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Collection of airborne materials by a water surface

Abstract—The collection of major ions, N and P compounds, and particulate and organic materials by a water surface was compared with collection of the same substances by an equal area of dry inert surface such as that used in precipitation chemistry collectors. The water surface proved to be a much more efficient collector of Na⁺, K⁺, Ca²⁺, and Cl⁻ and a less efficient collector of SO₄²⁻ and NH₄⁺ than the dry surface. The estimated transport of some atmospheric materials to natural water surfaces may be in error by a significant amount if computed from traditional precipitation chemistry collectors.

Early appreciation of the ecological importance of atmospheric transport can be found in the works of Gorham (1958) and Hutchinson (1954), both of whom recognized that chemical mass balance of freshwaters could be affected significantly by this mechanism. Gorham (1961) demonstrated that atmospheric transport could even dominate freshwater chemistry under some conditions. It has now become routine to consider atmospheric transport as part of any comprehensive study of chemical mass balance in freshwater systems.

Atmospheric transport to aquatic systems is usually estimated from bulk (= wet + dry) precipitation collections, which have been made with a variety of simple devices (Galloway and Likens 1976; Lewis and Grant 1978). The dryfall component, which accounts for an important fraction of total loading for many constit-

uents (Gorham 1976; Grant and Lewis 1982), is typically collected on a dry surface. Numerous investigators have recognized the likelihood that natural terrestrial surfaces are much more efficient collectors of atmospheric materials than the uniform flat collecting surfaces used to make approximations of transport (Eaton et al. 1973; Hicks 1980; Wiman 1981), but it has seemed more reasonable to assume that water surfaces are adequately represented by collectors with dry, smooth surfaces. Such a collector surface obviously differs in several important respects from a water surface, however, and there is apparently very little literature that would support a direct comparison. Removal of materials from the atmosphere by rain, snow, and cloud droplets has been very extensively studied (Englemann and Slinn 1970), but occurs under conditions that are physically very different from those of interest here. Volchok et al. (1970), attempting to explain anomalously high delivery of ⁹⁰Sr to the sea, compared the accumulation of this isotope in Crater Lake with approximations based on terrestrial collectors; they found no suggestion of special removal by water. Comparable information for the broad spectrum of ecologically important materials is apparently not available.

I report here the transport rates of ecologically interesting materials to wet and dry surfaces from the atmosphere. The results can be viewed from two perspec-

tives. First, there is a purely methodological consideration: collections made on a dry surface may not very well represent transport to a water body if water surfaces have especially high or low collection efficiencies for atmospheric materials. Second, the results are potentially of fundamental interest, insofar as they might reveal that water surfaces differentially facilitate or impede transport for various classes of airborne materials.

The study was conducted in the Como Creek watershed at 2,900-m elevation, 6 km east of the Continental Divide in north-central Colorado. Precipitation chemistry, watershed characteristics, and standard collection methods have been dealt with elsewhere (Lewis and Grant 1978, 1980). Two collectors were used in the study. The first of these, here called the dry-surface collector, has been in use at Como Creek since 1975. The square collecting surface has an area of 0.2 m² and consists of an inverted Plexiglas pyramid that opens into a small funnel. The funnel is connected by a surgical rubber hose to a glass storage vessel. The hose between the funnel and the collecting vessel is looped to form a vapor barrier. The second collector, here called the wet-surface collector, was designed specifically for this study and consists of a watertight Plexiglas box 12 cm deep with a square opening of the same dimensions as the dry-surface collector. Distilled water was added to the wet-surface collector at the beginning of each collecting period to a depth of 7.5 cm.

In a container blank for the wet-surface collector, distilled water was added and left in the laboratory for 3 days under a shield that prevented it from being influenced by dust or air currents. The water was then treated as a sample, i.e. compared with laboratory distilled water. Change in the container blank was <5% of values for field collections for all constituents. The vapor barrier hose of the dry-surface collector was also leached (1 week) to see whether it released sulfate. Sulfate was released in amounts equal to only 3% of the average values observed in the field.

The two collectors were mounted side by side on a tower 3 m from the ground surface. The tower was situated in a natural clearing in conifer forest at a standard collecting site for the Como Creek watershed. Surrounding vegetation is effective as a natural wind shield for the collectors but is not near enough to them to influence precipitation chemistry (Grant and Lewis 1982). Collections were made weekly between 23 June and 21 September 1981, the snow-free period for this watershed. At weekly intervals the storage vessel draining the dry-surface collector was removed, the water in it was measured, and the collecting surface was rinsed with 500 ml of distilled water which was collected in a separate vessel. The water in the wet-surface collector was poured off, measured, and stored in a hard glass vessel. The wet-surface collector was then rinsed thoroughly with 500 ml of distilled water; the rinse was stored in a separate vessel. The reservoir and hose of the dry-surface collector were replaced with identical ones that had been thoroughly cleaned in the laboratory. The wet-surface collector was cleaned in the field with distilled water.

Chemical analyses were all done within 48 h. Alkalinity and pH were measured immediately before the samples were mixed with the rinses. The pH was determined with a Radiometer model 29 meter and combination electrode in an unstirred sample (Galloway and Likens 1979). Alkalinity was determined by electrometric titration to a fixed end point of 4.4. This titration is likely to overestimate the bicarbonate concentration slightly, but alkalinity was almost zero, so this is not important here.

After pH and alkalinity determinations, each sample was mixed with its rinse. The rinse was a relatively small proportion of the samples in most cases (5–10%). Dilution was accounted for by a correction factor applied to the concentration data. Each sample was filtered through pre-weighed Whatman GF/C glass-fiber paper. The filters were dried at 60°C to constant weight and reweighed to provide an estimate of total particles. The filtrate was

Table 1. Comparison of mean loading values for wet-surface and dry-surface collectors (mean of weekly values, 12 weeks).

	Wet			Dry		
	mg·m ⁻² ·wk ⁻¹	SE	meq·m ⁻² ·wk ⁻¹	mg·m ⁻² ·wk ⁻¹	SE	meq·m ⁻² ·wk ⁻¹
Na ⁺ *	9.50	3.08	0.413	2.81	0.62	0.122
K ⁺ *	6.88	2.45	0.176	3.11	0.90	0.080
Ca ²⁺ *	9.46	1.56	0.461	7.20	1.42	0.359
Mg ²⁺	0.91	0.21	0.075	0.94	0.21	0.077
H ⁺	0.84	0.21	0.840	0.68	0.14	0.680
Cl ⁻ *	35.3	16.3	0.997	8.52	2.53	0.240
SO ₄ ²⁻ *	8.00	2.17	0.167	36.9	8.34	0.768
HCO ₃ ⁻ *	10.0	1.34	0.151	0.75	0.46	0.011
NO ₃ ⁻ -N	9.29	2.66	0.664	6.90	1.42	0.493
NO ₂ ⁻ -N	0.15	0.03	0.011	0.18	0.06	0.013
NH ₄ ⁺ -N*	4.39	0.97	0.314	5.96	1.13	0.426
H ₂ PO ₄ ⁻ -P	0.12	0.04	0.004	0.15	0.03	0.005
DOP	0.11	0.03	—	0.07	0.02	—
SiO ₃	2.26	0.94	—	0.56	0.27	—
Absorbance, 360 nm	0.87	0.26	—	0.93	0.19	—
Total	290	77.2	—	315	102	—

* Dry and wet significantly different at $P = 0.05$.

analyzed for major cations by atomic absorption after lanthanum addition to suppress interference. Sulfate was analyzed by a turbidometric method (Colterman 1969), chloride by a colorimetric method (U.S. EPA 1979), nitrate by the cadmium reduction-azo dye method (Bendschneider and Robinson 1952; Wood et al. 1967), soluble reactive phosphorus by an ascorbic acid-molybdate method (Murphy and Riley 1962), dissolved organic phosphorus by the pyrolysis method of Solórzano and Sharp (1980), ammonium by a phenol-hypochlorite method (Koroleff 1976), and silicate by a molybdate method (Armstrong and Butler 1962). Absorbance at 360 nm was taken as an indication of soluble organic matter. The relation of absorbance to the amount of dissolved organic matter depends on the type of organic matter (Stewart and Wetzel 1980), but, since the present purposes are comparative, absorbance will be used as a relative index.

Table 1 summarizes the results, which are expressed in terms of loading rates (concentration data for bulk precipitation at this site are summarized by Lewis and Grant 1980 and Grant and Lewis 1982). There was rain in all weeks except the first. The average rain per week over the

study period was 20 mm. On the basis of ion balance, the results seem analytically sound. For both collectors anions total 88% of cations; this is not unreasonable in view of the wet chemical methods used for anions and the unknown effect of weak acids (Grant and Lewis 1982). Statistical comparisons can be made between individual components in the table on the basis of a pairing design *t*-test. The null hypothesis is that the mean loading rates are the same for the two collectors. The results of this test are included in the table.

The results for the hydrogen and bicarbonate ions cannot be interpreted in a straightforward manner because uncontrolled amounts of these ions are present in the water initially used in the wet-surface collector, and because concentrations of these ions are directly affected by the addition of other ions. The latter effect is unpredictable because it varies with the chemistry of the water in the collector, which is in turn influenced by bulk precipitation constituents. Inclusion of the hydrogen and bicarbonate ions in the table is thus principally intended to show the complete ion balance.

The loading rates for sodium, potassium, and calcium were significantly greater for the wet-surface than for the

dry-surface collector. The size of the difference is especially impressive for sodium. Together these differences account for a considerably higher total metal cation loading for the wet-surface collector than for the dry-surface collector.

Among the major anions, the loading rates for chloride and sulfate differ very considerably between the two collecting surfaces. Sulfate loading was five times higher on the dry than on the wet surface. In contrast, chloride loading was four times higher on the wet than on the dry surface. There is a suggestion of higher nitrate loading on the wet surface, but the difference is not significant.

Among the quantitatively minor constituents, only ammonium shows a significant difference between the two collectors; the dry surface was more efficient than the wet, but the difference is slight. Orthophosphate and soluble organic phosphorus were not detectably different for the two collecting surfaces. Collection of silicate seemed higher on the wet-surface collector, but the difference is not quite significant ($P = 0.11$) because of high variances. Collection of particles by the two collector surfaces was essentially identical. Also the absorbance readings do not suggest any major difference in the collection of soluble organic substances from the atmosphere.

To provide more insight into the association of chemical constituents for both dry- and wet-surface collectors, I obtained a matrix of Spearman rank correlation coefficients, which shows the following. The collection rates for a given constituent are often positively correlated for the two types of collector, but the major cations, chloride, sulfate, and total particles show no such correlations. For both types of collector there is a cluster of significant positive associations among the nitrogen species and another for particles and major cations. Chloride and sulfate are positively associated with particles and major cations for the dry-surface collector, but the wet-surface collector shows only an association of chloride, sodium, and magnesium.

Since the collectors are unlikely to ac-

cumulate wet deposition differently, the differences in statistical associations between the two collectors must be explained by their differential collection of dry deposition. The correlations provide added evidence for the special ability of water surfaces to collect metal cations and chloride in forms such as aerosols not associated with insoluble particles. This difference and the more efficient collection of sulfate by the dry surface account for the lack of association across collector types for major cations, sulfate, and chloride.

The differences between collectors in collection rates each week for each constituent were calculated and compared by Spearman rank correlation with the amount of rain. Amount of rain is negatively correlated with the degree of difference for absorbance, nitrite, particles, magnesium, calcium, and potassium, but not for sodium, chloride, or sulfate. The enhancement of sodium and chloride collection by the wet surface and of sulfate collection by the dry surface are evidently persistent and dominant through a range of atmospheric moisture conditions.

The results suggest that the water surface has significantly better collection abilities for sodium and chloride than the dry surface (possibly by taking up aerosols containing these ions) and to a lesser extent also for potassium and calcium. Surprisingly, the dry surface was a much better collector of sulfate and a somewhat better collector of ammonium. Thus if bulk precipitation collectors were used to estimate the influence of atmospheric loading on the chemical mass balance of freshwaters at this site, the mass balances would be erroneous in varying degrees of severity. Major errors would be made in estimation of sodium, potassium, chloride, and sulfate transport from the atmosphere to the water surface. If these results are general, the supply of metal cations and of chloride from the air to aquatic environments could be greatly underestimated from bulk precipitation samples collected by traditional methods.

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