 74 m	Station III 128 m	Station IV 141 m	Station V 195 m	Station VI 244 m	Station VIII 407 m	
Benthic chamber TPO₄ flux (F_{TPO4})* mmol m ⁻² d ⁻¹	1.04 ± 0.31	0.3 ± 0.05	0.23 -	0.12 -	0.44 ± 0.07	-0.07 -	
Potential (diffusive) TPO₄ flux (pot. F_{TPO4}) mmol m ⁻² d ⁻¹	1.07 ± 0.23	2.0 ±	0.5 ±	1.6	1.5 ±		
Relative abundance of Marithioplococci-related bacteria* copies g ⁻¹ (0-5 cm sediment depth)	4159		1687	3072		190	
Benthic chamber DIC flux (F_{DIC})** mmol m ⁻² d ⁻¹	65.9 ± 21	20.4 ± 7	8 ± 0.4	3.2 ± 1	4.7 ± 1	2.2 ± 0.3	
POC rain rate (RR_{POC})** mmol m ⁻² d ⁻¹	79.5 ± 33	28.2 ± 12	10.5 ± 3	12.5 ± 6	10.6 ± 4	2.7 ± 1	
Sediment accumulation rate (ω_{acc})** cm yr ⁻¹	0.45 ± 0.09	0.2 ± 0.04	0.04 ± 0.008	0.1 ± 0.02	0.07 ± 0.014	0.01 ± 0.002	
Mass accumulation rate (MAR)** g m ⁻² yr ⁻¹	1800 ± 360	600 ± 120	128 ± 26	320 ± 64	182 ± 37	44 ± 9	
Ratios for particulate matter from the water column (2 to 5 m above the sea floor):							
POC/TPP*	76 ± 4	68 ± 9	94 ± 10	132 ± 36	62 ± 9	96 ± 9	
POC/PIP*	197 ± 17	125 ± 34	291 ± 79	385 ± 7	217 ± 34	209 ± 34	
POC/POP*	126 ± 17	149 ± 29	142 ± 3	214 ± 87	87 ± 29	178 ± 29	
(4) TPP rain rate (RR_{TPP})	1.00 ± 0.31	0.40 ± 0.09	0.11 ± 0.02	0.09 ± 0.02	0.17 ± 0.02	0.03 ± 0.01	

mmol m ⁻² d ⁻¹							
(5) PIP rain rate (RR_{PIP})	0.39 ± 0.14	0.22 ± 0.04	0.04 ± 0	0.03 ± 0.02	0.05 ± 0.01	0.01 ± 0.01	
mmol m ⁻² d ⁻¹							
(6) POP rain rate (RR_{POP})	0.61 ± 0.18	0.18 ± 0.05	0.07 ± 0.02	0.06 ± 0.01	0.12 ± 0.01	0.01 ± 0.01	
mmol m ⁻² d ⁻¹							
(7) Terrigenous P input (RR_{Pterr})	0.10 -	0.02 -	0.01 -	0.02 -	0.01 -	0.00 -	
(8) Burial flux (F_{Pbur}) in 11 cm sediment depth	0.23 -	0.09 -	0.02 -	0.08 -	0.04 -	0.13 -	
mmol m ⁻² d ⁻¹							
Avg. Al conc. (0-1 cm sediment)							
(Al₀₋₁)*	0.99 -	0.70 -	1.10 -	0.97 -	0.72 -	0.66 -	
mmol g ⁻¹							
Avg. P conc. (0- 11 cm sediment)							
(P₁₁)*	0.05 -	0.05 -	0.07 -	0.09 -	0.08 -	1.05 -	
mmol g ⁻¹							
(10) P burial efficiency (PBE) at 11cm sediment depth	26 ± 8	23 ± 4	23 ± 5	92 ± 20	23 ± 2	490 ± 100	
%							
(11) P release from POP degradation according to Redfield (F_{P(Red)})	0.62 ± 0.2	0.19 ± 0.06	0.08 ± 0.01	0.03 ± 0.01	0.04 ± 0.02	0.02 ± 0	
mmol m ⁻² d ⁻¹							
(12) P release from POP degradation (F_{P(POP)})	0.52 ± 0.16	0.14 ± 0.05	0.06 ± 0.01	0.02 ± 0.01	0.05 ± 0.02	0.01 ± 0	
mmol m ⁻² d ⁻¹							
(13) P release from TPP degradation (F_{P(TPP)})	0.87 ± 0.17	0.3 ± 0.1	0.09 ± 0.01	0.02 ± 0.01	0.08 ± 0.02	0.02 ± 0.01	
mmol m ⁻² d ⁻¹							
Benthic diffusive TPO₄ flux (potential P flux)*	1.08 ± 0.23	2.0 -	0.5 -	1.6 -	1.5 -	- -	
Diffusive Fe²⁺ flux (F_{Fe2+})*	0.04 ± 0.02	0.01 -	0.02 -	0.0 -	0.03	0.0	

(14) P release from								
Fe (oxyhydr)oxides ($F_{P(Fe)}$)	0.004	± 0.002	0.001	0.002	0.0	0.003	0.0	
mmol m ⁻² d ⁻¹								
(15) P required to outbalance the P								
budget ($F_{P(deficit)}$)	-		-	0.12	0.09	0.3	-	
mmol m ⁻² d ⁻¹								

1079 * this study

1080 **published data from Dale et al. (2015)

1081 **Figure captions**

1082 **Figure 1:** Study area, sampling stations and O₂ concentration in μM along the 12°S transect.

1083 **Figure 2A:** Concentration profiles of TPP, PIP, POP and POC of the water column particles
1084 and the surface sediments along the 12°S transect. Water column particle concentrations
1085 (upper panel) are given in $\mu\text{mol L}^{-1}$ and surface sediment concentrations (lower panel) are
1086 shown in $\mu\text{mol mg}^{-1}$. Note that the water column particle concentrations shown for station VI
1087 (244 m) at 10 m water depth are ~ 5 times higher than at the other stations.

1088 **Figure 2B:** Ratios of POC to TPP, PIP and POP (POC/xP) along the 12°S depth transect of
1089 water column particles and surface sediments (0 – 5.5 cm depth) of station I to VIII (74 to 407
1090 m).

1091 **Figure 3:** Average distribution of POP and PIP (%) per station in the water column particles
1092 and in the top 5.5 cm of the sediments.

1093 **Figure 4A:** Measured benthic TPO₄ fluxes ($\text{mmol m}^{-2} \text{d}^{-1}$) at 12°S. The black line shows the
1094 theoretical TPO₄ flux generated from organic matter degradation with a Redfield POC/POP
1095 ratio of 106.

1096 **Figure 4B:** Potential TPO₄ fluxes ($\text{mmol m}^{-2} \text{d}^{-1}$) calculated from porewater profiles
1097 compared to the measured benthic TPO₄ fluxes ($\text{mmol m}^{-2} \text{d}^{-1}$) at stations I to VIII (74 to 407
1098 m). The black line with triangles depicts the TPO₄ flux that could be generated during
1099 degradation of total particulate phosphorus.

1100 **Figure 4C:** P percentages of the different P sources and the missing P that is needed to
1101 maintain the measured TPO₄ release rates and P burial fluxes for stations IV, V and VI (141,
1102 195 and 244 m) of transect section II. The missing P is assumed to be supplied by sulfide-
1103 oxidizing Marithioploca-related bacteria (see Discussion).

1104 **Figure 5:** Mass balance calculations and measured benthic TPO₄ fluxes for stations I to VIII
1105 (74 to 407 m). All fluxes are in $\text{mmol m}^{-2} \text{d}^{-1}$.

1106 **Figure 5A:** POP rain rates, TPO₄ fluxes and P burial rates only. The number in percent
1107 denotes missing P needed to sustain the benthic TPO₄ fluxes.

1108 **Figure 5B:** Mass balance calculations including the POP and PIP rain rates, the terrigenous P
1109 input, P release from the reductive dissolution of Fe (oxyhydr)oxides and the benthic TPO₄
1110 fluxes into the bottom waters as well as the P burial rates.

1111 **Figure 6:** Measured benthic TPO₄ fluxes versus relative abundance of Marithioploca in cells
1112 g⁻¹ in the upper 5 cm of the sediment. Highest abundance and TPO₄ flux was found at station
1113 I. The other data points are for the stations IV, VI and VIII (with decreasing abundance and
1114 TPO₄ flux).

1115 **Figure 7:** Comparison of porewater PO₄³⁻ concentrations (blue) before and after the
1116 freeze/thaw experiments (red) in μmol L⁻¹.