Reports

Acid Precipitation: Natural Versus Anthropogenic Components

Abstract. *The concentrations of* H^+, SO_4^{2-}, *and* NO_3^- *in the precipitation of eastern North America are greater now than they were historically as a result of fossil-fuel combustion. Because of a lack of data prior to 1950, the absolute increases in the concentrations of these three ions are unknown. This problem can be addressed by comparing the composition of precipitation from areas sensitive to acidic deposition with that of precipitation from remote areas. An analysis of precipitation data indicates that many areas of eastern North America receive precipitation with substantially greater* H^+, SO_4^{2-}, *and* NO_3^- *concentrations than remote areas. For example,* SO_4^{2-}, *the most ecologically significant indicator of change, is enriched 2 to 16 times in eastern North American precipitation relative to its concentration in remote areas.*

Several different approaches have been used to determine that precipitation in eastern North America is more acidic now than it was in the past. In one recent investigation, it was shown that precipitation acidity has increased in the eastern United States over the period from 1955 to 1982 (*1*). Although useful, these trends have too short a time frame and are too recent to be of use in establishing a background acidity of precipitation in the eastern United States. In another investigative approach, a natural acid concentration in precipitation was assumed. There have been two estimates. When H_2CO_3 was used as a reference acid, a *p*H of 5.6 was commonly accepted as the natural *p*H of precipitation (*2*, *3*). More recently, Charlson and Rodhe (*4*) selected a range of *p*H of natural precipitation of 4.5 to 5.6, based on background concentrations of SO_2, NO_x (oxides of nitrogen), and CO_2 in the atmosphere. The third approach uses data from remote regions of the world. Using this method, Galloway *et al.* (*5*) estimated that the lower limits of the natural mean *p*H of precipitation in marine and continental areas were ≥ 5.

The agreement among the three measures is poor, as the *p*H estimates range from 4.5 to 5.6. In addition, all these approaches suffer from a common flaw—they focus on H^+ to describe the change in precipitation composition due to anthropogenic activities. Since H^+ is produced by a host of acids (H_2SO_4, HNO_3, HCOOH, and others) and bases (NH_3 and $CaCO_3$), the H^+ concentration of precipitation in a remote area may be controlled by an entirely different mixture of acids and bases than the concentration in eastern North America. It is thus clear that, in order to compare the precipitation composition between remote areas and eastern North America, the element used should be more conservative than H^+, that is, should be one whose concentration is negligibly affected by chemical and biological interactions. The element should also be directly linked to effects on aquatic and terrestrial ecosystems.

In this report, using data from the Global Precipitation Chemistry Project (GPCP) and North American precipitation chemistry networks, we address three specific questions:

1) What are the concentrations of SO_4^{2-} * (defined as non–sea salt SO_4^{2-}), NO_3^-, and H^+ in precipitation in remote areas?

2) How does the composition of precipitation in remote areas compare to that in eastern North America?

3) Which ion is the most ecologically significant in assessing the magnitude of the change in precipitation composition due to anthropogenic activities?

The data that we used in characterizing the chemistry of precipitation for remote areas were collected at five sites of the GPCP (Fig. 1). Summaries of these data and the sampling and analytical techniques are reported elsewhere (*5*, *6*). Although data from other remote locations were available, the number of storm events at these sites was small and often seasonally biased; we did not use data from these other sites because we felt that our samples may not have represented the true range of variation in precipitation chemistry at these locations. At some of the sites (Poker Flat and Bermuda), the data base was edited to remove storms that were likely to exhibit considerable anthropogenic influences. At Poker Flat, storms associated with air mass trajectories from the Arctic or nearby Fairbanks were eliminated (*7*); at Bermuda, storms associated with air masses arriving from North America were eliminated (*6*).

The data used in characterizing the precipitation chemistry of eastern United States were collected at five sites from the MAP3S Program (*8*) (Fig. 1). We computed the statistical characteristics by using all the data that had been collected through 1981. A more specific comparison of SO_4^{2-} * in remote areas and eastern North America was accomplished with the use of data from several North American precipitation programs (*9*).

Observed concentrations and precipi-

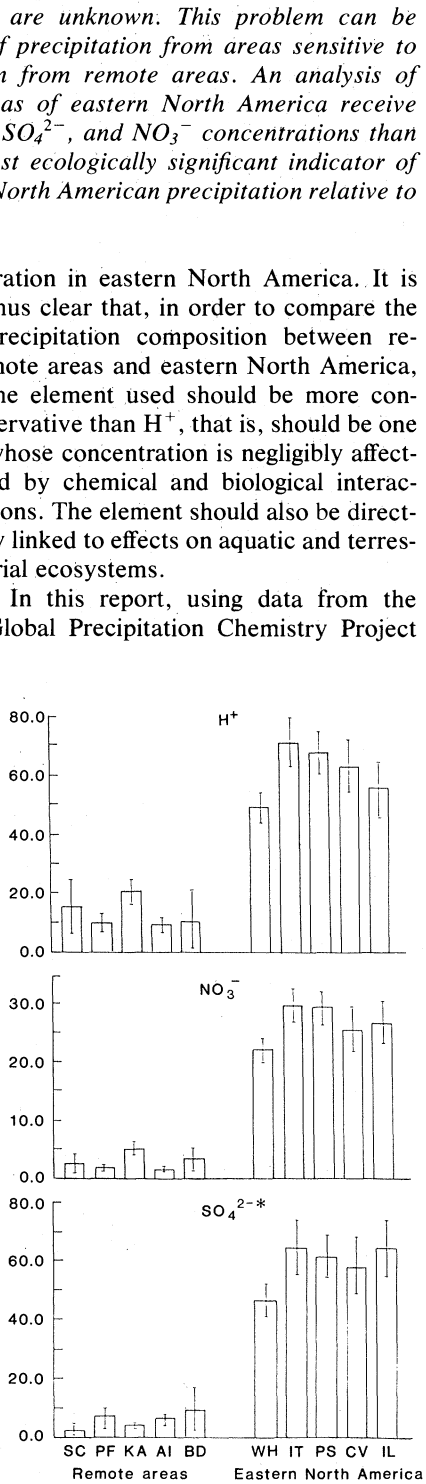

Fig. 1. A comparison of the volume-weighted mean concentrations with 95 percent confidence intervals for five sites in remote areas and five sites in eastern North America. The remote sites are as follows: SC, San Carlos, Venezuela (*n* = 14); PF, Poker Flat, Alaska (*n* = 22); KA, Katherine, Australia (*n* = 125); AI, Amsterdam Island, Indian Ocean (*n* = 73); and BD, Bermuda, Atlantic Ocean (*n* = 23). The eastern North American sites are as follows: WH, Whiteface Mountain, New York (*n* = 329); IT, Ithaca, New York (*n* = 295); PS, State College, Pennsylvania (*n* = 373); CV, Charlottesville, Virginia (*n* = 239); and IL, Champaign, Illinois (*n* = 186).

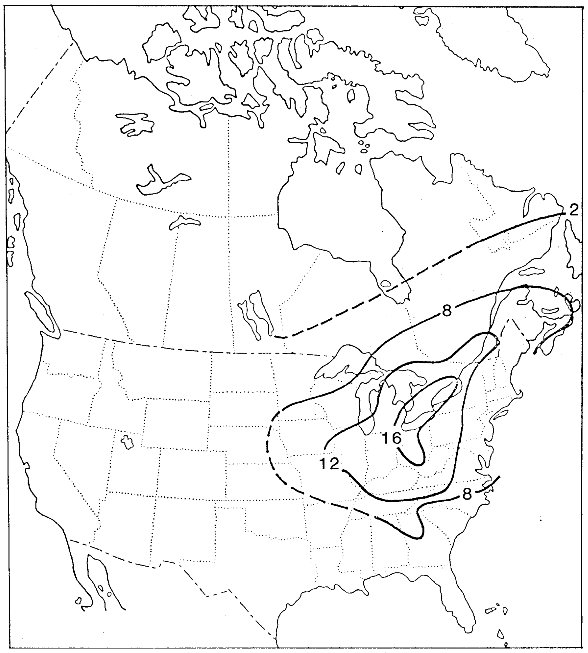

Fig. 2. A plot of enrichment factors for SO_4^{2-} * concentrations in eastern North American precipitation relative to that in remote areas (*14*).

tation amounts were used to calculate the volume-weighted mean (VWM) and the standard error of the VWM at each site for H^+, SO_4^{2-} *, and NO_3^- (Fig. 1) (*10*). We compared the VWM values for each ion among the five sites in each group by using analysis of variance techniques. These comparisons test the null hypothesis that there is no difference in VWM concentration from site to site within each group. Using a 5 percent level of significance, we found that the null hypothesis was rejected for all three ions in the eastern United States group and for H^+ and NO_3^- in the remote group. The VWM concentration of SO_4^{2-} does not appear to vary significantly among the remote sites. These comparisons are illustrated in Fig. 1, where each VWM is graphed along with the associated 95 percent confidence interval.

In remote areas, the primary proton donors in precipitation are H_2SO_4, HCOOH, HNO_3, and CH_3COOH. In marine areas, H_2SO_4 dominates the acidity. In continental areas, HCOOH dominates (*5*). In remote areas organic acids are important proton donors; however, since precipitation acidity is dominated by H_2SO_4 and HNO_3 in eastern North America (*3, 11*), we will concentrate only on the comparison of SO_4^{2-} *, NO_3^-, and H^+ for remote areas and eastern North America. Organic acids will be considered only in the context of their variable control on H^+ in precipitation at remote areas.

The VWM concentrations of SO_4^{2-} *, NO_3^-, and H^+ vary from 3 to 10, 2 to 5, and 10 to 20 μeq/liter, respectively, at the remote sites (Fig. 1). There appear to be significant differences in VWM for both H^+ and NO_3^- among the five remote sites. In the case of SO_4^{2-} *, irrespective of locality (marine versus continental; Southern versus Northern Hemisphere), the VWM values among the five sites are not significantly different.

A comparison of the precipitation composition in remote areas with that at five sites in the eastern United States that have similar sample collection protocols according to *t*-tests shows that there are significant differences between the VWM statistics for the two groups of sites for each ion. The differences between the two regions (eastern United States versus remote) are much greater than the differences for any ion within a region. The differences in H^+ between remote areas and the eastern United States are lower limits. In the latter, since biological activity in the samples was not eliminated, the organic acids were oxidized between collection and analysis, thus raising the *p*H (*5*). Preliminary estimates of the contribution of organic acids to precipitation-free acidity in the eastern United States range from 16 to 35 percent (*12*).

The above analysis shows that the concentrations of H^+, NO_3^-, and SO_4^{2-} * are elevated in eastern North American precipitation as compared to remote areas. We are interested, however, not only in the increase but also in the chemical parameter that is the best indicator of the change, relative to the potential ecological effects caused by acid deposition. Such an indicator should be conservative (unaffected by processes unrelated to the acidification phenomenon) and should have ecological significance.

We believe that SO_4^{2-} * in precipitation is a better indicator of change in precipitation composition than H^+ and NO_3^-. It is misleading to use H^+ for comparison because remote areas have a different mixture of acids and bases than eastern North America (*5, 12*), and H^+ is therefore not a conservative tracer. In the case of NO_3^-, because of its rapid uptake by biota in terrestrial and aquatic ecosystems, it does not promote long-term acidification of aquatic ecosystems as much as SO_4^{2-} * (*13*). Because SO_4^{2-} * is conservative, does not vary significantly among the remote sites, and is the primary control on the acidification of aquatic ecosystems (*13*), we believe that it is the best indicator of change in precipitation composition between remote areas and eastern North America. To demonstrate the magnitude of change, we have calculated enrichment factors by normalizing the 1980 VWM concentrations of SO_4^{2-} * in eastern North American precipitation (*9*) to those observed in remote areas. The enrichment factors vary from <2 to >16 (Fig. 2).

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9. Data from several precipitation chemistry networks in eastern North America were used: Air and Precipitation Network, Canada; Ontario Ministry of the Environment, Canada; Canadian Network for Sampling Precipitation; and the U.S. National Atmospheric Deposition Program.
10. The VWM concentrations were calculated as follows:

$$\mathrm{VWM[X]} = \frac{\sum_{i=1}^{n} P_i\,[\mathrm{X}]_i}{\sum_{i=1}^{n} P_i}$$

where X is the ion considered, P_i is the precipitation depth for storm event i, $[X]_i$ is the concentration measured in the precipitation from storm event i, and n is the number of storm events. The formula used in calculating the variance of the VWM is

$$\mathrm{Var(VWM)} = \frac{n}{\left(\sum_{i=1}^{n} P_i\right)^2} \times \left[\frac{n \sum_{i=1}^{n} P_i^2 \, [X]_i^2 - \left(\sum_{i=1}^{n} P_i \, [X]_i\right)^2}{n\,(n - 1)} \right]$$

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14. Because there is substantial local variation in SO_4^{2-} * due to variations in altitude and other factors, this map is useful only for the depiction of regional trends.
15. This is a contribution to the Global Precipitation Chemistry Project and the MAP35 Program supported by the National Oceanic and Atmospheric Administration. This work was also supported by the Department of Energy and the National Science Foundation. We thank W. Keene, J. Miller, and R. Linthurst for helpful comments.

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Holocene Sea Level Changes at the Coast of Dor, Southeast Mediterranean

Abstract. *Geological, geomorphological, and archeological data of changes in sea level during the Holocene at the Mediterranean coast of Dor provide a eustatic curve of the region. This curve shows that sea level was approximately 2 meters below the present level 4000 years ago, rose to 1 meter below the present level 3000 years ago, and was 1 meter higher than the present level 1500 years ago. It then dropped to 1 meter below the present level about 800 years ago.*

Paleogeographic and morphologic evidence of elevated coasts during the Holocene time as compared with recent sea level is available from a variety of locations around the world. The findings are based mostly on high notches, terraces with coastal sediments, coral shells, and fossils. Archeological evidence of elevated and low coasts has come mostly from the Mediterranean, which provides numerous archeological structures at its shores and at the near shore. The main archeological findings consist of marine installations built to adapt to sea level at the time of their construction—for example, quays, moles, shipyards, mooring stones, fish tanks, and salt tanks.

Many researchers (*1–8*) have concluded that sea levels have been rising and falling in historic times. Opinions about sea level height at the Roman period (that is, from the third century B.C. to 476 A.D. in the western Mediterranean and from 37 B.C. to 324 A.D. in Israel) range from 1.0 m below (*8*) to 2.0 m above the present level (*5*). Opponents of the theory that sea level is higher today than in historical times emphasize the instability of the Mediterranean and the seismic movements that took place either in historical or more recent times (*9–12*). Archeological excavations have exposed marine installations that do not coincide with present sea level and yet do not prove eustatic movement. Therefore, the possibilities of regional tectonic movement, or even local tectonic movements, must be considered.

The coast of Dor (the research area) is located at the southeastern part of the Mediterranean (142°400′N and 225°250′E). At the research area, there is a sharp transition from a relatively sandy area with wide beaches in the south to another area composed of embayments, cliffs, and islets in the north. It has been suggested that a recent movement was responsible for the creation of embayments (*13*). There is another proposal suggesting that a local vertical movement, relatively recent, lifted the coast of Dor (*12*). However, in the case of Caesarea (*14*), 13 km to the south, the Roman harbor is 5 m or more below the present sea level (*7*).

Paleogeographic evidence indicates that when the coastline of Dor was west of the present coast, about 12,000 years ago, the inlets were topographic depressions with sandstone (Kurkar) at the bottom, at least 5 m below today's sea level. These depressions gradually filled with water as sea level rose. Radiocarbon dating of organic clay samples taken from the bottom of the marshland, 4.4 m below present sea level, were given an age of 11,400 ± 420 years (*15*). The influence of the neighboring sea (to the south) is indicated by remnants of marine fauna, foraminifera, and brackish water. The clay 3.8 m below present sea level is given an age of 9415 ± 480 years (*15*). At this period the coast of Dor formed a transition from an aquatic stage (the source of its water being inland) to a marine stage with the water source from the sea. In samples from 3 m below present sea level in the south and 1.5 m

Table 1. Archeological marine installations. Height is given as above or below current sea level.

Type	Age	Number of stages	Height (m)	Function	Sea level at time of building
Sea wall	Pre-Byzantine		−0.40*	Probably an ancient mole	Low
Warehouses	Roman ceramics (*28*)	>1	0.50*		
Three drainage channels	Pre-Roman	2	−0.70† −0.120†	Prevent clogging of anchorage; circulation	Low (−1.20 m)
	Post-Roman	1	0.50 + 0.80†		High (0.50)
Shipyard, three slipways	Persian 2250 years (*28*)		2.5 + 0.10†	Anchored on land	Low
Wave catcher; rock-cut pools; canal	Persian	2 or 3	−0.30† −1.50†	Breakwater; piscina or salt tanks (?); drainage	Low Low
Fish tanks	Byzantine ceramics 1600–1400 years	2 or 3	−0.30† 0.90† 1.00†	Marine agriculture or small piscina	High
Quay	3200 years (*28*)	2 or 3	−0.37* 0.30* 0.50*	Harbor	Low
Well	Several 100 years	1	0.14	Sweet water	Low

*Measurement from the top of the walls. †Measurement at the base of the installation.