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How to develop a bio-based phosphorus mining strategy for eutrophic marine sediments: Unlocking native microbial processes for anaerobic phosphorus release

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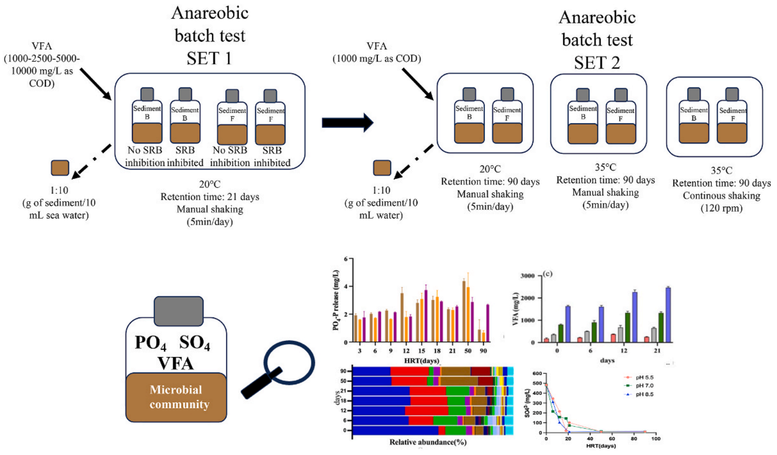
HIGHLIGHTS

- Introducing waste derived VFA to marine sediment triggered anaerobic P release.
- Temperature, pH and HRT affected P release efficiencies.
- *Desulfomicobiaceae* were found as dominant SRB in the batch bioreactors.
- Low P releases could be attributed to the complex nature of marine sediment.
- PAOs were not enriched during batch bioreactor operation.

GRAPHICAL ABSTRACT



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ABSTRACT

This study examined the anaerobic release of phosphorus (P) from two different Baltic Sea sediments (B and F), focusing on the impact of initial concentration of externally introduced waste-derived volatile fatty acids (VFA) as the carbon source, temperature, pH, and mixing conditions. The first batch bioreactor set was operated to demonstrate the effect of VFA on anaerobic P release at different concentrations (1000–10000 mg/L as COD) at 20 °C. A notable P release of up to 15.85 mg/L PO_4–P was observed for Sediment B at an initial carbon concentration of 10000 mg COD/L. However, VFA consumption in the bioreactors was minimal or no subsequent. The second batch bioreactor set was carried out to investigate the effect of temperature (20 °C-35 °C), pH (5.5,

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Anoxic sediment
Eutrophication

7.0 and 8.5) and mixing conditions on P release by introducing lower initial carbon concentration (1000 mg COD/L) considering the potential risk for VFA accumulation in the bioreactors. Maximum P releases of 4.4 mg/L and 3.5 mg/L were for Sediment B and Sediment F, respectively. Two-way ANOVA tests revealed that the operation time and pH and their interactions were statistically significant ($p < 0.05$) for both sediments while the effect of mixing was not statistically significant. Most of the sulfate was reduced during batch bioreactor operation and *Desulfomicobiaceae* became dominant among other sulfate-reducing bacteria (SRB) possibly shows the importance of SRB in terms of anaerobic P release. This study gives an insight into future implementations of phosphorus mining from eutrophic environment under anaerobic conditions.

1. Introduction

Phosphorus (P) is a crucial source for living organisms and it plays a fundamental role in synthesizing genetic and cellular components as well as for other metabolic activities and energy transfer (Sosa, 2018). Besides, it stands as an irreplaceable element for anthropogenic activities, especially in the domain of crop production. One of the major concerns for sustaining agricultural activities with the increasing global population is the food security risk due to finite phosphate ore reserves and their uneven distribution in the world (Schoumans et al., 2015). European Union has very limited P sources and the supply chain is predominantly dependent on imports, so; P was announced as a critical raw material in 2014 (European Commission, 2014). Meanwhile, poor agricultural practices and deficient wastewater treatment led to the accumulation of nutrients in European water bodies and consequently, compounded the eutrophication problem. Notably, the Baltic Sea is facing a severe eutrophication problem with more than 97% of the marine region being subjected to eutrophication (European Commission, 2023).

Bio-based P recovery using mussels, algae, plants or microorganisms from polluted natural resources (i.e., eutrophic water bodies) can be considered a win-win approach for ensuring P for global human consumption while simultaneously remediating water bodies to mitigate eutrophication (Cakmak et al., 2022). The profound research gap concerning P recovery from polluted marine environments can be addressed by harnessing well-established applications in wastewater treatment and the learning-from-nature concept. For instance, phosphate accumulating microorganisms (PAOs) in marine sediment could play a key role in developing a P recovery strategy from marine sediments. In enhanced biological phosphorus removal (EBPR) processes, an anaerobic stage is employed through the addition of an organic carbon source (volatile fatty acids) to synthesize polyhydroxyalkanoates (PHA) and release of PO_4–P by hydrolysis of intracellular poly-P (Seviour et al., 2003). Likewise, in marine environment, the poly-P can serve as an energy source for PAOs as well as heterotrophs under anaerobic conditions leading to phosphate release (Ingall and Jahnke, 1997). Sulfate-reducing bacteria (SRB) can be another key player in P recovery from marine sediment. They initiate sulfate reduction by using carbon as the energy source and lead to sulfide formation followed by Fe reduction, precipitation of Fe (II) with S/S_2 and, eventually, release of P which are previously bonded to Fe under anoxic conditions (Pan et al., 2019; Wijsman et al., 2002). So, research focusing on employing key microorganisms for P release from marine sediment under anaerobic conditions with the addition of external carbon will give insight for future implementations. Subsequently, the P released from the marine sediment can be recovered from the liquid phase via physical adsorption and chemical precipitation such as struvite, vivianite and hydroxyapatite (Zhu et al., 2023).

Beyond the role of microorganisms for anaerobic P release from marine sediment, operational conditions such as temperature, pH, and mixing conditions also play a crucial role in designing engineering systems. In both fresh and marine water bodies, the rate of P release increases along with temperature increase due to the stimulation of mineralization, reducing redox potential at the surface sediment and increase in diffusion rates (Gibbons and Bridgeman, 2020). Phosphorus fractions in the sediment are also sensitive to pH alterations that can lead to P release from the marine sediment (Nyguen and Maeda, 2016). Finally, mixing in natural marine environments such as water movements and bioturbation is stated to promote P release (Vaalama et al., 2019). Although some studies explored the effect of temperature, pH and mixing on P release from sediments, the investigations in the context of engineering applications for phosphorus recovery remain unclear especially when an external organic carbon source is introduced.

The primary focus of this paper is to investigate the applicability of a bioengineering approach to release P from eutrophic marine sediments under anaerobic conditions. The specific objectives of this paper include i) investigation of the effect of waste-derived VFAs as a carbon source and operational conditions (temperature, pH, time, mixing) on P release from the marine sediments and ii) monitoring of microbial community shifts along the anaerobic operation and revealing key microorganisms for P release. To reach these specific objectives above, batch scale anaerobic bioreactors were operated at various conditions, including different VFA concentrations, operation time, pH, temperature and continuous mixing vs. manual mixing conditions. Importantly, the changes in PO_4–P, VFA and SO_4^{2-} concentrations were monitored to reveal underlying mechanisms of the P release under anaerobic batch bioreactor operation. Furthermore, the microbial community were also monitored during the anaerobic batch bioreactor operation to observe their response to different operational conditions and to understand the relationship between PO_4–P release, SO_4^{2-} consumption and microbial community change.

2. Materials and methods

2.1. Experimental setup for anaerobic batch tests

Seawater and sediment samples were collected from two different areas located in Stockholm Archipelago, the Baltic Sea: Baggensfjärden (B) (59.319561 N, 18.34675 E) and Farstaviken (F) (59.32628 N, 18.35872 E), respectively (Supplementary Material Figure S1). Both seawater and sediment samples were kept at 4 °C before characterization and batch experiments. Two sets of anaerobic batch tests (Table 1 and Supplementary Material Figure S2) were conducted to evaluate the anaerobic P release from the marine sediments at different operational conditions, including VFA concentration, temperature, pH, operation time, and mixing. In the first set, the influence of the carbon source (VFA) concentration was examined. VFA-rich effluent (COD_{ave}: 37618 mg/L; VFA content: 10–16% of COD; TN_{ave}: 1257 mg/L, TP_{ave}: 238 mg/L, PO_4-P_{ave}: 206 mg/L) was taken from a pilot-scale reactor from Hammarby Sjöstadsverk (Stockholm, Sweden) (Owusu-Agyeman et al., 2022). COD concentrations in the anaerobic batch bioreactors were adjusted as 1000, 2500, 5000 and 10000 mg COD/L by adding the required amount of VFA-rich effluent. Herein, the COD originating from the sediment were not taken into account in the calculations due to the negligible amount in the liquid phase. Furthermore, the stated concentrations represent not only VFA but also incorporate other carbon sources. In this set, the effect of SRB on P release mechanisms was also investigated by inhibiting the SRB through the addition of 2 mM of ammonium molybdate to some batch bioreactors. The experiments were conducted at 20 °C with manual shaking (5 min each day). Initial pH was not set after addition of the VFA mixture (Table 1). Samples were taken at three-day intervals until the end of the experiment (21 days). For the SRB inhibition experiment, samples were only taken at the end of the experiment (21 days). In the second set, the effect of temperature (20 °C, 35 °C), pH (5.5, 7.0 and 8.5), operation time and mixing regime (continuous at 120 rpm vs. manual at 35 °C) on the release of anaerobic P were tested. In this set, COD concentrations in the batch bioreactors were adjusted to 1000 mg/L by adding VFA-rich effluent. In this set, samples were taken at three-day intervals until 21 days. An additional two sets of samples at days 50 and 90 were also collected to observe the effect of long-time operation on VFA consumption and P release. Both anaerobic batch experiment sets were performed in 20–50 mL serum bottles that contained both sediment and seawater mixture with a ratio of 1:10 (g of sediment: mL of seawater) Anaerobic conditions were provided via purging with N_2 gas for 4 min. The allocation of bottles was determined considering destructive sampling and triplicate setup. Control experiments (duplicate) with sediment and seawater mixture were also performed without adding VFA-rich effluent.

2.2. Analytical methods

The seawater and porewater samples (overlying water after centrifugation of the sediment at 2500 rpm for 15 min) were filtered with a 0.45 μm cellulose membrane filter for detailed characterization. PO_4–P levels in both seawater and porewater were measured by spectrophotometric analysis with the Hach Lange test kit (LCK 349) and the method stated in Murphy and Riley (1962). Cations and anions concentrations were also measured with an Ion Chromatography (850 Professional IC, 2.850.2030, Metrohm) instrument equipped with a Metrosep A Supp 5–150/4.0 (6.1006.520, Metrohm) for anions, conductivity detector and 863 Compact IC Autosampler (2.863.0010, Metrohm) with injection volume of 10 μL for sample measurement. Sample eluents of 2.5 mM HNO_3 and 1 mM $NaHCO_3$ + 3.2 mM Na_2CO_3 were used for cations and anions measurements respectively, at a flow rate of 0.9 mL/min in both cases. Total and volatile solids for sediment and seawater samples were measured by Standard Methods (APHA, 1998). P content and its fractions in the sediment were measured by the Standards in Measurements and Testing (SMT) protocol stated by Pardo et al. (2003). Total nitrogen content in the sediments was measured by Hach Lange kits (LCK 138) by using Hach Lange DR 3900 Spectrophotometer. The pH was measured with the Mettler Toledo pH meter.

The batch bioreactor samples were centrifuged at 2500 rpm for 15 min and the supernatant were filtered by 0.45 μm cellulose membrane filter prior to PO_4–P (Hach Lange kit, LCK 349 and Murphey and Riley, 1962) and SO_4^{2-}(IC) measurements. PO_4–P releases were calculated by subtracting initial (at day 0) concentrations from the PO_4–P concentrations for each operation time. This calculation was done to eliminate the PO_4–P due to the addition of VFA-rich effluent (See Section 2.1). pH of the bioreactor samples was measured with the Mettler Toledo pH meter. For determination of VFA, the supernatant was filtered with a 0.2 μm cellulose membrane filter, and the filtered samples were acidified with phosphoric acid. VFA concentrations including (acetic acid, butyric acid, propionic acid etc.) in the bioreactors were analyzed by gas chromatography (GC 6890, Agilent) as reported elsewhere (Atasoy et al., 2019).

2.3. Microbial community analysis

The sediment samples from the second anaerobic batch set were screened for microbial community analysis to assess the change in the microbial community and define the key species for P release. The sediment samples (triplicate) from batch bioreactors were collected at day 0, 6, 12, 18, 21, 50 and 90, and were stored at −20 °C. For DNA extraction, composite samples (a mix of duplicates/triplicates of each sampling day) were weighted and approximately 0.3 g of the sediment from the composite sample was used for DNA extraction in duplicates. DNA extraction protocol was performed with the Nucleospin Soil Kit (Macherey-Nagel, Germany) and the extracted DNA samples were stored at −20 °C before PCR amplification was performed. PCR amplification was carried out as reported elsewhere (Owusu-Agyeman et al., 2021). Briefly, primers 515F (GTGYCAGCMGCCGCGGTAA) and 806R (GGACTACNVGGGTWTCTAAT) (Caporaso et al., 2010) as well as Red Taq DNA Polymerase Master Mix (VWR international) were used. Also, a thermal cycler (Techne® Prime) was utilized for amplification (Initial denaturation at 95 °C for 5 min, 28 cycles at 95 °C for 1 min, 55 °C for 1 min, 72 °C for 1.5 min, and a final elongation step at 72 °C for 5 min). Later, index PCR was done using the PCR product from the previous step, Red Taq DNA Polymerase Master Mix (VWR international) as well as different index primers to label each sample uniquely. With this approach, sequencing libraries were prepared. The amplification conditions for this step were initial denaturation at 95 °C for 5 min followed by 5 cycles of 95 °C for 30 s, 60 °C for 30 s, 72 °C for 30 s, and a final elongation step at 72 °C for 5 min. Finally, normalization was performed using SequalPrep TM Normalization Plate (96) Kit (Invitrogen, Life Technologies, Thermo Fisher, USA). The normalized samples were sent to Science for Life Laboratory (Stockholm, Sweden) for the sequencing by Illumina MiSeq. After the data are received from the laboratory, bioinformatic analysis was performed using QIIME2, and the SILVA database was used for the taxonomy assignments for bacteria and archaea (97% similarly cut-off value). The raw sequence data is available at NCBI (PRJNA1105638).

2.4. Statistical analysis

A *t*-test and an ANOVA test (alpha level:0.05) were conducted to find the significance of independent variables on the PO_4–P releasing efficiency. Correlation analysis was done to reveal the relationship between PO_4–P and VFA concentration in the first set of batch bioreactors. Redundancy analysis (RDA) was run to find out the relationship between PO_4–P release and SO_4^{2-} reduction as well as the microbial community in the second set of batch reactors. Furthermore, a one-way PERMANOVA test was conducted to evaluate the effects of operational conditions on the microbial community. RDA was accomplished using XLSTAT. Other statistical tests as well as visualization of graphs were performed in GraphPad Prism 9.

3. Results and discussion

3.1. Characterization of sea water, sediment and porewater

The results of the characterization of the seawater, sediment and porewater samples are presented in the Supplementary Material (Table S1). Briefly, the dissolved oxygen level was found to be

Table 1

Experimental setup for the anerobic batch experiments.

Set number	VFA (mg/L as COD)				Temperature		pH			Mixing	
	1000	*2500*	*5000*	*10000*	*20 °C*	*35 °C*	*5.5*	*7.0*	*8.5*	*Continuous*	*Manual*
1	[a]	[a]	[a]	[a]	[a]		variable pH (5.6-7.2)				[a]
2	[a]				[a]	[a]	[a]	[a]	[a]	[a]	[a]

[a] Operational conditions of the set 1 and 2.

completely depleted at Farstaviken (0 mg/L) and the PO_4–P concentration in the seawater sample was 0.33 mg/L which could be expected under anoxic conditions. The PO_4–P concentration in the seawater sample from Baggensfjärden was lower (0.03 mg/L) and the dissolved oxygen level was relatively higher. The PO_4–P concentrations in the pore water were measured as 1.52 mg/L and 2.68 mg/L for Baggensfjärden and Farstaviken, respectively showing the effect of oxygen availability on P release. Particularly, dissolved oxygen has a notable role in the transformation of Fe/Al bounded P. In aerobic conditions, Fe/Al bounded P was intensely adsorbed onto surface sediments, on the contrary; anoxic conditions lead to Fe/Al bounded P release followed by triggered growth of algae that can release also other P (Ca bounded P or organic P) (Jiang et al., 2008).

Total sedimentary P in both samples (1096–1225 μg P/g) were similar. Inorganic P (%) was higher than organic P in both sediment samples and the ratio of non-apatite inorganic P (i.e., Al and Fe bounded P) was higher than apatite inorganic P (i.e., Ca bounded P). In engineering applications such as P recovery from sewage sludge, the efficiency of P recovery predominantly relies on the P dissolution potential (Saoudi, 2022). Indeed, it is also essential to classify the speciation of P in marine sediment for investigating P recovery applications. The presence of non-apatite P is important in terms of P release under anaerobic conditions because of Fe reduction potential (Adhikari et al., 2015). On the other hand, apatite inorganic P shows limited P release especially under acidic conditions (Adhikari et al., 2015) and they are also extremely stable under alkaline conditions (Diaz et al., 1994; Barik et al., 2019). Moreover, organic P is formed due to the mineralization of organic matter (Barik et al., 2019) and it can either serve as a major source of dissolved P in the water column or it can serve as a sink for permanent P burial in sediments (Rydin et al., 2023).

3.2. *Effect of initial VFA concentration on anaerobic P release*

The effect of different initial VFA concentrations on the anaerobic P release from the sediment samples is shown in Fig. 1(a and b). The highest P release of 6.14 mg PO_4–P/L on day 21 was observed for sediment F with a VFA loading of 1000 mg COD/L. Conversely, the control bioreactor (no VFA addition) exhibited the lowest PO_4–P/L release at each operation time and the highest P release from the control was 1.09 mg PO_4–P/L on day 12. In the bioreactors operated with sediment B, the highest P release was observed with the addition of 10000 mg COD/L after 21 days, which was 15.85 mg PO_4–P/L. The control bioreactor for sediment B presented the maximum P release (0.69 mg PO_4–P/L) on day 18. As the P release was compared with total phosphorus (TP) in the sediment, the maximum P release was 5.6% and 14.5% of the TP in sediment F and sediment B, respectively. It can be argued that the differences in biochemical composition of the sediments (i.e., organic matter, particle size) might influence the P release. For instance, the granulometry and organic matter content were found to be the major factors for the distribution of the P forms in the Netravathi-Gurupur estuary on the southwestern coast of India (Saha et al., 2023). In another study (Ma et al., 2023), P increase related to nitrogen inputs varied depending on the sediment type and temperature. Furthermore, the microbial community can vary depending on the concentrations of organic carbon, nitrogen and phosphorus in the sediment (Sinkko et al., 2013) which can directly affect P release in

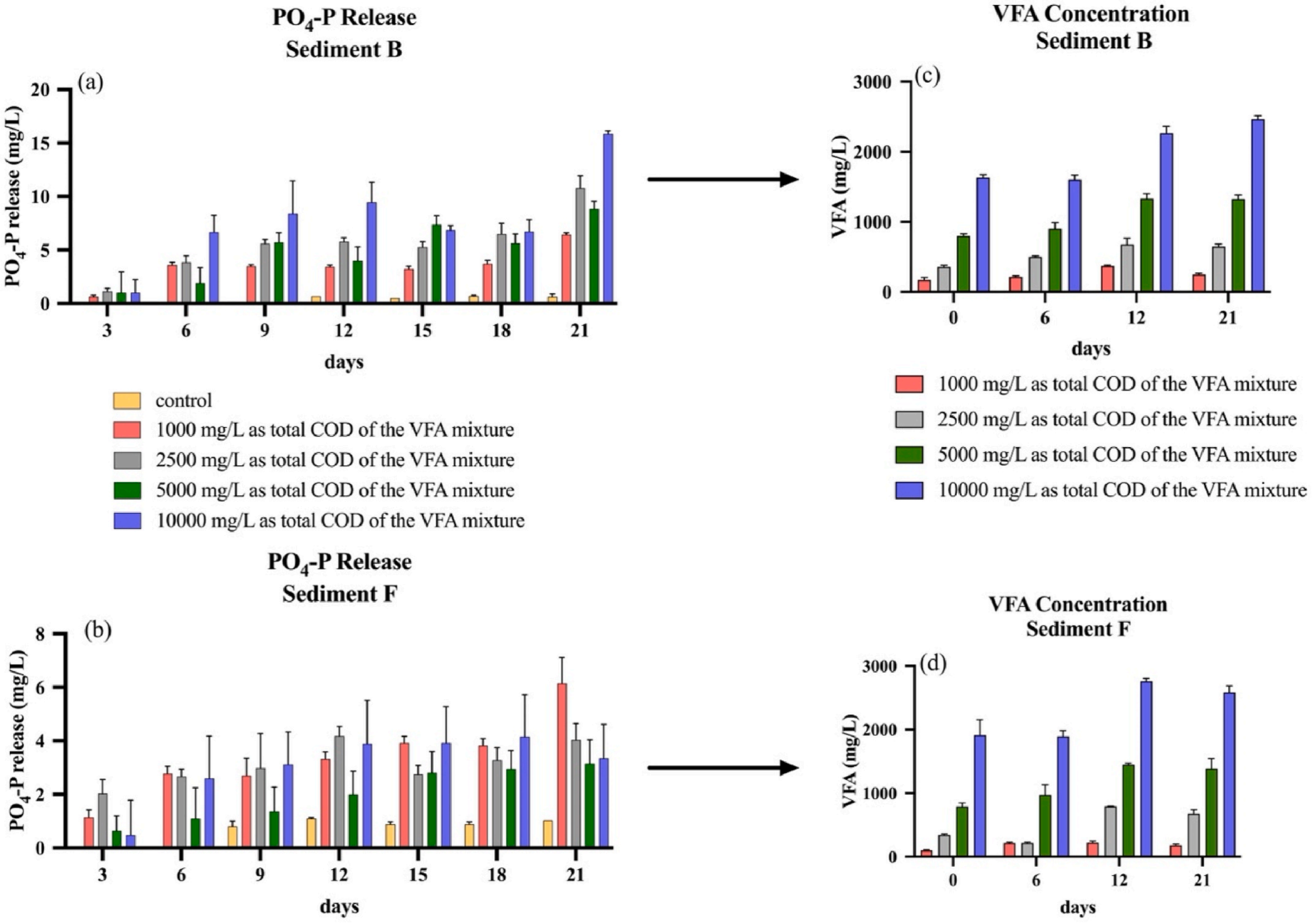


Fig. 1. P releases (a–b) and VFA concentrations (c–d) in the bioreactors operated with different VFA loading.

anaerobic conditions.

In this set, SRB inhibition was also tested. Accordingly, PO_4–P release was not observed for both sediment B and sediment F batch bioreactors after day 21 with the inhibition, and the PO_4–P concentrations in the liquid phase were below the initial PO_4–P concentrations in the bioreactors (data not shown). This result held significance in terms of the role of SRBs in anaerobic bioreactor operation. In marine sediments, SRBs are able to catalyze the reduction of sulfate into sulfide followed by the oxidation of organic matter and P release. Furthermore, sulfide can also form a precipitate with iron (FeS/FeS_2) that stimulates P release in anoxic conditions (Rozan et al., 2002; Pan et al., 2019). So, inhibition of the aforementioned pathways likely resulted in either the oxidation of organic matter by SRBs or the breaking down of Fe-bounded P in the marine sediment to form FeS/FeS_2.

VFA concentrations in batch bioreactors were also monitored (Fig. 1c and d, the results for the control bioreactors are not given due to very low concentrations). The correlation analysis between VFA concentration and P release (See Supplementary Material, Table S.2) showed that the correlation between initial VFA concentration in the bioreactors and P release was moderately positive ($r = 0.6677$) for the experiments operated with Sediment B. However, there is a very weak linear correlation ($r = -0.1502$) between VFA concentration and P release in the bioreactors operated with sediment F. In the batch bioreactors operated with sediment F, VFA concentrations increased steadily until day 12. Subsequently, a minor portion of VFA was consumed, resulting in a decrease up to 17%. In the bioreactors operated with sediment B, a VFA increase was observed until day 12 followed by minimal or no subsequent VFA consumption. VFA accumulation during the bioreactor operation can be likely attributed to the characteristics of the VFA mixture. The presence of other organic carbon sources in the VFA-rich effluent could be degraded by the marine microbiome and possibly result in the accumulation of VFA in the bioreactors. In anoxic marine sediments, organic matter is degraded via sequential steps including extracellular hydrolytic degradation of polymers, fermentation of monomers to VFAs and H_2, and terminal oxidation of VFA and H_2 into CO_2 and H_2O (Finke and Jørgensen, 2008). Both batch bioreactor sets showed notable accumulation of VFAs (in mg/L) due to organic matter mineralization and the most dominant VFA was acetic acid during the initial days of the experiment. Especially, acetic acid is a key intermediate product for SRBs and methanogens (Sansone and Martens, 1982). After the initial days of the experiment, other VFAs such as caproic acid, butyric acid and propionic acid started to accumulate. The accumulation of longer chain VFAs at a later stage is attributed to the shift in the fermentation pathways towards higher chain VFAs (Finke and Jørgensen, 2008). Furthermore, as the concentration of the VFA mixture introduced to the system increased, the accumulation of other VFAs was much more prevalent at the end of the experiment (Supplementary Material, Figure S3). Our study also showed that VFA consumption was very limited in the experiments. In natural aquatic environments, the concentrations of fermentation products (i.e., VFAs) are generally very low since thermal oxidizers such as sulfate reducers or methanogens have a higher capacity to oxidize fermentation by-products more efficiently than the rate at which fermentation occurs (Finke and Jørgensen, 2008). However, in this study, introducing excess organic carbon sources could lead to the accumulation of VFAs and the rate of consumption was not as visible as VFA production based on the data we obtained. At this point, longer retention time (longer than 21 days) could help to observe VFA consumption in the long terms. Furthermore, the use of pure VFA can be more applicable to deeply investigate the VFA reduction capacity of the mixed microbiome and P release and uptake mechanisms. Additionally, continuous bioreactor systems with anaerobic-aerobic operation would provide better organic carbon consumption and P release than batch bioreactor systems due to improved microbial activity.

3.3. Effect of temperature, pH, and mixing conditions on anaerobic P release

The results of the previous batch bioreactor set showed that waste-derived VFA addition improved P release efficiency from the sediment samples. However, one of the main limitations of using waste-derived VFAs was the presence of other carbon sources and nutrients in the mixture at high concentrations. Although additional P input to the bioreactors would make the P recovery more feasible, it was observed that there was no significant consumption of VFA for metabolic activities. Consequently, introducing high concentrations of VFA mixture (i.e., 10000 mg/L as COD) could lead to excess carbon in the bioreactor systems. Considering all of the above, the minimum tested VFA loading (1000 mg/L as COD of the VFA mixture) was selected for further process optimization in terms of other operational conditions.

Fig. 2(a–f) depicts the P release from the bioreactors operated with sediment B and sediment F at three different initial pHs (5.5, 7.0, and 8.5), two different temperatures (20 °C and 35 °C) and certain mixing conditions at 35 °C. For the bioreactors operated with sediment B, the highest P release was 4.4 mg PO_4–P/L at pH 5.5 (20 °C, at day 50 as well as 35 °C mix, at day 50). Remarkably, there was also a prompt release (4.3 mg PO_4–P/L) at day 3 (pH 5.5, 35 °C mix). Control bioreactors showed lower P releases at each of the assayed conditions. At 35 °C, regardless of the mixing conditions, the P releases were higher than those found at 20 °C up to 9 days. Two-way ANOVA tests for the bioreactors operated with sediment B revealed that the operational conditions (operation time and pH) and their interactions were statistically significant ($p < 0.05$) for all data sets when the experimental setups were analyzed within the same temperature. Additionally, unpaired *t*-test results showed that the effect of mixing was insignificant ($p > 0.05$) at all pH values regarding the P release.

In the case of the bioreactors operated with sediment F, the highest P release was measured as 3.5 mg PO_4–P/L (20 °C, pH 7.0, at day 15). At 35 °C, the highest P was observed as 3 mg PO_4–P/L (pH 8.5, at day 12). Two-way ANOVA tests showed that operational conditions (operation time and pH) and their interactions were statistically significant ($p < 0.05$) for 20 °C and 35 °C when the experimental setups were analyzed at the same temperature. Unpaired *t*-test results also revealed that the effect of mixing was not significant ($p > 0.05$) at all pH values.

In this set, VFA concentrations were also monitored (See Supplementary Material, Figure S4-S5). The VFA concentrations slightly increased in the first 6 days, and acetic acid was the dominant species at all the operational conditions in the bioreactors containing sediment F as observed in the first set of anaerobic batch reactors. Remarkably, there was no significant consumption of acetic acid during bioreactor operations, whereas propionic, butyric and caproic acids accumulated and later decreased in most of the cases. Besides that, VFAs were consumed in the bioreactor experiments with sediment B, especially after day 50 in most of the cases. However, the same trend was not observed for sediment F.

In this study, changes in SO_4^{2-} concentrations in the batch bioreactors were also monitored to investigate possible anaerobic sulfate reduction (Fig. 3). At all the operational conditions, the SO_4^{2-} concentrations started to decrease from the first day and most of the bioreactors showed a decreasing trend through operation. This data revealed that SO_4^{2-} consumption was probably related to the presence of the SRBs. Interestingly, microbial sulfate reduction can take place via two pathways: anaerobic oxidation of methane and organoclastic sulfate reduction. For some bioreactors (i.e., sediment B at 20 °C, pH 5.5 and pH 7.0, day 90) SO_4^{2-} concentrations increased which could be explained by the oxidation of SO_4^{2-} via sulfur compounds of intermediate oxidation state, which occurs by means of complex chemical and biological reactions. In literature, it was speculated that bacterial metabolism can form sulfate by using elemental sulfur and amorphous ferric hydroxide as the substrates (Thamdrup et al., 1993). Furthermore, it was also observed that increasing MnO_2/H_2S ratios promotes thiosulfate and sulfate production

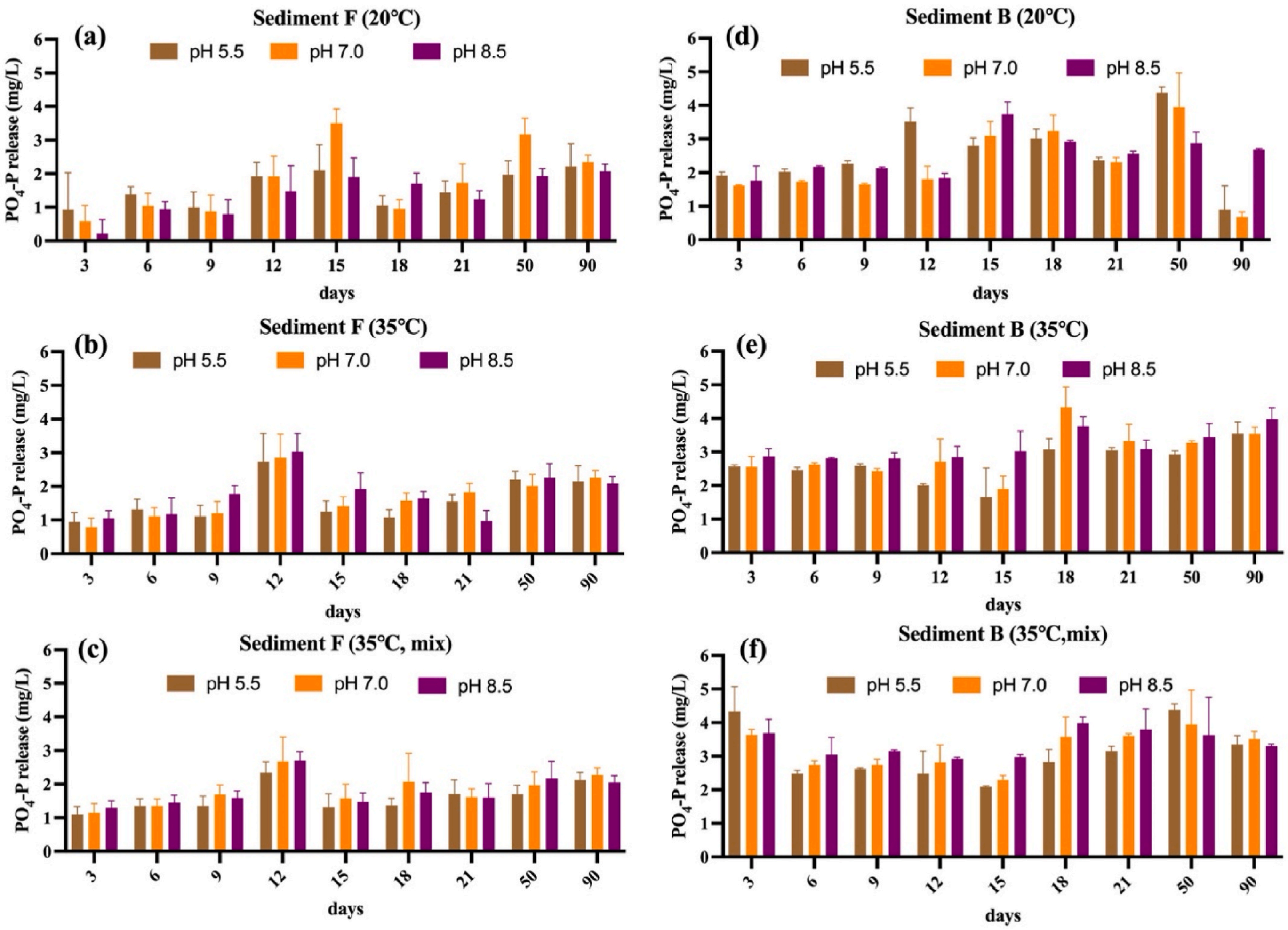


Fig. 2. Effect of different temperatures, pHs, operation time, and mixing conditions on the average P release in bioreactors operated with sediment B and sediment F.

in anaerobic marine sediments (Zopfi et al., 2004). A deep investigation was not done in this study to reveal the increase in sulfate concentrations under anaerobic conditions. However, SO_4^{2-} concentrations were reduced in most of the cases, which was an indicator of the activity of SRBs.

This batch set was conducted in order to optimize operational conditions (temperature, pH and mixing conditions) towards enhancing P release. To start with, pH is an important factor that affects several biochemical reactions, such as sorption-adsorption and oxidation-reduction (Jin et al., 2006). In our study, pH was found to be one of the significant parameters for P release, however; it is hard to conclude the optimum pH for the bioreactor operation due to complex interactions with other operational conditions (temperature, operation time and mixing) as well as biological activities. In literature, the research investigating the relationship between pH and P release mostly focuses on lake sediments under oxic conditions. For instance, Jin et al. (2006) observed that alkaline conditions favored P release from lake sediments under oxic conditions. In another study, Wu et al. (2014) found out that both acidic and alkaline (most favorable) conditions favored P releasing from the lake sediments under oxic conditions and the lowest P release was at neutral pH. In theory, higher P release at both acid and alkaline conditions can be explained by the phosphorus retention capacity of the sediment. P binding capacity of Fe^{2+} and Al^{3+} decreases in alkaline conditions in both overlying water and sediment due to predomination by the ligand exchange reactions which refers to the replacement of *ortho*-phosphate by hydroxide ions (Lijklema, 1993). On the other hand, higher pH also promotes the formation of $CaCO_3$ as well as Ca–P minerals leading to the retention of P in the sediments and low pH favors the release of Ca–P (Zhao et al., 2022). In order to have a better understanding of the effect of P release mechanisms under different pH conditions, Fe^{2+}, Ca^{2+} and Al^{3+} can be monitored in the bioreactors in future studies to clarify underlying P release and uptake mechanisms under different pH conditions.

In this study, temperature was also found to be an important parameter for P release. Previous studies (oxic conditions) also showed that P release was promoted with respect to increased temperature (Wu et al., 2014; Jiang et al., 2008). Temperature increase improves biomass growth of the bacteria as well as benthic alga and phytoplankton (Jiang et al., 2008). Especially, increased temperatures (from 5 °C to 15–25 °C) promote abundance for SRBs due to an increase in labile sulfide concentrations and inhibiting the growth of iron-reducing bacteria (IRB) due to the competition between SRBs and IRBs in terms of organic matter and ferric iron. Consequently, the microbial sulfate reduction is promoted followed by S-induced chemical iron reduction which results in P release (Han et al., 2023). In this study, while microbial/chemical Fe reduction was not explored, the discussion in the next section highlights the positive role of SRBs in P release and their relationship with temperature.

3.4. Marine microbial community change during batch bioreactor operation

Initially, the bacterial community at the phylum level of the bacterial taxa for sediment B were dominated by *Proteobacteria (53.5%),* followed

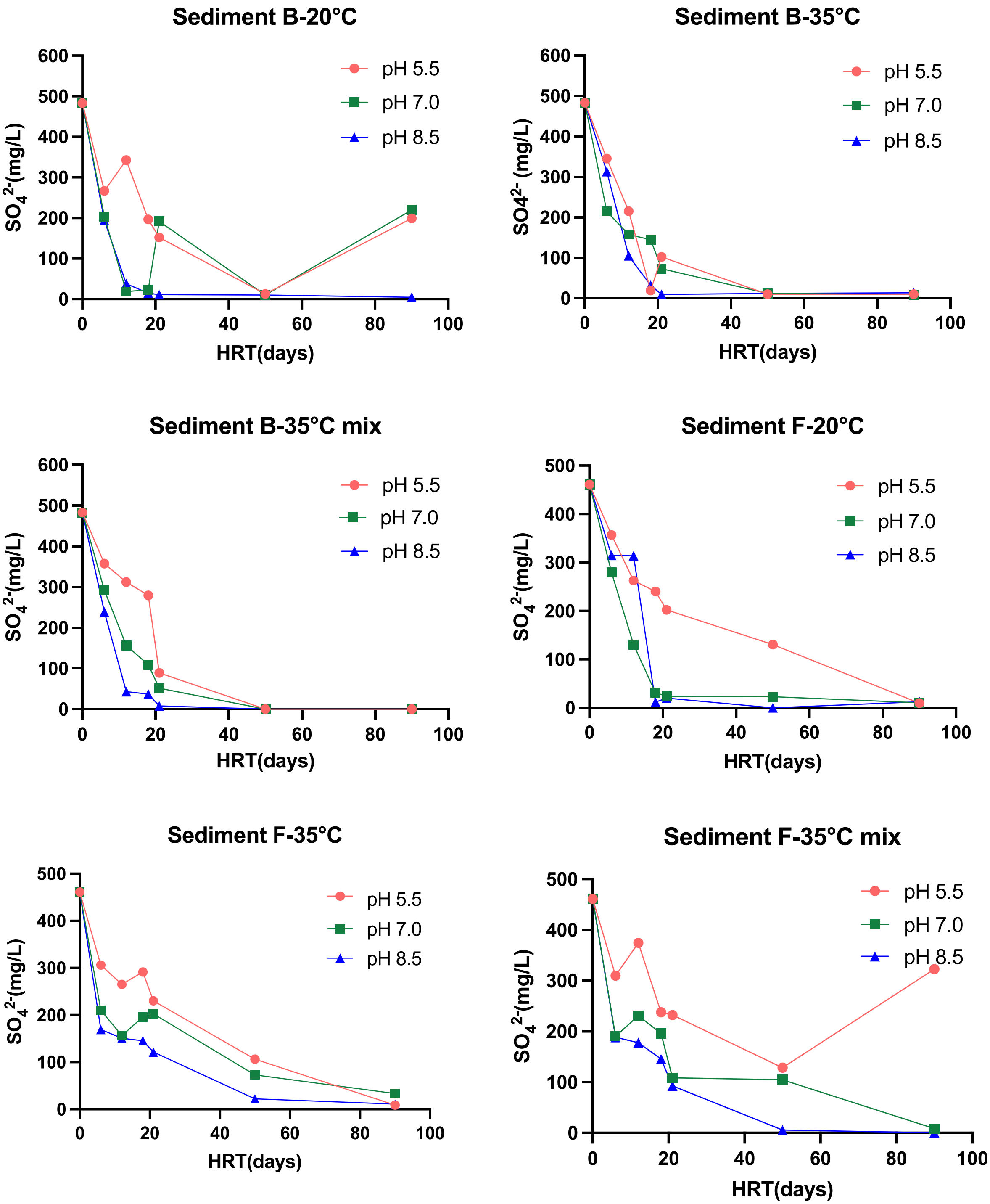
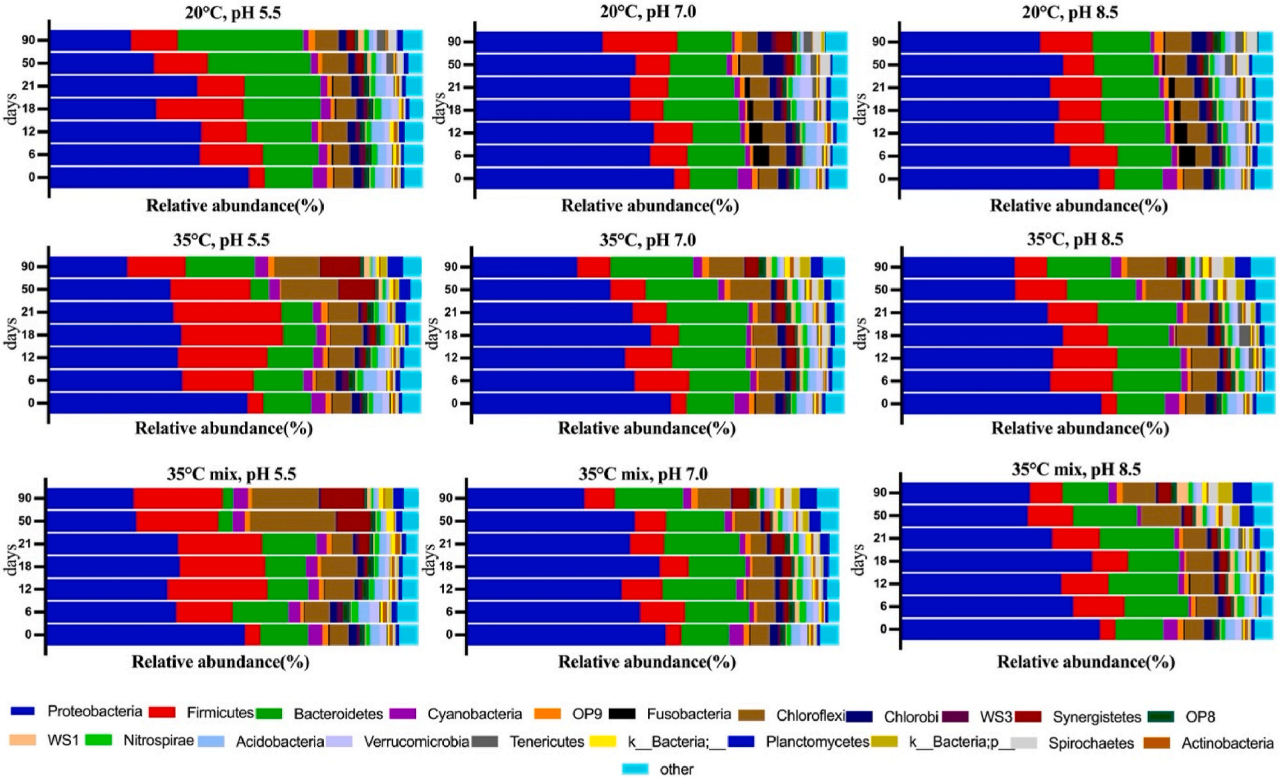


Fig. 3. Mean change in SO_4^{2-} concentrations in the bioreactors operated with sediment B and sediment F (N = 2).

by *Bacteroidetes* (12.8%). *Firmicutes* and *Chloroflexi* had relative abundances of 4.2% and 5.2%, respectively. The dominant ones in sediment F were *Proteobacteria (54.2%),* followed by *Bacteroidetes* (13.83%). The microbial community shift in phylum level with regards to operation time, temperature, pH and mixing conditions for both sediments are depicted in Fig. 4(a and b). A one-way PERMANOVA test was performed to evaluate the effect of operational conditions on the microbial community. The results showed that, for the bioreactors operated with sediment B, different temperatures resulted in significant differences in the microbial community ($p < 0.05$). However, mixing conditions did not show statistically significant differences. In addition, the microbial community at pH 7.0 and 8.5 were also not significantly different ($p > 0.05$). When operation times were compared, there was a significant difference between the microbial community on day 90 and the other sampling days ($p < 0.05$). In the bioreactors operated with sediment F, the temperature fluctuations did not yield a notable variance in microbial communities. Nonetheless, significant disparities ($p < 0.05$) were observed in microbial communities under different mixing conditions. The difference in the microbial community at pH 5.5 and pH 7.0–8.5 was significant ($p < 0.05$); whereas the difference in the microbial community between pH 7.0 and pH 8.5 was not significant. When operation times were compared, there was no significant difference between microbial communities between day 6 and 21 ($p > 0.05$).

Redundancy Analysis (RDA) was also performed to evaluate the

(a) Sediment B



(b)Sediment F

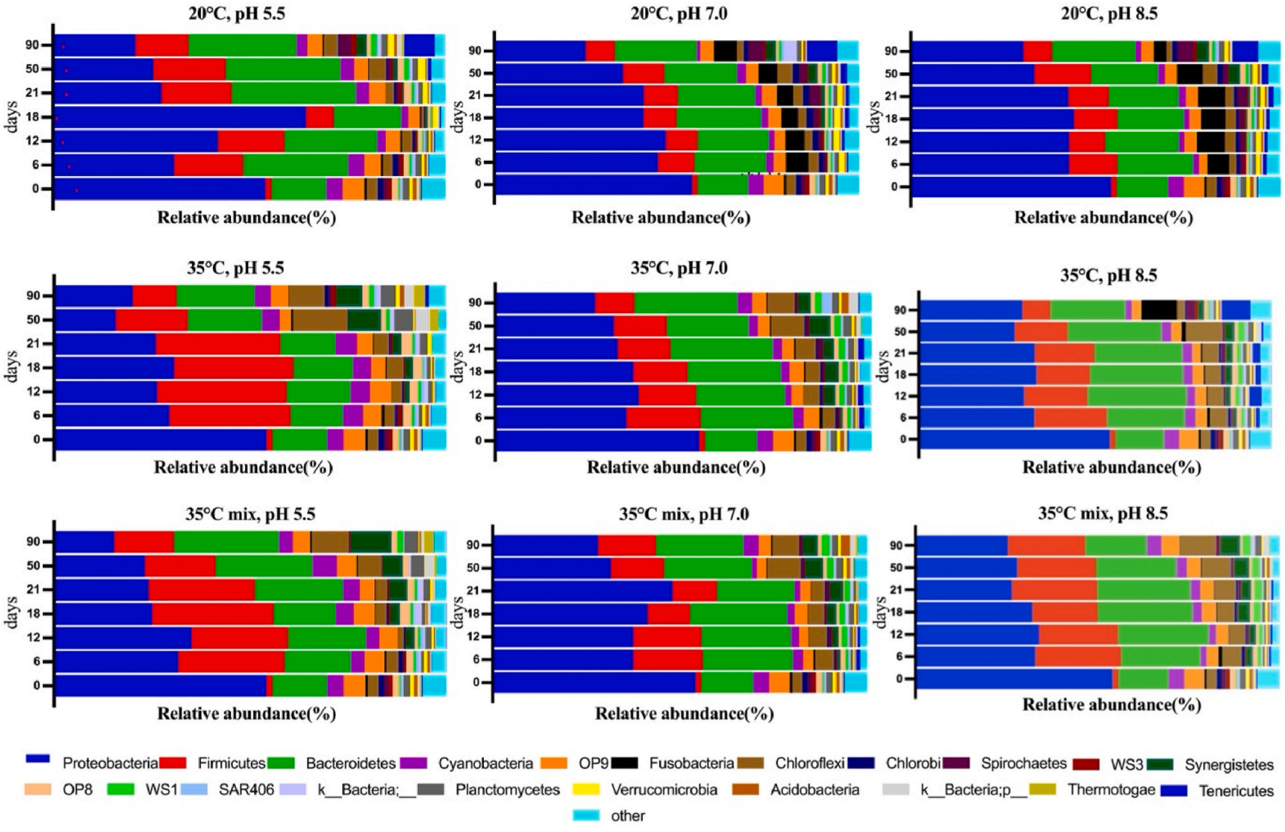


Fig. 4. Shift in microbial communities (expressed as the relative abundance, %) in the bioreactors operated with sediment B (a) and sediment F(b).

relationship between P release and sulfate reduction as well as operational parameters and the microbial community at the family level of bacterial taxa (Fig. 5). Notably, only families whose relative abundancies were more than 2% were considered in the analysis. Explanatory variables were set as both quantitative (P release and sulfate reduction) and qualitative (temperature, pH). RDA results showed that the microbial community and environmental variables (temperature, operation time and pH) were linearly correlated with each other ($p < 0{,}0001$; 999 permutations), and 48% and 50% of the species community variability could be explained by these environmental variables for sediment B and

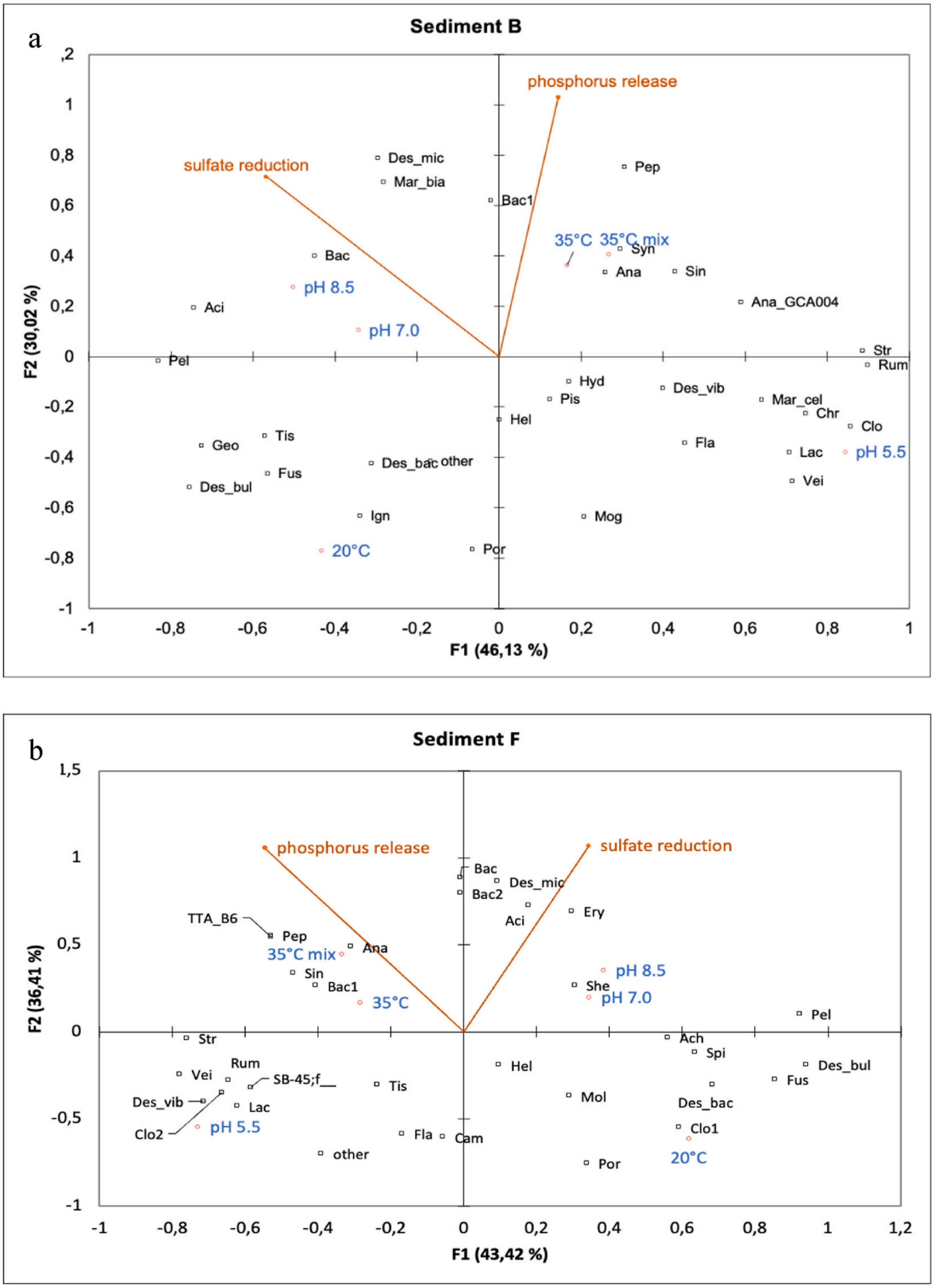


Fig. 5. RDA of the family level bacterial community observed for (a) sediment B and (b) sediment F. (**Abbrevations:** *Acidaminobacteraceae*:***Aci***;*Anaerolinaceae*:***Ana***; *Acholeplasmatales*; ***Ach***;*Bacteroidales;f_*:***Bac***;*Campylobacteraceae*:***Cam***; *Chromatiales;f_*:***Chr***; *Clostridiaceae*:***Clo***;*Desulfomicrobiaceae*: ***Des_mic***; *Desulfobacteraceae*: ***Des_bac***; *Desulfobulbaceae*:***Des_bul***;*Desulfovibrionaceae*:***Des_vib***; *Erysipelotrichaceae*:***Ery***; *Fusobacteriaceae*: ***Fus***; *Flavobacteriaceae*: ***Fla*** *SB-45;f_*: ***SB-45_***: *Helicobacteraceae*: ***Hel***; *Hydrogenophilaceae*: ***Hyd***; *Ignavibacteriaceae*: ***Ign***; *Lachnospiraceae*: ***Lac***; *Marinicellaceae*:***Mar_cel***; *Marinilabiaceae*:***Mar_bia***; *Mollicutes;o_;f_*: ***Mol***; *Piscirickettsiaceae*: ***Pis***; *Porphyromonadaceae*:***Por***; *Pelobacteraceae*:***Pel***; *Peptococcaceae*: ***Pep***; *Ruminococcaceae*: ***Rum***;*Sinobacteraceae*:***Sin***; *Shewanellaceae*: ***She***; *Stramenopiles;f_*:***Str***; *Synergistales;f_TTA_B6*: ***Syn***; *Spirochaetaceae*:***Spi***; *Tissierellaceae*: ***Tiss***; *Veillonellaceae*: ***Vei***; *k_Bacteria;p_;c_;o_;f_*: ***Bac 1***; *k_Bacteria;p_WS1;c_;o_;f_*:***Bac 2)***.

sediment F, respectively. The RDA results for the bioreactor samples with both sediments showed that P release was clustered at 35 °C with/without mixing conditions. Sulfate reduction was in turn clustered with both pH 7.0 and pH 8.5.

Microbial community plays an essential role for P cycling in the sediments and one of the main mechanisms is associated with sulfur cycle, which relies on the biological dissimilatory sulfate reduction (DSR) to sulfide under anaerobic conditions (Jørgensen and Kasten, 2006). Sulfate reducing bacteria (SRB) presents a diverse group of microorganisms, mainly including the phylum of the *Deltaproteobacteria* and *Firmicutes* (Zouch et al., 2017). According to RDA (Fig. 5), sulfate reduction could be attributed to the presence of *Desulfomicrobiaceae* and *Acidaminobacteraceae* (for Sediment B and Sediment F), which are known to be sulfate reducers (Rosenberg et al., 2014) as well as *Marinilabiaceae* (for Sediment B) and *Shewanellaeae* (for Sediment F). Especially, *Desulfomicrobiaceae* were found as the most abundant phylum regarding SRBs in both sediments during batch bioreactor operations. The relative abundancy of the *Desulfomicrobiaceae* were observed to be <1% at the beginning of the experiment, and mostly showed an increasing trend during anerobic bioreactor operation for both sediments. *Desulfomicobiaceae* are mesophilic/moderately thermophilic (Rosenberg et al., 2014), which can be related to higher increase in the abundancy at mesophilic temperature. The highest relative abundancy was observed at 35 °C with mixing conditions at day 18 for both sediment B and sediment F with 17.6% (at pH 8.5) and 16.9% (at pH 7.0) increase, respectively. The acetate accumulation in the bioreactors (See Supplementary Material, Figure S4-S5) was also obvious, which can be partially attributed to the activity of *Desulfomicobiaceae*. Notably, *Desulfomicrobiaceae* are characterized as being able to oxidize organic substrates into acetate using sulfate as the electron acceptor (Rosenberg et al., 2014). pH can also be considered as an important parameter for *Desulfomicobiaceae*; the relative abundancies were measured to be lower for pH 5.5 than those at pH 7.0–8.5 (as correlated in RDA). Apart from sulfate reducers, *Marinilabiaceae* were correlated with sulfate reduction in sediment B. They could represent a role for initial hydrolysis and fermentation and could contribute to sulfate reduction process. For sediment F, *Shewanellaeae* were also correlated with the sulfate reduction. Notably, *Shewanellaeae* can do a dissimilatory reduction of manganese, iron oxide, and other metal compounds (Satomi, 2014).

P cycling in marine sediments also relies on other biological uptake and release mechanisms. For instance, poly-P accumulating organisms in sediments can transfer P into the benthic food chain as well as can influence the permanent P mineral deposition via inducing rapid P release (Hupfer et al., 2007). In EBPR systems, a wide range of PAOs are well known, such as *Ca. Accumulibacter Halomonas*, *Tetrasphaera*, *Microlunatus phosphovorus*, *Dechloromonas*, *Ca. Obscuribacter*, *Thiothrix caldifontis*, *Tessaracoccus Bendigoensis*, as well as *Comamonadaceae* members (Chen et al., 2022). However, in marine sediments, the PAOs and their roles in P cycling are not yet well studied as EBPRs. Brock and Schulz-Vogt (2011) showed that *Beggiatoaceae*, the marine sulfur-oxidizing bacteria (family level), can store poly-P and hydrolyze it under anoxic and sulfidic conditions. It is also stated that *Thiomargarita* can release P into the anoxic sediment for precipitation of hydroxyapatite (Schulz and Schulz, 2005). In our study, the relative abundances of *Comamonadaceae* for both bioreactor samples decreased when compared to initial conditions. In addition, *Beggiatoaceae* were not found in the bioreactor samples, whereas *Thiotrichaceae* were found initially at 1.7% and 0.3% (RA) in sediment B and sediment F, respectively, and it decreased during bioreactor operation. So, we can conclude that the current strategy did not improve the abundance of the PAOs. Apart from PAOs, P solubilizing bacteria (PSB) could also play a key role in the solubilization of inorganic forms of P. *Pseudomonas, Serratia, Bacillus, Flavobacterium, Corynebacterium, Enterobacteriaceae* are some of the examples found in soil and water ecosystems (Dastager and Damare, 2013; Qian et al., 2010; Kannapiran and Sri Ramkumar, 2011). During the bioreactor operation, the stated examples were not found or were found at very low abundances.

RDA also showed that *Anaerolineaceae* were found to be correlated with the P release in both sediments. Importantly, *Anaerolineaceae* were found abundant in the heavily eutrophic Gulf in the Baltic Sea, which was stated as a possible role for methane production. In that study, this family was positively correlated with Al-bound P, which is an indicator for P sink with erosion material (Sinkko et al., 2013). *Sinobacteraceae* (or *Solimonadaceae*) were also positively correlated with P release and they are known for degrading chemical pollutants (i.e, atrazine, chlorinated hydrocarbons and hexane) (Zhou et al., 2014); but, to the best of our knowledge, no studies investigating the relationship between P solubilization and *Sinobacteraceae* have been found so far.

4. Conclusion

The study demonstrated that VFA addition as the carbon source improved P release from marine sediment samples under anaerobic conditions. pH, temperature and operation time had significant influences on P release, on the other hand; the mixing did not affect the P release notably. Furthermore, SRBs were critical players in terms of P release from the marine sediment and the role of PAOs were very limited due to very low abundancies. This study showed the importance of conducting more studies for a deeper understanding of P uptake and release during bioreactor operation to improve the P release efficiency. The suggestions for future studies include i) monitoring of Ca^{2+}, Fe^{2+}, Mn^{2+} and Al^{3+} in the liquid medium as well as different forms of P in the sediment to clarify P release mechanisms and the effect of operational parameters, ii) testing with carbon sources as pure VFA and continuous bioreactor operation.

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CRediT authorship contribution statement

Ece Kendir Cakmak: Writing – original draft, Visualization, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Chen Chen:** Writing – review & editing, Data curation. **Maria Cuartero:** Writing – review & editing. **Zeynep Cetecioglu:** Writing – review & editing, Supervision, Methodology, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.chemosphere.2024.142188.

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