Climatically induced rapid acidification of a softwater seepage lake

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TO establish a relationship between levels of atmospheric pollutants such as SO_2 and the acid–base chemistry of lakes is an important but elusive goal of studies on acid precipitation. But the direct effect of acid deposition on the acid-neutralizing capacity (ANC) of lake waters is difficult to isolate, because rates of change of the latter are small[1] and ANC is also influenced by other factors[2,3]. We report here the observation of changes in the ANC of a seepage lake in Michigan driven by the effects of drought on the local hydrology. While levels of acidic wet deposition at the lake remained at a constant, moderate level over a five-year period, a rapid, major loss of ANC occurred because of changes in the input of ANC-rich groundwater. Thus even modest climate fluctuations can have substantial effects on lake chemistry, and must be taken into account when interpreting temporal trends. Sustained drought conditions might similarly alter the acid–base chemistry of other softwater systems.

The ANC of softwater lakes is determined by four main factors: the geological setting, the hydrological paths of inputs, internal alkalinity generation, and the atmospheric loading rates of mineral acids. Seepage lakes are defined hydrologically by the absence of permanent inlets and outlets of surface water, and their sensitivity toward acidification is closely related to the relative amount of ANC-rich groundwater they receive[3]. For many of the low-ANC seepage lakes that receive ≤10% of their water from groundwater, internal alkalinity-generating processes such as sulphate reduction become an important source of ANC[4]. Seepage lakes occur worldwide, commonly in glacial outwash deposits, coastal dunes and karst topography. In geologically sensitive (that is, slowly weatherable) regions of the United States sampled during the National Surface Water Survey, >25% of the lakes were seepage lakes. More important from an impact perspective, 56% of the acidic lakes (ANC < 0 $\mu eq\,l^{-1}$) and 41% of the lakes with ANC < 50 $\mu eq\,l^{-1}$ were seepage systems[5].

Nevins Lake (46°31′00″ N, 86°14′34″ W) is a small (110 ha), continually mixed seepage lake (maximum and mean depths of 4.9 and 1.8 m) located in the eastern Upper Peninsula of Michigan. The lake lies on a highland glacial outwash plain of sand and gravel[6] within 10 km of Lake Superior and is surrounded by white pine and hardwood forest. The watershed is relatively remote, but 30 seasonal cottages and one year-round residence are present on the northern shore. The region receives ~95 cm yr^{-1} of precipitation, and the influence of Lake Superior is reflected in the wide range of snowpack measurements from two nearby stations (530-627 cm).

As part of a continuing study designed to detect trends related to acid deposition[7], water chemistry variables were analysed between autumn 1983 and autumn 1988 on samples collected at 1.0 m depth each spring (after the ice thawed), mid-summer and autumn. To evaluate time trends, we applied the seasonal Kendall τ-test (with correction for serial dependence)[8] to the SO_4^{2-}, Ca^{2+}, Mg^{2+}, ANC, pH, conductance and dissolved organic carbon (DOC) data. For variables showing significant trends, the median rate of change was calculated using the seasonal Kendall slope estimator[9].

During the study period, there was a striking change in the acid–base chemistry of the lake. The ANC decreased by a factor of 8 from a peak concentration of 178 $\mu eq\,l^{-1}$ in autumn 1983 to a low of 22 $\mu eq\,l^{-1}$ in autumn 1988 (Fig. 1), a highly significant

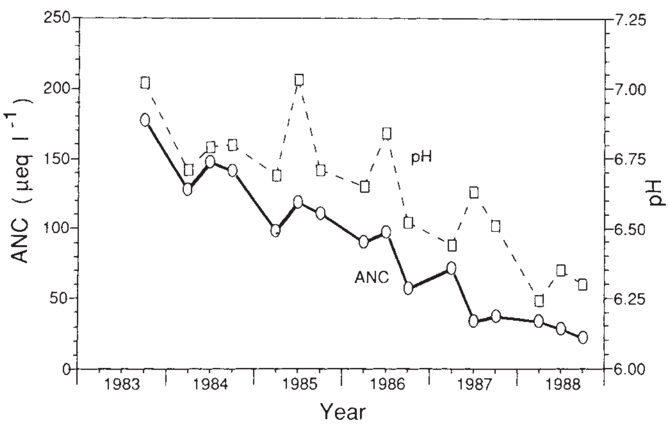

FIG. 1 ANC and pH measured in samples collected at 1.0 m depth from Nevins Lake between autumn 1983 and autumn 1988. Trend slopes were $-30\,\mu eq\,l^{-1}\,yr^{-1}$ for ANC, (95% confidence interval −17 to $-40\,\mu eq\,l^{-1}\,yr^{-1}$; $p=0.007$) and −0.14 units yr^{-1} for pH (95% confidence interval −0.04 to −0.21; $p=0.011$). ANC was determined by Gran titration to pH 3.5 and pH samples were not aerated.

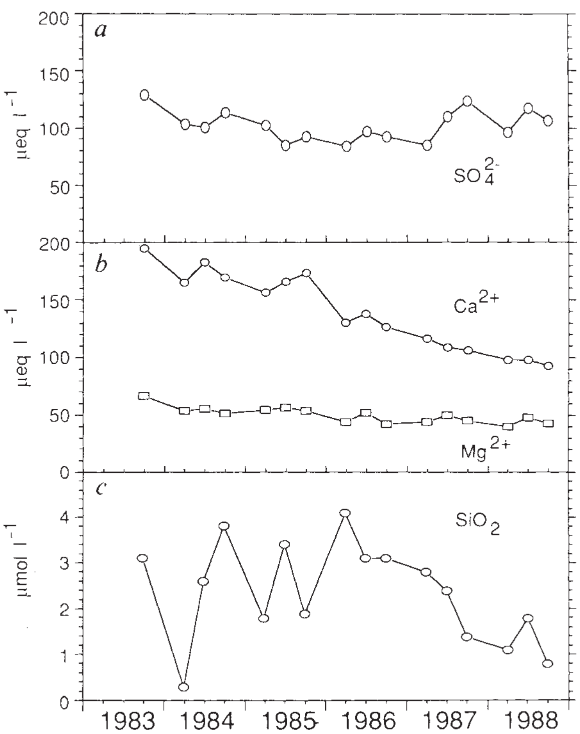

FIG. 2 Concentrations of *a*, SO_4^{2-}, *b*, Ca^{2+} and Mg^{2+} and *c*, SiO_2 in samples collected at 1.0 m depth from Nevins Lake. Trend slopes were $-20\,\mu eq\,l^{-1}\,yr^{-1}$ for Ca^{2+} (95% confidence interval −12 to $-28\,\mu eq\,l^{-1}\,yr^{-1}$; $p=0.010$), $-3\,\mu eq\,l^{-1}\,yr^{-1}$ for Mg^{2+} (95% confidence interval −1 to $-5\,\mu eq\,l^{-1}\,yr^{-1}$; $p=0.028$), and $-23\,\mu eq\,l^{-1}\,yr^{-1}$ for $\Sigma Ca^{2+}+Mg^{2+}$ (95% confidence interval −16 to $-32\,\mu eq\,l^{-1}\,yr^{-1}$; $p=0.011$). No significant trend was detected for SO_4^{2-} ($p=0.641$). Analytical methods: SO_4^{2-}, ion chromatography; base cations (dissolved), atomic absorption spectrophotometry; SiO_2, oxalic acid/molybdate method.

change ($-30\ \mu eq\ l^{-1}\ yr^{-1}$). This was mirrored by a significant decrease in the pH from 7.03 to 6.24 (Fig. 1). Parallel decreases in Ca^{2+} and Mg^{2+} (19 and 3 $\mu eq\ l^{-1}\ yr^{-1}$, respectively) accounted for most of the loss of ANC, with the balance attributable either to variance about these slope estimates or to small undetected trends in other variables. Of the remaining variables, a significant trend was detected only for conductance ($-2.3\ \mu S\ cm^{-1}\ yr^{-1}$, $p = 0.007$, where P is the probability that $\tau = 0$); DOC, Na^+, K^+ and Cl^- remained relatively constant at low concentrations.

Several lines of evidence support our hypothesis that the acidification (loss of ANC) was driven by fluctuations in climate and hydrology, and not by increases in atmospheric pollutant loading, shifts in internal alkalinity-generating processes, or watershed disturbance. Nevins Lake receives moderate loadings of mineral acids; based on interpolation of data from the National Atmospheric Deposition Program, wet SO_4^{2-} deposition is 15.1 kg $ha^{-1}\ yr^{-1}$ and the volume-weighted pH of the precipitation is 4.6 (T. Olsen, personal communication). Wet-deposition rates of base cations and strong-acid anions remained stable between 1979–1987 (seasonal Kendall τ-test) at the closest NADP stations (Trout Lake, Wisconsin and Douglas Lake, Michigan)[10]. Further, we observed no significant trend in lake SO_4^{2-} during the study period (Fig. 2*a*). Nitrate was detectable only in spring samples and then concentrations were low ($<10\ \mu eq\ l^{-1}$). The magnitude of ANC loss, combined with stable SO_4^{2-} concentration in the lake, discount a change in internal alkalinity generation by sulphate reduction as the primary explanation for the patterns we observed. Low concentrations of soluble reactive phosphorus ($<3\ \mu g\ l^{-1}$) and the lack of change in land use during the study period suggest that shoreline dwellings were not a factor inducing the chemical changes.

The monotonic decreases in Ca^{2+}, Mg^{2+} and SiO_2 (Fig. 2*b*, *c*) strongly suggest that the rapid acidification of Nevins Lake was linked to reduced groundwater discharge. Superimposed on the progressive loss of ionic strength, we observed summer maxima in ANC and Ca^{2+} (Figs. 1, 2*b*) which may reflect pulsed inputs of groundwater following the melting of the snow. The absence of this seasonal pattern after 1986, concurrent with a decrease in SiO_2 (Fig. 2*c*), probably marks the end of the flow of groundwater into the lake. Low-ANC seepage lakes receive a large portion of their ANC, Ca^{2+}, Mg^{2+} and SiO_2 from groundwater, although their hydrological inputs are dominated by precipitation rather than groundwater[11-14]. Elimination or reduction of groundwater discharge combined with continued inputs of mineral acids from precipitation, gradually depletes the ANC, primarily through dilution[12,15]. Ion-enrichment calculations[11] predict that prolonged absence of groundwater inputs to Nevins Lake would eventually result in acidic conditions (ANC ≤ 0).

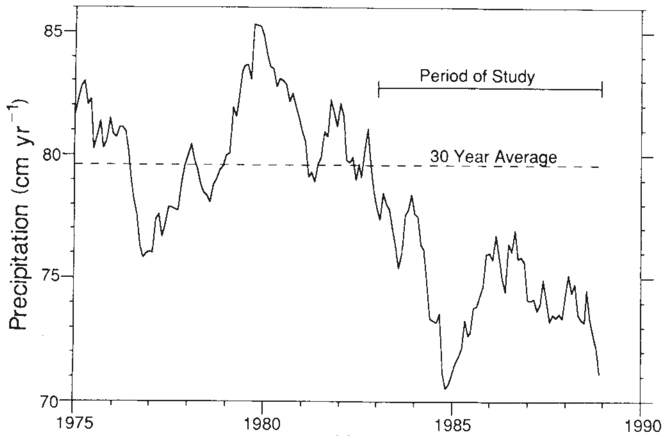

FIG. 3 Five-year running means of annual precipitation at Grand Marais, calculated monthly. The dashed line indicates the 30-yr average annual precipitation at the site. NOAA climatological data 1970–88 (National Climatic Center, Asheville, North Carolina).

Climate data further support our interpretation of the chemical trends. Five-year running averages of annual precipitation at Grand Marais (22 km to the northeast of the study site) were far below normal during the entire study period (Fig. 3). Hydrological records are unavailable, but the lake level in 1988 was as much as 0.5 m below that of previous years (local residents' and our observations), corresponding to ~10% loss of volume. In addition, the water table at three US Geological Survey monitoring wells 13 to 95 km from Nevins Lake had decreased significantly (seasonal Kendall τ-test) since 1975.

The speed and magnitude of a lake's chemical response to drought seems to be related to the initial percentage of groundwater input, which determines ANC, and water residence time. During the same period, drought-related decreases in the lake level and in the water table, followed by cessation of groundwater inflow, were observed at Vandercook Lake and Little Rock Lake, two low-ANC (20–25 $\mu eq\ l^{-1}$) seepage lakes in north central Wisconsin (D. A. Wentz and W. J. Rose, personal communication). During this time, however, a drought-related decrease in ANC of 10 $\mu eq\ l^{-1}$ occurred only in the untreated basin of Little Rock Lake (C. Watras, personal communication). This decrease in ANC was much less than that observed at Nevins Lake (150 $\mu eq\ l^{-1}$) owing to Little Rock Lake's lower initial ANC (25 $\mu eq\ l^{-1}$), longer residence time (~3 yr) and smaller groundwater contribution. The relatively short inflow-based water residence time (~1.6 yr) of Nevins Lake, the result of a shallow mean depth combined with large annual inputs of precipitation, explains its rapid response. Lakes with longer water residence times, such as Vandercook Lake (~5 yr)[16], would be expected to exhibit lags in their chemical response to hydrological fluctuations.

The data from Nevins Lake demonstrate that changes in hydrological flowpaths caused by climate fluctuations—in this case a shift in the relative inputs of groundwater and direct precipitation—can cause ANC changes exceeding those expected in response to acidic deposition[1,17]. It is likely that the chemical changes in Nevins Lake represent an extreme in terms of the magnitude and the speed of the response. Nevertheless, the process we describe is generally applicable to systems that rely on small inputs of groundwater to sustain their ANC, especially low-ANC seepage lakes and peatlands[18]. Uncertainties about the effects of drought on overland and stream flow (hydrological inputs absent from seepage lakes) complicate but do not preclude extrapolation to low-ANC drainage lakes. Our results suggest that reduced groundwater inputs related to sustained drought or to global warming increase the risk of acidification to many softwater systems. □

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1. Schindler, D. W. *Science* **239**, 149–157 (1988).
2. Eilers, J. M., Glass, G. E., Pollack, A. K. & Sorenson, J. A. *Can. J. Fish. aquat. Sci.* **46**, 1929–1944 (1989).
3. Eilers, J. M., Glass, G. E., Webster, K. E. & Rogalla, J. A. *Can. J. Fish. aquat. Sci.* **40**, 1896–1904 (1983).
4. Baker, L. A. & Brezonik, P. L. *Wat. Resour. Res.* **24**, 65–74 (1988).
5. Baker, L. A., Kaufmann, P. R., Herlihy, A. T. & Eilers, J. M. *Current Status of Surface Water Acid-Base Chemistry, Rep. SOS/T 9* (National Acid Precipitation Assessment Program, Washington, DC, 1990).
6. Vanlier, K. E. *Reconnaissance of the Ground-water Resources of Alger County, Michigan, Water Investigation 1* (Michigan Department of Conservation, Geological Survey Division, Lansing, 1963).
7. Newell, A. D., Powers, C. F. & Christie, S. J. Rep. EPA/600/4-87/014. (US Environmental Protection Agency, Washington, DC, 1987).
8. Hirsch, R. M. & Slack, J. R. *Wat. Resour. Res.* **20**, 727–732 (1984).
9. Hirsch, R. M., Slack, J. R. & Smith, R. A. *Wat. Resour. Res.* **18**, 107–121 (1982).
10. *NADP/NTN Annual Data Summaries 1980–1987* (Colorado State University, Fort Collins, 1981–1988).
11. Baker, L. A., Eilers, J. M., Cook, R. B., Kaufmann, P. K. & Herlihy, A. H. in *Acidic Deposition and Aquatic Ecosystems* (ed. Charles, D. F.) (Springer-Verlag, New York, in the press).
12. Anderson, M. P. & Bowser, C. J. *Wat. Resour. Res.* **22**, 1101–1108 (1986).
13. Wentz, D. A. *et al.* in *Acid Rain* (eds Perry, R., Harrison, R. M., Bell, J. N. B. & Lester, J. N.) 309–316 (Selper, London, 1987).
14. Hurley, J. P., Armstrong, D. E., Kenoyer, G. J. & Bowser, C. J. *Science* **227**, 1576–1578 (1985).

15. Garrison, P. J. *et al. Lake Reservoir Management* **3**, 356-364 (1987).
16. Wentz, D. A. & Rose, W. J. *Arch. envir. contam. Tox.* **18**, 147-155 (1989).
17. Dillon, P. J., Reid, R. A. & de Grosbois, E. *Nature* **329**, 45-48 (1987).
18. Gorham, W., Bayley, S. E. & Schindler, D. W. *Can. J. Fish. aquat. Sci.* **41**, 1256-1268 (1984).

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Emission of electromagnetic radiation preceding the Ito seismic swarm of 1989

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THERE have been several reports[1-8] of electromagnetic radiation being detected in air and/or underground before large earthquakes or volcanic eruptions. Unfortunately, such measurements are often plagued by contamination from other sources of noise. We have developed an electrode system that is effective at filtering out urban and atmospheric background noise. Here we report the detection of anomalous electromagnetic signals several hours before the occurrence of large earthquakes near Ito city, Japan, about 150 km from the location of the electrodes. We have also detected anomalous signals about one day before an undersea volcanic eruption that constituted part of the same seismic swarm near Ito. Although the mechanism responsible for such signals is still unclear, these results indicate that their monitoring could be valuable for the prediction of seismic activity.

Conventional methods of measuring underground electromagnetic radiation (EMR) associated with seismicity are not effective in a highly industrialized area with high levels of urban noise. Measuring EMR using a steel pipe in a deep borehole as an electrode was therefore proposed, especially to measure the vertical component of the underground electric field[9]. This configuration is very effective for reducing signals caused by lightning discharges or other atmospheric effects[9]. Such signals propagate between the ionosphere and the ground in a 'waveguide mode', which means that the associated electric fields under the ground surface are predominantly horizontal. The electrode system was installed in late March 1989 at Tsukuba, ~60 km northeast of Tokyo. One electrode is a steel pipe in a borehole 603 m deep and the other is a circle of grounded wire, 40 m across, which surrounds the hole at a depth of 1 m. Although we have no means of knowing the exact extent of earthing of the casing pipe at an arbitrary depth, we suspect that the finite value of earth resistivity would cause partial grounding. At Tsukuba, the surface of the pre-Tertiary basement[10] is at a depth of 400 m. Below the ground surface the resistivity is several tens of ohm metres, but lower down, it is an order of magnitude more conductive owing to the high salinity of fossil water[11]. The lowest layer below the basement surface has a high resistivity of several hundreds of ohm metres. The vertical inhomogeneity in the resistivity enables the electrode system to be sensitive to vertical gradients of the electric field.

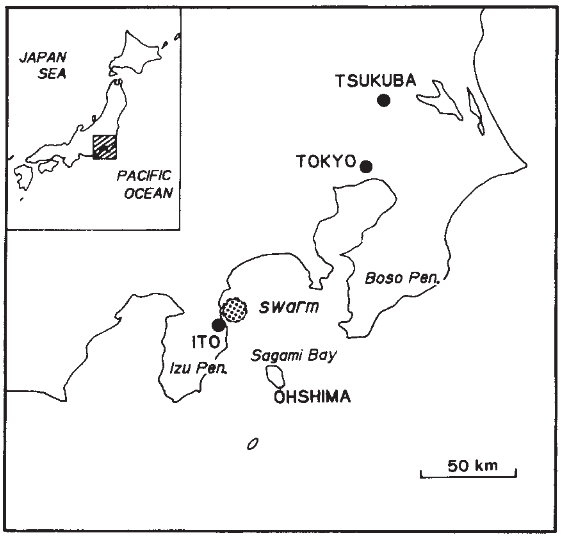

FIG. 1 The electromagnetic radiation recording system is installed at Tsukuba. The 1989 seismic swarm occurred off the coast of Ito on the Izu peninsula.

We have observed EMR in three frequency bands—the d.c. range (~12 Hz), the ultra-low-frequency (ULF) range (0.01-~12 Hz), and the extremely-low-frequency (ELF) and very low-frequency (VLF) ranges (1-~9 kHz)—since last March. We detected no anomalous record in the ULF ranges with our recording method, however, and the following discusssion is limited to the ELF/VLF bands. Amplitude envelopes of the ELF/VLF band have been recorded on strip charts. Criteria for determining abnormal radiation were tentatively selected by examining the normal patterns before and after events.

The most anomalous precursory EMR was observed during the seismic swarm and the undersea volcanic eruption that took place in 1989 off the coast of Ito (Fig. 1)[12]. (Seismic swarms have been occurring almost annually in the western area of Sagami Bay since 1978[13].) Last summer's swarm activity started at the end of June and on 5 July 1989 a moderate earthquake of magnitude $M = 4.9$ occurred near Ito, at 02:28 local time. Figure 2*a* shows the EMR amplitude from ~16:00 on 4 July to ~05:00 on 5 July. At ~20:00 the radiation pattern suddenly changed; the first burst in radiation level was maintained for half an hour and in the second burst the level was maintained for about an hour. These bursts occurred ~6 h and 4 h before the earthquake, respectively. Typical radiation patterns of normal conditions are shown in Fig. 2*b*. Normal patterns consist almost entirely of short-lived pulses, and are thought to be the result of atmospheric activity.

The anomalous radiation is characterized by sporadic bursts lasting half an hour, together with numerous large pulses. By inspecting the data with an event-recorder we found that the durations of the pulses were >50 ms, much longer than the ~5-ms duration of pulses caused by atmospheric activity. The pulses continued until the earthquake occurred. There were no appreciable abnormal fluctuations in the magnetic field data from Ohshima, which is in the vicinity of the seismic swarm at the time of the anomalous radiation.

The largest shallow earthquake ($M = 5.5$; focal depth, 17 km) during the swarm occurred at 11:09 on 9 July. The EMR recorded before this earthquake is shown in Fig. 3. Prominent, sporadic emission bursts, about half an hour long, occurred intermittently for ~10 h before the earthquake. Because 108 earthquakes were recorded on this day (Japan Meteorological Agency), it is not clear whether or not the bursts were related to a particular earthquake. The regularity of the bursts, however, suggests that the abnormal radiation was related to the largest earthquake.

The seismic swarm peaked between 4 and 10 July with prominent crustal motions, such as observed by the Global Positioning System (GPS) technique[14]. On 11 July a volcanic tremor started without any appreciable crustal motion, however, causing concern among the disaster prevention communities in Japan. Our EMR data showed a distinctive abnormal radiation pattern from ~13:00 to ~17:00 on the day before the eruption on 13 July (Fig. 4). The radiation pattern is obviously different from that