

Acidic Lakes and Streams in the United States: The Role of Acidic Deposition

LAWRENCE A. BAKER, ALAN T. HERLIHY, PHILIP R. KAUFMANN, JOSEPH M. EILERS

A statistically designed survey of lakes and streams conducted by the Environmental Protection Agency in acid-sensitive areas of the United States, the National Surface Water Survey (NSWS), was used to identify the role of acidic deposition relative to other factors in causing acidic conditions in an estimated 1180 lakes and 4670 streams. Atmospheric deposition was the dominant source of acid anions in 75 percent of the acidic lakes and 47 percent of the acidic streams. Organic anions were dominant in one-fourth of the acidic lakes and streams; acidic mine drainage was the dominant acid source in 26 percent of the acidic streams. Other causes of acidic conditions were relatively unimportant on a regional scale. Nearly all the deposition-dominated acidic systems were found in six well-delineated subpopulations that represent about one-fourth of the NSWS lake population and one-third of the NSWS stream population.

THERE IS NOW LITTLE QUESTION that acidic deposition can cause surface water acidification (1), although many surface waters are acidic for reasons unrelated to acidic deposition, such as acidic drainage from mine tailings or natural production of organic acids. Thus, a major policy question regarding emissions reductions is: What is the role of acidic deposition, in relation to other factors, in the occurrence and distribution of acidic (2) waters in the United States?

If adequate historical data were available, determining the role of acidic deposition would be reasonably straightforward. But historical water quality data are sparse, questions regarding comparability of data are often unresolvable, and exogenous factors may have contributed to observed changes (3). Consequently, with a few exceptions, studying the direct association between long-term (>10 years) water quality trends and deposition trends has not been a productive approach for assessment of acidification on a regional scale. Paleolimnological research has been valuable, particularly in the Adirondacks, where a statistically designed study has been used to make a quantitative assessment of historical acidification

(4, 5); in other regions, too few lakes have been studied to make quantitative regional assessments. Thus, in this paper, we base our assessment of the causes of acidic conditions largely on inferences from current chemical composition (6).

Our analysis is based on the Environmental Protection Agency's National Surface Water Survey (NSWS), a statistically designed synoptic survey of lakes and streams conducted in acid-sensitive areas of the United States (7, 8) (Fig. 1). We segregated acidic NSWS surface waters into three subpopulations: (i) organic-dominated surface waters, in which organic anions (A^-) exceed $SO_4^{*} + NO_3^-$ on an equivalent basis (9), (ii) waters dominated by watershed sources of sulfate, in which measured SO_4^{2-} concentrations are more than twice as high as concentrations predicted from evapoconcentration of atmospheric inputs (10), and (iii) deposition-dominated waters, in which $SO_4^{2-} + NO_3^-$ from atmospheric deposition are the dominant acid anions. Although Cl^- is a strong acid anion and is important in coastal areas of the NSWS, we did not identify a chloride-dominated class because chloride generally enters watersheds as a neutral salt (sea spray or road salt), rather than as HCl .

The deposition-dominated group includes 75% of the acidic lakes and 47% of the acidic streams in the NSWS (Table 1). Within this group, 67% of the lakes and 88% of the streams had $SO_4^{*}:(C_B - Cl^-)$ ratios greater than 1.0 (11) (C_B is base cations). Ratios greater than 1.0 imply that H_2SO_4 inputs exceed the capacity of water-

sheds to neutralize acid inputs by C_B production (12). Therefore, H_2SO_4 inputs alone are sufficient to cause acidic conditions in most acidic deposition-dominated surface waters in the NSWS. Deposition-dominated, acidic surface waters typically had SO_4^{*} concentrations of 70 to 150 $\mu eq/liter$, and low concentrations of NO_3^- and dissolved organic carbon (DOC) (Table 1). For 97% of the streams and 60% of the lakes in this category, $[A^-]$ is less than 20% of $[SO_4^{*} + NO_3^-]$.

One-fourth of both the acidic lakes and the acidic streams are organic-dominated (Table 1). Most of these are naturally acidic, indicated by the observation that half the lakes and 75% of the streams in this category had $A^-(C_B - Cl^-)$ ratios greater than 1.0 (13). Lakes and streams in this group had much higher DOC and lower SO_4^{2-} than those in the deposition-dominated category (Table 1). This difference reflects the more frequent occurrence of wetlands in watersheds of the organic-dominated systems (14). In all, 80% of the organic-dominated acidic lakes are in Florida and the Upper Midwest; all sampled acidic streams in this category are in the Mid-Atlantic Coastal Plain and Florida.

One-fourth of the acidic NSWS streams are in the watershed sulfate-dominated category; nearly all these streams are acidic because of mine drainage. Sulfate and $C_B - Cl$ were typically much higher in these streams than in deposition-dominated streams (Table 1). There was evidence of mining activity in every mine drainage stream watershed, and many had characteristic "yellow boy" (iron hydroxide) deposits. In the NSWS, streams impacted by acidic mine drainage were found primarily in the coal mining region of the Mid-Atlantic Highlands (15). Only 3% of the acidic lakes are in the watershed sulfate-dominated category (Table 1) (16).

Nearly all the deposition-dominated acidic NSWS lakes and streams were found in six well-delineated subpopulations (Fig. 1 and Table 2). The two NSWS subpopulations most clearly affected by acidic deposition are lakes in the southwest Adirondack Mountains and lakes and streams in forested watersheds of the Mid-Atlantic Highlands.

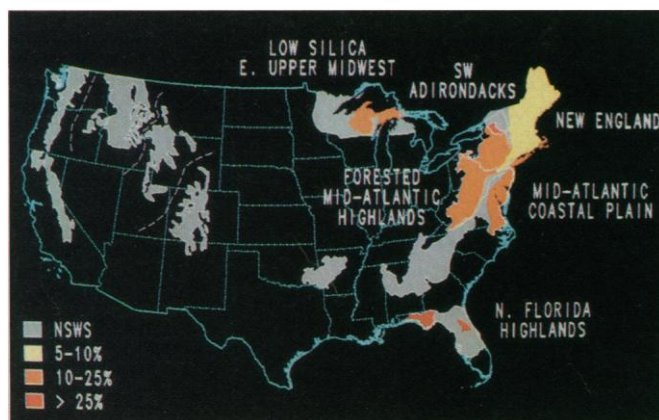
All acidic NSWS lakes in the Adirondacks are located in the southwestern third of the subregion. Most are rapidly flushed drainage systems; sensitivity to acidification in this region is controlled largely by depth of overlying glacial till and bedrock type (17). Paleolimnological studies (5, 18) in this region have shown that although some lakes were naturally acidic, the number of acidic lakes has tripled since preindustrial times, with concomitant increases in levels of inor-

L. A. Baker, Minnesota Water Resources Research Center, c/o U.S. Environmental Protection Agency Environmental Research Laboratory, 200 Southwest 35th Street, Corvallis, OR 97333.

A. T. Herlihy and P. R. Kaufmann, Utah State University, c/o U.S. Environmental Protection Agency, Environmental Research Laboratory, 200 Southwest 35th Street, Corvallis, OR 97333.

J. M. Eilers, E&S Environmental Chemistry, Incorporated, Post Office Box 609, Corvallis, OR 97339.

Fig. 1. Map of the United States showing the percentage of acidic waters in areas sampled in the NSWS and the high-interest regions that contain nearly all deposition-dominated acidic systems. High-interest regions are labeled. Other survey areas are shaded gray. In the eastern Upper Midwest, lakes in the high-interest subpopulation have silica less than 1 mg/liter; in the Mid-Atlantic Highlands, the high-interest subpopulation comprises streams and lakes in forested watersheds only.



ganic monomeric aluminum (Al_i), which is toxic to fish. Nearly all cored lakes that are deposition-dominated and have $SO_4^{2-}:(C_B - Cl)$ ratios greater than 1.0 have become more acidic since preindustrial times. Thus, paleolimnological studies corroborate inferences from lake chemistry.

Nearly all deposition-dominated acidic streams and lakes in the Mid-Atlantic Highlands are in forested watersheds with areas less than 30 km² and at elevations greater than 300 m; waters in lowland valleys are well buffered. Reliable historical data documenting acidification caused by acidic deposition in this region are sparse. However, for deposition-dominated acidic streams, SO_4^* and Al_i concentrations were high (mean of 148 μ eq/liter and 202 μ g/liter, respectively), and A^- concentrations were low (mean of 10 μ eq/liter). Thus, the current chemical composition overwhelmingly implicates deposition-induced acidification.

Acidic NSWS lakes in New England are a heterogeneous population, and watershed cultural disturbances complicate geochemical interpretations for many lakes. Most acidic lakes in this subpopulation are deposition-dominated; about half had $SO_4^*:(C_B$

$- Cl^-)$ ratios >1.0 (Table 2). Paleolimnological studies in lakes that have acidified indicate that the timing of acidification coincides with increases in fossil fuel combustion (19).

Nearly all (93%) deposition-dominated acidic lakes in the Upper Midwest are low-silica lakes. Most are seepage lakes (defined as lakes with no mapped inlets or outlets) located in the eastern part of the region (Fig. 1). Here, silica concentration is a surrogate for ground-water input, which in turn determines sensitivity to acidification (20). The acidification signal is not as strong here as in other regions: 82% of the acidic lakes in this group are deposition-dominated, but in half of these, $[A^-]$ constituted more than 30% of $[SO_4^* + NO_3^-]$. Historical surveys and paleolimnological studies show that pH and ANC have declined in a few lakes, although pH and ANC have increased in many lakes whose watersheds have been disturbed (21).

In Florida, 94% of the deposition-dominated acidic lakes and all sampled deposition-dominated acidic streams are in the northern highlands area (22) (Fig. 1). Most of these had low DOC (<3 mg/liter). Paleolimnological data indicate that recent acid-

ification has occurred in the northern peninsula of Florida, but some deposition-dominated acidic lakes in the Panhandle appear to be naturally acidic (23).

The sixth area of interest is the Atlantic Coastal Plain. Although many streams in this area are organic-dominated, there is also a substantial population of deposition-dominated acidic streams, mainly in the Pine Barrens of New Jersey. Of perhaps greater interest than acidic streams in the Coastal Plain are the many nonacidic streams with pH less than 6.0, about half the population. These streams are an important resource for anadromous fish, which are particularly sensitive to acid stress. Although evidence of fish loss due to acidification in this region is inconclusive, over half the streams had acid-base chemistry unsuitable (low pH, high aluminum, low calcium) for sensitive indigenous species, such as blueback herring (24).

Taken together, these six high-interest subpopulations represent about one-fourth of the lake population and one-third of the stream population in the NSWS, but they include nearly all the deposition-dominated acidic surface waters (95% of the lakes and 84% of the streams). In several areas of the NSWS, few acidic systems were found. No acidic lakes were sampled in Minnesota; only one acidic lake, affected by a geothermal spring, was sampled in the West; and less than 2% of the lakes and streams sampled in the Interior Southeast were acidic (Fig. 1).

We examined only three potential causes of acidic conditions, but it is unlikely that other mechanisms are important on a regional scale. Among other possible causes, forest regrowth following cutting in the early 1900s has been the most widely debated (5, 25–27). However, in the Adirondacks, where paleolimnological studies are most complete, the timing of acidification corresponds better with the increase in industrial emissions than with forest cutting and regrowth (27). Furthermore, there is no evidence that forest regrowth has caused surface waters to become acidic in regions with low SO_4^{2-} deposition.

Retention of sea-salt cations (28) is probably unimportant as a cause of chronic acidic conditions in Northeast coastal lakes and Mid-Atlantic streams, and it is a minor contributor of H^+ in low-ANC waters in Florida (29); however, short-term acidification caused by retention of marine salts during storms is well documented in coastal areas (30). Hydrologic changes, such as droughts, can have a profound effect on acid-base chemistry (31), but there is no evidence that long-term hydrologic change alone has increased the number of acidic surface waters on a regional scale.

Table 1. Characteristics (medians) of acidic NSWS lakes and streams, by chemical class. All units are in microequivalents per liter, except DOC, which is in milligrams per liter; N is the estimated number of acidic lakes and streams in the NSWS target population; stream data are for upstream ends of reaches.

Chemical dominance	N	Chemical parameter				
		SO_4^*	NO_3^-	DOC	A^-	$C_B - Cl^-$
Deposition						
Lakes	881	102	1.0	2	15	83
Streams	2190	117	2.4	2	11	86
Organic acids						
Lakes	260	27	0.9	11	78	57
Streams	1250	44	0.5	25	179	128
Watershed sulfate						
Lakes	39	419	0.3	6	41	610
Streams	1230	3520	1.2	1	6	3110

Table 2. High-interest subpopulations in the NSWS. These were developed using physiographic maps, land-use data, and chemical data in an attempt to narrowly circumscribe deposition-dominated acidic lakes and streams (8). Streams were not sampled in the Adirondacks, New England, or the Upper Midwest. A dash indicates that there were no sampled systems in that category.

Subpopulation	Acidic systems		Chemical dominance for acidic systems			SO ₄ *: (C _B - Cl ⁻) > 1 (%)
	N	Percent of total	Deposition (%)	Organic (%)	Watershed-S (%)	
SW Adirondack lakes*	176	38	100	—	—	100
New England lakes	207	5	83	17	—	70
Mid-Atlantic highlands						
Forested lakes†	41	10	100	—	—	57
Forested streams†	1640	14	82	—	18	90
Atlantic Coastal Plain						
Lakes	20	11	100	—	—	100
Streams	1100	13	32	65	3	35
N. Florida highlands‡						
Lakes	327	63	80	20	—	36
Streams	185	28	75	25	—	17
E. Upper Midwest						
Low-silica lakes§	200	16	82	14	4	61

*The southwest was defined as the part of the Adirondack physiographic province that receives >110 cm/yr precipitation. This is about one-third of the NSWS Adirondack lake population. †About half the total population of streams and one-third of the lakes were in predominantly forested watersheds. ‡This includes about one-fourth of the lakes and half the streams in the Florida NSWS. §We used silica as an indicator of ground-water input. Low-silica lakes are defined as those with <1 mg/liter SiO₂, about 43% of the NSWS lake population in the eastern Upper Midwest.

Finally, Krug and Frink (26) proposed that many clear-water, high-sulfate, acidic lakes were always acidic and that the major change resulting from acidic deposition has been the replacement (anion substitution) of organic anions with sulfate. Analysis of current chemistry cannot determine whether this process is important. Paleolimnological studies in the Adirondacks indicate, however, that inferred DOC concentrations have not declined substantially in acidified lakes (5, 18). Other lines of evidence suggest that this process is significant mainly in waters with rather high initial DOC concentrations (32).

We have identified populations of surface waters likely to have become chronically acidic as a result of acidic deposition. We emphasize that the population of chronically acidic NSWS surface waters is not the same as the population of surface waters whose biota have been impaired by acidic deposition. Acidic waters (2) usually have pH values less than 5.0 to 5.5, whereas biological effects can appear when pH declines below 6.0 or even 6.5 (24, 33). On the other hand, aluminum concentrations in acidic lakes in the Upper Midwest and Florida were lower than in lakes with comparable pH in the east, and some sport fishes (yellow perch, largemouth bass) in these lakes are relatively acid-tolerant. We have not considered short-term episodic acidification that may occur during peak flow periods (30, 34) or chronically acidic lakes and streams not represented in the NSWS (35). Taken as a whole, these considerations suggest that the

population of surface waters impacted by acidic deposition is considerably larger than the population of chronically acidic systems in the NSWS; but available information indicates that the geographic distribution of waters impaired by acidic deposition in the United States corresponds closely with the high-interest areas shown in Fig. 1 (36).

REFERENCES AND NOTES

1. D. W. Schindler, *Science* **239**, 149 (1988).
2. Following common convention, we define acidic waters as those having acid neutralizing capacity (ANC) ≤ 0 $\mu\text{eq/liter}$, based on Gran titration. Recent acidification is defined as a loss of ANC that has occurred since the onset of industrial emissions approximately 100 years ago.
3. J. R. Kramer *et al.*, in *Acid Deposition: Long-Term Trends* (National Academy Press, Washington, DC, 1986), pp. 231–299. An excellent example of the challenge of interpreting historical changes is seen in the dialogue between J. R. Kramer [*Environ. Sci. Technol.* **24**, 387 (1990)] and C. E. Asbury, M. D. Mattson, F. A. Vertucci, and G. E. Likens [*ibid.*, p. 387] regarding the historical analysis of Adirondack lakes by C. E. Asbury *et al.* [*ibid.* **23**, 362 (1989)].
4. Much of the paleolimnological analysis of lake acidification in the United States has been conducted as part of the Paleolimnological Investigation of Recent Lake Acidification (PIRLA) studies. The PIRLA-I included small groups of low-ANC lakes in the Adirondacks, New England, Florida, and the Upper Midwest [D. F. Charles and D. R. Whitehead, *Hydrobiologia* **143**, 13 (1986)]. In PIRLA-II, cores from 37 statistically representative lakes were analyzed to quantify lake acidification in the Adirondacks [D. F. Charles and J. P. Smol, *Verh. Int. Verein. Limnol.* **24**, 474 (1990)].
5. T. J. Sullivan, *Historical Changes in Surface Water Acid Base Chemistry in Response to Acidic Deposition* [(Rep. 11, NAPAP State of Science and Technology, National Acid Precipitation Assessment Program (NAPAP), Washington, DC, 1990, 181 pp.)].
6. The assessment approach presented in this paper is

used in the aquatic part of the NAPAP Integrated Assessment (NAPAP, Washington, DC, in press).

7. The NSWS included three parts: the Eastern Lake Survey [D. H. Landers, W. S. Overton, R. A. Linthurst, D. F. Brakke, *Environ. Sci. Technol.* **22**, 128 (1988)]; the Western Lake Survey [J. M. Eilers, D. F. Brakke, D. H. Landers, P. E. Kellar, *Verh. Int. Verein. Limnol.* **23**, 144 (1988)]; and the National Stream Survey [P. R. Kaufmann, A. T. Herlihy, M. E. Mitch, J. J. Messer, W. S. Overton, *Water Resour. Res.* **27**, 611 (1991)]. Samples were collected from 2,311 lakes, representing a population of 28,300 lakes, and 500 streams, representing a population of 64,300 streams. Data that we present are population estimates. Sampling was conducted at a time of the year in which chemical conditions are relatively stable (fall mixis in lakes and spring baseflow in streams); thus, the data represent chronic conditions in contrast to snowmelt or rainstorm episodes, when waters are generally more acidic. Details of this analysis are in (8).
8. L. A. Baker, P. R. Kaufmann, A. T. Herlihy, J. M. Eilers, *Current Status of Acid Base Chemistry* (Rep. 9, NAPAP State of Science and Technology, NAPAP, Washington, DC, in press).
9. Concentrations of major anions are compared on an equivalence basis. Sea-salt-corrected sulfate concentration $[\text{SO}_4^*]$ was calculated from measured $[\text{SO}_4^{2-}]$ by subtracting the marine contribution using a marine $\text{SO}_4^{2-}:\text{Cl}^-$ ratio of 0.103. Because some waters were impacted by road salt, marine chloride contributions were calculated from a statistically derived distance-from-coastline equation (8). We used the model of B. G. Oliver, E. M. Thurman, and R. L. Malcolm [*Geochim. Cosmochim. Acta* **47**, 2031 (1983)] to calculate organic anion concentrations (A^-) from measured dissolved organic carbon (DOC) and pH. Two methods of calculating (A^-) were also examined: the anion-deficit approach and a regionalized calibration of the Oliver model for lakes [C. T. Driscoll, R. D. Fuller, W. D. Schecher, *Water Air Soil Pollut.* **43**, 21 (1989)]. Classification by these alternative methods resulted in slightly lower percentages of organic-dominated waters (8).
10. This classification step was surprisingly robust. For example, no acidic streams changed categories when the classification criterion was changed from greater than 2 times the expected $[\text{SO}_4^{2-}]$ to greater than 1.5 times the expected $[\text{SO}_4^{2-}]$. Furthermore, all deposition-dominated acidic streams had $[\text{SO}_4^{2-}]$ less than 250 $\mu\text{eq/liter}$, whereas all watershed sulfate-dominated acidic streams had $[\text{SO}_4^{2-}]$ greater than 450 $\mu\text{eq/liter}$ (8).
11. In examining $\text{SO}_4^*:\text{C}_B$ ratios, values of $[\text{C}_B]$ were adjusted for sea and road salt influence by the assumption that cations from these sources are equivalent to measured $[\text{Cl}^-]$ (8). Chloride-corrected C_B values are labeled $(\text{C}_B - \text{Cl}^-)$.
12. Assumptions and limitations regarding the use of ion ratios are discussed by R. B. Husar, T. J. Sullivan, D. F. Charles, in *Acidic Deposition and Aquatic Ecosystems: Regional Case Studies*, D. F. Charles, Ed. (Springer-Verlag, New York, 1991), chap. 3.
13. Most acidic, high-DOC lakes that have been included in paleolimnological studies exhibit little recent acidification, although there are exceptions (Suggs Lake in Florida; Doe Lake in the Adirondacks) (5). High-DOC waters may be relatively resistant to acidification compared to low-DOC waters with comparable C_B because of the buffering effect of the organic acid system [D. C. L. Lam, A. G. Bobba, R. A. Bourbonniere, G. D. Howell, M. E. Thompson, *Water Air Soil Pollut.* **46**, 227 (1989)]. Nevertheless, there is a significant mineral acid component in many acidic, organic-dominated NSWS systems: for about 40% of the streams and 60% of the lakes in this category, $[\text{SO}_4^* + \text{NO}_3^-]$ is greater than 50% of $[\text{A}^-]$. Acidification of some high-DOC waters as a result of industrial emissions cannot be ruled out.
14. About 80% of the organic-dominated acidic lakes had mapped wetlands in their watersheds. In contrast, 70% of the deposition-dominated acidic lakes had no mapped wetlands in their watersheds (8).
15. A. T. Herlihy, P. R. Kaufmann, M. E. Mitch, D. D. Brown, *Water Air Soil Pollut.* **50**, 91 (1990).
16. In the eastern United States, lakes with apparent

- watershed sources of sulfate are found primarily in watersheds with agricultural or urban land disturbances. Most have higher pH and ANC than do lakes in the general NSWs population (8).
17. C. T. Driscoll, R. M. Newton, C. P. Gubala, J. P. Baker, S. W. Christensen, in *Acidic Deposition and Aquatic Ecosystems: Regional Case Studies*, D. F. Charles, Ed. (Springer-Verlag, New York, 1991), chap. 6.
 18. T. J. Sullivan *et al.*, *Nature* **345**, 54 (1990).
 19. As of 1989, 14 New England lakes have been included in paleolimnological studies. Although this group is biased toward smaller, high-DOC lakes that are more likely to be naturally acidic, 6 have undergone significant pH declines; only 1 showed a significant increase in pH [D. F. Charles, R. W. Battarbee, I. Renberg, H. Van Dam, J. P. Smol, in *Soils, Aquatic Processes, and Lake Acidification*, vol. 4 of *Acidic Precipitation*, S. A. Norton, S. E. Lindberg, A. L. Page, Eds. (Springer-Verlag, New York, 1989), pp. 207–276].
 20. Hydrologic budgets for about a dozen seepage lakes (mostly in northern Wisconsin) show that C_B concentrations are linearly related to ground-water inputs. Acidic seepage lakes in the Upper Midwest generally receive less than 10% of their water input from ground water; the rest is from precipitation to the lake surface [L. A. Baker, J. M. Eilers, R. B. Cook, P. R. Kaufmann, A. T. Herlihy, in *Acidic Deposition and Aquatic Ecosystems: Regional Case Studies*, D. F. Charles, Ed. (Springer-Verlag, New York, 1991), chap. 17]. Some Florida lakes also have low ground-water input [L. A. Baker, P. L. Brezonik, E. S. Edgerton, *Water Resour. Res.* **22**, 715 (1986)], but an ongoing study suggests that ground-water in some areas of Florida is so depauperate of base cations that lakes with large ground-water inputs might also be sensitive to acidification (C. D. Pollman *et al.*, in preparation).
 21. J. C. Kingston *et al.*, *J. Paleolimnol.* **4**, 153 (1990); J. M. Eilers, G. E. Glass, A. K. Pollack, J. A. Sorenson, *Can. J. Fish. Aquat. Sci.* **46**, 1929 (1989).
 22. We use the term “northern Florida highlands” to include the northern part (north of 29°N) of the Central Lake District and the Panhandle Districts [H. K. Brooks, *Physiographic Divisions of Florida* (Center for Environmental and Natural Resources, University of Florida, Gainesville, 1981)].
 23. P. R. Sweets, R. W. Bienert, T. L. Crisman, M. W. Binford, *J. Paleolimnol.* **4**, 103 (1990); additional data in (5).
 24. J. P. Baker, J. Freda, S. W. Christensen, M. J. Sale, *Biological Effects of Changes in Surface Water Acid-Base Chemistry* (Rep. 13, NAPAP State of Science and Technology, NAPAP, Washington, DC, in press).
 25. I. Rosenqvist, *Sci. Total Environ.* **10**, 39 (1978).
 26. E. C. Krug and C. R. Frink, *Science* **221**, 520 (1983).
 27. D. F. Charles *et al.*, *J. Paleolimnol.* **3**, 195 (1990).
 28. E. C. Krug, P. J. Isaacson, and C. R. Frink [*J. Air Poll. Control Assoc.* **35**, 109 (1985)] argued that chronic acidic conditions in coastal areas may be caused by this mechanism, in which H^+ is produced by retention of base cations caused by cation exchange or vegetative uptake; also see counterargument by S. A. Norton, D. F. Brakke, and A. Henriksen [*Sci. Total Environ.* **83**, 113 (1989)].
 29. T. J. Sullivan, C. T. Driscoll, J. M. Eilers, D. H. Landers, *Environ. Sci. Technol.* **22**, 185 (1988); L. A. Baker, C. D. Pollman, J. M. Eilers, *Water Resour. Res.* **24**, 1069 (1988); A. T. Herlihy, P. R. Kaufmann, M. E. Mitch, *ibid.* **27**, 629 (1991).
 30. P. J. Wigington, Jr., T. D. Davies, M. Tranter, K. N. Eshleman, *Episodic Acidification of Surface Water Due to Acidic Deposition* (Rep. 12, NAPAP State of Science and Technology, NAPAP, Washington, DC, 1990, 200 pp).
 31. K. E. Webster, A. D. Newell, L. A. Baker, P. L. Brezonik, *Nature* **347**, 374 (1990).
 32. Experimental acidification studies [R. F. Wright, E. Letse, A. Semb, *ibid.* **342**, 670, (1988); L. O. Hedlin, G. E. Likens, K. M. Postek, C. T. Driscoll, *ibid.* **345**, 798, (1990)] and observations of lake recovery following emissions reductions [B. D. LaZerte and P. J. Dillon, *Can. J. Fish. Aquat. Sci.* **41**, 1664 (1984)] suggest that buffering by anion substitution is far less important than buffering by other processes, except perhaps in highly organic systems, such as the KIM basin in Norway discussed by Wright *et al.*
 33. See D. W. Schindler *et al.*, *Science* **228**, 1395 (1985); J. M. Eilers, G. J. Lien, R. G. Berg, *Aquatic Organisms in Acidic Environments: A Literature Review* (Tech. Bull. 150, Wisconsin Department of Natural Resources, Madison, WI, 1984).
 34. The number of streams in the NSWs regions and lakes in the Adirondacks that are acidic during episodes may be three times the number that were acidic during the NSWs sampling periods [K. N. Eshleman, *Water Resour. Res.* **24**, 1118 (1988)].
 35. Roughly 4000 additional acidic lakes in the eastern United States are smaller than the NSWs 4-ha nominal lower size limit (8). In the Adirondacks, lakes less than 4 ha are more likely to be acidic than are larger lakes, but they are also more strongly influenced by organic acids [T. J. Sullivan *et al.*, *Water Resour. Bull.* **26**, 1 (1989)]. There are four to nine times as many streams as are represented on the 1:250,000-scale maps from which the NSWs stream target population was drawn, although many of these unmapped streams are small ephemeral or intermittent streams unsuitable for fish. More importantly, we estimate that 1700 acidic streams in the Northeast were not sampled in the NSWs (8).
 36. We thank M. Mitch and J. Blick for statistical analysis, C. Johnson for GIS support, and S. Christie for editorial assistance; and D. Schindler, J. Stoddard, D. Charles, P. Brezonik, and D. Landers for their critical reviews of an earlier draft of this manuscript. This paper has been prepared at the U.S. EPA Environmental Research Laboratory in Corvallis, OR, through cooperative agreements CR813999 with the University of Minnesota and CR815168 with Utah State University and work plan AR 51-21 under contract no. 68-03-3439 with Kilkelly Environmental Associates. This manuscript has been subjected to the Agency's peer and administrative review and approved for publication.

28 November 1990; accepted 19 March 1991

Alkali-Fulleride Superconductors: Synthesis, Composition, and Diamagnetic Shielding

KÁROLY HOLCZER, OLIVIER KLEIN, SHIOU-MEI HUANG, RICHARD B. KANER, KE-JIAN FU, ROBERT L. WHETTEN, FRANÇOIS DIEDERICH

The recent report of a superconductivity onset near the critical temperature $T_c = 18$ K in potassium-doped C_{60} raises questions concerning the composition and stability of the superconducting phase. The effects of mixing and heat treatment of $K_x C_{60}$ samples prepared over a wide range of initial compositions on the superconducting transition was determined from shielding diamagnetism measurements. A single superconducting phase ($T_c = 19.3$ K) occurs for which the composition is K_3C_{60} . The shielding reaches a maximum of greater than 40 percent of the perfect diamagnetism, a high value for a powder sample, in samples prepared from 3:1 mixtures. A $Rb_x C_{60}$ sample prepared and analyzed in an analogous way exhibited evidence for superconductivity with $T_c = 30$ K and a diamagnetic shielding of 7 percent could be obtained.

THE RECENT DISCOVERY (1) AND separation (2, 3) of molecular forms of solid carbon has made possible the formation of new semiconducting (4) and conducting (5) π -anionic charge-transfer compounds of C_{60} (and C_{70}) with molecular and alkali counterions, respectively. From the latter studies, Hebard *et al.* (6) have provided unambiguous evidence for superconductivity in solids composed of icosahedral C_{60} molecules “doped” with potassium ($K_x C_{60}$) with an onset near $T_c = 18$ K. They combined three experiments on two different morphologies (microwave absorption and magnetic susceptibility χ of powders, and dc resistivity of films) to assert superconductivity under unusually difficult, poorly controlled chemical conditions. As the powder is prepared by a solid-state reaction, only the initial composition is known, so no claim could be made about the

homogeneity of the end product. Therefore, the actual composition of the superconducting phase was not directly determined, and the lower bound of 1% superconducting phase, established by shielding diamagnetism measurements, leaves open questions about the compositional stability of this phase within the K- C_{60} phase diagram.

We report measurements of the shielding diamagnetism curves (χ versus T) conducted over a range of compositions and treatments with the aim of separating and identifying the superconducting phase. In an attempt to narrow the composition range of the superconducting material, the initial composition was systematically varied to locate the maximum fraction of shielding diamagnetism, which is a measure of the actual quantity of superconducting material. This maximum, found at a composition K_3C_{60} , is >40%, a high value for a powder sample. This phase appears to be stable, that is, it is present after indefinitely long heating and mixing, for all nominal sample compositions, $x < 6$. When this same procedure

Departments of Physics and of Chemistry and Biochemistry and Solid State Science Center, University of California, Los Angeles, CA 90024-1569.