A STUDY ON PHOSPHORUS FLUX FROM SEDIMENT IN A SHALLOW HOMOGENEOUS LAKE

Paolo VIOTTI[1], Luigi GALEOTTI[1], Elisa MARTORELLI[1] and Vincenzo TORRETTA[2*]

Abstract. *A study on phosphorus release dynamics was conducted into a shallow homogeneus and mesotrophic lake. The purpose was to investigate physical- chemical factors which contribute to the nutrient release-adsorption from sediments. Water and sediment samples were analyzed under different conditions: aerobic and anoxic, static and mixed. Results in both last cases (anoxic/aerobic conditions) show that the nutrient release- sorption dynamics are strictly linked to the iron- manganese associated phosphorus contents within the sediments but the low overall phosphorus release is largely linked to the sediment's calcareous nature (phosphorus precipitation as hydroxyapatite and co-precipitation/adsorption with carbonates). In the mixed tests cases, as expected, the release is higher compared to static aerobic ones: the sediments re-suspension allows for a higher contact surface area with water leading to a higher phosphorus desorption. In case of shallow lake the wind can therefore play an important role in influencing phosphorus balance in the waters. This aspect can be even more important when suspended fine clay particles are involved since they can be considered a support for phosphorus forms. It follows that surficial sediments when re-suspended play a double role: they can redistribute phosphorus along the water column but they can re-adsorb it.*

Key words: *Phosphorus release; Shallow Lake; Aerobic-anoxic conditions; Lake sediment.*

Introduction

Eutrophication, which is characterized by a massive and harmful algal bloom and an excessive nutrient loading, is a common but problematic phenomenon in freshwater ecosystems (Zhu M. et al., 2013). More specifically, this issue can be linked to excessive phosphorus loading, which can be identified as external loading from wastewater treatment plants (Raboni M. et al., 2013; Zhang Y. et al., 2013; Raboni M. et al., 2014a; Torretta V. et al., 2014; Raboni M. et al., 2014b) and/or from uncrotrolled discharged, or from its release from lake sediments (internal loading) (Wang C. et al., 2012). In fact,

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[1] Dept. of Civil, Building and Environmental Engineering, "Sapienza" University of Rome, Via Eudossiana 18, 00184 Rome, Italy

[2] Dept. of Biotechnologies and Life Sciences, Insubria University Via G.B. Vico 46, Varese, Italy. Author to whom correspondence should be addressed; E-Mail: vincenzo.torretta@uninsubria.it; Tel: +39- 0644585512

since phosphorus is often a growth-limiting element for aquatic organisms, it is not only a cause of a lake's trophic state (Perrone U. et al., 2008), but it is often the key element responsible for eutrophication in many lakes (Xiang S. and Zhou W., 2011).

Many studies have shown that monitoring external loading was not enough in order to control and avoid water bodies eutrophic conditions (Jin X. et al., 2006). Accordingly, they mainly focus on monitoring phosphorus release from sediments into water as well as internal nutrient loading (Beutel M.W. et al., 2008). Lake sediments play a key role in the internal P cycle (Kowalczewska-Madura K. et al., 2010): depending on many different parameters, some of them well known, as pH, dissolved oxygen, redox potential, organic matter, temperature, nitrates, sulfates, salinity, bacteria activity, others linked to the different elements with whom phosphorus interacts, they can represent a sink or a source for phosphorus (Rzepcki M., 1997). Several studies have been conducted to investigate conditions (Gunnars A. and Blomqvist S., 1997), as well as parameters that influence phosphorus retention and release from sediments of freshwater environments. In this work phosphorus release processes were investigated taking into account experimental techniques, which can evidence the relation between phosphorus, metals and environmental conditions. For the samples collection it was chosen an Italian Lake. Lake Trasimeno (central Italy) is classified as a mesotrophic lake with the tendency to eutrophication (Martinelli A., 2013), where the anthropic pressure and drought have led to a lowering of its water level and a deterioration of its water quality during last years (Giordano R. et al., 2013). Lake Trasimeno has a peculiarity: because of its very shallow waters (Bresciani M. et al., 2011), it is influenced by wind- wave disturbance (ARPA, 2012). In addition to re-oxygenation of the water body, wind influence and low water levels lead to the nutrient remixing across the water column and to the surficial sediments re-suspension (Niemistö J. et al., 2011), which increase, more or less continuously, the contact between sediment and water (Sondergaard M., 2003). It follows that the estimation of potential internal phosphorus load is particularly elaborated in shallow lakes since it is largely controlled by wind mixing. It should be also emphasized that lakes sediments can be highly variable in chemical composition: lakes show different phosphorus release dynamics depending on many factors which are linked to the mineralogical and lithological nature of the sediments, such as content of iron, manganese, calcium and clay.

The aim of this work is to give a quantitative description on how these factors can contribute to phosphorus release- sorption dynamics in a no stratified lake and to underline how even close sites in a well mixed basin can result in very different behavior when the phosphorus release from sediment is considered. Results are obtained through simulation of different conditions, such as aerobic, anoxic, static and mixed environments, followed by a study of phosphorus fractionation in the sediments at the end of each test. Particular attention was paid to surficial sediments because they represent the larger potential phosphorus source for the water column (Petterson K., 1998).

Experimental Section

Site description and sampling

Lake Trasimeno is the fourth most extensive Italian lake, with a surface area of 121 km^2. It is the main water body in central Italy. In addition to directly rain and runoff waters, Trasimeno basin is fed by a small aquifer that surrounds it. However, because of the low permeability nature of the hallow substratum (Ludovisi A. and Gaino E., 2010), the lake catch basin almost corresponds to its hydrogeological one (ARPA, 2012). Lake Trasimeno is de facto considered a closed basin, with no natural outlets (Burzigotti R. et al., 2003). Trasimeno is a large but shallow lake, with a nearly flat bottom and a maximum depth of almost 6 meters.

Table 1 summarizes the main characteristics of Lake Trasimeno.

Table 1. Main characteristics of Lake Trasimeno (ARPA, 2012).

Avarage water level (meters above sea-level)	Lake perimeter (km)	Sinuosity index	Average depth (m)	Mean lake volume (m^3)	Total basin area (km^2)	Mean rain falling on water surface (mm year^{-1})	Hydraulic retention time (years)
257.1	53.1	1.34	4.75	490*10^6	383.5	723	24.4

Water and sediment samples were collected in different sites of the lake (Fig. 1): Albaia area (samples will be indicated by “A”) and Torricella area (indicating the collected samples by “B”). Both areas are situated east of the lake. Despite being only a few kilometers from each other, the two beaches are very different in features. More specifically, the “A” shore is mainly characterized by sandy soil while “B” beach is mainly characterized by loam. Further samples, which will be indicated by “C”, were collected in the S. Vito area. The procedure of sample collection was the same in all the experiences. The A and B samples were collected 7- 10 meters away from the shoreline, while the C samples were collected 30 meters away. More specifically, since mass exchange on the water- sediment interface mainly occurs on the surficial sediments within 5-10 cm (Qin B. et al., 2004), the first 10 cm of the sediments were considered.

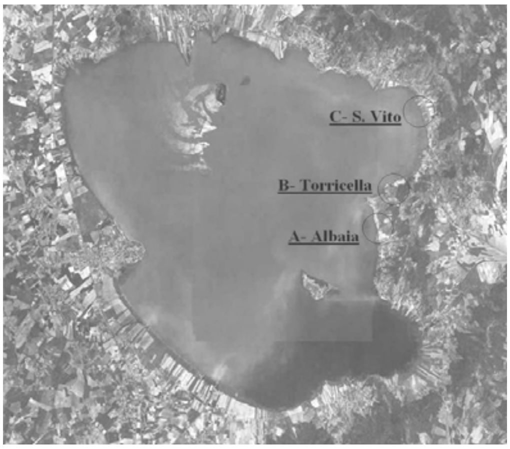

Fig. 1 - Study area- Lake Trasimeno. "A, B and C" letters respectively indicate Albaia, Torricella and S. Vito localities.

Sediment samples were collected using a sampler with dimensions (10×8×6 cm long) shown in Fig.2.

Fig. 2 - Sampler used to draw surficial sediments.

Water analysis

Water samples were analyzed in order to obtain Total Phosphorus (TP), Soluble Reactive Phosphorus (SRP) and Total Dissolved Phosphorus (TDP) contents, TP content was measured in the unfiltered samples using the acid digestion method (ASTM, 1997). Water samples were filtered through a 0,45 μm membrane filter to obtain SRP and TDP contents. More specifically, the SRP, which consists primarily of orthophosphates and represents the most available fraction, was determined by means of a colorimetric method using ammonium molybdate (ASTM, 1997). In order to obtain TDP content, samples were submitted to digestion (ASTM, 1997); the digestion method leads to a

TDP conversion in orthophosphates and the colorimetric method was then applied. Finally, Fe, Mn, Ca and P contents were determined by atomic absorption spectroscopy.

Sediment analysis

TDP was also determined in interstitial water for the A and B samples. Interstitial water was obtained using a centrifugation method on sediments belonging to B. Because of the sandy nature of the “A” shore, there was no need to use the centrifugation method on sediments to extract excess water. Afterwards, in order to characterize sediments and to better understand how phosphorus binds to the solid matrix, sediment samples were analyzed by Psenner’s sequential extraction method (Pettersson K. et al., 1988). This method classifies phosphorus fractions as follows (Dondajewska R., 2011):

- NH_4Cl-P: it consists in “loosely-sorbed” P for interstitial water and in $CaCO_3$ bound P for lake water. It gives an estimate of the immediately available phosphorus;
- BD-P (Buffered Dithionite extractable phosphorus): it includes different redox potential sensitive forms such as iron or manganese associated P and organic phosphorus forms. It is known as “reducing soluble phosphorus”;
- NaOH-P: it’s the metal oxide bound P and includes exchangeable against hydroxide ions OH^- phosphorus such as Al bound P and organic in bacteria incorporated phosphorus;
- HCl-P: it represents Ca bound P and it includes organic phosphorus which is soluble with HCl and phosphorus forms that are sensitive to low pH such as apatite;
- Res-P: it is the residual P and it includes both refractory organic phosphorus and the inorganic inert fraction. It is calculated as the difference between total phosphorus and the sum of other phosphorus fractions.

Furthermore, the extracted solutions were analyzed by atomic absorption spectroscopy in order to better characterize sediments. Once characterized the different P forms bound to the soil, to investigate phosphorus release under different conditions, tests on the sediments under aerobic and anoxic environments were carried out. The following tests were carried out on the sediment samples:

- leaching test under aerobic static conditions (for A, B and C samples).
- sequential extraction after the aerobic leaching test (for A and B samples).
- leaching test under anoxic static conditions (for A, B and C samples).
- sequential extraction after the anoxic leaching test (for A and B samples).
- desorption test under mixed aerobic conditions (for A, B and C samples).
- sequential extraction after the desorption test (for A and B samples).

Aerobic environment was obtained by using no capped flasks while anoxic environment was performed by a continuous stream of nitrogen into the capped flasks and it was checked by monitoring redox potential and dissolved oxygen concentration (DO<1mg L^{-1}).

Regarding mixed tests, they can be used for studying the effects brought from sediments re-suspension due to wind-influence on phosphorus concentrations and release- sorption dynamics. Mixed conditions were obtained by using a mechanical stirrer, which continuously worked for the 21-day duration of the jar test. The rotation speed was about 85 rpm. For the leaching and the desorption tests, 40 gr of undisturbed wet sediment samples from each beach were placed into 500 ml flasks and were put in contact with 500 ml of distilled water for 21 days. Withdrawals were carried out on the 7th, 14th, 21st day and TDP content was obtained by samples previously filtered by a 0,45 µm membrane filter. Once known phosphorus concentration, a new solution made of distilled water and KH_2PO_4 was prepared and in prior taken solution added so as to maintain always the same liquid-solid ratio.

Results and Discussion

Water analysis results

Concerning the mineral composition of the lake water, samples were analyzed by atomic adsorption spectroscopy. The results show a large calcium concentration (average 40 mg L^{-1}), a very low iron (<0.1 mg L^{-1}) and manganese content (<0.05 mg L^{-1}). Regarding phosphorus contents, Total Phosphorus (TP), Total Dissolved Phosphorus (TDP=SRP+NRP), Soluble Reactive Phosphorus (SRP) and No Reactive Phosphorous (NRP) are the different forms which are encountered in the waters. TP, TDP and SRP, which is the directly available phosphorus for algal growth, were analyzed in the A and B water samples.

The results reported in Fig. 3 show TP contents in the B1 and B2 samples higher than in the A1 and A2 samples. This means that B beach contains a major amount of phosphorus in particulate form. It is furthermore possible to observe that in B the difference between TP and TDP content shows an high value leading to the conclusion that in B shore we found the no directly available phosphorous mainly in a particulate form. If the further difference (TDP-SRP) is compared between the shore A and B it is possible to notice that in B samples the NRP fraction is larger. The summarized differences between A and B are due to the different characteristics of the soils in the two areas. Clay adsorbs phosphorus, which therefore becomes not directly available for algal growth. Regarding the large difference between the TP and TDP contents in the B samples, it is linked to the higher re-suspension capacity of fine clay grains (Jönsson A., 2005), that characterize B shore.

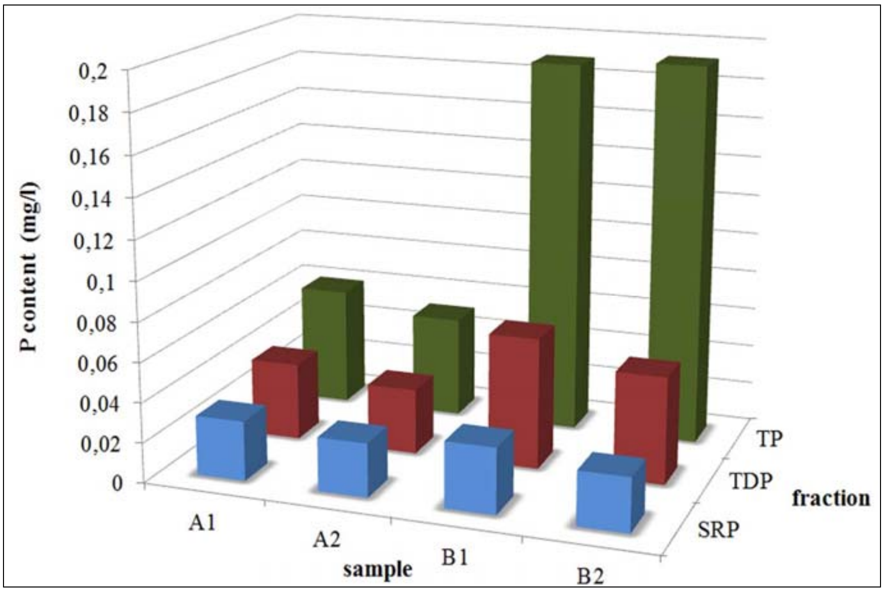

Fig. 3 - TP, TDP and SRP contents in A and B beaches.

Sediments analysis results

Sediment samples features. Moisture, organic content (O.C.) and phosphorus content were measured in sediment samples. The values are reported in Tab. 2.

Table 2. Moisture (%), organic content (%) and phosphorus content [mg P $kg^{-1}{}_{dry\ weight}$] in sediment samples.

Sample	Organic content(O.C.)	Phosphorus content	Moisture
A1	0.75	188.20	22.50
A2	0.92	193.15	22.28
A3	0.71	139.38	22.50
B1	3.06	244.50	36.33
B2	3.27	202.50	41.96
B3	3.11	219.00	41.11
C	10.4	446.70	-

Interstitial water results. TDP content in interstitial water was determined in the A and B sediment samples (Figures. 4a and 4b).

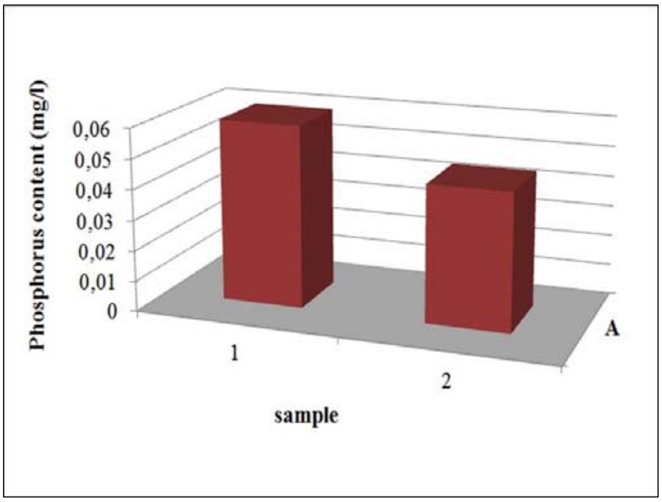

Fig. 4a - TDP content in interstitial water (A1-A2 samples).

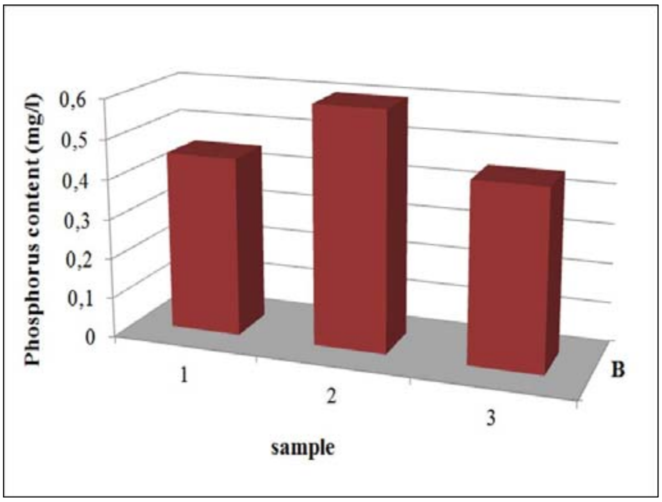

Fig. 4b - TDP content in interstitial water (B1-B2-B3 samples).

Phosphorus contents in the A1 and A2 samples are of the same order of magnitude of measured lake water TDP contents, while in the B1, B2, B3 samples show a higher value. This last result, obtained in case of low permeable bottom, is confirmed by Enell and Löfgren (1998) and Boström *et al.* (1982), who report that interstitial phosphorus concentration generally exceeds phosphorus concentration in the overlaying water. Because of this concentration gradient between interstitial and lake water, an upward diffusion flux can take place towards the overlaying water (Qin B. et al., 2006).

Sequential extraction results. The sequential extraction carried out had the aim of understanding how and in which proportion phosphorus fractions into sediments are bound. Tab. 3a shows content [mg P kg $^{-1}$$_{\text{dry weight}}$] of the various phosphorus forms in sequentially extracted samples.

Table 3a. Sequential extraction. Total P contents [mg P kg $^{-1}$$_{\text{dry weight}}$] into extracted solutions.

Sample /P- fraction	NH_4Cl	BD-P	NaOH-P	HCl-P	Res-P
A1	3.87	28.62	15.86	31.33	104.81
A2	1.93	22.44	27.08	71.95	66.35
B1	4.98	58.81	30.4	116.12	34.19
B2	5.48	47.34	39.87	95.68	14.12

Also in this case due to the lithological nature of A shore, in the A1 and A2 samples residual phosphorus (Res-P) is higher than in the B1 and B2 samples. Accordingly to other similar lakes data in literature (Petterson K., 1998), the results show a negligible NH_4Cl-P content while concerning the other forms it is possible to summarize that B shore presents an average content of phosphorus higher than A and that in the A shore phosphorus is mainly in the inert form, while in the B shore it is bounded mainly to metal and Ca. Regarding iron, manganese and calcium contents in the extracted solutions, the results of the atomic adsorption spectroscopy are reported in Tab. 3b.

Table 3b. Results of the atomic adsorption spectroscopy on the extracted solutions. Iron, Manganese and Calcium contents [mg L^{-1}] in the extracted solutions after the sequential extraction procedure on sediments.

	Fe [mg L^{-1}]	Mn [mg L^{-1}]	Ca [mg L^{-1}]
BD A1	10,00	0.2	0.75
BD A2	11.10	0.22	0.74
BD B1	16.70	1.15	2.75
BD B2	18.30	1.17	3.83
HCl A1	68,4	0.79	18
HCl A2	64	0.68	15.6
HCl B1	77.2	2.18	118.4
HCl B2	90	1.83	143.6
NaOH A1	0.24	< 0.05	1.31
NaOH A2	0.37	< 0.05	0.65
NaOH B1	0.88	< 0.05	1.14
NaOH B2	1.05	< 0.05	1.4
NH_4Cl A1	0.16	0.07	20.8
NH_4Cl A2	< 0.1	0.06	26.4
NH_4Cl B1	< 0.1	0.18	123.2
NH_4Cl B2	< 0.1	0.08	91.2

Leaching test under aerobic static conditions. Information on phosphorus release dynamics is obtained by means of a leaching test. The results are shown on Tables 4 and 5 and on Fig. 5.

Table 4. Leaching test under aerobic static conditions results. Released P concentrations [mg P L^{-1}] after 7, 14, 21 days from the start of the test and release rates [mg m^{-2} d^{-1}] for each sample.

Samples	Released P concentration after 7 days	Released P concentration after 14 days	Released P concentration after 21 days	Release rates
A1	0.024	0.03	0.048	0.381
A2	0.024	0.03	0.048	0.381
A3	0.024	0.03	0.036	0.286
B1	0.036	0.078	0.078	0.349
B2	0.012	0.042	0.024	0.619
C	0.075	0.094	0.088	0.698

Table 5. Leaching test under aerobic static conditions results. Average concentrations of dissolved P [mg P L^{-1}] at the different collecting times and average release rates [mg m^{-2} d^{-1}].

Samples	Released P average conc. after 7 days	Released P average conc. after 14 days	Released P average conc. after 21 days	Average release rates
A	0.024 ± 0	0.03 ± 0	0.044 ± 0.006	0.349
B	0.024 ± 0.012	0.06 ± 0.02	0.051 ± 0.027	0.405
C	0.075	0.094	0.088	0.698

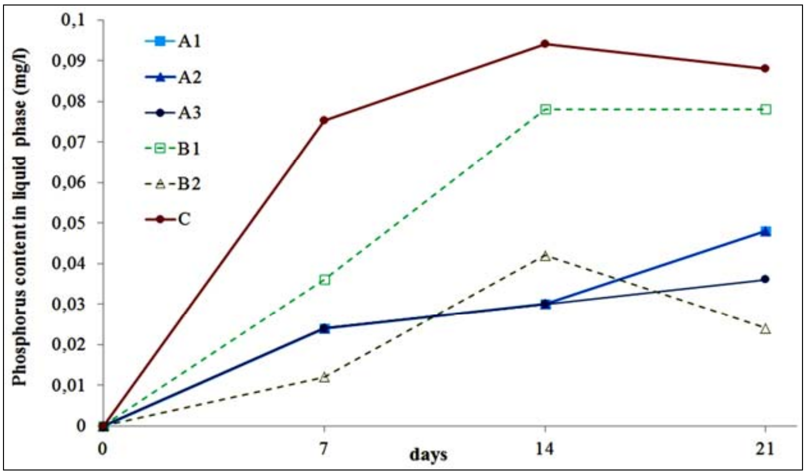

Fig. 5 - Leaching test in aerobic static conditions. TDP contents after 7, 14 and 21 days.

The difference in the average release rate between B, C and A is surely due to the greater initial phosphorus content but also to the higher quantity of organic substance in C and B. The high organic content leads to an increase in oxygen demand by microorganisms as well as a decrease in redox potential. Because of the lowering of redox potential, the oxidized trivalent iron (Fe^{3+}) is reduced into divalent iron (Fe^{2+}) and iron bound phosphate is released from sediments into the overlaying water, as evidenced also from Wauer *et al.* (2005).

For the B and C samples it can also be evidenced a steady-state or even a further adsorption that can be described by means of the sequential extraction tests described below. Tab. 6 shows content [mg P kg $^{-1}{}_{\text{dry weight}}$] of the various phosphorus forms in sequentially extracted samples before and after the leaching test.

Table 6. Sequential extraction. Total P contents [mg P kg $^{-1}{}_{\text{dry weight}}$] into extracted solutions before (Init. A1, Init. B1) and after (A1, B1) the leaching test under aerobic static conditions. The sign (-) on percentages indicates a P release, while the sign (+) indicates a P adsorption.

Sample /P- fraction	TP	NH_4Cl	BD-P	NaOH-P	HCl-P	Res-P
Init. A1	184.50	3.87	28.66	15.88	31.37	104.72
A1	165.75	1.55	8.51	19.73	40.18	95.78
% P- release (-)	-10%	-60%	-70%	-	-	-
% P- sorption (+)	-	-	-	+24%	+28%	-
Init. B1	244.50	4.71	55.60	28.74	109.79	45.65
B1	214.50	3.6	21.30	11.93	155.29	22.38
% P- release (-)	-12%	-24%	-62%	-58%	-	-
% P- sorption (+)	-	-	-	-	+41%	-

In the A1 sample the release is mainly due to Fe bound P (BD-P) and “loosely-sorbed” P (NH_4Cl-P). In the B1 sample the BD-P fraction substantially decrease as well as NaOH-P and Res-P ones. The BD-P is therefore the most involved fraction in release, as confirmed by literature (Rydin E., 2000). The NaOH-P decrease in the B1 sample is probably linked to the organic content and lithological nature of B sediments, which lead the limy beach (B) to be more sensitive to redox potential variation due to bacterial activity so that, in addition to Fe, Al contributes to the phosphorus release. The HCl- P fraction increases during the test for both samples. Since B has a higher organic content than A, it could be hypothesized that, with a pH increase due to the oxygen consumption by microorganism, the phosphorus adsorption on calcite was favored. In fact, phosphorus co-precipitation with calcium carbonate and carbonate adsorbed phosphorus precipitation are favored by higher pH (Otsuki A. and Wetzel R.G., 1972). This characteristic is relevant in calcareous lakes such as Trasimeno in which the pH average value amounts to

8-8.5 (ARPA, 2012), playing therefore a possible important role towards phosphorus sorption/co-precipitation on calcite dynamics.

Leaching test under anoxic static conditions. Tabs. 7 and 8 and Fig. 10 show the anoxic test results.

Table 7. Leaching test under anoxic static conditions results. Released P concentrations [mg P L^{-1}] after 7, 14, 21 days from the start of the test and release rates [mg m^{-2} d^{-1}] for each sample.

Samples	Released P concentration after 7 days	Released P concentration after 14 days	Released P concentration after 21 days	Release rates
A2	0.132	0.228	0.240	1.905
A3	0.072	0.114	0.132	1.048
B1	0.12	0.33	0.372	2.952
B2	0.15	0.234	0.252	2.000
B3	0.258	0.378	0.498	3.952
C	0.178	0.125	0.0273	2.163

Table 8. Leaching test under anoxic static conditions results. Average concentrations of dissolved P [mg P L^{-1}] at the different collecting times and average release rates [mg m^{-2} d^{-1}].

Samples	Released P average conc. after 7 days	Released P average conc. after 14 days	Released P average conc. after 21 days	Average release rates
A	0.102 ± 0.03	0.171 ± 0.057	0.186 ± 0.054	1.476
B	0.176 ± 0.069	0.314 ± 0.072	0.374 ± 0.123	2.968
C	0.075	0.094	0.088	2.163

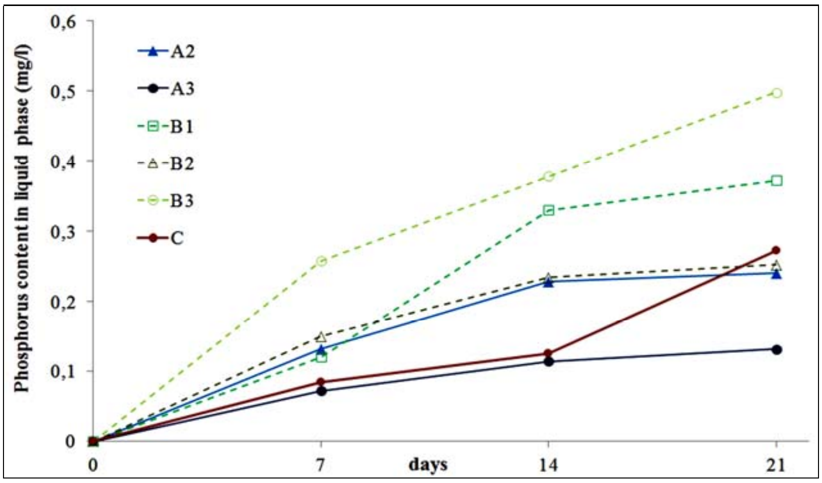

Fig. 6 - Test in anoxic static conditions. TDP contents after 7, 14 and 21 days.

If the results of the tests are compared with the aerobic ones, the encountered differences can be pointed in:

A) the continuous release observed in all the samples (B samples in the previous described test were reaching a “plateau” in the dissolved concentration values vs time);

B) the difference in the released amount (in the anoxic test the amount of released P is one order of magnitude greater than in the aerobic test).

Concerning the point B) it is evident the strong contribution from the reducing conditions existing in the anoxic test (it is possible to evidence that, if the B tests of the total amount of released P are compared, a range between 78% and 90 % can be attributed to the reducing system and, if compared the A and C results of the total amount of released P, the range is between 68- 78 %).

Regarding the point A), the continuous release can be partly linked to the greater contribution of the BD-P fraction and to the lower sorption as HCl-P fraction, as described below in the sequential extraction tests, while in the aerobic tests a qualitative mass balance can evidence the important role of the P sorption as HCl-P in the “plateau” shape of the leaching curve (Fig. 5).

It can be also observed that, while in the aerobic test the C sample showed the highest average release rate, under anoxic conditions it shows a lower P average release rate than B. It can be explained by the fact that in the anoxic test the higher organic content in the C sample plays a minor role on P release since the whole test is performed in reducing conditions.

Finally, the A and B samples were sequentially extracted. Results are shown in Tab. 9.

Table 9. Sequential extraction. Total P contents [mg P kg $^{-1}{}_{\text{dry weight}}$] into extracted solutions before (Init. A1, Init. B1) and after (A1, B1) the leaching test under anoxic static conditions. The sign (-) on percentages indicates a P release, while the sign (+) indicates a P adsorption.

Sample/P- fraction	TP	NH_4Cl	BD-P	NaOH-P	HCl-P	Res-P
Init. A1	184.50	3.87	28.66	15.88	31.37	104.72
A1	162.75	3.09	5.80	10.83	44.87	98.15
% P- release (-)	- 12%	- 20%	- 80%	- 32%	-	-
% P- sorption (+)	-	-	-	-	+ 43%	-
Init. B1	244.50	4.71	55.60	28.74	109.79	45.65
B1	199.50	3.60	15.00	13.20	120.30	47.40
% P- release (-)	- 18%	- 24%	- 73%	- 54%	-	-
% P- sorption (+)	-	-	-	-	+ 9%	-

Compared to leaching test results (Tab. 6), the minor TP content into sediment samples after the leaching test under anoxic conditions (Tab. 9) confirms the higher phosphorus release during the latter. In both the A1 and B1 samples under anoxic environment phosphorus release is mainly due to redox potential sensitive fractions (BD-P and NaOH-P). However, compared to sequential extraction under aerobic conditions, in A1 sample NaOH-P presents different behaviors. More specifically, it increases in the aerobic condition while it decreases in the anoxic one. The behavior in anoxic conditions could be due to the reducing environment that can either contribute to the release of this fraction or inhibit its increase. Conversely, in the B1 sample NaOH-P fraction decreases in both environments.

Desorption test. Desorption tests in mixed conditions were conducted. For testing the behaviour of the sediments in long times the adsorption/desorption tests were carried out on 21 days. Desorption test results regarding the A1, B1 and C samples are shown in Fig. 7.

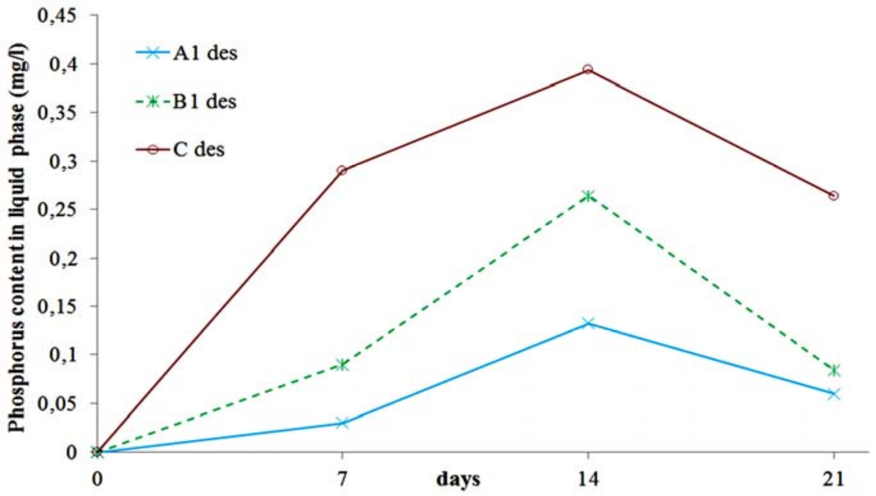

Fig. 7 - Desorption tests under aerobic mixed conditions.

Comparison between TDP contents during the test. As expected, phosphorus release is higher under mixed conditions than in static aerobic ones (Fig. 5). The main reason why the release is higher during the mixed test is probably linked to particles re-suspension, which could increase phosphorus dispersion into the overlaying water because of a rise of specific surface area in contact with water. Moreover, after 14 days from the beginning of the mixed test, an adsorption phase follows the desorption one. Our results therefore show that under mixed conditions suspended materials could represent a support for phosphorus, which can be re-adsorbed on them. In fact, different authors (Holdren, G.C. and Armstrong D.E., 1980) demonstrate that phosphorus release and TDP content in liquid phase generally increase until sediments re-suspension. Hence the TDP content decreases until it reaches values smaller than those in non-mixed conditions. Conversely, TP content continues to increase therefore the released phosphorus is mainly linked to particulate matter. From Fig. 7 it is also worth noting that the B1 sample shows an higher initial P desorption than the A sample; however, the adsorption phase leads the B phosphorus concentration [mg L^{-1}] to be the same order of A phosphorus concentration at the end of the test. This result can be explained by the mineral composition of B particles and by the high specific surface area which characterize this soil (clay). In fact, because of its slow sedimentation velocity and its specific surface area, average fine clay fraction plays an important role in adsorption processes (Giovanardi F., 1995).

Finally, it can also be evidenced that under mixed conditions the C sample presents a higher tendency to phosphorus desorption, compared to the B1 and A1 samples. This behaviour is probably linked to the greater organic content in C and its mineralization by microorganisms (O.C.(C) > O.C.(B) > O.C.(A) on table 2). More specifically, organic substance mineralization leads to an increase in carbon dioxide and, because of the calcareous nature of Lake Trasimeno, calcium carbonate dissolution occurs. Previously with calcium carbonate co-precipitate phosphorus into the overlaying water is simultaneously solubilised (Boström B. et al., 1988). The same remarks can be made for the B1 sample as the A1 sample.

As in the other cases, the A and B samples were sequentially extracted. Tab. 10 shows the content [mg P kg $^{-1}{}_{\text{dry weight}}$] of the various phosphorus forms in sequentially extracted samples.

Table 10. Sequential extraction. Total P contents [mg P kg $^{-1}{}_{\text{dry weight}}$] into extracted solutions before (Init. A1, Init. B1) and after (Des.A1, Des. B1) the desorption test under aerobic mixed conditions. The P release or sorption on percentages is indicated within round brackets for each P fraction. The sign (-) indicates a P release, while the sign (+) indicates a P adsorption.

Sample /P-fraction	TP	NH_4Cl	BD-P	NaOH-P	HCl-P	Res-P
Init. A1	184.50	3.87	28.62	15.86	31.33	104.81
Des. A1	174.70	2.32	17.41	11.99	76.20	66.83
% P- release (-)	- 5%	- 40 %	- 40 %	- 24%	-	-
% P- sorption (+)	-	-	-	-	+ 143 %	-
Init. B1	244.50	4.98	58.81	30.40	116.12	34.19
Des. B1	228.00	5.48	84.72	20.43	87.21	30.15
% P- release (-)	- 7%	-	-	- 33 %	- 25 %	-
% P- sorption (+)	-	+ 10 %	+ 44 %	-	-	-

The TP content slightly decreases in both samples. The BD- P reduction in the A1 sample is minor compared to the leaching and anoxic tests. This may be explained by the minor influence of redox potential variation on phosphorus release under mixed conditions. NaOH- P decrease occurs in both the A1 and B1 samples. Since redox potential plays a small role under mixed conditions, the decrease is probably linked to organic substance presence. This is confirmed by the higher NaOH- P decrease in the B1 sample, which has a greater organic content that leads to a pH increase, compared to the A1 sample. At high pH the ability of phosphorus to bind with Aluminum and Iron compounds decreases because of the ionic exchange reactions which occur when phosphate ions are replaced by idroxide ones (Boström B. et al., 1982). Finally, HCl- P fraction shows an anomalous pattern. Generally, this fraction increases during tests. However, during the B1 desorption test HCl- P fraction decreased. This may be explained by the increasing BD- P fraction during the desorption test. More specifically, a part of released phosphorus may be re-adsorbed and stored in BD- P fraction rather than HCl- P fraction. In fact, released phosphorus forms do not necessarily remain in solution. In many cases the mobilization leads to phosphorus transfer from one fraction into another.

Comparison with other data. The comparison between literature data and our results in the different tests can be pointed in:

- the aerobic leaching test results (Tab. 5), compared with other data reported in literature (Boström B. and Petterson K, 1982), confirm that the average concentration of P in waters resulting in the Lake Trasimeno is slightly lower than the others, as shown in Fig. 8;
- from the anoxic test results (Table 8) it can be evidenced that Lake Trasimeno shows the same order of magnitude of phosphorus release rate as other lakes under anoxic conditions. However, Holdren and Armstrong (1980) use water from the same lake to carry out their experiments. In this latter case it is obvious that the nutrient concentration gradient decreases if compared to the use of distilled water and the release is lower than in our case. In addition, in these tests the SRP content was measured, instead of TDP one.
- the desorption test results for Lake Trasimeno show a lower or equal tendency to phosphorus release compared to studies carried out on Lake Balaton (Istvànovics, V. et al., 1989). Desorption rates are comprised between 0,47 and 2,09 [mg m^{-2} d^{-1}] for Lake Trasimeno and 0,9-1,7 [mg m^{-2} d^{-1}] for Lake Balaton. The analogy derives from the fact that both are defined as calcareous lakes.
- sequential extraction results in the different tests show that the nutrient is mainly adsorbed as HCl-P form. This result is analogous to the results on Balaton Lake (Istvànovics, V. et al., 1989), in which the co-precipitation with $CaCO_3$ process is considered an important contribution to the flux of P to the sediments.

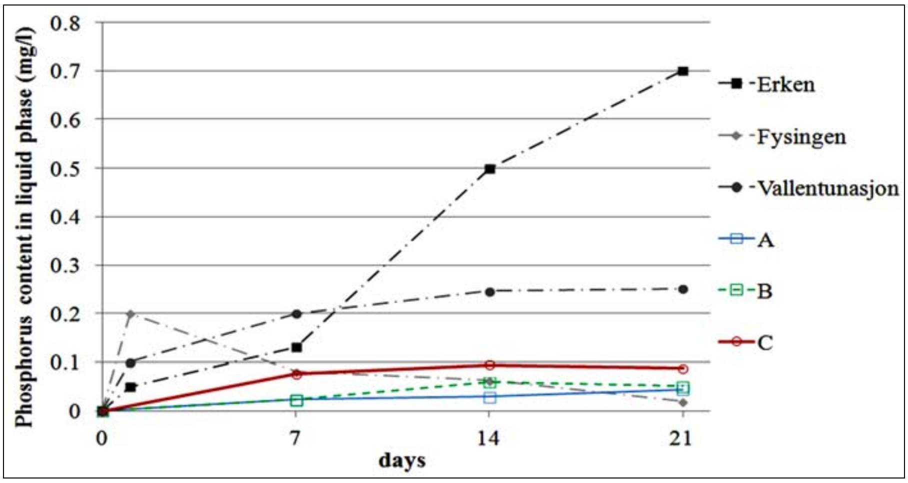

Fig. 8 - Leaching test. Comparison between phosphorus release of Lake Trasimeno (A, B and C average concentrations) and that of other lakes data by literature [46].

Conclusions

It can be concluded that phosphorus release dynamics can be considered influenced also from many mineralogical- lithological factors. Three of them are often of particular importance: (i) iron- manganese content, (ii) calcium content and (iii) presence of clay. In addition to the mineralogical factors, the re-oxygenation of the water column and the sediments re-suspension due to the wind mixing play an important role in the equilibrium concentration of phosphorus in the lake waters. More specifically, the results show the following statements:

- the different redox potential sensitive forms such as iron or manganese associated P are strictly involved in the nutrient release;
- during the leaching test under aerobic conditions, the phosphorus release is mainly linked to the nutrient concentration gradient between pore and overlaying water and to the organic content into sediments.;
- when we face calcareous sediments, the phosphorus precipitation as apatite as well as the co-precipitation/adsorption on carbonates is favored. The clay presence increases the adsorption capacity towards phosphates;
- nearby sites in a well mixed basin can be different in chemical composition and it is possible to evidence different behavior in phosphorus release-sorption dynamic;
- another element which can contribute to maintain an equilibrium in phosphorous concentrations is the limited depth of the water body; in this case the good transfer of oxygen and the re-suspension effects of the wind generated currents can favor phosphorus distribution across the water

column, as confirmed by literature (Sondergaard M. et al., 1992), but at the same time a re-adsorbtion of the phosphorus from the waters.

The maximum phosphorus release rate, which amounts to 3 [mg m^{-2} d^{-1}], was found under anoxic environment, while aerobic static conditions brings a release rate of 0,7 [mg m^{-2} d^{-1}] confirming that the oxygen presence limits the fluxes. The former condition is however hardly present in shallow lakes, if not in a compromised state, where the wind influence leads to re-oxygenation of the water column. As an example, Lake Trasimeno presents a dissolved oxygen concentration higher than 9 [mg l^{-1}] (ARPA, 2012), disadvantaging therefore possible anoxic and reducing conditions.

In mixed conditions tests, the phosphorus initial desorption phase is higher if compared to static aerobic ones.

It can be concluded that, even for sediments from nearby sites in the same well mixed basin, the mineralogical- chemical composition of lake sediments influences phosphorus fluxes from the bottom sediments, while the limited depths of the water column, allowing for oxygen redistribution and sediment re-suspension, can be considered a valid element for phosphorus release-sorption equilibrium in shallow homogeneus lakes. These considerations must be taken into account when a monitoring phase for the eutrophic state of a lake must be planned as well as when a mass balance of the internal–external loading of phosphorus must be carried out.

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