An investigation of the origin and mobility of phosphorus in freshwater sediments from Bort-Les-Orgues Reservoir, France

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In order to assess the origin and the potential mobility of phosphorus (P) in the sediment of the Bort-Les-Orgues Reservoir, France, two sequential extraction schemes, *i.e.*, the SMT (modified Williams method) and the Golterman schemes, were compared. Finally, the potential mobility of P in this sediment was estimated from results of sequential extraction. The SMT method appeared to be more satisfactory than the Golterman method, which is in accordance with results from a study currently carried out in the framework of the European programme Standards, Measurements and Testing. Iron-bound P and organic P were the dominant forms of P in the sediment; these forms are likely to be released at the sediment/water interface in case of anoxia and could diffuse into the water column, thus increasing the risk of eutrophication in this sensitive reservoir. The P stock (330 ± 66 t) is not negligible and should be taken into account in any restoration project of the reservoir. The SMT procedure seems promising and will provide, in the near future, a valuable tool for water managers in the field of lake restoration.

Introduction

Water management of lakes, reservoirs and watercourses has become an increasing problem due to the development of eutrophication. This excessive supply of phosphorus (mainly from anthropogenic origin) to water systems, induces a degradation of their quality through the proliferation of algae, thus hindering various water uses. Much effort and money have been spent on combating this form of pollution, but eutrophication remains one of the most important water quality problems in Europe. This clearly appears through the Urban Wastewater European Directive of May 21, 1991, in which eutrophic waters are defined as 'sensitive areas' requiring stricter standards for phosphorus and nitrogen discharge to receiving waters.

Phosphorus is regarded as the key factor in freshwater eutrophication.[1-3] It has two origins, *i.e.*, external and internal. Phosphorus from external origin comes from diffuse sources (natural, agricultural) or point sources (industrial and domestic effluents). This nutrient is also released from the sediment, which acts as an internal source.[4] Sediment can contribute phosphate to the overlying waters at levels comparable to the external source.[5]

However, not all the forms of P are likely to be released and thereby increase eutrophication. The ability of a sediment to store or release P has repercussion on the trophic state of a lake, hence on its productivity. The study of the sediment behaviour is, therefore, a key factor which helps understanding the P cycle in rivers and lakes. It is also of prime importance in the framework of water management and restoration of water bodies.

The various forms in which P occurs in sediments has received considerable attention during the past decades and many extraction schemes have been developed. Good extraction methods are operationally defined on the basis of the reactivity of a particular phase in a given extractant. There are two types of methods: the 'strong' ones using HCl–NaOH[6-9] and the 'soft' ones in which chelators such as nitrilo triacetic acid or EDTA are used.[10,11]

Extraction methods not only provide information on the potential mobility of P species, they also allow the assessment of the origin of the sediment phosphorus.

In this paper, two sequential extraction schemes, modified Williams (SMT) and Golterman, aimed at determining the origin of phosphorus in the sediment of the Bort-Les-Orgues Reservoir (France) are compared. Finally, the potential mobility of phosphorus in this sediment is assessed.

Description of the study site

The hydroelectric reservoir of Bort-Les-Orgues is located in the upper part of the Dordogne River, not far from its source; it is the largest reservoir of the French Massif Central. The drainage basin is 1745 km² (1010 km² for the Dordogne River, 735 km² for the Rhue River). The reservoir is 20 km long with a mean depth of 43.7 m and a maximum depth of 110 m. For the normal elevation of exploitation (542.5 m above sea level), it has an area of 10.91 km² and a volume of 477×10^6 m³. It should be noted that these data apply for 1996, the year during which this study was carried out. The main set of characteristics regarding hydrology, land use and population are given in Ruban and Demare.[12]

Sampling and preservation

Three sediment cores were taken in the reservoir in 1997, down to a depth of 25 cm, the CEMAGREF sampler was used. A surface sample (0–5 cm) was also collected by means of a grab sampler. The cores were sliced as follows : 0–2 cm, 2–5 cm, 5–10 cm and then every 5 cm to the bottom. The samples were put into glass bottles and stored at a temperature of 4 °C until analysis. The sediment was passed through a 200 μm sieve in order to eliminate coarse plant fragments and then freeze dried. Though not perfect, this technique induces little change in the sediment and allows reproducible analyses even after several months, which is not always the case with fresh sediment.

pH and redox potential (Eh) were measured *in situ* by means of Ponselle probes (Ponselle PVRT).

Sample analysis

The following determinations were carried out on the fraction of the sediment with a particle size of less then 200 μm: (i) loss on ignition (calcination at 550 °C for 2 h); (ii) water content (drying at 105 °C until stable weight); (iii) particle size distribution (laser diffraction, Malvern Mastersizer MS1005) Kjeldahl nitrogen[13] (distillation with concentrated H_2SO_4); (iv) iron, calcium (FAAS, Varian Spectra A300); (v) organic carbon[14] (oxidation with potassium dichromate); (vi) total phosphorus (persulfate digestion + colorimetry according to Murphy and Riley[15]); and (vii) sequential extraction of P. Two operationally defined extraction schemes were used in this study, i.e., a modified version of the Williams method (SMT), which has been proposed in the frame of the 'Standards, Measurements and Testing' programme of the European Commission, and the Golterman method (G). The initial version of the Williams method and the Golterman scheme are widely recognised for the determination of P compounds in lake sediments,[10,11,16–18] and the SMT protocol seems promising[19] because it is relatively easy to implement, can be used for all kinds of sediments (either calcareous, siliceous or organic), and has a good reproducibility.

The SMT method is composed of five steps and involves the use of aqueous solutions of NaOH and HCl[19] (Table 1). The following forms are determined : iron-bound P, calcium-bound P, inorganic P, organic P and total P.

The Golterman method, (G) utilises chelators (Ca–EDTA, Na_2EDTA) and is carried out at a pH similar to the sediment pH. It also comprises five steps as shown in Table 1: labile P, iron-bound P, calcium-bound P, acid soluble organic P and reductant organic P.

Both methods have shortcomings, e.g., the partial resorption of P extracted by NaOH onto $CaCO_3$ in the case of SMT, and possible solubilisation of a very small part of organic matter by NaOH in the first step. In the case of the G method, chelators interfere with P determination and the method is very long and lacks precision.

The detection limits were 0.01 mg g^{-1} for the forms of P and total phosphorus (TP), 1 mg g^{-1} for Fe and 0.1 mg g^{-1} for Ca.

Five replicate determinations were made for each form of P (for both methods). The coefficient of variation ranged from 0.5 to 5%. For the SMT scheme, the precision of the method is $\pm 5\%$ for HCl–P, inorganic P and concentrated HCl extractable P, $\pm 10\%$ for NaOH–P and organic phosphorus (OP). Regarding the G method, the precision is around $\pm 20\%$, $\pm 50\%$ for labile P because of the very small quantities extracted in this step.

The Murphy and Riley colorimetric method[15] was used to measure P in the extracts. The quantification of phosphate was based upon calibration curves of standard solutions. These curves were determined several times during the period of analysis.

All the reagents used were analytical-reagent grade; the glassware and plasticware were soaked in 0.3% HCl and rinsed with de-ionised water. A quality control procedure was applied throughout the different steps of sample preparation and analysis. The quality control procedure mentioned was that in use at the Water Division of Laboratoire Central des Ponts et Chaussées. The materials and equipment (e.g., glassware, balances, pH meters, pipettes, spectrophotometers) were regularly checked and the traceability of the samples was ensured thanks to data reported in specific books. Furthermore, blanks and standards were regularly run with each series of analyses in order to check the validity of the data.

Characteristics and origin of the sediment

Fig. 1 shows the main characteristics of the sediment in the Bort-Les-Orgues Reservoir. The sediment was mainly silt (87% on average) and was homogeneous with depth. Furthermore, there was little variation from upstream to downstream. Organic carbon slightly increased from upstream (5.4%) to downstream (6.2%); these values are in the range of concentrations for sediments in reservoirs from crystalline watersheds (4.9–6.4%) as reported by Rofes.[20]

Calcium concentration was low (7.2 mg g^{-1}), whereas iron concentration was high (58 mg g^{-1}). Again, these elements were homogeneous with depth (Table 2). As the iron concentration was much higher than the calcium concentration, iron would probably be a key factor in phosphorus exchange at the sediment/water interface. Note that the abundance of iron is characteristic of crystalline regions such as the French Massif Central.

The C/N ratio is a good indicator of organic carbon sources.[17] Sediments of terrestrial origin have a C/N ratio of around 14–20 (by weight), while phytoplankton, the major source of autochthonous organic matter in lakes, produces ratios of from 5 to 9. In the Bort-Les-Orgues sediment, C/N averaged 13 upstream and 11 downstream. These values are slightly higher than the average for the Pareloup Reservoir (9.8) located about 100 km south from Bort-Les-Orgues. This ratio results from the mixing of two pools of organic matter (OM), autochthonous and allochthonous, on which is superimposed biogeochemical modification of the particulate matter. Allochthonous organic matter prevailed but it can be seen that autochthonous material increased downstream.

Sequential extraction of P

Comparison of the SMT and Golterman methods

Total phosphorus (TP) concentrations in the surface sediment (SMT method) are presented in Fig. 2. Although TP concentrations were rather high ($2–2.5 \pm 0.1$ mg g^{-1} on average), these values are comparable to those reported by Boström et al.[21] for lake sediments and they are in the upper range of concentrations for sediments from crystalline reservoirs as reported by Rofes.[20] There was no significant tendency with depth as shown in Table 2. The small variations observed probably resulted from changes in phosphorus inputs over

Table 1 Reagents used and corresponding P fractions in the two sequential extraction procedures tested in this study

	Step 1	Step 2	Step 3	Step 4	Step 5
SMT	NaOH 1 mol L^{-1}, iron-bound P, bioavailable	HCl 1 mol L^{-1} + 3.5 mol L^{-1}, Ca-bound P, non-available	HCl 3.5 mol L^{-1} + calcination, total P	HCL 1 mol L^{-1}, inorganic P	HCl 1 mol L^{-1} + calcination, organic P, partly available
Golterman	H$_2$O, labile P, bioavailable	Ca–EDTA + dithionite 0.05 mol L^{-1}, iron-bound P, bioavailable	Na$_2$–EDTA 0.1 mol L^{-1}, Ca-bound P, non-available	H$_2$SO$_4$ 0.25 mol L^{-1}, acid soluble organic P bioavailable	NaOH 2 mol L^{-1}, reductant organic P, non-available

$S = 10.45 \text{ km}^2$
$V = 477 \times 10^6 \text{ m}^3$
mean depth = 43.7 m
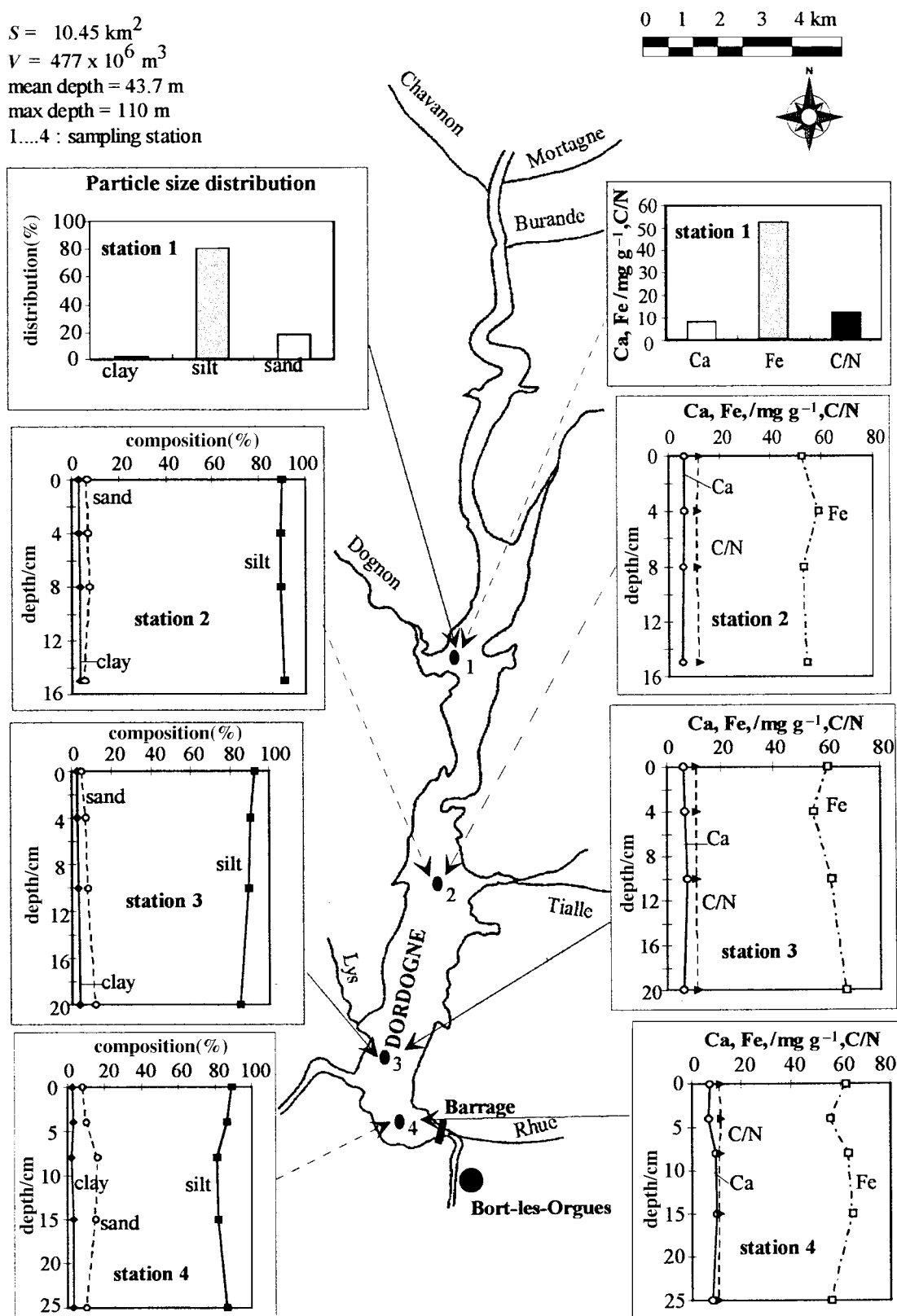max depth = 110 m
1....4 : sampling station

0 1 2 3 4 km

N

Chavanon

Mortagne

Burande

Particle size distribution

distribution(%)

station 1

clay   silt   sand

Ca, Fe /mg g⁻¹,C/N

station 1

Ca   Fe   C/N

composition(%)

depth/cm

sand

silt

station 2

clay

Dognon

Ca, Fe,/mg g⁻¹,C/N

depth/cm

Ca

C/N

Fe

station 2

composition(%)

depth/cm

sand

silt

station 3

clay

Ca, Fe,/mg g⁻¹,C/N

depth/cm

Fe

Ca

C/N

station 3

Tialle

Lys

DORDOGNE

Barrage

Rhue

composition(%)

depth/cm

clay   silt

sand

station 4

Bort-les-Orgues

Ca, Fe,/mg g⁻¹,C/N

depth/cm

C/N

Ca

Fe

station 4

Fig. 1 Characterization of the sediment in the Bort-Les-Orgues Reservoir.

time (dry year/wet year), but these changes remained small, within the precision of the method. Besides, TP concentrations tended to increase from upstream (1.99 ± 0.1 mg g⁻¹) to downstream (2.55 ± 0.13 mg g⁻¹), as did organic C concentrations. This has been observed in other reservoirs, e.g., in St Etienne Cantalès Reservoir.[22] In the case of Bort-Les-Orgues, the increase in P could result from inputs from the Rhue River

since P concentration in the Rhue River is higher than that of other tributaries of the lake. The influence of the Rhue River was observed up to station 3, 2 km from the dam.[23]

In order to know whether the difference between upstream and downstream TP was significant, a statistical test was carried out. Because the number of observations was small, the non-parametric test of White was used. For $\alpha = 0.05$, the

Table 2 Concentration of the forms of P, Fe, and Ca in a sediment core collected at station 4 (deeper part of the lake)

| Depth/ cm	Ca/ mg g^{-1}	Fe/ mg g^{-1}	TP/ mg g^{-1}	HCl–P/ mg g^{-1}	NaOH–P/ mg g^{-1}	OP/ mg g^{-1}
0	7.3	5.8	2.69	0.38	1.55	0.67
2–5	7.2	59	2.65	0.42	1.60	0.62
5–10	7.1	58	2.60	0.40	1.62	0.65
10–15	7.2	58	2.70	0.40	1.50	0.69
15–20	7.2	57	2.72	0.42	1.65	0.63
20–25	7.3	59	2.67	0.42	1.60	0.63
Mean	7.2	58	2.67	0.41	1.59	0.65
SD	0.08	0.75	0.05	0.02	0.05	0.03
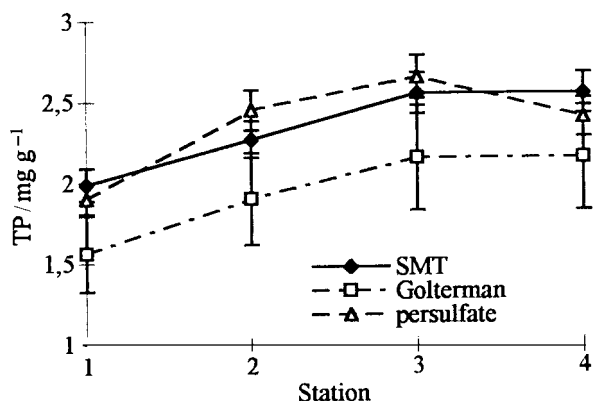
Fig. 2 Total phosphorus concentrations in the Bort-Les-Orgues Reservoir. TP was measured by the SMT and Golterman extraction schemes, and by persulfate digestion. Five replicates were made, the mean value and standard deviation are reported on the figure.

hypothesis of equality between the means was rejected, therefore, it can be admitted that upstream P values are different from downstream P values.

Fig. 3 shows the distribution of phosphorus forms at the four stations in the Bort-Les-Orgues sediments, the SMT and Golterman methods were used. Concentrations were homogeneous within a core (Table 2), consequently, average values are presented here. The test of White was again applied to test the difference between the two methods. As shown in Table 1, step 1 (SMT) and 2 (G) are equivalent, so are step 2 (SMT) and 3 (G), and step 4 (SMT) and 4+5 (G). Consequently, for each station, HCl–P (SMT)/Ca–P (G), NaOH–P (SMT)/Fe–P (G), OP (SMT)/acid soluble OP + reductant OP (G) were compared. For $\alpha = 0.05$ the comparison of means carried out according to this test showed a significant difference. This confirms that the SMT and Golterman methods are not equivalent.

The validity of the SMT scheme and the accuracy with which it has been carried out may be tested by comparing the sum of the single fractions with the total (concentrated HCl–P) measured separately.[24] Such a comparison shows that TP − Σ(NaOH–P + HCl–P + OP) = 0.05, the mean difference is thus negligible. Furthermore, TP values measured by persulfate digestion were close to those obtained following the SMT protocol.

As TP was not measured separately in the G method, it is not possible to check the validity of this scheme as was done for the SMT scheme. However, it has to be noted that the sum of the different fractions yielded by the G method is significantly lower than TP measured by persulfate digestion and SMT method (Fig. 2). It seems reasonable to conclude then, that the SMT method gives better results in the case of the Bort-Les-Orgues sediments. This is not surprising as the G method was mainly designed for calcareous sediment and the Bort-Les-Orgues sediments are crystalline. Also, it is important to note that the better results of the SMT scheme
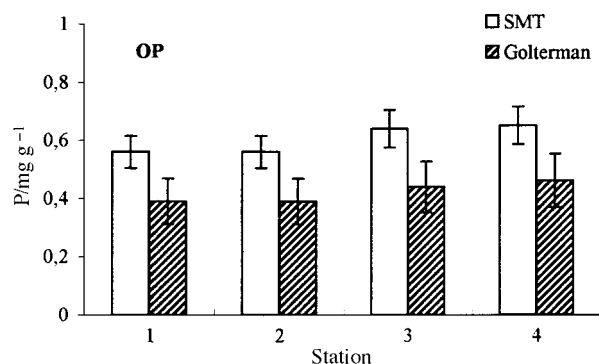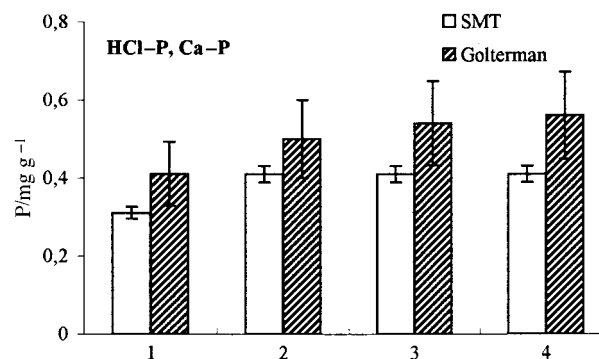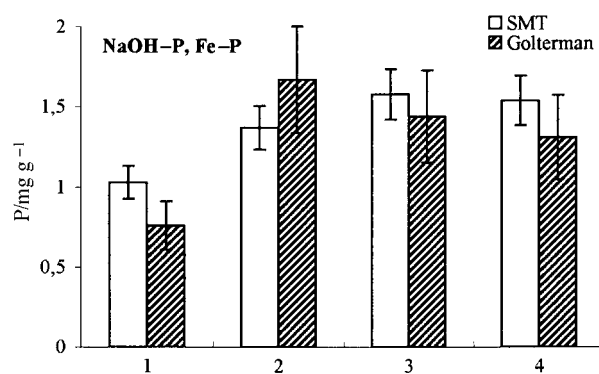
Fig. 3 Sequential extraction of phosphorus (SMT and Golterman schemes) at the 4 stations in the Bort-Les-Orgues Reservoir. Five replicates were made, the mean value and standard deviation are reported on the figure.

are in agreement with a series of interlaboratory comparisons currently carried out in the framework of the European project SEPHOS (sequential extraction of phosphate in freshwater sediments) supported by the Standards, Measurements and Testing Programme of the European Commission.[19] The discrepancy between the two methods enhances the necessity of a harmonised sequential extraction scheme, which would enable water managers and researchers to compare their results.
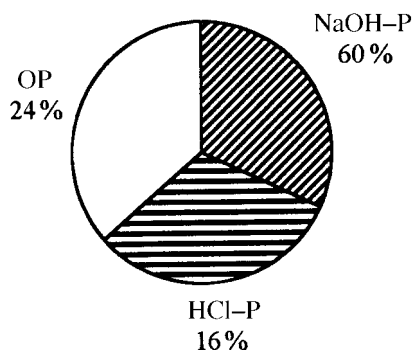
Fig. 4 Relative distribution of phosphorus according to the SMT protocol, in the Bort-Les-Orgues Reservoir.

The relative percentages of phosphorus forms according to the SMT method are presented in Fig. 4 for the Bort-Les-Orgues Reservoir. NaOH–P was 60% of TP, OP 24%, and HCl–P 16%. The potentially releasable P (NaOH–P+OP) in the sediment is around 80%, which is in agreement with previous results[12].

Therefore, in the Bort-Les-Orgues Reservoir, phosphorus is mainly of anthropogenic origin (NaOH–P+OP partly), whereas Ca–P, which is of detrital origin, accounts for less than 20%. These results also show that most sediment P in the lake is allochthonous. Brigault and Ruban[25] have shown that among the sources of allochthonous P, about 30% comes from domestic or industrial effluents (mostly NaOH–P), 60% from agriculture (NaOH–P+OP).

Estimation of the phosphorus stock in the sediment

An estimation of the sediment stock in the reservoir of Bort-Les-Orgues was made.

Taking into account the volume (477×10^6 m^3) and the mean depth (43.7 m) of the reservoir (the surface of the sediment was estimated to 10.91 km^2) and assuming that P is active in the upper 5 cm of the sediment,[26] it is possible to calculate the available P stock, since the concentration is known. The sediment stock (5 cm) was 545 500 m^3, with a mean water content of 75%, the volume of dry sediment was $130\,625 \pm 10\%$ m^3. The density of the sediment was 1.1, hence the sediment mass was 150 012 t. The concentrations of NaOH–P and OP were 1.62 and 0.58 mg g^{-1}, respectively, and their mass in the sediment was then:

$$m_{\text{NaOH–P}} = 1.62 \; 10^{-3} \times 150\,012 = 243 \pm 48 \text{ t}$$

$$m_{\text{OP}} = 0.58 \; 10^{-3} \times 150\,012 = 87 \pm 18 \text{ t}$$

The stock of P likely to be released averaged 330 ± 66 t, which is far from negligible if compared to the annual TP input of 121 t.[25] However, this value is only indicative as it supposes that the release occurs on the whole reservoir, which is probably not the case.

Nurnberg[27] has shown that significant correlations between anoxic release rates and sediment P fractions can be used to predict phosphate release rates in lakes with known sediment P concentrations. Applying this relationship to the sediment of Bort-Les-Orgues leads to a release rate of about 5 mg m^{-2} d^{-1}, which is typical of meso-eutrophic lakes in this area. It has to be noted that a much higher flux

(18 mg m^{-2} d^{-1}) was measured through a laboratory experiment[12] before the reservoir was emptied in 1995. The partial emptying of the reservoir induced a reduction of P release due to the oxidation of iron compounds to which P was adsorbed.

Also, it is important to keep in mind that a large releasable P stock exists in the reservoir, which could delay the recovery of the lake even when measures to reduce P inputs are taken. Quantification of the P stock, together with the release rate will help in predicting this restoration delay.

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Paper 9/02269D