Supplementary material

Vivianite as phosphorus source in lake sediments: Importance of increased sulfate reduction on phosphorus mobilization

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Data Collection:

Surface water: Surface water concentrations were measured at regular time intervals for SRP, sulphide and sulphate by drawing 20 mL of surface water. The obtained values were all calculated into µmol L^{-1}. The water was refilled with lake water and at certain times a fixed volume of stock sulphate solution.

Loss on ignition and dry weight : Around 1g of wet sediment was weighed in a pre-weighed aluminium crucible. The sediment was dried at 105 ^{o}C overnight and weighed again to measure the dry weight (DW) value, in g per g wet weight where the water fraction was 1-DW. Then, the crucibles were placed in an oven at 450 ^{o}C for 3 h, cooled down and weighed again for the Loss On Ignition (LOI) value.

Solid phase concentrations: Sequential extractions were performed on wet sediment, with set volumes of extract and washing steps. 20 mL of the extract was filtered (.45 µm) and acidified with sulfuric acid. The concentration of SRP was measured photometrically in the H2O, NaOH and HCl fractions. Fe was measured in Bipy and BD fractions within 24h after extraction by Atomic Absorption Spectroscopy. P was measured photometrically in the Bipy, BD and NaOH fractions after digesting 5 mL of (diluted) extract with $K_2S_2O_8$.

A fixed weight (70 mg) of dry sediment was digested following the reverse aqua regia meth (DIN 38 414-S7, 1983). The sediment was weighed directly in the Teflon microwave vessels, subsequently 2 mL 37% HCl and 6 mL of 65% HNO3 was added, the vessels were closed and placed in the microwave. The microwave followed a standard program, 40 min of heating and a cooling period. The digestate was transferred to 50 mL Greiner tubes, the microwave vessels and caps rinsed 3 times with MQ water, adding the wash to the digestate. After cooling overnight, the volume was adjusted to 50mL with MQ water and the concentration was measured by inductively coupled plasma optical emission spectroscopy (ICP-OES) for Fe, P, S, Mn, Ca, Al and Ti.

All concentrations were measured in mg L^{-1}, and calculated into µmol L^{-1} for mass balancing.

Calculations:

Surface water concentrations

In order to calculate the release from the sediment independent from variations in water column height, the measured mol L^{-1} values were used to calculate the cumulative load L_j at each timestep j in mol cm^{-2}:

$$L_j = \frac{1}{A}\sum_{i=1}^{j} N_i - N_{i-1;corr} \quad (1)$$

With A the surface of the SWI and N_i the total mass of the respective parameter in the water column with volume V_{water} at timestep i, with concentration C_i:

$$N_i = C_i V_{water} \quad (2)$$

And the previous timestep corrected for the replaced sampling volume (20 mL), and - in the case of sulphate – added stock:

$$N_{i-1;corr} = \llbracket (V) \rrbracket_{water} - 20) C_{i-1} \; + \; 20 C_{lake} + \left[V_{stock,i-1} \llbracket (C) \rrbracket_{stock} - C_{lake}) \right] \quad (3)$$

The rate of release over time in µmol cm^{-2} d^{-1} was calculated from the cumulative load using a linear model (LN).

Solid phase quantification

Per dry weight concentrations

The measured concentrations from the extracts or digestate were used to calculate dry weight concentrations.

$$C\left(\mu mol/_{gDW}\right) = \frac{C\left(\mu mol/_{L}\right) V}{W} \quad (4)$$

Where C is the concentration of the element in µmol per gram dry sediment and µmol per litre extract, respectively. V is the total volume of extract used to extract a weighed mass of sediment, W. In the case of the sequential extraction, wet sediment was used so the value was calculated into per dry weight by multiplying by the DW value.

Sediment chemistry change

To quantify the change in sediment composition (ΔC_{sed}) - in particular the P and S content - the measured concentrations for each depth at the end of the experiment (C_{meas}) had to be compared with the composition at the start (C_{start}).

$$\Delta C_{sed} = C_{meas} - C_{start} \quad (5)$$

However, the composition profile at the start of the experiment was not measured directly, so a theoretical starting composition was used (*Theoretical* in Fig 4A). The composition, LOI and DW were determined of the two sediment types ($C_{OM;\ start}$ and $C_{Viv;\ start}$) before filling the mesocosms, and with a few assumptions these values were used to estimate the starting composition as function of depth for each tube.

Assumptions

- The concentrations of the treatments at the start of the experiment was the same as that of the two respective sediments before filling.
- Treatment Viv. contained only one of the two sediments while Viv. + OM contained both. Treatment Qs + OM contained also quartz sand, but this was assumed to have a concentration of 0 for all measured elements.
- If the concentration of a certain element is the same as the starting sediment at every depth, it did not change as result of the experiment.

For treatment Viv., there was only one type of sediment supplied at the start of the experiment, so the theoretical starting composition was equal to that of the Viv. sediment at every depth.

$$C_{start} = C_{Viv;\ start} \quad (6)$$

For treatment Qs + OM, the depths of interest were only the top cm with OM, as below 1.5 cm the Qs was found. Regarding only the top OM sediment, the starting composition would have been that of the OM sediment.

$$C_{start} = C_{OM;\ start} \quad (7)$$

Treatment Viv. + OM, however, is a bit more complicated. While the top and bottom were clearly defined by respectively the OM and Viv. sediments, there is a contact zone between the sediments which is characterized by a compositional transition. The switch from OM to Viv. sediment can be seen in the composition profile as a steep gradient in elemental concentration, LOI and DW around 2 cm depth (Fig. 3). The sediment around the contact zone is also where the largest chemical changes were expected as result of the experiment. Thus accurate quantification of treatment effects required distinguishing the gradient between OM and Viv. sediment.

To determine the compositional variation resulting from the difference between the initial OM and Viv. sediment, a theoretical starting composition was calculated for each depth as function of the two starting sediment concentrations. The calculation was based on the assumption that some parameters did not change during treatment, and any variation in concentration is a result of mixing of the two sediment. The unchanged parameters were determined as follows: If above 2cm depth the concentrations followed the OM sediment starting values, and below 3cm the composition of the Viv. sediment, then it was assumed the composition did not change over the course of the experiment and the gradient was purely from mixing between the sediments at the transition zone. This was the case for Al, Ti, Fe and Mn, which all followed the same pattern.

From the concentration of the unchanged elements, the mixing between the two sediments was calculated as mass fraction ($w_{Viv.}$) of Viv. sediment:

$$w_{Viv.} = \frac{C_{meas(Al;\,Ti;\,Fe;\,Mn)} - C_{OM;\,start}}{C_{Viv;\,start} - C_{OM;\,start}} \tag{8}$$

Where C_{meas} represents the concentration of an unchanged parameter at a specific depth. The Viv. mass fractions were calculated for all four elements (Al, Ti, Fe and Mn, Table 4), and the average value was used as estimation of the sediment proportions, shown in Fig. 3 as function of depth with errors from the four values. The $w_{Viv.}$ value is unitless, and a value of one means the composition is equal to the of the Viv. sediment at the start of the experiment, while zero means equal to the OM sediment. Values between 0 and 1 imply a degree of mixing between the two sediments. While mixing was most striking at the depth interval between 2-2.5 cm, the calculated proportion was used in all slices of the Viv. + OM sediment to calculate a theoretical starting composition of the changed parameters (P and S) via:

$$C_{start} = w_{Viv.}\, C_{Viv;\,start} + [\![(1 - w]\!]_{Viv.})C_{OM;\,start} \tag{9}$$

Per volume and surface area concentrations

For mass balance purposes, the elemental composition was calculated per volume wet sediment, which was used to calculate total mass changes of the sediment for P and S. Starting with the per dry weight concentrations, the corresponding concentration per volume wet sediment could be calculated using the density and the DW:

$$C\left(\mu mol/_{cm^3}\right) = C\left(\mu mol/_{g}\right) \times DW \times \rho \tag{10}$$

With DW the measured dry weight fraction and ρ the density of the bulk sediment (solid + liquid phase) in g cm^{-3}. The density was not measured directly, but estimated from the LOI and dry weight values, assuming the LOI as the organic fraction and the remaining 1-LOI as the inorganic fraction of the solid phase:

$$\rho = 1 \times (1 - DW) + 1.25 \times LOI \times DW + 2.65 \times (1 - LOI) \times DW \tag{11}$$

Which is a weighted average of the densities of water (1 gcm^{-3}), OM (1.25 gcm^{-3}) and inorganic particular fraction (2.65 gcm^{-3}), values from Avnimelech et al. (2001).

The P and S concentration per volume wet sediment was calculated for each sediment slice, and is depicted in Fig. 4A. The change in P and S content per volume wet weight is shown in Fig 4B. The total change of P and S per surface area in the analysed sediment (up to 10 cm depth) was calculated by the sum of the mass change in each slice i:

$$\Delta C_{sed;\,tot} = \sum_{i=0}^{10} \Delta C_{sed;\,i}\, d_i \qquad (12)$$

Where $\Delta C_{sed;\,tot}$ is the total change in µmol cm^{-2} within the first 10 cm of sediment. $\Delta C_{sed;\,i}$ is the concentration change for slice i in µmol cm^{-3}, and d_i the thickness of the slice in cm.

Tables

Table 3: Measured concentrations (C) of SRP, Sulphide and Sulphate in the water column at each timestep. The cumulative load (L) to the water column was calculated with equations 1-3. In the case of sulphate, the added stock was taken into account to calculate the load. The errors show the standard deviation based on replicate incubations (N=3).

		SRP		Sulphide		Sulphate		
Treatment	Incubation time (days)	C ($\mu mol\ L^{-1}$)	L ($\mu mol\ cm^{-2}$)	C ($\mu mol\ L^{-1}$)	L ($\mu mol\ cm^{-2}$)	C ($\mu mol\ L^{-1}$)	L ($\mu mol\ cm^{-2}$)	Added sulphate stock (mL)
Viv. + OM	1	120 ± 5	0.1 ± 0.2			1464 ± 26	2.6 ± 4	1
	5	140 ± 64	0.6 ± 1			1526 ± 78	0.7 ± 4.7	
	8	64 ± 8	-0.8 ± 0.3			1467 ± 20	0 ± 3.9	
	11	79 ± 50	-0.5 ± 1.1	-2 ± 0	0 ± 0	1339 ± 30	-2.1 ± 4.1	1
	13	47 ± 7	-1.1 ± 0.4	-2 ± 0	0 ± 0	1394 ± 18	-4.3 ± 3.2	
	18	54 ± 8	-0.9 ± 0.4	26 ± 24	0.6 ± 0.5	1388 ± 33	-3.9 ± 3.2	
	22	69 ± 3.5	-0.6 ± 0.2	102 ± 86	2.1 ± 1.7	1123 ± 44	-8.7 ± 3.9	1
	25	70 ± 18	-0.5 ± 0.6	50 ± 82	1.2 ± 1.7	1136 ± 47	-11.9 ± 3.3	2.5
	29	76 ± 33	-0.4 ± 0.4	39 ± 51	1 ± 1.1	1381 ± 53	-15.8 ± 3.8	
	39	110 ± 45	0.3 ± 0.7	168 ± 110	3.6 ± 2.5	1115 ± 30	-20.7 ± 3.7	1
	42	110 ± 43	0.4 ± 0.7	165 ± 126	3.7 ± 2.8	1134 ± 40	-23.5 ± 3.9	2.5
	46	120 ± 46	0.7 ± 0.7	234 ± 159	5.2 ± 3.7	1479 ± 66	-25.5 ± 4.9	
	56	140 ± 45	1.2 ± 0.7	432 ± 239	9.4 ± 5.5	1023 ± 61	-34.2 ± 2.1	
	61	140 ± 49	1.2 ± 0.9	277 ± 126	6.5 ± 3.3	966 ± 87	-35 ± 5.1	
	75	160 ± 37	1.7 ± 0.6	425 ± 121	9.7 ± 3.3	746 ± 23	-39.3 ± 3.4	
	78	160 ± 35	1.9 ± 0.6	466 ± 91	10.8 ± 2.9	703 ± 22	-40.1 ± 3.6	4.5
	103	210 ± 33	3.1 ± 0.6	812 ± 241	18.2 ± 6	963 ± 25	-51.3 ± 2.8	
	117	220 ± 30	3.4 ± 0.5	553 ± 71	13.5 ± 3.3	758 ± 31	-55.2 ± 3	3.5
	140	250 ± 26	4.2 ± 0.5	436 ± 91	11.4 ± 3.1	1002 ± 100	-63.1 ± 1.6	3
	152	280 ± 29	4.8 ± 0.5	488 ± 91	12.8 ± 3.2	1933 ± 404	-54.8 ± 12.2	
	203	340 ± 20	6.3 ± 0.4	536 ± 62	14.1 ± 2.6	1103 ± 258	-70.4 ± 7.8	3
	218	340 ± 11	6.6 ± 0.3	559 ± 113	14.9 ± 3.6	1200 ± 184	-79 ± 7.5	
	242	360 ± 8	7.2 ± 0.3	287 ± 119	9.8 ± 3.6	812 ± 143	-86.5 ± 6.6	
Viv.	1	30 ± 18	-0.5 ± 0.3			1398 ± 15	0.8 ± 0.8	1
	5	44 ± 15	-0.1 ± 0.2			1554 ± 21	1.4 ± 0.7	
	8	2.6 ± 2	-1.1 ± 0.6			1478 ± 10	0 ± 0.4	
	11	3.6 ± 2	-1.1 ± 0.5	-2 ± 0	0 ± 0	1408 ± 21	-1.1 ± 0.1	1
	13	3.6 ± 2	-1.1 ± 0.5	-2 ± 0	0 ± 0	1526 ± 36	-1.4 ± 1.2	
	18	2.8 ± 1.2	-1.1 ± 0.5	-2 ± 0	0 ± 0	1530 ± 10	-0.8 ± 0.8	
	22	3.0 ± 0.9	-1.1 ± 0.5	-2 ± 0	0 ± 0	1397 ± 40	-3.4 ± 1.2	1
	25	1.9 ± 1.3	-1.1 ± 0.5	-2 ± 0	0 ± 0	1395 ± 48	-6.6 ± 1.6	1
	29	0.5 ± 0.2	-1.2 ± 0.5	-2 ± 0	0 ± 0	1458 ± 10	-8.3 ± 0.3	
	39	0.7 ± 0.7	-1.2 ± 0.5	-2 ± 0	0 ± 0	1304 ± 94	-11.6 ± 1.8	1
	42	0.4 ± 0.3	-1.2 ± 0.5	-2 ± 0	0 ± 0	1444 ± 35	-11.2 ± 1.3	1
	46	0.6 ± 0.5	-1.2 ± 0.5	-2 ± 0	0 ± 0	1595 ± 24	-12.6 ± 0.6	
	56	1.4 ± 1.2	-1.1 ± 0.5	-2 ± 0	0 ± 0	1307 ± 15	-19 ± 0.8	
	61	0.6 ± 0.3	-1.2 ± 0.5	-2 ± 0	0 ± 0	1243 ± 23	-20.1 ± 0.7	
	75	1.1 ± 1.1	-1.2 ± 0.5	-2 ± 0	0 ± 0	1234 ± 68	-19.9 ± 2	
	78	0.7 ± 0.4	-1.2 ± 0.5	-2 ± 0	0 ± 0	1315 ± 27	-17.5 ± 1.1	2.5
	103	4 ± 3	-1.1 ± 0.6	-2 ± 0	0 ± 0	1587 ± 16	-19.6 ± 0.7	
	117	3 ± 2	-1.1 ± 0.6	0 ± 0	0 ± 0	1520 ± 55	-20.6 ± 1.2	
	140	5 ± 4	-1.1 ± 0.6	0 ± 0	0 ± 0	1437 ± 6	-22 ± 0.4	0.33
	152	3 ± 3	-1.1 ± 0.5	0 ± 0	0 ± 0	1545 ± 320	-20 ± 5.4	
	203	16 ± 13	-0.8 ± 0.7	0 ± 0	0 ± 0	1423 ± 200	-22 ± 2.7	
	218	20 ± 16	-0.7 ± 0.9	1 ± 0	0 ± 0	1318 ± 227	-23.9 ± 3.4	
	242	8 ± 6	-1 ± 0.7	0 ± 0	0 ± 0	1243 ± 200	-25.2 ± 3	
Qs + OM	1	58 ± 10	-0.4 ± 0.4			1329 ± 6	0.8 ± 0.4	1
	5	61 ± 19	-0.3 ± 0.6			1502 ± 21	1.7 ± 1.1	
	8	46 ± 1	-0.6 ± 0.1			1384 ± 36	-0.7 ± 0.3	
	11	43 ± 6	-0.7 ± 0.2	1 ± 5	0.1 ± 0.1	1270 ± 27	-3 ± 0.2	1
	13	43 ± 7	-0.7 ± 0.2	10 ± 21	0.3 ± 0.5	1342 ± 27	-4.5 ± 0.8	
	18	43 ± 7	-0.6 ± 0.3	74 ± 71	1.9 ± 1.8	1339 ± 53	-4.2 ± 0.9	
	22	48 ± 2	-0.5 ± 0.2	97 ± 109	2.5 ± 2.8	1148 ± 38	-8.3 ± 0.5	1
	25	48 ± 4	-0.5 ± 0.2	188 ± 97	4.8 ± 2.7	1185 ± 68	-10.8 ± 1.4	2.5
	29	48 ± 3	-0.4 ± 0.2	387 ± 160	9.8 ± 4.5	1427 ± 31	-13.8 ± 0.4	
	39	48 ± 2	-0.4 ± 0.2	562 ± 86	14.3 ± 2.9	905 ± 49	-26 ± 1.1	1
	42	47 ± 1	-0.4 ± 0.2	587 ± 79	15.3 ± 2.7	1099 ± 11	-24.6 ± 0.1	4.5
	46	47 ± 3	-0.4 ± 0.2	640 ± 178	17.1 ± 5.3	1642 ± 54	-27.6 ± 1.9	
	56	49 ± 3	-0.3 ± 0.2	1071 ± 90	27.9 ± 3.1	1246 ± 114	-36.6 ± 2.6	
	61	46 ± 2	-0.3 ± 0.2	711 ± 181	20 ± 5.6	1292 ± 64	-35.1 ± 1.3	
	75	46 ± 2	-0.3 ± 0.2	961 ± 123	26.6 ± 4.5	1008 ± 65	-41.5 ± 1.4	
	78	47 ± 2	-0.2 ± 0.2	1130 ± 186	31.4 ± 6.3	945 ± 44	-42.9 ± 0.9	3.5
	103	48 ± 2	-0.2 ± 0.2	1332 ± 214	37.2 ± 7.2	1070 ± 45	-52.4 ± 1	
	117	49 ± 2	-0.1 ± 0.2	1190 ± 214	34.6 ± 7.3	790 ± 110	-58.9 ± 2.4	3.5
	140	49 ± 2	-0.1 ± 0.2	1188 ± 220	35.4 ± 7.6	1017 ± 165	-66.1 ± 4	3
	152	50 ± 6	0 ± 0.3	1164 ± 215	35.7 ± 7.6	1157 ± 509	-73.2 ± 12.3	
	203	50 ± 1	0 ± 0.2	1459 ± 348	43.8 ± 11.2	632 ± 512	-85.4 ± 12.3	3
	218	35 ± 24	-0.3 ± 0.7	1455 ± 364	44.7 ± 11.9	977 ± 442	-88 ± 11.2	
	242	49 ± 4	0 ± 0.3	1148 ± 369	38.3 ± 11.9	675 ± 430	-95.1 ± 11	

Table 4: The concentrations of Mn, Fe, Al and Ti in the solid phase of the sediment of treatment Viv. + OM after incubation, as shown in Fig. 3. The concentrations of the elements were used to calculate the proportion of Viv. vs OM sediment for each depth, by comparing with the composition of the two sediments at the start of the experiment (equation 8). The two starting sediment composition are shown below.

Treatment Viv. + OM	Mn		Fe		Al		Ti		
Depth	C ($\mu mol\ g^{-1}$)	$w_{Viv.}$	C ($\mu mol\ g^{-1}$)	$w_{Viv.}$	C ($\mu mol\ g^{-1}$)	$w_{Viv.}$	C ($\mu mol\ g^{-1}$)	$w_{Viv.}$	Mean $w_{Viv.}$
0.25	18	0.06	212	0.13	177	0.09	5	0.11	0.096 ± 0.03
0.75	13	-0.008	140	-0.0006	134	-0.07	4	-0.10	-0.04 ± 0.05
1.25	16	0.03	178	0.07	159	0.02	4	-0.05	0.02 ± 0.05
1.75	18	0.07	212	0.13	162	0.03	5	0.09	0.08 ± 0.04
2.25	45	0.45	518	0.67	290	0.50	8	0.66	0.57 ± 0.11
2.75	77	0.90	738	1.07	425	0.98	10	1.06	1.00 ± 0.06
3.50	88	1.06	731	1.05	444	1.05	9	0.90	1.01 ± 0.08
4.50	89	1.06	730	1.05	425	0.98	9	0.93	1.01 ± 0.06
6.00	87	1.05	744	1.08	439	1.03	8	0.78	1.0 ± 0.1
8.00	87	1.05	741	1.07	428	0.99	9	0.98	1.02 ± 0.04
Start sed:									
OM	14		140		152		4		
Viv.	84		701		430		10		

Table 5: Measured concentrations (C_{meas}) of total P and S in the solid sediment, per gram dry weight and per volume of sediment. With an estimation of the starting composition (C_{start}) based on the compositions of the Viv. and OM sediments, the change in P and S content after incubation (ΔC_{sed}) was calculated (equations 5-9). See also Fig. 4.

		P				S			
Treatment	Depth	C_{meas} (µmol g^{-1})	C_{meas} (µmol cm^{-3})	C_{start} (µmol cm^{-3})	ΔC_{sed} (µmol cm^{-3})	C_{meas} (µmol g^{-1})	C_{meas} (µmol cm^{-3})	C_{start} (µmol cm^{-3})	ΔC_{sed} (µmol cm^{-3})
Viv. + OM	0.25	44	2.6	4.8	-2.2	440	26	17	9.4
	0.75	43	3.0	4.5	-1.4	360	25	19	6.1
	1.25	49	3.8	5.5	-1.7	350	27	21	5.6
	1.75	52	4.3	6.7	-2.4	400	33	24	9.5
	2.25	42	4.7	16	-11	710	78	36	42
	2.75	110	14	24	-10	620	75	45	30
	3.50	190	26	28	-2	430	60	52	8
	4.50	200	31	31	0.25	360	56	58	-1.7
	6.00	200	32	31	1.3	360	57	59	-2
	8.00	200	33	33	-0.066	350	58	61	-3.3
B	0.25	180	17	19	-1.4	380	36	35	0.83
	1.25	200	26	26	0.016	370	49	49	-0.52
	1.75	200	29	29	0.76	360	53	54	-1.3
	2.75	200	31	31	0.46	350	56	58	-2.7
	3.50	200	31	31	-0.061	360	57	59	-2.4
	4.50	230	37	32	4.8	360	57	60	-2.2
	6.00	200	33	32	0.36	380	61	61	0.61
	8.00	200	34	34	0.69	360	61	63	-1.9
C	0.25	31	1.9	3.3	-1.4	490	30	13	17
	0.75	33	2.4	3.6	-1.2	330	23	14	9.2
	1.25	40	4.1	4.7	-0.58	260	27	18	8.1
	1.75	7.8	4.7	8.8	-4	46	27	35	-7.1