Environmental Health Perspectives
Vol. 89, pp. 153-158, 1990

The Effects of Acid Precipitation Runoff Episodes on Reservoir and Tapwater Quality in an Appalachian Mountain Water Supply

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The aluminum concentration and Ryznar Index increased and the pH decreased in a small Appalachian water supply reservoir following acid precipitation runoff episodes. Concomitant increases in tapwater aluminum and decreases in tapwater pH were also observed at two homes in the water distribution system. Lead concentrations in the tapwater of one home frequently exceeded recommended levels, although spatial and temporal variation in tapwater copper and lead concentrations was considerable. Since source water and reservoir water copper and lead concentrations were much lower, the increased copper and lead concentrations in tapwater were attributed to corrosion of household plumbing. Tapwater copper concentration correlated well with tapwater pH and tapwater temperature. Asbestos fibers were not detected in tapwater. The asbestos-cement pipe in the water distribution system was protected by a spontaneous metallic coating that inhibited fiber release from the pipe. Several simultaneous reactions were hypothesized to be taking place in the distribution system that involved corrosion of metallic components and coating of asbestos-cement pipe components in part with corrosion products and in part by cations of watershed origin. Greater water quality changes might be expected in areas of higher atmospheric deposition.

Introduction

Acidification of streams by atmospheric deposition in the Appalachian Mountains of Pennsylvania may be threatening the quality of surface drinking water supplies. Headwater streams typically used as water supplies in this region originate from acidic soils derived from sandstones and shales, which offer little neutralization or buffering capacity. Many of these headwater streams exhibit episodic declines in pH (*1-4*) and increases in dissolved aluminum leached from soils during rainfall or snowmelt runoff events (*1,4,5*). Elevated aluminum concentrations in source streams could directly affect quality of tapwater in homes, but perhaps more serious is the potential for increased corrosion of the water distribution system caused by increased acidity of source water. Increased corrosivity of source water as indicated by increased values of Ryznar's (*6*), Langelier's (*7*) or aggressiveness (*8*) indices could cause increased concentrations of toxic metals (*9-11*) and possibly asbestos.

This paper summarizes the results of several studies of the impacts of acid atmospheric deposition on a small surface water system serving several thousand people in central Pennsylvania. Observations of water quality in the source stream, reservoir water, and household tapwater were made in 1983, 1984, and 1986 with specific emphasis on pH and lead, copper, aluminum, and asbestos fiber concentration. The 1053 hectare (ha) watershed for the source water, Galbraith Gap Run or GGR, is forested with little or no disturbance since logging at the turn of the century.

Methods

Water quality samples were collected from the system during the period March 3 to April 1, 1983 (4 homes) and March 20 to April 12, 1984 (2 homes) and on several occasions in 1985 and 1986 (6 homes). Samples were collected in 1983, before, during, and subsequent to a rain-caused runoff event on the source stream. During 1984, sampling took place before, during, and after several rainstorms and a spring snowmelt event. Samples were collected by hand in polyethylene bottles at the same time each day, usually morning. Samples were collected in the source stream at the water supply intake for the reservoir, in the reservoir at the distribution system intake, at the cold water kitchen taps of study homes (first flush sample), and at a convenient outside tap for each home. When outside taps were frozen, no sample was obtained. All inside kitchen tap samples were collected by the homeowner. Outside tap samples were collected by project staff. Outside taps were flushed daily throughout the study so that the water in the outside line was representative of the water in the rest of the

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Table 1. Water analysis.[a]

Parameter	Detection limit	Procedure	Equipment
Alkalinity	0.5 mg/L	EPA titrimetric 310.1	Fisher titrimeter
Asbestos	—	EPA interim methods	ISI SX40 SEM, Philips EM-300 TEM
pH	—	EPA electrometric 150.1	Orion Ionalyzer 901
Specific conductance	0.1 mhos	EPA specific conductance 120.1	YSI conductance meter model 32
Aluminum	0.003 mg/L	EPA AA furnace 202.2	Perkin-Elmer HGA 500 graphite furnace
Calcium	0.01 mg/L	EPA AA direct aspiration 215.1	PE 2380 spectrophotometer
Copper	0.02 mg/L	EPA AA direct aspiration 220.1	PE 2380 spectrophotometer
Lead	0.01 mg/L	EPA AA furnace 239.2	PE HGA 500 graphite furnace
Temperature	—	EPA thermometric 170.1	Mercury in glass thermometer

[a] Designated procedure from EPA 600/4-70-020, Methods for Chemical Analysis of Water and Wastes, March 1983 (*12*).

household system. Daily samples were obtained during runoff episodes with samples collected less frequently at other times.

Samples were transported to the Water Laboratory of the Environmental Resources Research Institute within 2 hr of collection, and analysis for pH and alkalinity, metals preservation, and filtration were accomplished immediately, except on weekends. Weekend samples were refrigerated and held until the following Monday for analysis. Aliquots were removed from each sample for preservation with nitric acid (Baker Instra-Analyzed).

Streamflow stages were recorded at the time of water quality sampling from a staff gauge at the reservoir intake and were converted to discharge values using flow rating curves obtained by periodically gauging the stream with a current meter.

Thirty-five samples collected in 1983 were digested with nitric acid (EPA procedure 4.1.4) to determine total recoverable metals concentrations (*12*). All other 1983 metals samples were decanted into two aliquots, one of which was filtered through 0.45 μm membrane (Millipore) filter paper prior to analysis. Samples for metal analysis collected after 1983 were not filtered prior to acid preservation.

A section of asbestos-cement pipe was recovered from the water distribution system. The pipe had been in service for approximately 40 years. An ISI scanning electron microscope was used to examine the inside surface of the exposed pipe. Elemental composition of the coating on the inside of the pipe was determined by energy dispersive X-ray analysis.

Determinations of asbestos fiber concentrations in the tapwater of six homes were made wth a Philips EM-300 transmission electron microscope. The revised U.S. EPA interim method (*18*) for asbestos was followed with two exceptions. First, after the 47-mm Nucleopore filter was coated with carbon, the entire filter was examined with the scanning electron microscope as a first-level screening procedure. Second, only the aspect ratio of a fiber and its elemental composition as determined by energy dispersive X-ray analysis were used for positive identification of asbestos fibers. A complete listing of methods and analysis equipment is presented in Table 1.

Results and Discussion

Partial summaries of the results of this work have been

Table 2. Mean (range) values of selected water quality parameters by sampling location.

				Water quality parameter						
Location	*n*	*pH*	*SPC, μmhos*	*Temperature, °C*	*Total alkalinity, mg/L $CaCO_3$*	*Ca, mg/L*	*Al, μg/L*	*Cu, μg/L*	*Pb, μg/L*	*Ryznar index*
Home 1, inside	11	7.08 (6.85–7.19)	36.7 (31.0–37.7)	16.3 (14.0–17.0)	7.0 (5.6–10.8)	3.1 (2.7–3.4)	17 (BD-36)	309 (170–400)	BD[b] (BD)	13.4 (13.0–14.5)
Home 1, outside	7	7.23 (7.13–7.33)	33.6 (30.2–37.0)	15.2 (13.0–18.0)	6.5 (5.8–7.0)	3.1 (2.8–3.4)	16 (14–20)	233 (170–280)	BD (BD)	— —
Home 2, inside	27	6.75 (6.49–7.27)	36.0 (27.4–41.5)	16.0 (10.0–20.0)	5.6 (3.8–10.2)	2.8 (2.3–4.8)	13 (BD-29)	443 (100–710)	3.4 (BD-10)	13.9 (13.0–14.8)
Home 2, outside	29	6.99 (6.59–7.47)	35.7 (30.1–41.6)	7.0 (4.0–10.0)	4.9 (1.8–14.7)	2.7 (2.3–3.4)	25 (10–53)	108 (20–220)	2.5 (BD-7)	14.8 (14.3–15.4)
Home 3, inside[a]	28	6.83 (6.54–7.23)	36.1 ((31.3–41.2)	17.7 (10.0–21.0)	5.1 (2.8–9.8)	2.8 (2.3–4.6)	17 (9–56)	471 (120–640)	23 (4–49)	13.9 (13.0–14.6)
Home 3, outside[a]	28	6.97 (6.59–7.57)	36.3 (31.5–41.3)	14.0 (10.0–18.0)	4.9 (2.8–9.8)	2.8 (2.3–4.3)	18 (BD–63)	297 (100–490)	13 (BD-30)	14.3 (13.8–14.8)
Home 4, inside[a]	8	7.15 (7.05–7.30)	34.0 (30.9–37.1)	18.9 (17.0–26.0)	6.1 (4.9–7.2)	2.8 (2.3–3.3)	21 (BD-48)	160 (130–210)	BD (BD)	13.22 (13.0–13.6)
Reservoir	29	6.80 (6.58–7.13)	31.8 (27.6–36.3)	6.4 (2.0–7.5)	3.2 (1.8–5.5)	2.5 (2.0–3.5)	43 (12–77)	5 (30–50)	BD (BD)	15.0 (14.0–15.7)
Source stream	30	6.73 (6.47–7.01)	30.8 (25.5–35.4)	4.6 (2.5–8.0)	2.9 (0.8–5.5)	2.5 (1.9–3.6)	30 (11–95)	5 (BD-40)	BD (BD)	15.2 (14.4–16.5)

[a] Not sampled in 1984.

[b] BD, below detection limit.

published previously (*10,11*). These papers report on changes in source water quality following a 1983 acid precipitation runoff episode and on attempts to correlate 1984 tapwater copper and lead concentrations to tapwater Ryznar Index values. Results reported herein compare the relative quality of source water, reservoir water, and tapwater during acid runoff episodes, detail attempts to improve on the prediction of tapwater copper and lead concentration using more easily measured parameters, and discuss the relationship between asbestos-cement pipe corrosion and acid precipitation runoff.

Selected water quality data for all sampling locations are summarized in Table 2. The corrosiveness of water entering the distribution system was always reduced at the residential tap, probably as a result of the passive corrosion control (asbestos-cement and cement-lined pipe) present in the water distribution system. Lead and especially copper increased in the household taps, indicating that the household water distribution system was probably their origin.

Large streamflow increases were recorded on Galbraith Gap Run, the source stream for the water supply under study in March 1983 and 1984. Water quality in the storage reservoir at the water distribution system intake changed in response to these events. Dissolved aluminum and Ryznar Index (RI) increased and pH decreased in the reservoir water as a consequence of the runoff events. Reservoir aluminum concentrations correlated positively ($R^2 = 95\%$) with streamflow rates, and reservoir pH and stream water pH were also highly correlated (Fig. 1).

Mean tapwater and reservoir pH (March–April 1984) were well correlated (Fig. 2). Tapwater pH tended to decline in conjunction with declining pH of the reservoir. Tapwater RI increased concomitantly with pH decline. Outside tapwater aluminum concentrations rose as stream aluminum concentrations rose (Fig. 3). Inside tapwater did not show as strong a relationship with stream pH and aluminum concentrations, possibly due to the uncontrolled use of these taps during the study. Reservoir total-recoverable aluminum concentration was also positively correlated with tapwater total recoverable aluminum concentration ($R^2 = 98.2\%$). However, reservoir dissolved aluminum did not correlate well with tapwater dissolved aluminum, indicating that most of the aluminum in tapwater is probably in particulate form. The relatively high pH of tapwater supports this hypothesis. It is clear from the data that tapwater aluminum concentration increased during acid precipitation runoff episodes in Galbraith Gap Run while tapwater pH declined.

Copper and lead concentrations in the tapwater of four homes sampled in 1983 and the two homes studied in 1984 were variable, and no clearcut relationship to acid precipitation runoff was evident. Lead concentrations routinely exceeded U.S. EPA Recommended Maximum Contaminant Level (RMCL = 20 μg/L) at the home 3 location. Similar results were obtained at the home 3 location in 1983, but lead concentrations were smaller.

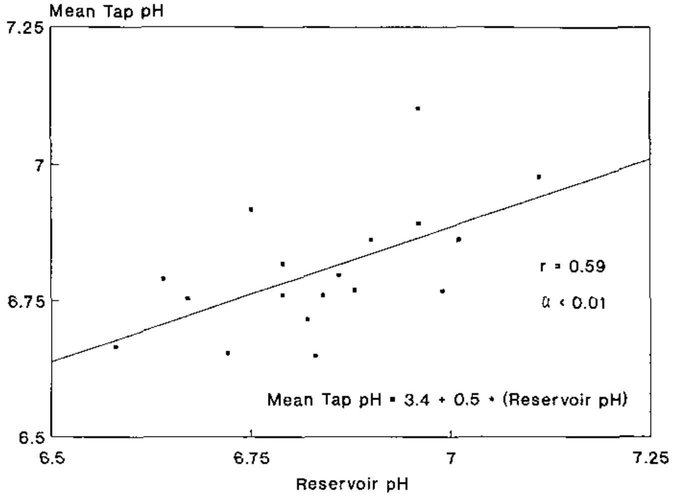

FIGURE 2. The relationship of tapwater pH to reservoir pH.

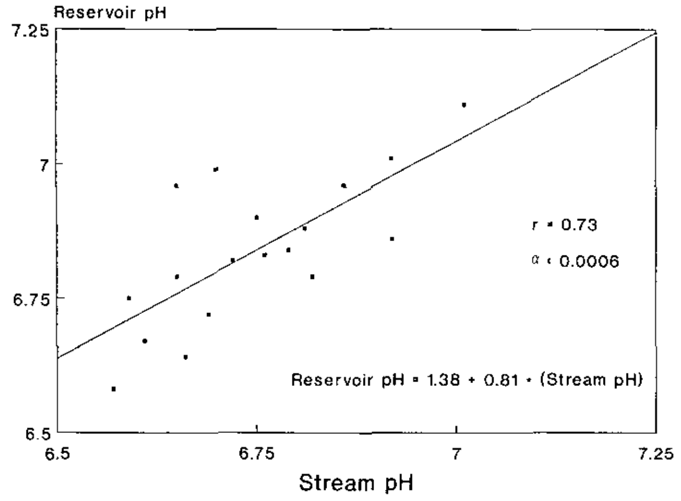

FIGURE 1. The relationship of reservoir pH to stream pH.

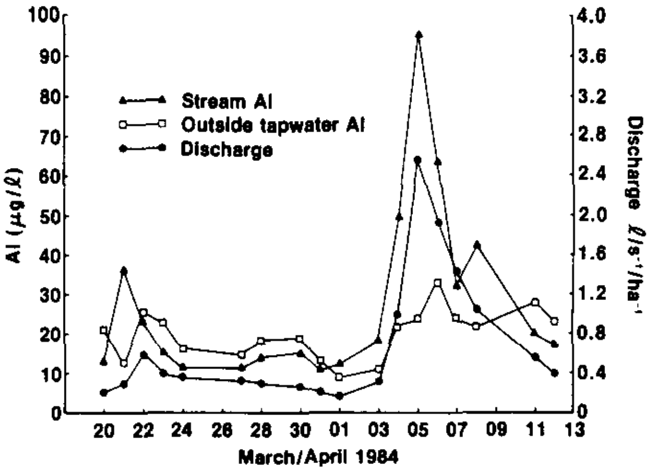

FIGURE 3. Variation of source stream aluminum, outside tapwater aluminum, and stream discharge with time.

When indicator variables were used to distinguish between inside and outside taps, copper concentration in tapwater correlated well with reservoir pH, tapwater pH, and tapwater temperature. Temperature differences between inside and outside taps were significant; consequently, it was important to distinguish between the two in the regression analysis. The prediction equations were:

$$\text{Cu concentration} = 1.2\text{-}0.18\ \text{pH (tap)} + 0.02\ T\text{(tap)} + 0.08\ \text{Tap}\ (R^2 = 70.4\%)$$

$$\text{Cu concentration} = 0.54\text{-}0.08\ \text{pH (reservoir)} + 0.02\ T\text{(tap)} + 0.10\ \text{Tap}\ (R^2 = 66\%)$$

Where T is the temperature of the tapwater (°C) and Tap is the indicator variable for outside (Tap = 0) versus inside taps (Tap = 1).

Figure 4 is a plot of the data showing the relationship between tapwater copper concentration and tapwater pH. It appears that decreases in the pH of tapwater were related to increases in tapwater copper concentration. The range of pH change is also important. For a range of pH of 7.0 to 7.5, little relationship between pH and copper concentrations was evident; however, for a range of pH from 6.5 to 7.5, a stronger relationship appeared to exist. Prediction of lead concentration in tapwater based on reservoir and tapwater pH and tapwater temperature was less successful, with a maximum of 37% of the variation in lead concentration explained by these variables for home 3.

The presence of asbestos-cement pipe and aggressiveness index (AI) values less than 10.0 indicated a strong likelihood that asbestos fibers would be found in tapwater downstream of segments of asbestos-cement pipe in the water distribution system. However, this was not the case when the tapwater of six homes was examined on two separate occasions. No asbestos fibers were positively identified in any of the samples. The asbestos-cement pipe in use was reported to be Transite (a registered trademark of the Johns-Manville Corporation). American Water Works Association standard C400-77 established criteria for the use of asbestos-cement pipe based on AI values. Autoclaved asbestos-cement pipe (Transite) is not recommended for waters with AI values less than 10.0. The mean AI of the source water in the system studied was 7.8 with values never exceeding a maximum of 8.2. Buelow et al. (*18*) reported positive tests for asbestos fibers in two water systems containing asbestos-cement pipe where the AI values were 5.3 and 9.5, respectively, but they caution that AI values alone may not be sufficient to predict asbestos-cement pipe corrosion. Millette and Kinman (*14*) have reported that some waters, particularly those high in iron, do not corrode asbestos-cement pipe even though they may have AI values that indicate a corrosion potential.

In an attempt to verify whether or not this was the case, a section of asbestos-cement pipe was obtained from the distribution system in conjunction with the planned replacement of a section of asbestos-cement pipe. The pipe section had been in service for approximately 40 years.

Visual inspection of the inside wall of the pipe revealed the presence of a brown coating. The pipe wall and coating were scrutinized by scanning electron microscopy and energy dispersive X-ray analysis. Results are illustrated in Figures 5 and 6. Scattered asbestos fibers and a surficial coating of crystals are evident in Figure 5. Because sampling of tapwater failed to reveal asbestos contamination, it would appear that the coating shown in Figure 5 was effective in reducing fiber exposure to water conveyed through the pipe.

The results of energy dispersive X-ray analysis of the coating are depicted in Figure 6. The principal components of the coating are silica, calcium, iron, and manganese. Holtschulte and Schock (*15*) performed energy dispersive X-ray analysis on the surface of asbestos-cement pipe from a New England water system utilizing zinc orthophosphate for iron corrosion control. The surface coating of their pipe also had relatively large amounts of silica, calcium, iron, and manganese; however, there are some differences in the composition of the coatings from GGR and their pipe. The predominant component of their coating was zinc, which they attributed to the zinc orthophosphate treatment. Silica was the largest component and calcium content was smaller rela-

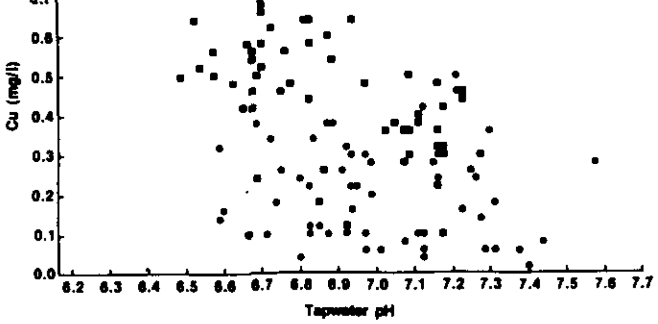

FIGURE 4. The relationship of copper concentration and tapwater pH for taps of the two homes studied in both 1983 and 1984.

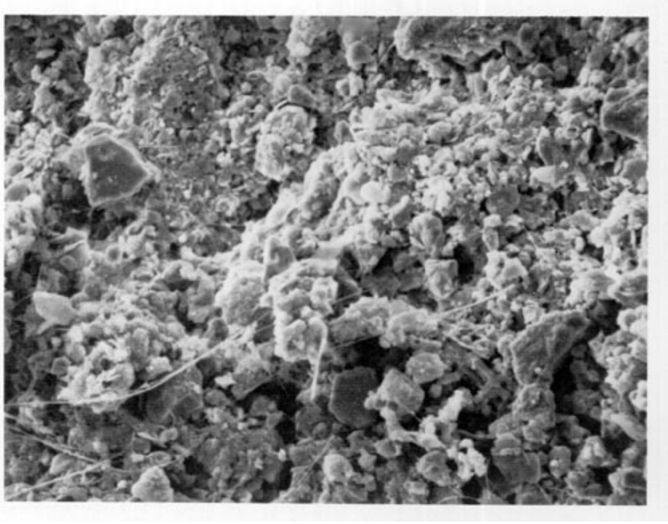

FIGURE 5. Scanning electron micrograph view of the interior wall of asbestos-cement pipe from the study water supply. × 600. (Bar = 16.5 μ).

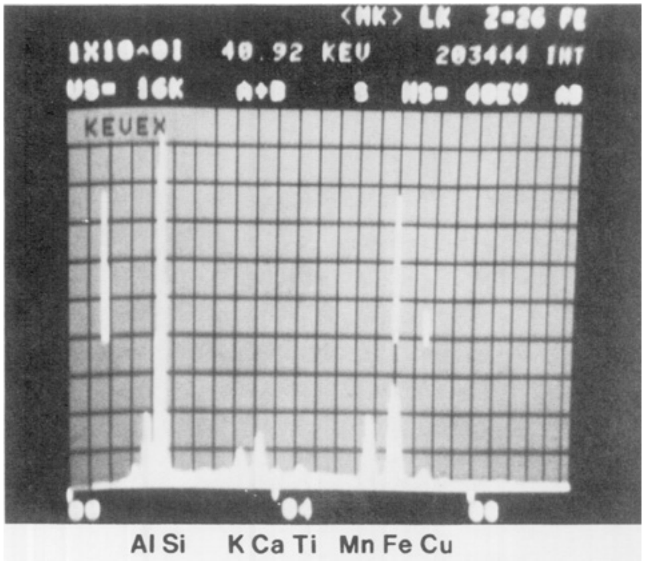

FIGURE 6. Energy dispersive X-ray spectrum of the surface of the interior wall of a section of asbestos-cement pipe from the study water supply.

tive to iron or manganese in the surface layer of the GGR pipe. Although the GGR source water is very low in iron, iron from the corrosion of the iron pipe in the distribution system was thought to be acting as an asbestos-cement corrosion inhibitor. Silica and calcium are both thought to be part of the original pipe with possibly small additions from water carried by the pipe. Other surface layer components in the GGR pipe are also major components of GGR soils. Aluminum, potassium, titanium, and manganese are all abundant in forest soils of the Northeast, and aluminum, calcium, potassium, and manganese are exported from acidified soils (*5*).

The data suggest that cation export from acidified watersheds may be beneficial in preventing the release of asbestos fibers from asbestos-cement pipe. Limited analysis of GGR source water for potassium, manganese, and titanium revealed concentrations of 1.51 mg/L, below detection limit, and 0.03 mg/L, respectively. Since the concentrations of these elements would be expected to fluctuate in GGR source water, more extensive sampling may show greater or lesser amounts than indicated here.

Summary

Acid runoff episodes lowered the pH and increased the aluminum concentration of water entering the distribution system. Although the small number of homes involved in this study precludes any definitive conclusions, the data presented suggest that tapwater quality changed in concert with the episodic changes in reservoir water chemistry. A concomitant increase in the aluminum concentration of tapwater was observed, as was a decrease in tapwater pH. Tapwater copper concentration appeared to increase slightly in response to the acid runoff episodes on the source stream.

Asbestos fibers were apparently not released from asbestos-cement pipe present in the water distribution system despite AI values indicative of such a problem. The presence of a protective coating of metallic elements which appeared to be at least in part a consequence of cation export during acid runoff episodes was thought to prevent asbestos fiber release.

This work was supported in part by The Pennsylvania State University, the Richard King Mellon Foundation, and the United States Forest Service. The authors also wish to thank those homeowners and township officials who assisted with the necessary data collection. The work of Marie Francois-Walk on data analysis and Thomas Doman on SEM and TEM analysis is also appreciated. Carol Spangenberg and Howard Halverson were also instrumental in data collection.

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