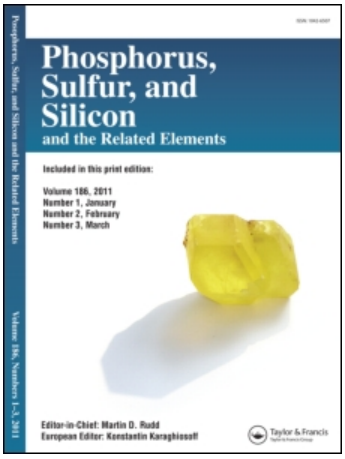

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Qualitative and quantitative study of various forms of phosphorous in storm and runoff waters in Toulouse (31) and Florensac (34), France

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ABSTRACT

Storm water and runoff water has been analyzed. Phosphorous was measured in three forms : orthophosphates, hydrolysable phosphate (polyphosphates), and total phosphorous. The difference [total phosphorous] - {[hydrolysable phosphorous] + [orthophosphates]} gives a good idea of the organic origin phosphorous content.

The qualitative and quantitative assessment of different phosphorous amounts enabled us to find that the irreducible part (organic soluble phosphorous) is about 23% of total phosphorous for runoff waters. Annual loads of orthophosphates, total phosphorous and so phosphorous known as organic were evaluated in the case of the motorway site at 3,3 kg of total phosphorous of which 0,60 kg of orthophosphates and 1,1 kg of soluble phosphorous known as organic for a catchment area of 1 hectare: motorway runoff waters are three times less loaded in total phosphorous than treated waters. As the urban site is much more loaded than a motorway site, it seems very important to supervise urban runoff waters.

INTRODUCTION

The work described was undertaken in collaboration with the Compagnie Générale des Eaux and more particularly its research center Anjou-Recherche. It concerns the phosphorous amounts in the storm and runoff waters in the city of Toulouse and in the mediterranean motorway site (A9). The goal of this work was to carry out a qualitative and quantitative assessment of the various forms of phosphorous per site and per different kind of sampling waters. Another goal was to differentiate between the phosphorous form considered irreducible and the phosphorous forms (1) which are possible to reduce through appropriate treatments.

1 METHODOLOGY

1.1 Sampling

Runoff water: For the three Toulouse sites, the study was made on the first thirty litres of runoff water which reached the mouth of the sewer from the start of the rainfall event (2).

For the motorway site, the (2 x 3 lane) motorway road bed surface area is 13000m^2. recovered in a drain channel lower down.

Storm water: Rain gauges were installed at five sites round Toulouse

For the motorway site, the cone of the rain gauge was not protected during dry spells and so collected all that fell (wet and dry).

1.2 Analyses

The phosphorous was measured in three forms : orthophosphates, hydrolysable phosphorous (polyphosphates) and total phosphorous. The difference [total phosphorous] - {[hydrolysable phosphorous] + [orthophosphates]} gives a good idea of the organic origin phosphorous content. We note that the polyphosphates which come first from detergents change through hydrolysis into orthophosphates and the kinetics of change depend on the ambient conditions (temperature, pH, weather etc.,).

Orthophosphates measurement

Ammonium molybdate, double antimony tartrate and potassium react in an acid medium with the orthophosphates to produce phosphomolybdic acid. This is reduced through ascorbic acid and produces a blue complex. Colorimetric measurement is carried out at 630 nm wave length by means of a UV - Visible Perkins Elmer lambda 2 spectrophotometer. The measurement range extends to 0.01 to 1 mg/l.

Polyphosphates measurement

Polyphosphates are converted into orthophosphates by hydrolysis on boiling in a 15% sulphuric acid medium. Spectrophotometer measurement is done after addition of soda until a pH value of 2 is obtained. Phosphorous concentration coming from hydrolysable phosphates was calculated by the difference between the phosphorous content measured in this way and the orthophosphate content previously determined.

Total phosphorous measurement

The sample was mineralized by hydrolysis at 480°C in a concentrated sulphuric acid medium in the presence of sodium persulphate as catalyst. After neutralization with concentrated soda at a pH = 1.5 to 2.5, the orthophosphates liberated by mineralization were measured by colorometer by means of a UV - Visible Perkin Elmer lambda 2 at 700 nm wave length.

The total soluble phosphorous was measured on filtered water. The total phosphorous corresponds to the total soluble phosphorous content increased by the phosphorus content in the suspended matter. It was measured for a more limited number of samples.

2 RESULTS AND DISCUSSION

2.1 Qualitative and quantitative assessment of different phosphorous amounts according to the source of analyzed waters.

Total phosphorous can be found in sediment form and in soluble form. Total soluble phosphorous contains soluble orthophosphates, polyphosphates, and the soluble part of the organic phosphorous. Total organic phosphorous content is equal, then, to the difference between the total phosphorous and the orthophosphates and polyphosphates in the suspended solids and the soluble phase. It is not possible to directly reach it with the carried out analysis because the orthophosphates contained in the sediments cannot be known. On the other hand, the organic soluble phosphorous is completely defined by the difference between the total soluble phosphorous amount and the soluble orthophosphates and polyphosphates amounts. The means obtained for each site are shown in the Tables 1 and 2 . The sites « Argoulets, Palayre and South Ring Road » whose means are very close together, have been regrouped under the name « South East » which corresponds to the geographical characteristics.

The mean values obtained for each site are shown in Tables 1 and 2.

Mean contents per site	unity	South South-East	North ring road	Saint Simon (South-west)	Motorway A9
Orthophosphates	(mgP/l)	0,14	0,18	0,12	0,04
Total soluble phosphorous	(mgP/l)	0,59	0,29	0,43	0,31
Organic phosphorous	(mgP/l)	0,44	0,11	0,31	0,27

Table 1: Storm water

Mean contents per site	unity	Urban	North ring road	Semi-urban	Motorway A9
Orthophosphates	(mg P/l)	1,17	0,79	0,41	0,13
Total soluble phosphorous	(mg P/l)	2,10	1,30	0,69	0,38
Organic phosphorous	(mg P/l)	0,93	0,51	0,28	0,25
Total phosphorous	(mg P/l)	2,83	1,34	0,62	0,68

Table 2: Runoff water

The insoluble part can , for the most part, be eliminated by settling. The soluble part can be treated by a physico-chemical process which consists of precipitation of phosphates inducted by, for example, alumina sulphate and ferric chlorid (flocculation process).
Concerning organic phosphorous, no simple or cheap process allowing its elimination is known for the moment. Consequently it represents the part of the phosphorous irreducible in water treatment. Some work is being done at the moment to characterize this phase.
Therefore, it is interesting to note what the respective percentages are (figure 1) for the insoluble and soluble parts as well as for the organic soluble part in the runoff water, knowing that rainfall, when it flows on the ground, fills up primarily with orthophosphates.
The phosphorous irreducible amount remains between 19 and 27 % of the total phosphorous amount. Approximately one quarter of the total phosphorous pollution inducted by the runoff water is never actually treated.

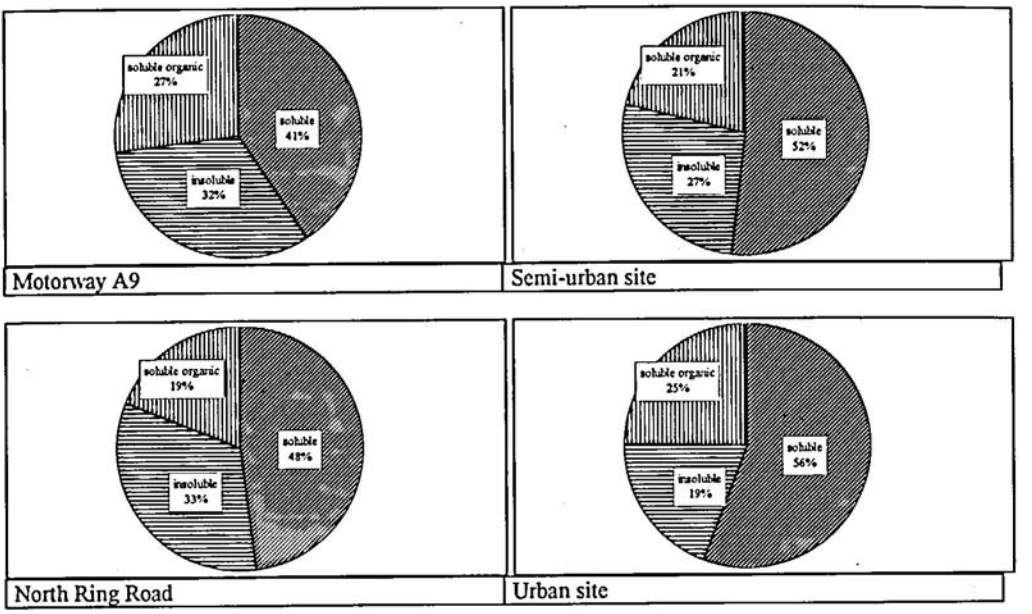

figure 1 :Respective percentages of different parts of phosphorous in runoff waters

2.2 Comparison of loads

Annual loads of orthophosphates, total phosphorous and so phosphorous known as organic were evaluated in the case of the motorway site for a catchment area of 1,3 hectares (table 3).

Year 1993-1994	Yearly soluble load	Yearly particule-like load	Total yearly load	Yearly soluble load/ha	Yearly particle-like load/ha	Total yearly load/ha
PO4 kgP	0,8	?	?	0,6	?	?
Porg kgP	1,4	?	?	1,1	?	?
Ptot kgP	2,2	2,1	4,3	1,7	1,6	3,3

Table 3 : Phosphorous loads (motorway site A9)

The irreducible phosphorous percentage is about 30% for the samples collected during one year of analysis. The percentage previously mentioned for the concentration values is very close to this last percentage.

Sampled waters	Year 1993-94	Total annual load (KgP)	Number of Equivalent/ inhabitant
runoff waters	Motorway A9	4,3	2600*
waste waters	Inlet B400	8271,0	400000
	Inlet B150	3148,0	150000
	General outlet	2641,0	550000

Table 4:Total phosphorous annual loads of runoff waters (A9) and waste waters (Toulouse 1994)

The total phosphorous loads obtained for the runoff waters are clearly inferior to those obtained for the waste waters (table 4). In order to compare them, it is necessary to evaluate the total annual load of COD (Chemical Oxygen Demand) knowing that 100 g of COD corresponds to 1 equivalent/inhabitant. The annual load of COD for the motorway catchment area studied is 261 kg which corresponds to 2600 equivalent/inhabitant. Motorway runoff waters are therefore three times less loaded in total phosphorous than treated waters.
As the urban site is four times loaded in total phosphorous than the motorway site (table 2), it seems very important to supervise urban runoff waters which are therefore close to treated waters..

3 CONCLUSION

71 samples of storm water were analysed. By site or overall, 14% of samples have a total phosphorous content higher than 1 mg P/l. This content is never higher than 2 mg/l.Orthophosphate contents were always less than 1 mg/l.
Samples were taken of run off water at four sites. 57 samples were analysed. Phosphorous contents were higher at the urban site (mean total phosphorous content : 2,8 mg/l) than at the semi urban site (mean total phosphorous content : 0,62 mg/l), at the ring road site (mean total phosphorous content : 1,30 mg/l) and at the motorway site (mean total phosphorous content : 0,68 mg/l) without allowing for atmospheric fallout (rain and dry deposits). We note that in one case, at the urban site, the total phosphorous content reached 8 mg/l. Phosphorous contents in suspended matter were calculated for 33 samples. In 65% of the samples analysed the phosphorous content was higher than 1 mg/l and in 25% of cases higher than 2 mg/l.
The qualitative and quantitative assessment of different phosphorous amounts enabled us to find that the irreducible part (organic soluble phosphorous) is about 23% of total phosphorous for runoff waters.
Annual loads of orthophosphates, total phosphorous and so phosphorous known as organic were evaluated in the case of the motorway site at 3,3 kg of total phosphorous of which 0,60 kg of orthophosphates and 1,1 kg of soluble phosphorous known as organic for a catchment area of 1 hectare. These values were compared to mean values obtained in 1994 at the city of Toulouse purification plant outlet. If we take the number of equivalent inhabitants as the point of reference (100 g of COD corresponds to 1 equivalent/inhabitant), motorway runoff waters are three times less loaded in total phosphorous than treated waters. As the urban site is much more loaded than a motorway site, it seems very important to supervise urban run off waters.

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