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PRELIMINARY STUDIES OF ADSORPTION LOSSES OF PHOSPHATE FROM DILUTE SOLUTIONS

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PREFACE

The exercise outlined in the following note was carried out as part of a project studying geochemical cycling in an upland grassland catchment near Plynlimon, mid Wales (ITE Project 594). A general introduction to this project is available as Bangor Research Station Occasional Paper No. 4.

Preliminary Studies of Adsorption Losses of Phosphate from Dilute Solutions

Introduction

Losses of phosphate from dilute solutions such as river and lake water during sample storage have been extensively documented in the literature, see e.g. Annett and D'Itri 1973. Various mechanisms have been proposed to account for the losses, for example adsorption to container walls (Hassenteufel et al 1963), (Ryden et al 1972), uptake by organisms sorbed to container surfaces; (Heron 1961, Annett and D'Itri 1973), precipitation and adsorption onto suspended particulate, (Annett and D'Itri 1973). Various techniques have been recommended for overcoming this problem; such as the use of polycarbonate containers in preference to acid washed glass ones (Ryden et al 1972), surface impregnation of polythene bottles to retard bacterial growth (Heron 1962), and the use of mercuric chloride (20-40 mg/1) as a preservative with storage either frozen or at 4°C. (Klingaman and Nelson 1976, Jenkins 1968, Grunnet 1971).

The majority of the authors quoted recommend that filtration or centrifugation to separate off suspended particulates should be performed as soon as possible after collection of the sample, preferably within six hours. This is particularly important if the samples are to be frozen, as death of any micro-organisms present can cause release of P and enhancement of the soluble phosphate concentration. Increases in soluble phosphorus concentrations in filtered samples have been observed however, Philbert (1973), and losses of phosphorus to filters have also been reported Schierup et al (1979).

In view of these problems, and the very low levels of soluble phosphate encountered in water samples from Plynlimon, some preliminary experiments were designed to study phosphate losses from dilute solutions. A radiotracer technique, using ^{32}P was chosen after discussion with Dr. Harrison from ITE Merlewood. The method relies on the principal that the radio-active isotope, ^{32}P in this case, is chemically identical to and will exchange with its stable counterpart in solution. Thus the radioisotope can be used to "tag" or "label" a compound such as PO_4^{2-}. The object of these experiments was to assess the losses of phosphorus from dilute solutions by adsorption onto polypropylene sample bottles, cellulose acetate membrane filters and glassware to be used for the Geochemical Cycling project.

Experiment 1

A solution of potassium orthophosphate containing 5 µg/ml P in deionised water (DIW) was serially diluted (1:1) to give solutions containing the following concentrations:

Sample No.	Dilution	Concentration of P (µg/ml)
100 - 102	x 1	5
103 - 105	x 2	2.5
106 - 108	x 4	1.25
109 - 111	x 8	0.625
112 - 114	x 16	0.313
115 - 117	x 32	0.151
118 - 120	x 64	0.076
121 - 123	x 128	0.038
124 - 126	x 256	0.019
127 129	x 512	0.009

Three replicates of 100 ml of each dilution were placed in 125 ml polypropylene bottles and 10 µl of P^{32} added to each replicate. The solutions were left to stand for 16 hours at room temperature (18 - 20°C). Aliquots of 20 ml of each solution were then transferred to counting vials and their activities determined using a scintillation spectrometer. A counting period of ten minutes was employed and the data were corrected for decay, background and counting efficiency by M. Smith at Merlewood.

The activity of the ^{32}P was standardised on the 20th., June 1979 at 12 noon. The ^{32}P was in a solution containing 100 μg/ml stable P as "carrier".

Results

The final concentrations of P in solution after the addition of the ^{32}P are shown below, Table I. The mean corrected "Total Counts" are also given and these values represent the absolute activity per counting vial standardised to 12 noon on June 20th., 1979. The full data are given in Appendix I.

Table 1

Mean Corrected Total Counts for Phosphate Solutions Labelled with 10 μl of P^{32}

Sample Number	Concentration of P (μg/ml)	Mean Total Counts
100 - 102	5.01	59042.56
103 - 105	2.51	57102.09
106 - 108	1.26	56304.44
109 - 111	0.635	56159.12
1112 - 114	0.323	56160.98
115 - 117	0.161	55156.27
118 - 120	0.086	53425.36
121 - 123	0.048	54276.69

Overall Mean = 55628.32
S.D. = 1709.77
C.V.(%) = 3.1

Discussion

Ideally all the corrected total count values should be equal as the same activity of ^{32}P was added to each solution. Losses of P by adsorption might be expected from the more dilute solutions, thus causing a reduction in the measured activity of these solutions. There is a slight decrease in the number of counts in the more dilute solutions. However the majority of the variation, which is in itself quite small, is probably attributable to errors derived from sample handling (A. F. Harrison, pers commun). The losses of P from solution by adsorption to bottle walls are probably neglible over the period of 16 hours.

Experiment 2

Sixteen samples of streamwater (100 ml) were collected from Finsthwaite, High Dam, Cumbria in 125 ml acid washed polypropylene bottles. The stream at Finsthwaite is small and the flow at this time was low. In consequence, the water was clear with little suspended particulate matter.

On return to the laboratory, 10 µl aliquots of ^{32}P solution were added to the samples which were then left at room temperature for 12 hours. Eight samples were vacuum filtered through 0.45 µm cellulose acetate membrane filters supported on glass filtration apparatus. The filtrate was returned to the sample bottle which had been rinsed with a small volume, c. 30 ml, of DIW Aliquots of 20 ml were then transferred to counting vials.

Five of the serially diluted phosphate solutions from Experiment 1 were also filtered through 0.45 µm membranes. Aliquots of 20 ml of the filtrate were transferred to counting vials, as were 20 ml aliquots of the remaining eight water samples. The activities of the solutions were determined using a scintillation spectrometer with a counting period of ten minutes. Corrections were applied to the data as for experiment 1.

Filters were soaked in DIW overnight prior to use. The glassware was washed in 10% v/v nitric acid and rinsed four times with distilled water before use. Between successive samples, the filtration apparatus and measuring cylinders were rinsed with a small volume of 1% v/v hydrochloric acid followed by three rinses with DIW.

Results

The total corrected counts for the filtered solutions and the filtered and unfiltered water samples, corrected for volume differences, are given in Table 2.

Table 2

Overall Mean Corrected Total Counts for Filtered Solutions and Filtered and Unfiltered Water Samples

Filtered Solutions	Concentration of P(µg/ml)	Mean Corrected total count
100/2 - 102/2	5.01	53480.53
103/2 - 105/2	1.26	53633.39
106/2 - 108/2	0.323	53010.39
109/2 - 111/2	0.086	50403.75
112/2 - 114/2	0.029	50053.02

Streamwater Samples

	Unfiltered Samples	Filtered Samples
Overall Mean Corrected Count	51989.84	52609.74
S.D.	1522.31	1067.53
C.V. (%)	3.0	2.0

Discussion

Comparing unfiltered and filtered phosphate solutions, there is a difference of 5% to 6% between the mean corrected total counts for the two groups. The filtered solutions have the lower counts, but there are too few replicates to warrant statistical analysis. From observation of the data, the differences are probably significant. Thus there appears to be a slight loss of P either to the filters, the filtration equipment or to the container walls with the increased storage time.

There is little difference in counts between filtered and unfiltered water samples. The coefficients of variation for both data sets are low and comparison by a t-test indicated no statiscally significant difference between the batches.

Conclusions

Losses of P as PO_4^{2-} from dilute solutions in DIW by adsorption to polypropylene bottles are negligible over a period of storage of 16 hours at 18 - 20°C. There are slight losses of P as PO_4^{2-} from solution after membrane filtration, either to the filters or the filtration glassware. The work of Ryden et al (1972) would tend to suggest the latter as being responsible for the losses. Adsorption losses from dilute natural water samples after filtration appear to be negligible, however,

The results of this experiment although valid have limited application due to the short storage period. Future experiments using water samples collected at Plynlimon and following the technique for sample storage and treatment used for project 594, are planned as follow up to this work.

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Appendix I

Listing of Total Corrected Counts for Experiments 1 and 2

A. Phosphate Solutions - Expt. 1

Sample No.	Concentration of P (µg/ml)	Counts
100	5.01	57854.06
101		61137.09
102		58136.52
103	2.51	55467.93
104		58057.89
105		57780.45
106	1.26	57528.93
107		56441.78
108		54942.62
109	0.635	55987.49
110		56825.34
111		55664.54
112	0.323	55392.73
113		57382.93
114		55706.28
115	0.161	53614.07
116		55443.51
117		56411.22
118	0.086	53308.65
119		54478.45
120		52488.98
121	0.048	52691.29
122		55614.74
123		54524.05
124	0.029	53615.89
125		53210.04
126		53860.22
127	0.019	54062.91
128		54515.67
129		56702.46

B. Filtered Phosphate Solutions - Expt. 2

Sample No.	Concentration of P (μg/ml)	Total Corrected Counts
100/2		54463.33
101/2	5.01	111638.2
102/2		52497.73
103/2		54276.07
104/2	1.26	53334.55
105/2		53289.54
106/2		53441.04
107/2	0.323	51624.96
108/2		53965.16
109/2		51720.37
110/2	0.086	50133.50
111/2		49357.37
112/2		48993.36
113/2	0.029	49865.86
114/2		51299.85

C.<u>Unfiltered Water Samples - Expt. 2</u>

Sample No.	Total Corrected Counts
116/2	51735.52
117/2	51833.95
118/2	52317.08
119/2	50637.63
120/2	52350.44
121/2	50163.58
122/2	54890.66

D. Filtered Water Samples - Expt. 2

Sample No.	Total Corrected Counts
123/2	52455.22
124/2	53189.38
125/2	53001.95
126/2	52385.50
127/2	51038.67
128/2	54668.76
129/2	52311.85
130/2	51824.41