Evidence that filterable phosphorus is a significant atmospheric link in the phosphorus cycle

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Deposition of phosphorus from the atmosphere was measured weekly over 7 annual cycles in the montane region of Colorado, USA. Deposition of phosphorus consistently reached a sharp peak in early summer, near the beginning of maximum biological activity. The peak is associated with soluble phosphorus capable of passing through a filter. Pollen studies show that the peak cannot be accounted for by leaching of phosphorus from pollen, and the amounts of miscellaneous mineral and organic particulate materials are too small to account for the peak. The study thus indicates transport of filterable, water-soluble phosphorus substance, probably of biogenic origin, in large amounts over a short period of time. This transport mechanism, heretofore unsuspected, may account for significant long-distance phosphorus transport.

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Осаждение фосфора из атмосферы измеряли еженедельно в течение 7 годовых циклов в горном районе Колорадо (США). Осаждение P достигало высокого максимума в начале лета, примерно, совпадая с началом пика биологической активности. Пик связан с растворенным фосфором, способным проходить через фильтр. Исследование пыльцы показало, что пик не связан с выщелачиванием P из пыльцы, а количество смешанного минерального и органического размельченного материала слишком мало для обеспечения этого пика. Таким образом, исследование показало, наличие транспорта фильтрующегося водорастворимого фосфора, очевидно биогенного происхождения в больших количествах в короткий период времени. Этот транспортный механизм до того неизвестный, может обеспечить значительный транспорт фосфора на большие расстояния.

Introduction

In studying the deposition of total phosphorus and phosphorus fractions at the Como Creek watershed in Colorado since 1975, we have repeatedly observed high deposition of phosphorus early in the growing season. In this paper we describe the phosphorus deposition pulse at the Como Creek watershed and show that it also occurs with similar timing at another site. We also show that the phosphorus deposition pulse coincides with biological activity, is accounted for by phosphorus that passes through a filter of 2 μm pore size, and cannot be explained by pollen deposition.

Methods

Phosphorus deposition was measured at two different sites in Colorado: Como Creek watershed (Boulder County) and Lake Dillon (Summit County). The Como Creek watershed collection site is located at an elevation of 2900 m just to the east of the Continental Divide. The site is heavily vegetated with conifers (*Pinus contorta, Abies lasiocarpa, Picea engelmannii, Pinus flexilis*) and has not been significantly disturbed by fire, logging, or development for more than 40 yr. The Lake Dillon site is located at 2800 m elevation in Summit County, 60 km southwest of the Como Creek site in the opposite side of the Continental Divide. The vegetation in the vicinity of the Lake Dillon site is very similar to that at Como Creek but is disturbed to some degree by residential development.

Bulk deposition of phosphorus at both locations was sampled over weekly intervals with a large collector (0.2 m²). This collector, which has been used in other studies of precipitation chemistry (Lewis and Grant 1980, Grant and Lewis 1982), consists of an inverted plexiglas pyramid under a square opening rimmed with plexiglas. The collection surface remains continuously open to the air, thus collecting both wet and dry deposition. The plexiglas funnel opens into a vapor trap (loop of tubing that holds water) and a hard glass receiving vessel underneath. A box surrounds the receiving vessel and the plexiglas collection surface. The box is insulated and contains thermostatically controlled heaters that keep the collecting surface at a sufficiently high temperature to melt incoming snow in the wintertime.

For all years except 1982, when only one collector was in operation, there were two collectors at Como Creek, and the data we report here are the averages of these two. The collectors were mounted 3 m above the ground on platforms in two separate clearings (2500 m²) within a forested area. The surrounding forest provided wind shielding, but the collectors were placed a sufficient distance from the nearest tall vegetation that there was no contact of wet precipitation with vegetation before the precipitation reached the collecting surface. At Lake Dillon there was a single collector sit-uated 0.5 km from the lake and 0.3 km from the nearest vegetation.

The collectors were usually serviced once a week, although the Lake Dillon collector was serviced less often in the wintertime. Each time a collector was serviced, the plexiglas pyramid was rinsed with deionized water of known quantity and the vapor barrier and collecting vessel were both replaced with clean substitutes. The sample was then taken to the chemical laboratory in Boulder and analyzed immediately. Although the analyses were comprehensive, only the phosphorus analyses are relevant here.

For the phosphorus analysis, a portion of the sample was filtered onto Whatman GF/C fiber paper (pore size, ca. 2 μm). The filtrate was analyzed for total P. This fraction is traditionally called "total soluble P" (Strickland and Parsons 1968), but we will refer to it here as "filterable P" to encompass the possibility of very fine particles passing the filter. The filter was analyzed for particulate phosphorus. In 1982, particulate phosphorus determinations were done by the method of Solorzano and Sharp (1980). Prior to 1982, particulate phosphorus was analyzed by sulfuric acid digestion (see below) followed by molybdate determination of orthophosphate (Murphy and Riley 1962), and filterable phosphorus was degraded by ultraviolet oxidation and then analyzed by the molybdate method. All results are expressed as deposition rates (mass deposited per unit area per unit time).

Analysis of pollen was required for calculation of the role of pollen in producing the seasonal maximum each year. Pollen of lodgepole pine (*Pinus contorta*) was collected directly from trees in the vicinity of the Como Creek site at the time of maximum pollen release. For determination of total P, 5–7 mg of air-dried pollen was weighed on an analytical balance and placed in a Kjeldahl flask. The pollen was not oven-dried because volatile compounds might have been lost by such treatment. The digestions were run in triplicate along with blanks and a National Bureau of Standards orchard leaf standard to test the efficiency of digestion. At the beginning of the digestion, 1.0 ml of 1:1 H_2SO_4 solution was added along with 1.0 ml of K_2SO_4/Se solution. The flasks were heated until the solution cleared (3 h). After the samples cooled, 7 ml of deionized water was added and the samples were boiled for 5 min. The samples were cooled again and 5 ml of water was again added along with 2.0 ml of 35% w/v sodium hydroxide solution. Samples were then diluted to 50 ml and analyzed for soluble reactive phosphorus using the molybdate method. Results were expressed as phosphorus per unit weight of pollen.

Determinations were also made of the amount of phosphorus that could be liberated by rinsing or soaking pollen with water having a strong acid composition similar to that of rain at Como Creek. The solution for rinsing and soaking consisted of deionized water with strong acids in amounts equal to Como Creek averages (HNO_3

10 μ eq l^{-1} and H_2SO_4 19 $\mu eq l^{-1}$; Grant and Lewis 1982). For the rinse experiment, 75 mg of fresh pollen was added to 0.5 l of the acidified water (pH 4.2–4.4). The rinse was then shaken and filtered to remove the pollen. The filtrate was analyzed for filterable P by the same method as used for precipitation samples. For the soaking experiment, 75 mg of pollen was added to 0.5 l of acidified water and the mixture was allowed to stand for 7 d at room temperature. The mixture was then filtered and the filtrate was analyzed for filterable P.

Results

Fig. 1 shows the deposition of filterable phosphorus at Como Creek over 6 yr (1981 data are missing) and the deposition at Lake Dillon in 1982. To facilitate comparisons, all plots have the same scale. The figure shows that peak deposition of filterable P consistently occurs between late June and early August. The magnitude of the peak varies greatly from year to year and site to site. In the most extreme instance, 1982 at Lake Dillon, 33% of total annual phosphorus transport occurred in one week, and 98% of the phosphorus deposited that week was soluble.

The filterable P at the time of peak deposition is composed 75–90% of soluble reactive P (SRP). Quantification of the fraction of filterable P that is accounted for by SRP is not very informative, however, as the SRP fraction includes certain soluble organic phosphorus molecules as well as inorganic phosphorus (Rigler 1968, Levine and Schindler 1980). Our focus here will thus be on total filterable P.

Peak pollen fall occurs near, but typically not coincident with, the time of the soluble phosphorus deposition peak. If the soluble P shown in Fig. 1 were simply leachate from pollen, the data would be merely confirming the known principle that P is transported over short to moderate distances in particulate form as pollen (e.g., Banks and Nighswander 1982). However, given the high amounts of P in relation to pollen, pollen cannot account for the transport. As a means of identifying the maximum possible contributions of pollen to the peak, the percentage of phosphorus in pollen was determined as specified in the methods section. The phosphorus data for pollen are summarized in Tab. 1, which shows not only the total P content of pollen, but also the
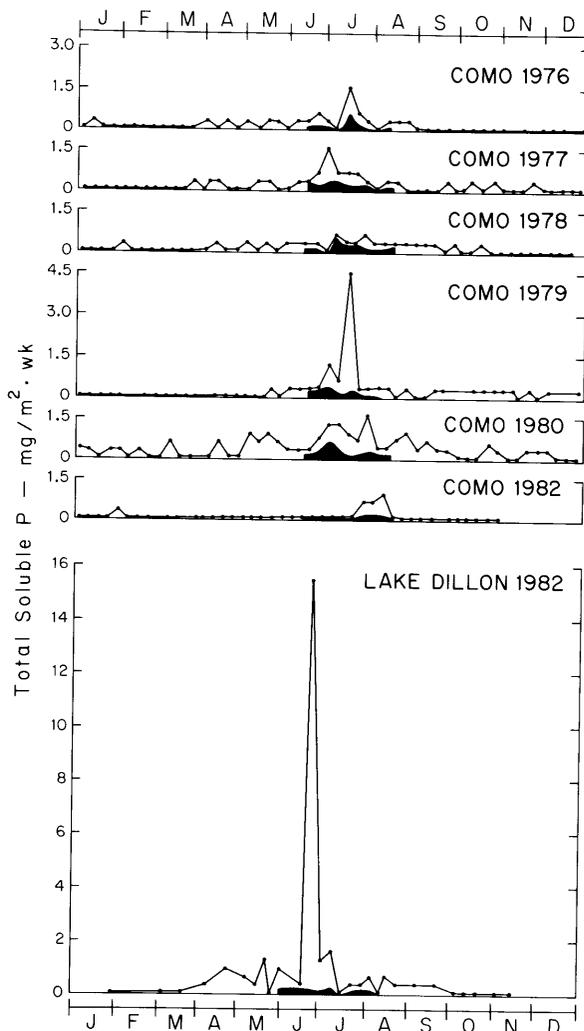

Fig. 1. Plot of total soluble (= filterable) phosphorus deposition at Como Creek watershed over 6 yr and of Lake Dillon over one year. Shaded area is the upper limit of possible leaching contribution from particulates to the total soluble P between 1 June and 15 August of each year.

amount that can be removed in filterable form. Brief contact of acidic rainwater with pollen removes very little P, but 7-d contact removes about 30% of the total P.

Results from the 7-d soak experiment were used to

Tab. 1. Total phosphorus in pollen of *Pinus contorta* and the amount that was removed by rinsing and soaking with synthetic rainwater.

Replicate	Total P(%)*	Amount removed* in rinse (%)	Amount removed* in soak (7 d)(%)
1	0.27	0.003	0.098
2	0.27	0.002	0.102
3	0.29	0.003	0.100
Mean	0.28	0.003	0.100

*Percentages computed as 100 times the mass of P divided by pollen dry weight.

compute the maximum contribution of pollen to the peak of filterable P deposition for the interval 15 June – 15 August of each year. The computation assumes that all particulates were pollen. This results in conservative (i.e., upper bound) estimates of the pollen contribution, since some of the particulate matter was not pollen. The computations also assume that P would leach from the pollen at a rate equal to that observed in the soak experiment. The shaded portions of Fig. 1 show, on the basis of these calculations, the maximum filterable P that could be accounted for by leaching. In most years, maximum possible pollen contributions are not nearly large enough to account for the phosphorus peak. In years with the most pronounced peaks, pollen can at most account for less than 10% of filterable P deposition.

Discussion

The results show that significant amounts of filterable phosphorus move through the atmosphere in the montane regions of Colorado for a brief period between the end of June and beginning of August. If this phenomenon is widespread, it might constitute an important mechanism as yet unconsidered in studies of the phosphorus cycle by which phosphorus moves into and out of ecosystems. The brief phosphorus peaks could, given the total P export from these watersheds (Lewis et al. 1984), account for as much as 25% of total P flux. Although published data typically do not resolve the temporal patterns of P deposition on a weekly basis, as is necessary to show the deposition peak most clearly and to separate it from pollen fall, early summer P deposition peaks have been noted at other locations (e.g. Rognerud 1979, Banks and Nighswander 1982). Since the phosphorus under consideration here is not particulate (as defined by filtration), and is produced over a relatively short time, its total deposition at a particular location in a given year may well be governed by the amount and timing of rainfall necessary to scrub it from the atmosphere. This offers an explanation of the year-to-year variation evident in Fig. 1. For example, in the year of the smallest peak at Como Creek(1978), rainfall during the relevant weeks was nil or exceptionally low.

The maximum of filterable P deposition is coincident with surges of spring plant growth and reproductive activity that begin in late June at montane elevations in Colorado. This suggests that the filterable phosphorus maximum is a by-product of biological activity. A biological cause helps explain varied timing of the peak, since years differ considerably in their spring weather. In fact the year of the earliest peak at Como Creek (1977) corresponds to the warmest May and the year of the latest peak (1982) corresponds to the coldest May.

It is impossible from the results of the present study to say what component of the biota might be producing the filterable phosphorus deposition maximum, but the conifers are obviously suspect because of their dominance and their known propensity for the release of volatile organic compounds (Squillace 1976, Anon. 1981). However, soil biota cannot be ruled out. It seems likely that the filterable phosphorus maximum is associated with biological release of a small volatile organic compound incorporating P, although possibly a very fine biogenic phosphorus aerosol could have similar effects. Existing information on release of volatile organic materials from higher plants provides no evidence for the movement of a significant amount of phosphorus-bearing compounds over short intervals of time. It would appear that the release of the phosphorus-rich compounds causing the deposition peak that we have observed is associated with some very specific function related to the onset of spring growth of plant or soil biota. Sustained release of phosphorus in these amounts would be disadvantageous in view of the relatively small phosphorus inventory available to organisms.

The release of significant amounts of filterable phosphorus opens up some new perspectives in the phosphorus cycle. Since filterable phosphorus is likely to move over much longer distances than particulate phosphorus, its release will magnify the fluxes into and out of watersheds. Furthermore, if the release of filterable phosphorus is indeed a biological phenomenon, then phosphorus transport by this mechanism may be a function of the amount and type of vegetation and of the successional state. Remaining questions to be studied include the identity of the filterable phosphorus-bearing materials, their exact source, and the breadth of ecosystem types that can be expected to release such materials.

References

Anon. 1981. National Academy of Sciences. Atmosphere-biosphere interaction: toward an understanding of the ecological consequences of fossil fuel combustion. – National Academy Press, Washington, DC, USA.

Banks, H. H., and Nighswander, J. E. 1982. The application of a new method for the determination of particle deposition onto a lake. – Ecology 63: 1254–1258.

Grant, M. C., and Lewis, W. M. Jr. 1982. Precipitation chemistry in the Colorado Rockies. – Tellus 34: 74–88.

Levine, S. N. and Schindler, D. W. 1980. Radiochemical analysis of orthophosphate concentrations and seasonal concentrations in the flux of orthophosphate to seston in Canadian Shield Lakes. – Can. J. Fish. Aquat. Sci. 37: 479–487.

Lewis, W. M. Jr., and Grant, M. C. 1980. Acid precipitation in the Western U. S. – Science 207: 176–177.

– , Saunders, J. F., Crumpacker, D. W. and Brendecke, C., 1984. Eutrophication and land use: Lake Dillon, Colorado. – Springer, New York, USA.

Murphy, J., and Riley, J. P. 1962. A modified single solution method for the determination of phosphate in natural waters. – Anal. Chem. Acta. 27: 31–36.

Rigler, F. H. 1968. Further observations inconsistent with the hypothesis that the molybdenum blue method measures orthophosphate in lake water. – Limnol. Oceanogr. 13: 7–13.

Rognerud, S. 1979. Hovedrapport fra undersökelsene i perioden 1975–1979. Norsk Inst. Vannforsk. Rap. 0–70112. (In Norwegian).

Solorzano, L., and Sharp, J., 1980. Determination of total dissolved phosphorus and particulate phosphorus in natural waters. – Limnol. Oceanogr. 25: 754–758.

Squillace, A. E. 1976. Analysis of monoterpenes of conifers by gas – liquid chromatography. P. 120–157. *In:* Miksche, J. P. (ed.), Methods in forest genetics. Springer, New York, USA.

Strickland, J. D. H. and Parsons, T. R., 1968. A pratical handbook of seawater analysis. J. Fish. Res. Bd. Can. Bull. 167.