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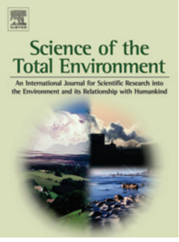

Groundtruthing and potential for predicting acid deposition impacts in headwater streams using bedrock geology, GIS, angling, and stream chemistry

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ABSTRACT

Atmospheric acid deposition is of environmental concern worldwide, and the determination of impacts in remote areas can be problematic. Rainwater in central Pennsylvania, USA, has a mean pH of ≈4.4. Bedrock varies dramatically in its ability to neutralize acidity. A GIS database simplified reconnaissance of non-carbonate bedrock streams in the Valley and Ridge Province and identified potentially chronically impacted headwater streams, which were sampled for chemistry and brook trout.

Stream sites ($n=26$) that originate in and flow through the Tuscarora had a median pH of 5.0 that was significantly different from other formations. Shawangunk streams ($n=6$) and non-Tuscarora streams ($n=20$) had a median pH of 6.0 and 6.3, respectively. Mean alkalinity for non-Tuscarora streams (2.6 mg/L $CaCO_3$) was higher than the mean for Tuscarora streams (0.5 mg/L). Lower pH and alkalinity suggest that the buffering capability of the Tuscarora is inferior to that of adjacent sandstones. Dissolved aluminum concentrations were much higher for Tuscarora streams (0.2 mg/L; approximately the lethal limit for brook trout) than for non-Tuscarora streams (0.03 mg/L) or Shawangunk streams (0.02 mg/L).

Hook-and-line methods determined the presence/absence of brook trout in 47 stream reaches with suitable habitat. Brook trout were observed in 21 of 22 non-Tuscarora streams, all 6 Shawangunk streams, and only 9 of 28 Tuscarora stream sites. Carefully-designed hook-and-line sampling can determine the presence or absence of brook trout and help confirm biological impacts of acid deposition.

15% of 334 km of Tuscarora stream lengths are listed as “impaired” due to atmospheric deposition by the Pennsylvania Department of Environmental Protection. 65% of the 101 km of Tuscarora stream lengths examined in this study were impaired.

1. Introduction

1.1. *Background*

Atmospheric acid deposition is a considerable environmental problem in many regions worldwide (Rodhe et al., 2002; Larssen et al., 2006) that are downwind of coal-fired power plants and other combustion sources. Data from 2004 showed that central Pennsylvania had average rainfall pH of 4.4, which has slowly increased in recent years (NADP, 2006). In the northeastern and eastern regions of the USA, sulfate deposition is declining and precipitation pH is increasing (NADP, 2006; Driscoll et al., 2003). However, the pH, sulfate and acid-neutralizing capacity (ANC) responses of streams and lakes have not followed the precipitation changes equally in all regions (e.g., Webb et al., 2004; Kahl et al., 2004; Palmer

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et al., 2004); these pH and ANC increases in streams lag behind decreases in atmospheric sulfate deposition due to complex soil/groundwater interactions.

Some aquatic ecosystems are protected by soils or bedrock geology that provide long-term buffering capability (Langmuir, 1997); the most typical example given is the essentially inexhaustible buffering capability of carbonate bedrock. Siliciclastic sedimentary, igneous, and metamorphic rocks commonly have much lower ANC and release alkalinity more slowly than carbonates. A Virginia, USA study showed that ANC is highest in crystalline bedrock and lowest in siliciclastic bedrock (Cosby et al., 1991). A German study concluded that in non-carbonate systems, rock acid-neutralizing capacities, ANC_s, from which streams derive ANC_{aq}, increased in order from quartzite, shale and greywacke, granite to gneiss (Frei et al., 1998). Schindler et al. (1986) concluded that in some Canadian lakes within-lake biological process provided more ANC than geological sources. Welsh and Perry (1997) concluded that West Virginia streams in two formations commonly had $pH<5.5$ due to inability to neutralize acid precipitation. Sharpe et al. (1987) found that sandstone formations in the Alleghany Plateau of Pennsylvania differed in their ability to provide ANC to streams.

In geological formations with ANC_s that experience acid precipitation, depressed pH values correlate with elevated aluminum concentrations, but the relationship is not governed by a single simple mineral solubility. Dissolved organic carbon (DOC), hydroxyl, fluoride, sulfate, and silica commonly can complex aluminum in acid streams (e.g., Nordstrom and May 1996; Lindsay and Walthall 1996; Driscoll and Postek 1996; Doucet et al., 2001), and the presence of such ligands causes the total dissolved aluminum concentration to increase. Aluminum solution chemistry is further complicated by the existence of polynuclear aluminum species (Bertsch and Parker 1996).

Aquatic macroinvertebrates and fish populations suffer or are eliminated in aquatic ecosystems where bedrock geology has little ability to neutralize the excess acid. The exact causes of fish disease, reproductive difficulties, and mortality are complex, as are the effects of aluminum speciation on toxicity (e.g., Parkhurst et al., 1990; Wood 1989; Wood et al., 1990; Ingersoll et al., 1990; Maitat et al., 2000). Increasing inorganic monomeric Al (Al^{3+} and its OH^- complexes) concentrations due to decreased pH are primary factors in fish population declines. The presence of dissolved organic carbon (DOC), fluoride, and silica tend to decrease aluminum toxicity given the same total concentrations of aluminum (e.g., Parkhurst et al., 1990; Baldigo and Murdoch 1997; Exley et al., 1997; Exley et al., 2002; McCartney et al., 2003). Measured or calculated acid-neutralizing capacity (ANC) is another value that is critical to understanding acid precipitation impacts. Various methods are used to determine ANC, including Gran titration and calculation of ANC from dissolved ions, but there is no complete agreement on which measurement or calculation is best (McCartney et al., 2003).

Although rainfall pH is rising in the northeast USA, ecological recovery also lags behind chemical recovery, but no long-term effort to monitor biological recovery exists in the USA (Kahl et al., 2004). Models based on assumptions of reduced acid emission suggest that ecological recovery will take decades after acid deposition is reduced (e.g., Driscoll et al., 2003). Ecosystem recovery can experience lag times of several decades following chemical recovery (NAPAP, 2005). Similar conclusions are drawn for northern European ecosystems (Forsius et al., 2003; McCartney et al., 2003; Clair and Hindar, 2005). Because of the dynamic nature of ecosystem changes relating to acid deposition, we need methods for targeting potentially impaired streams in remote areas and for rapidly and cheaply assessing chemistry and biology.

1.2. *Impairment assessments: Simple may not be better, but it may be more realistic*

Acid precipitation impacts on watersheds and biota are intriguing in their complexity, yet startlingly simple in effect: fish have been extirpated and ecosystems dramatically altered. Many impacted streams and lakes are often in remote (therefore infrequently-sampled) headwater areas with beautiful habitat and clear water, thus many impaired streams are not identified as such, and acid deposition has been referred to as a “silent killer” for this reason.

Governmental departments of environmental protection or environmental quality are charged with determining the extent of negative impacts on watersheds. In many cases, these agencies have nearly impossible tasks because of the time and money required to carefully examine a large number of streams, many of which are remote and/or on private land that is not easily accessed. For example, in Pennsylvania, 17% of the 1.3×10^5 km of streams had not been officially assessed for “impairment” of any nature (PA DEP, 2004; PSIE, 2004) as of 2004. The Pennsylvania Department of Environmental Protection (PA DEP) cannot continuously regularly reassess all of these streams, or even those already deemed impaired. In addition, some streams were assessed as “naturally acidic” when they were likely impaired due to atmospheric deposition (R. Ryder, pers comm, PA DEP, 2007).

When agencies do assess, they commonly rely on fewer data than many acid precipitation specialists would consider adequate (PA DEP 2007, PADEP undated). Extensive chemical analyses are the exception rather than the rule (R. Ryder PA DEP pers comm). Total or total dissolved aluminum may be the only aluminum data collected. Fluoride, DOC, and silica are not likely to be measured, and no aluminum speciation is determined by experiment or by geochemical computer programs. Alkalinity by fixed-pH endpoint titration may be the only approximation of ANC.

1.3. *This study*

We investigated the relationship between bedrock sandstone geology and acid neutralization in central and eastern Pennsylvania, USA. Pennsylvania receives some of the lowest pH rainfall in the USA (NADP, 2006). The headwater streams of the Valley and Ridge Geologic Province flow primarily through sandstones, which have low acid-neutralizing ability. After exiting the mountain regions, stream waters recover from acid deposition, receiving alkalinity from shales and carbonates.

Kirby and Turner (2005) found evidence that one sandstone, the Tuscarora Formation, was not able to neutralize acidity as well as the adjacent sandstones, none of which contained carbonate cement. Such preliminary work is essential to identify the importance of local geology in neutralizing acidity for a broader study, and this work led to McInerney and Kirby (2006) and the current study.

We hypothesized that 1) a geographic information systems (GIS) database could be used to target potentially impacted streams based on small differences in bedrock sandstone geology, and 2) stream chemistry results could be paired with data collected by highly experienced volunteer anglers in small headwater streams to assess wide regions rapidly and reliably. Angling information was used to establish the presence or absence of brook trout (*Salvelinus fontinalis*) as an indicator species for chronically acidified streams. This near-base flow "snapshot" sampling made no effort to determine whether streams might be episodically acidified. Streams identified as impaired could then be referred to regulatory agencies for further assessment and consideration of streams for treatment.

Agencies charged with protecting the environment are forced to simplify due to lack of time and money. In recognition of these constraints, the current study employs Occam's Razor to slice away complexity (e.g., aluminum speciation, heterogeneity of rock formation chemistry), and it presents an approach for screening streams that are likely candidates for acid precipitation impacts. Hopefully the simple approach presented here will increase the likelihood that it can be implemented at low cost, on a large scale, and with reliable results that can identify target streams that have not been previously identified as impaired.

2. Methods

2.1. Geologic setting and pre-sampling GIS reconnaissance

The study area encompassed much of the Valley and Ridge Geologic Province in Pennsylvania, a folded and faulted terrain in which the more weather-resistant sandstones form ridges. The Silurian-age Tuscarora Formation and the stratigraphically equivalent Shawangunk Formation commonly are found at the highest elevations. PBTGS (2001) describes the lithologies of rocks in the study area as follows. The Tuscarora is a nearly pure quartz sandstone that is locally conglomeratic with minor interbedded shales. The Shawangunk is a quartz arenite sandstone/conglomerate with thin shale interbeds. The Tuscarora is underlain by the Juniata Formation (a quartzofeldspathic greywacke sandstone and greyish red siltstone), and overlain by the Clinton Group (predominantly shale; calcareous near top); thus the Tuscarora is adjacent surficially to these formations. The quartz arenite Shawangunk is underlain by the Martinsburg Formation or Hamburg Formation (primarily shale and greywacke sandstone), and overlain by the Bloomsburg Formation (siltstone, shale; sandstone). The Juniata is underlain by the Bald Eagle Formation (a quartzofeldspathic sandstone).

ArcMap™ 9.1 was used to develop a GIS database that included bedrock geology (1:250,000), US Geological Survey 7.5-minute topographic maps (1:24,000), local roads, counties, and streams (data publicly available: PASDA, 2004). The lateral extent of the Tuscarora and Shawangunk Formations in Pennsylvania are shown in Fig. 1. The PA DEP 305(b) list (impaired waters) was used to display all currently assessed streams. This stream coverage was "clipped" to display only streams >1 km long that flowed through the Tuscarora and Shawangunk formations. Streams were then manually "clipped" if they flowed through but did not originate in the Tuscarora or Shawangunk. The 1 km cutoff was arbitrarily established assuming that many streams shorter than this length might be ephemeral. Soils at the 1:250,000 scale (the largest scale available digitally) were plotted and compared with the extent of the Tuscarora formation. Almost all of the soils within the Tuscarora Formation (as well as many surrounding formations) are classified alike as typic dystrochrepts, loamy skeletal, mixed, mesic (SRBC, 2006).

The geology and stream coverages were overlaid on topographic maps to target sample sites and to provide volunteers with detailed maps of the stream reaches targeted for hook-and-line fish sampling. Both stream chemistry sampling

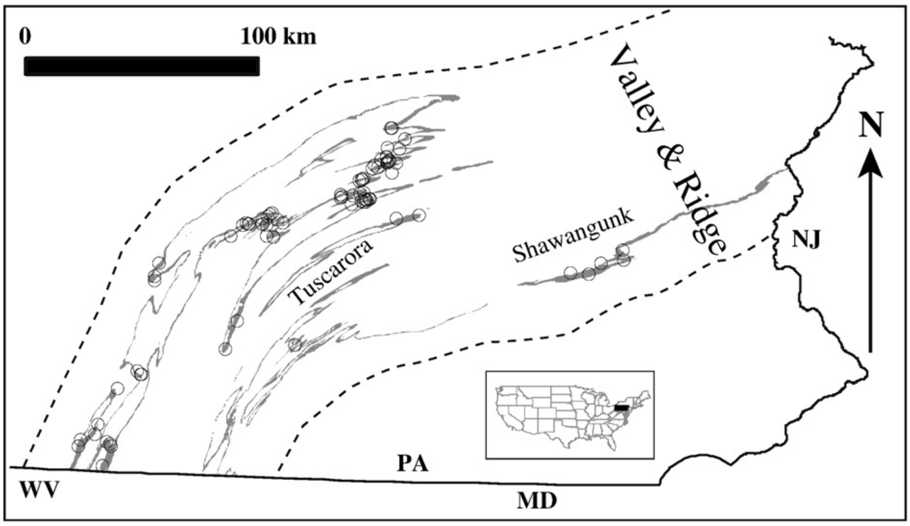

Fig. 1 – Index map of USA (inset) and lateral extent of the Tuscarora and Shawangunk Formations in Pennsylvania, USA. Circles indicate chemistry sampling sites ($n = 107$).

and fish sampling were targeted to occur at the farthest downslope mapped extent of Tuscarora or Shawangunk that was accessible. At the point of sampling all targeted streams in the Tuscarora and Shawangunk originated and flowed through only these formations. Other streams originated in various formations. Several streams in adjacent sandstones were included in the study for comparison. For brevity, we hereinafter refer to streams flowing through neither the Tuscarora nor the Shawangunk as "non-Tuscarora" streams.

2.2. *Field sampling for stream chemistry and rocks*

Water chemistry samples and data were collected in March through September of 2002, August 2004, and June through August of 2005 during near base flow conditions. A YSI™ multi-parameter instrument was used to measure pH, temperature, specific conductance, and dissolved oxygen (DO). The YSI meter was frequently calibrated with pH 7 and 4 buffers. DO was calibrated in the field with air saturated with water vapor. The pH, temperature, DO, and specific conductance were measured at all sites, other parameters at a subset of sites.

Alkalinity titrations were conducted in the field at stream locations with a $pH > 5.1$. Gran titrations (APHA, 1998) were performed for the 2002 samples, which resulted in negative values for some samples. Subsequent titrations were performed using a Hach™ digital titrator (0.16 N sulfuric acid IN in 1/800 mL increments) and a Hach™ Bromocresol Green–Methyl Red (BGMR) color indicator powder pillow (with KCl). The titrations used a $pH \approx 5.1$ (blue–grey) endpoint due to the low alkalinity and low CO_2 concentrations (APHA, 1998); these post-2002 titrations are constrained to return non-negative results, but had Gran titrations been performed, some of these later titrations would likely have given small negative values.

Two grab samples were collected in acid-rinsed HDPE bottles. A 125-mL raw, unpreserved (RU) sample was collected for the analysis of selected anions. A 60-mL sample was filtered (0.45 μm) and acidified with 3 drops of trace metal grade nitric acid (FA) for the analysis of major and minor metals. For the purposes of this study, "dissolved" metals are operationally defined as the fraction passing the 0.45 μm filter. Thus, "dissolved aluminum" is the sum of all aluminum species (organically or inorganically complexed, colloidal) passing the filter. All samples collected were immediately placed on ice and then put in refrigerated storage in the lab. 10% of samples were duplicates of both the RU and FA samples for quality control/quality assurance (QC/QA).

Grab samples of selected rocks through which streams flowed were collected for X-ray diffraction. Samples of road gravel were collected from backroads located near streams studied and tested for effervescence in dilute HCl solution to check for the presence of limestone gravel.

2.3. *Laboratory methods*

RU samples were analyzed for SO_4^{2-}, Cl^-, NO_3^-, and PO_4^{3-} using high performance liquid chromatography (HPLC). FA samples were sent to ActLabs, Inc. for an analysis of major and minor metals (68 elements) using inductively coupled plasma mass spectrometry (ICP-MS). Due to limited funding, only small subsets of samples were analyzed for F, Si, and DOC (ion chromatography, ICP-MS, and persulfate ultraviolet oxidation, respectively).

Field data showed that brook trout were present in 4 streams with an apparent $pH < 5.0$. Dissolved aluminum concentrations for those sites were much lower than expected based upon a solubility curve for aluminum hydroxide. Thus for any samples retained refrigerated in the lab (2005 samples, one month maximum), pH values were measured again in the lab after adding a BGMR indicator powder pillow (containing KCl to increase the ionic strength, Boyle et al., 1986). After the lab pH was recorded, another alkalinity titration was performed. The data analyzed throughout this study were based on the pH and alkalinity measurements performed in the lab, although field data are also shown graphically.

Rock samples from the Tuscarora, Juniata, and Bald Eagle Formations were crushed in a shatter box. Five grams of each powdered sample was placed in 200 mL of acidified distilled water (0.16 N H_2SO_4 to a pH of 4.5) to represent acid precipitation; samples were also placed in pH 4.5 rainwater collected in Lewisburg, PA. Each suspension was stirred for a week with the pH measured periodically until the system had reached equilibrium (no pH change after one week).

Powdered rock samples were placed in acetone slurry on a low-background silicon plate for powder X-ray diffraction from 5 to 80° 2Θ with 0.025° 2Θ steps (10 s/step) at 45 kV and 30 mA. No effort was made to separate or orient clay minerals. The results from a Philips™ search/match program were examined for high scores and compared to knowledge of likely minerals present. Unidentified peaks were compared manually to ICDD (2002) reference patterns.

2.4. *Fish sampling methods*

Some justification is in order for hook-and-line sampling. We sought an inexpensive, reliable sampling method that would do little harm to fish. Many other sampling methods are available, but we hypothesized that a carefully-designed hook-and-line method would meet the above criteria and establish the presence/absence of brook trout. Extensive personal experience suggested to the first author that experienced small-stream anglers would be able to establish presence/absence. In addition, using volunteers allowed greater local community involvement in studying local fisheries.

Numerous studies in the fisheries literature examine fish sampling methods. Hook-and-line methods have, for example, been used to estimate age composition, mean length, and mean length-at-age of rainbow trout in order to be representative of fish caught in the sport fishery (Rutz, 1993) and to target a particular age range of salmon (Bretz and Olson, 2003). Hilderbrand and Kershner (2004) used two-way traps, electrofishing, and hook-and-line to sample cutthroat trout, and Haggarty and King (2004) sampled for marine lingcod and rockfish by hook-and-line but neither study explained the rationale behind these choices. Hetrick et al. (2006) suggest that hook-and-line sampling provided a size-biased subset of a rainbow trout population and that the data supported the use of angling gear as a potentially viable sampling method for monitoring the size composition of rainbow trout in small southwest Alaskan streams. Hook-and-line sampling was found less effective than gillnetting and beach seining for sampling rainbow trout in a large Alaskan river (Schwanke and Hubert, 2004). Yellowstone National Park used data from volunteer flyfishers in an "incredibly successful program" (details were not provided) for data collection on fish populations (Koel et al., 2005). These studies in the fisheries literature suggest that hook-and-line methods can be effective for a very specific goal.

Electrofishing is an extremely common fish sampling technique. It was not used in this study because we lacked funding. Several studies have also documented negative health impacts on fish due to electrofishing (e.g., Tillma 1996; Henry et al., 2004; Keefe et al., 2000; Hollender and Carline 1994). Although electrofishing can be reliable and provide more size range information than angling, it can harm fish, especially fish that may already be under stress due to acid environmental conditions.

Fish sampling was performed by five Trout Unlimited (TU) volunteers. Because small-stream fishing for brook trout is quite a different endeavor from trout fishing on larger streams, the volunteers were carefully selected for their small-stream expertise. Volunteer hook-and-line sampling (by catch and release flyfishing) occurred during June, 2005. Whenever possible, volunteers sampled ≈100-m stream reaches targeted by the GIS work. If the stream reach was inaccessible, alternate downstream reaches were sampled as close to the Tuscarora or Shawangunk (usually less than 100 m) as possible, and volunteers returned a detailed map of the stream reach they sampled. Non-Tuscarora sites were sampled for comparison.

Volunteers used a tally sheet to indicate the number of strikes and fish caught. In some cases, the streams were either so small that trout were spooked before volunteers were able to fish for them or there was no way to cast to the fish due to thick vegetation. In such cases, volunteers relied upon visual methods to assess the presence of brook trout. Volunteers returned detailed notes of their sampling and noted that they saw and/or spooked fish even if they were unable to get them to strike. They also indicated whether habitat (flow, pools and riffles) appeared appropriate for brook trout.

Stream reaches were not included if the stream appeared likely to be ephemeral. Stream reaches with recent electrofishing data from the Pennsylvania Fish & Boat Commission did not correspond to any of the stream reaches in this study. Electrofishing by Pennsylvania Fish & Boat Commission personnel was planned for a small subset of study streams, but time constraints prevented electrofishing.

2.5. *Post-sampling computer analysis*

Sample sites were located on 7.5-minute US Geological Survey topographic maps, and the locations were transferred as points to the GIS coverage. Sample data were entered into spreadsheets and referenced to the sample locations to allow visual inspection of field and lab data to look for spatial trends, especially in pH, alkalinity, dissolved Al concentration, geology, presence of limestone roads parallel to streams, and the presence/absence of fish. A two-tailed unpaired Student's *t*-test was used to determine if pH, Al concentration, alkalinity and the number of fish significantly differed between formations.

3. Results and discussion

3.1. *Trends in chemistry and fish presence*

All chemistry data were first screened for anomalous results. Two Tuscarora pH measurements were quite high and were not included in the discussion below: One of the South Branch of Laurel Run (Perry Co.) sites was excluded because it had been treated with limestone sand and therefore supported a brook trout population (Botts, 2004). Although the pH value (7.8) did not fail Chauvenet's criterion (Taylor, 1997) to be defined as an outlier, Roaring Run (Huntingdon Co.) was excluded because, 1) its pH was >2 standard errors than the average, and 2) its metal and anion concentrations and specific conductance were considerably higher than other Tuscarora samples. The Al concentration of one non-Tuscarora sample was also excluded based on Chauvenet's criterion (Taylor, 1997); this sample was >4.5 standard errors higher than the mean although the pH was 5.8. We suspect this sample was incorrectly analyzed or was mistakenly not filtered in the field.

All streams had pool and riffle structures and were well-shaded. Mean stream temperatures were 13±3 (1σ) °C. Mean DO concentrations were 9.8±1.5 (1σ) mg L^{-1}, which included two extreme headwaters (DO=4.3 mg L^{-1}) that began as bogs.

Table 1 – Summary statistics (based on lab measurements only) including number of observations (in parentheses) for pH (converted to activity for averaging), activity of H^+, dissolved aluminum concentration, and alkalinity (as $CaCO_3$) by formation as well as fish sampling results

Formation	Tuscarora	Shawangunk	Non-Tuscarora
Mean pH	4.8	5.7	6.3
Mean activity H^+	$^{S,\,N}1.5\times10^{-5}$ (26)	$^{T}1.2\times10^{-6}$ (6)	$^{T}4.6\times10^{-7}$ (20)
Mean dissolved Al, mg L^{-1}	$^{S,\,N}0.2\pm0.2$ (35)	$^{T}0.02\pm0.01$ (6)	$^{T}0.03\pm0.02$ (27)*
Median dissolved Al, mg L^{-1}	0.2	0.02	0.03
Range dissolved Al, mg L^{-1}	0.01–0.58	0.01–0.05	0.01–0.06*
Mean alkalinity, mg L^{-1} as $CaCO_3$	$^{N}0.5\pm1.1$ (26)	$^{N}0.7\pm0.7$ (6)	$^{S}2.6\pm1.9$ (20)
Median alkalinity, mg L^{-1} as $CaCO_3$	0	0.5	2.1
Range alkalinity, mg L^{-1} as $CaCO_3$	0–4.2	0.1–1.9	0.7–9.0
Fish observed	9	6	21
No fish observed	19	0	1

Fewer streams were sampled for fish than for chemistry. * indicates one extreme outlier (0.34) was excluded due to Chauvinet's criterion (Taylor, 1997); ± indicates one standard error. Superscripts indicate significant differences ($P<0.01$; two-tailed unpaired Student's *t*-test) from Tuscarora (^{T}), Shawangunk (^{S}), and non-Tuscarora (^{N}) values.

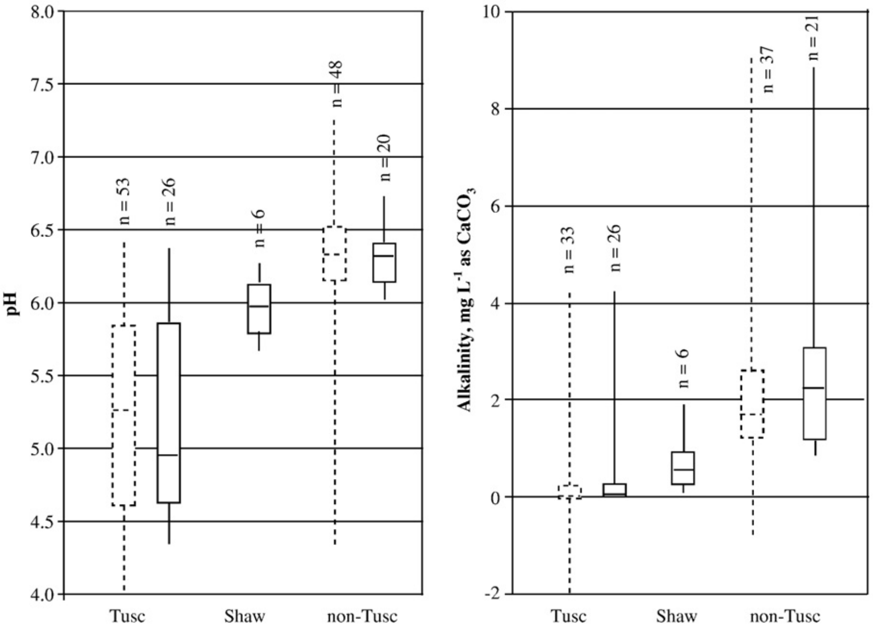

Fig. 2 – Box and whisker plots (median, quartiles, and range) for stream pH and alkalinity by formation. Dotted lines indicate both field and lab data used; solid lines indicate only lab data used.

Mean specific conductance was 30±20 (1σ) μS cm^{-1}. Very few streams appeared to be ephemeral. Table 1 summarizes chemical parameters likely to limit trout populations and shows whether brook trout were observed.

The Tuscarora streams commonly had lower pH values than either the Shawangunk or non-Tuscarora streams (Fig. 2 and Table 1), and the pH of eight of the Tuscarora stream sites were increased by either non-Tuscarora tributaries or by a parallel limestone road (see Section 3.4).

Dissolved Al concentrations in the Tuscarora streams averaged a factor of ten higher than other formations (Table 1), and Al concentrations increased with decreasing pH. Plotting log activity of Al *versus* pH on a diagram (not shown) with solubilities of gibbsite ($Al(OH)_3$), amorphous $Al(OH)_3$, and kaolinite

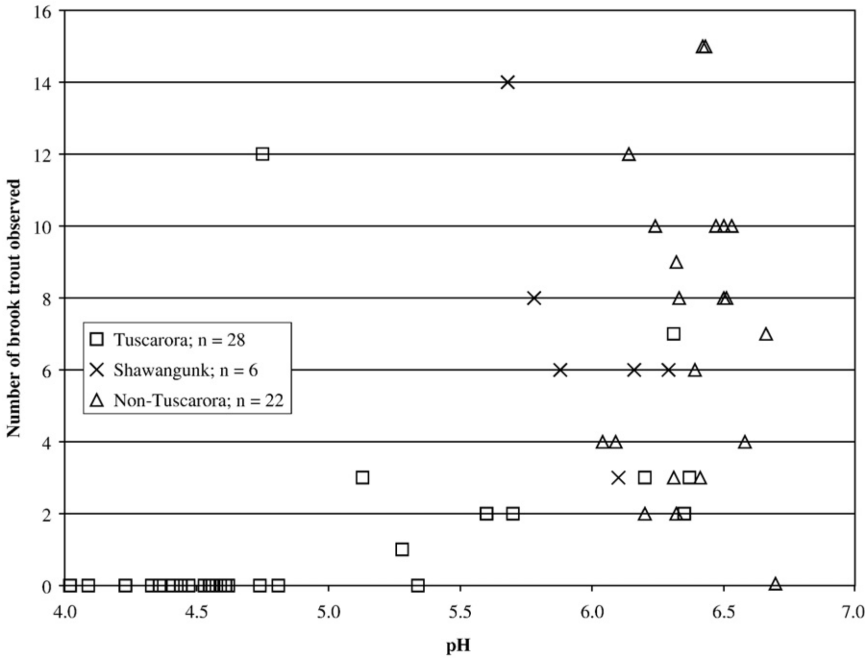

Fig. 3 – Number of brook trout observed *versus* pH by formation.

($Al_2Si_2O_5(OH)_4$) suggested that dissolved Al concentrations were not controlled by equilibrium with respect to a single solid Al-bearing phase. These results are not surprising given the complexity of aluminum speciation discussed in Section 1.1. A dissolved Al concentration of ≈0.2 mg L^{-1} is lethal to brook trout (Baker and Schofield 1982; Baldigo and Murdoch 1997), although health impairments start at lower concentrations. 15 stream sites (13 streams, all in the Tuscarora) had dissolved Al higher than 0.2 mg L^{-1}. 27 stream sites (18 Tuscarora and 4 non-Tuscarora streams) had dissolved Al concentration >0.05 mg L^{-1}.

The relationship between alkalinity and pH for streams flowing through the different formations (Fig. 3) shows that the Tuscarora Formation had many more samples with negative or zero alkalinity than other formations. None of the streams studied had alkalinity >10 mg L^{-1}, but nevertheless, several streams had apparently viable brook trout populations, suggesting that episodic acidification may not be a problem in many of the streams. Fig. 4 shows that with one exception (12 trout at pH 4.75), streams with pH<5 corresponded with zero fish observations, with all but one of the "no-fish" observations occurring in the Tuscarora. We cannot explain the 12-trout observation in the pH 4.75 stream; although several hypotheses might explain this phenomenon, but data are lacking to support any particular hypothesis.

Fluoride (n=10) was detectable (>0.01 mg L^{-1}) in four samples with a maximum of 0.03 mg L^{-1}. Silicon concentrations (n=20) averaged 1.56±0.07 (1σ) mg L^{-1}as Si. Only three samples were analyzed for DOC (1.5, 2.6, and 2.7 mg L^{-1} as C. Generalizations from such small sample sizes must be treated with much caution, but the concentrations observed are not likely to reduce aluminum toxicity dramatically, a view supported by the complete lack of fish in stream reaches with dissolved Al concentration >0.15 mg L^{-1} (Fig. 5).

Fig. 5 shows several phenomena commonly found in this study. Panther Run and the North Branch of Buffalo Creek originate in the Juniata, with initially low pH values in the extreme headwaters (in organic-rich boggy areas) rising (pH≈6.5 for most of their lengths) as the water flows for longer distances through the Juniata. Below the confluence of these two streams, the North Branch of Buffalo Creek flows through the Tuscarora, but its pH remains near neutral due to the Juniata-influenced headwaters. In contrast to most Tuscarora streams, the North Branch of Buffalo Creek is in an "exceptional value watershed" (PA DER, 1996) and is a Class A wilderness brook trout stream (PA F&BC, 2006) in a roadless area.

In contrast, the main branch of Buffalo Creek flows through an essentially roadless area (it is crossed by one gravel road that does not parallel the stream) in the Tuscarora for 7 km. The pH is less than 5 for at least 9 km. The main branch of Buffalo Creek is officially listed as impaired due to atmospheric deposition (PA DEP, 2004) and has no brook trout. The stream historically supported a brook trout population and had a pH of 7.0 and alkalinity of 61 mg L^{-1} as $CaCO_3$ (Robbins, 1953). By 1970, this location had a pH of 5.5, and the stream was judged to have too few brook trout to be stocked due to "natural acidity" (Reed and Hoopes, 1970), which was actually the impact of atmospheric deposition that continues today (pH=4.5 and no alkalinity).

3.2. Geological sources of alkalinity

Rock samples were grab samples, and a systematic investigation of the mineralogy of these formations, which are relatively but not completely homogeneous in their mineralogy, was beyond the scope of this project. No mineral separates or oriented clay samples were processed. The goal of the XRD work was to find likely candidate minerals as sources for alkalinity and aluminum released to the streams.

Quartz (SiO_2) was identified in all rock samples; dissolution of quartz would have no influence on pH or alkalinity. No

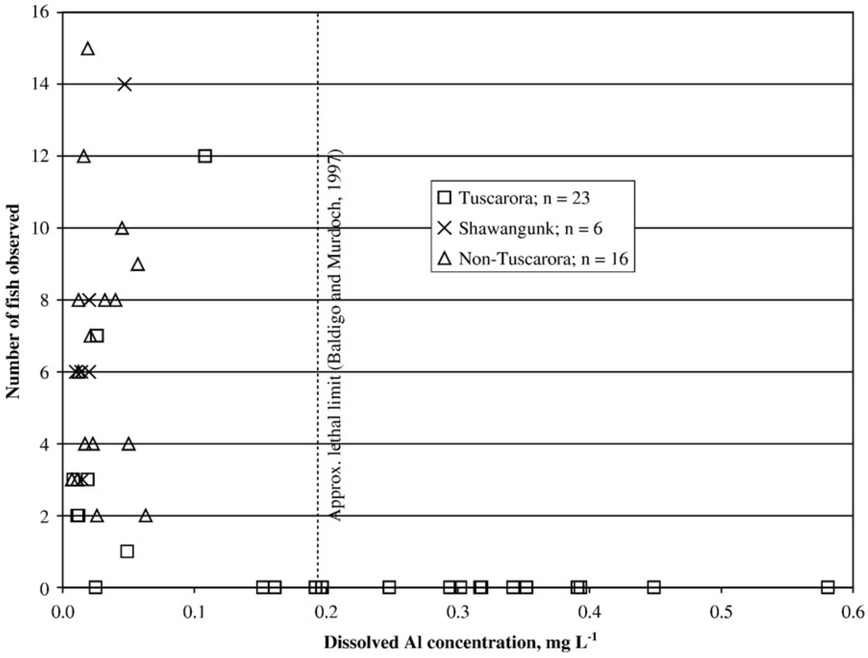

Fig. 4 – Number of brook trout observed *versus* dissolved Al concentration by formation.

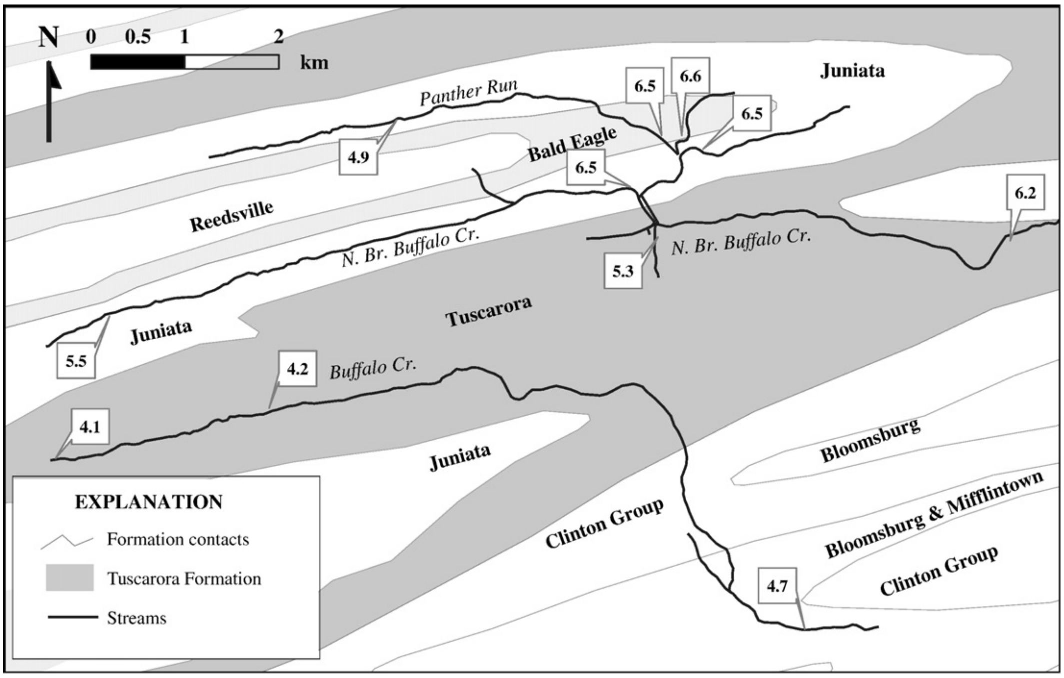

Fig. 5 – Geologic map with pH values for Buffalo Creek, North Branch of Buffalo Creek, and Panther Run, Union and Centre Counties, Pennsylvania, USA.

evidence for calcite ($CaCO_3$) or other carbonates, common sources for alkalinity, was found in any sample. We were not able to concentrate clay-sized particles and thus could not prepare oriented samples for XRD, the Tuscarora, Juniata and Bald Eagle Formation samples had peaks at ≈8.8° 2θ, suggesting the presence of the clay mineral illite. The Juniata (red sandstone/siltstone) contained hematite (Fe_2O_3). Evidence for feldspars ($NaAlSi_3O_8$ and $KAlSi_3O_8$) was found in the Juniata and Bald Eagle, respectively. The Tuscarora, Juniata and Bald Eagle showed weak evidence for the weathering product kaolinite ($Al_2Si_2O_5(OH)_4$). The Tuscarora and Bald Eagle are known to locally contain pyrite (FeS_2), a potential acid source, but there was no evidence for pyrite in the samples examined by XRD.

Although the dissolution of potassium feldspar into kaolinite could produce alkalinity, a buffering capacity graph (Eby, 2004) shows that this reaction should contribute negligible alkalinity at pH levels between 4 and 6. Illite (below referred to with the simpler formula for the mineral muscovite, $KAl_2(Si_3, Al)O_{10}(OH)_2$) weathering to kaolinite is more likely responsible for contributing alkalinity (HCO_3^-) to streams at these pH levels:

$$2KAl_2(Si_3, Al)O_{10}(OH)_2 + 5H_2O + 2CO_2 = 2HCO_3^- + 3Al_2Si_2O_5(OH)_4 + 2K^+. \qquad (1)$$

If illite or another buffering mineral is exhausted, especially along preferential flowpaths in fractured rock, pH can drop, and the acid dissolution of kaolinite can release Al to streams by

$$Al_2Si_2O_5(OH)_4 + 4H^+ + H_2O = 2AlOH_2^+(aq) + 2H_4SiO_4(aq) \qquad (2)$$

in concentrations harmful to brook trout.

Lynch and Dise (1985) described a strong correlation (r^2=0.95) between bedrock distribution and streamwater ANC in Shenandoah National Park, Virginia, USA; percentile distributions of streamwater ANC were distinctly different for five major bedrock types. In theory, the distribution of bedrock types within the region should provide a basis for predicting the ANC of unsampled streams in the region, as well as for explaining the ANC of sampled streams. In practice, this approach on regional scales is limited by the generality of much of the geologic information available for the Southern Appalachians. Herlihy et al. (1993) had little success in relating geological information at the 1:250,000 scale to stream ANC in data from the 1987 synoptic component of the Virginia Trout Stream Sensitivity Study (VTSSS); they concluded that this map scale was too coarse to adequately characterize small streams. Our data suggest that 1:250,000 geologic data can still be useful for reconnaissance if not for prediction.

Although our rock samples cannot be claimed to be samples representative of an entire formation, the ability of our single grab samples to neutralize acidity in the lab provides some insight into the neutralization potential in the field. All rock samples equilibrated with rainwater had some ability to release alkalinity and increase the pH above that of local rainwater when powdered and stirred (Table 2), thus all rocks

Table 2 – Final pH of powdered rock samples equilibrated with pH 4.5 rainwater

Crushed sample	"Equilibrium" pH	Lithology
Tuscarora	6.9	Quartz arenite sandstone
Juniata	8.2	Quartzofeldspathic sandstone/siltstone
Bald Eagle	7.1	Quartzofeldspathic sandstone
Reedsville	7.3	Black shale

in the study area must have some solid phase(s) present (illite?) that gives them some intrinsic ability to neutralize acidity. The powdering of the samples has two effects that cause the experiments to produce higher pH than observed in the field: 1) increased surface area increases reaction rates, and 2) the powdered lab samples had relatively unweathered surfaces exposed compared to *in-situ* field samples that have weathered from the outside to the inside. Groundwater flow through these well-cemented, low porosity rocks is very likely by fracture flow. These observations combine to suggest that inadequate time and fresh surface area are available for field pH values to be as high as lab pH values. Nevertheless, the Tuscarora formation produced the lowest equilibrated pH in the lab, and field pH values were significantly lower than for other formations.

3.3. *Potential non-bedrock influences*

Soil content and forest vegetation can also influence water chemistry. Older forests are much more likely to leach NO_3^- than younger forests, and coniferous tree litter is known to produce more acidification than deciduous tree litter (Sullivan, 2000). Sharpe et al. (1984) found the average pH values of throughfall, organic soil leachate, and mineral soil leachate in a Pennsylvania headwaters watershed were 3.94, 3.89, and 4.44, respectively. Therefore, the most significant change in pH was after the water percolated through the mineral soil, which is formed by weathering bedrock, suggesting that although the pH of water decreased slightly as it percolated through soil, the main factor controlling the pH changes was still bedrock geology. Sharpe et al. (1984) found that soil litter did not have a large influence on H^+ concentrations. However, Zawadzkas and Abrahamson (2003) found that the pH in the shallow soil zone on the ridges, slopes, and bottomland in the Swift Run headwaters area (an acidified Tuscarora stream in this study) were between 3.3 and 3.8. Because this pH is lower than the average rainwater (NADP, 2006), acidity must have been added while the water percolated through the shallow soil, presumably by microbial respiration of CO_2. The stream pH is ≈4.5, so as the water went through mineral soil and possibly bedrock, the acidity added from the shallow soil horizon must have been neutralized to some extent.

The nature of the forest canopy and soils was not investigated in this study. However, most of the forest canopy and soils likely differ relatively little in this region, which was largely timbered in the late 1800′s to early 1900′s.

3.4. *pH increase and alkalinity from limestone roads*

Fig. 6 shows evidence that a limestone gravel road running parallel to a stream in the Tuscarora can increase the pH and add alkalinity to such streams. In the roadless area near the headwaters of Bear Run, the pH is 4.7, but pH rises to 6.3 within 2 km below the point where the stream begins to parallel the road. No other Tuscarora streams showed such a large pH increase in this distance. No other sample sites had this unique combination of a parallel limestone gravel road in the Tuscarora, so this hypothesis could not be further tested.

3.5. *Fish sampling*

Volunteer hook-and-line fish sampling clearly demonstrated the presence or absence of brook trout in the studied streams. Fish were absent in 19 of 28 Tuscarora streams, absent in no Shawangunk streams, and absent in only 1 (an acidic, boggy extreme headwater) of 22 non-Tuscarora streams (Table 1).

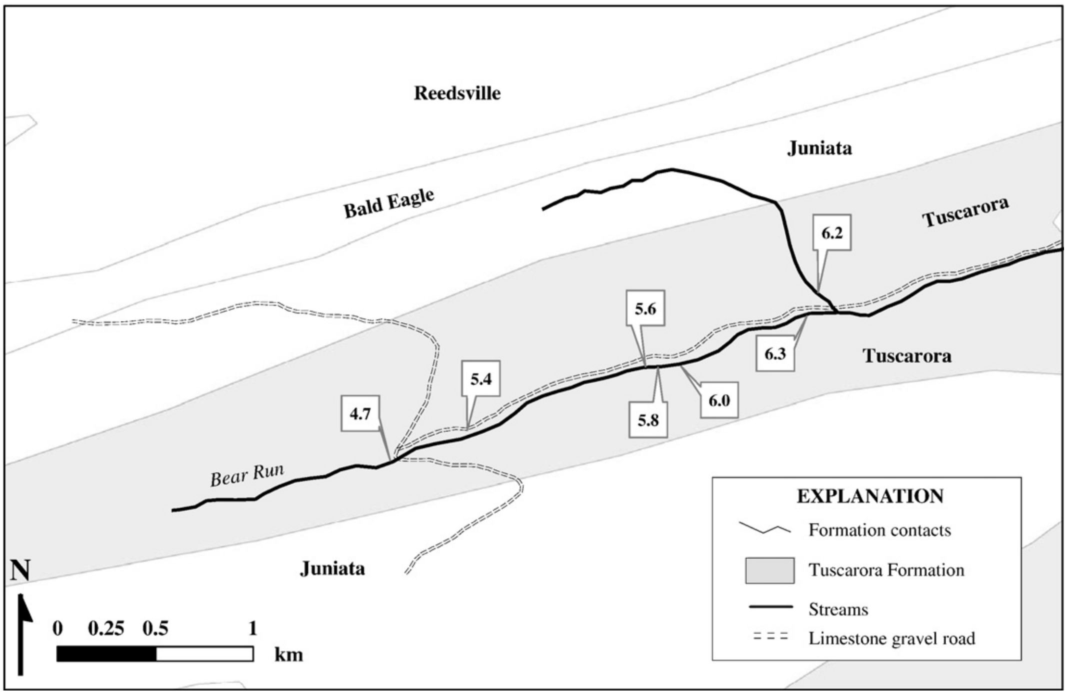

Fig. 6 – Geologic map with pH values for Bear Run, Union and Centre Counties, Pennsylvania, USA.

Poisoning is likely the only method that provides complete confidence for the no-fish condition. It could be argued that angling can only establish the presence of fish — it is possible that fish could be present but not counted in an angling survey. The first author's personal experience strongly suggests that experienced small-stream brook trout anglers will get strikes or at least see "spooked" brook trout if they are present under the conditions of this study. Therefore, we have high confidence in the results even if absence cannot be documented scientifically.

3.6. *Comparison with Pennsylvania DEP assessments*

There is no universal definition of impairment of streams. Ideally, streams would be labeled as impaired if humans caused the change from original conditions to conditions that have measurably declined for the original biota. In determining the impact of acid deposition, there commonly can be a question whether a stream was naturally acidic before acid deposition began. Headwater streams that begin as bogs are often naturally acidic due to organic acids. In this study, we found a few such streams, and these streams were slightly "tea-colored," suggesting the presence of organic acids. The mean concentrations of sulfate in the Tuscarora streams were higher than other streams, but this difference was not statistically significant, thus sulfate could not be used to distinguish acid deposition effects from natural effects. Most streams in this study likely had brook trout populations until sometime during the 1950's to 1970's, but documenting the historical presence of trout was not possible except in one case (Section 3.1).

The PA DEP maintains a list and GIS shapefile of assessed waters called 305(b) (PA DEP, 2004). PSIE (2004) also provides a GIS shapefile of all streams. Using GIS, we found that 83% of the total stream lengths in Pennsylvania have been assessed. Of the total stream lengths in the state (assessed and unassessed), 13% are listed as impaired, and 0.4% are listed as impaired due to atmospheric deposition. PA DEP (undated) states "The most important parameters for identifying acid precipitation impairment are pH and dissolved aluminum concentrations (with 0.1 μm filtration). Elevated dissolved aluminum concentrations (>150 μg/L) and low pH (<5.8) can be lethal to brook trout, depending on duration of exposure. When a stream survey documents pH depression and dissolved aluminum levels above 150 μg/L (after 0.1 μm filtration), it is probably appropriate to consider the stream to be biologically impaired due to acid precipitation." Ryder (pers comm, 2007) explained that the PA DEP did not list some streams meeting the above criteria because they were deemed "naturally acidic" by some regional offices, although the PA DEP

Table 3 – Comparison among PA DEP and this study's impairment acid deposition classifications

Stream	County	# of fish	Alkalinity	pH	Al, mg L^{-1}	DEP impaired?	Comments
Impaired this study, not impaired according to PA DEP							
Trib. To Raystown Br. Juniata R.	Bedford	0	0	4.8	0.32	**N**	
Trib. To Raystown Br. Juniata R.	Bedford	nd	0	5.6	nd	**N**	Ephemeral?
Pond Branch	Bedford	0	0	4.6	0.34	**N**	
Bear Run	Centre	nd	nd	4.7	nd	**N**	Ephemeral
Cherry Run	Clinton	nd	0	5.3	0.39	**N**	Ephemeral?
Croyle Run	Huntingdon	0	0	5.3	0.03	**N**	
Greenlee Run	Huntingdon	1	0	5.3	0.05	**N**	
Trib. To Laurel Run	Huntingdon	nd	nd	4.8	0.40	**N**	
Weikert Run	Mifflin	12	0	4.8	0.11	**N**	
Fowler Hollow Run	Perry	0	0	4.4	0.25	**N**	
Swift Run	Snyder	0	−1.1	4.4	0.30	**N**	Natural area
Trib. To Spruce Run	Union	nd	nd	5.5	nd	**N**	Ephemeral
Trib. To Rapid Run	Union	nd	nd	5.5	nd	**N**	
Trib. To N. Br. Buffalo Creek	Union	nd	0	5.3	nd	**N**	
Impaired this study, impaired according to PA DEP							
Pigeonroost Run	Bedford	0	0	4.6	0.39	Y	
Bear Gap Run	Bedford	0	0	4.5	0.58	Y	
Wildcat Run	Bedford	0	0	4.7	0.39	Y	
Laurel Branch	Bedford	0	0	4.6	0.35	Y	
Greens Valley Stream	Mifflin	0	0	4.6	0.16	Y	
S. Br. Laurel Run	Perry	0	0	4.6	317	Y	Above treatment
Buffalo Creek	Union	0	0	4.5	0.45	Y	
Not impaired this study, impaired according to PA DEP							
Lingle Stream (non-Tuscarora)	Centre	2	1.0	6.2	0.06	**Y**	Non-Tuscarora
S. Br. Laurel Run	Perry	2	6	6.4	0.06	**Y**	Below treatment

Streams in this study were categorized as impaired if a) number of fish = 0, b) alkalinity (mg L^{-1} as $CaCO_3$) ≤0, c) pH≤5.5, or d) Al concentration ≥0.05 mg L^{-1}Bold indicates disagreement with impairment status; nd indicates no data.
All streams except for Lingle Stream are in the Tuscarora. "Natural Area" indicates this stream flows through an area protected by the state. "Above treatment" and "below treatment" samples were taken upstream and downstream, respectively, of in-stream limestone sand addition. Only lab data for pH and alkalinity were used in this classification.

does not perform DOC determinations on such streams as part of the listing decision.

We did not collect all data for all parameters for every site due to the large number of sites, so we used a positive result for any of four criteria below to define impairment. The rationale and definitions follow. 1) Alkalinity of ≤ 0 suggests that pH should be less than 5.1, with a corresponding elevation of dissolved Al concentration above background. 2) pH$<$5.5 (commonly listed as a lower limit for brook trout). 3) Dissolved Al concentration ≥ 0.05 mg L^{-1} is close to the toxicity threshold for brook trout. 4) Zero fish suggests that there is not a viable brook trout population, which assumes that our anglers were able to correctly determine the fish/no-fish condition. The relationship between no fish, no alkalinity, low pH and high dissolved Al concentration presented herein suggest that this definition of impairment is, at the very least, a good starting point to suggest further investigation.

Table 3 lists streams found impaired by this study and whether those streams are impaired according to PA DEP. It also shows two streams listed as impaired by DEP that we did not find impaired. None of the Shawangunk or non-Tuscarora streams were found to be chronically impaired in this study or by the PA DEP. All streams judged “impaired” in this study except for Lingle Stream are in the Tuscarora, and all of these Tuscarora streams originate and flow through only the Tuscarora. Based on inspection of rainfall pH data (NADP, 2006), it is unlikely that atmospheric acid loading differs significantly within the study area. Although the Shawangunk lithology is similar to the Tuscarora, we suspect that minor (non-quartz) minerals in each formation differ enough that the Shawangunk neutralizes acidity better than the Tuscarora. Other formations adjacent to the Tuscarora, although sandstones, also appear to neutralize acidity to prevent chronic acidification.

Table 4 compares the stream km assessed in this study and by the PA DEP. Of the 334 km of stream originating and flowing through the Tuscarora, 15% of the stream lengths are officially listed as impaired due to atmospheric deposition. In this study, water and fish sampling was done as close as possible (within 100 m) to the farthest downstream extent of the mapped Tuscarora extent, and “impairment” was assumed to extend upstream because acidification was not expected to improve upstream (indeed, streams with more than one sample point had lower pH upstream). Although acid conditions could worsen upstream, reaches upstream of a sample site were assumed “not impaired” if the sample site did not fit the impairment criteria. Therefore it is likely that some stream reaches upstream of our unimpaired sampling locations are impaired, and our estimation of the stream length impaired is an underestimate. For example, if the farthest upstream site on a stream had a pH$>$5.5, it is quite possible that upstream reaches drop below pH 5.5 and would be classified as impaired if sampled. We did not sample or make habitat observations further upstream on the majority of streams, but streams (except those marked ephemeral in Table 3) were judged to have good brook trout habitat (pool/riffle structure, tree canopy, lack of obstructions such as waterfalls or dams, lack of excessive sedimentation, no other known pollution sources) up to the downstream Tuscarora extent. We did not calculate watershed areas for all streams, and small watershed area could suggest that streams are ephemeral. However, one sampled 2-km long stream (an unnamed Juniata stream marked as ephemeral on the USGS topographic map) that was not impaired contained at least 20 small brook trout in an approximately 1 km^2 watershed. This study examined 101 km of streams, and 65% of those stream lengths were found to be impaired (based on the criteria listed in Section 3.6). 22 km of streams were listed as impaired by PA DEP but not assessed in this study. Combining those 22 km with streams we found impaired gives 26% of Tuscarora stream lengths impaired. These data suggest that between 26 and 65% of Tuscarora streams are impaired.

Table 4 – Stream lengths originating and flowing through the Tuscarora, assessed, and impairment judgment; * indicates 22 km not assessed in this study were listed as impaired by PA DEP

Assessment by	Assessed, km	Not assessed, km	Impaired, km	Not impaired, km
This study	101	233*	65*	36
PA DEP	334	0	50	284

There are likely more impaired Tuscarora streams than those identified by this study. We focused on streams longer than 1 km, and many Tuscarora streams are shorter than 1 km because they tend to run directly off ridges due to the structural geology. While many of these short streams are likely ephemeral and thus may not provide good brook trout habitat, their aquatic macroinvertebrate populations may be impaired. Because there are demonstrably more Tuscarora stream lengths impaired due to acid deposition than the PA DEP officially counts, this study provides a rationale for DEP personnel or watershed groups to further investigate potential impairments.

The Tuscarora Formation has a relatively small areal extent (1.24×10^3 km^2, 1% of state area) in Pennsylvania, thus the number and lengths of streams potentially impacted by acid deposition in this formation are small. Although their study area was rather limited, Sharpe et al. (1987) suggest that the Alleghany and Pottsville Formations are likely to have trouble supporting brook trout populations due to acid deposition. They also contend that soil type is less of a predictor than bedrock geology. The extent of the Alleghany and Pottsville Formations combined cover 1.86×10^4 km^2 (16% of state area) in Pennsylvania and contain many more streams. Very few streams are listed as impaired by acid deposition according to the PA DEP. The approach in this study – combining geology, GIS reconnaissance, chemistry and angler fish sampling – could help delineate target streams for further study in Pennsylvania as well as in other regions.

4. Conclusions

At least 14 streams, and likely more, should be re-examined by the PA DEP for listing as officially impaired due to atmospheric acid deposition. The Tuscarora sandstone clearly was unable to neutralize acidity from atmospheric deposition as well as the Shawangunk sandstone or adjacent sandstones, although this result was not universally true due to chemical and mineralogical heterogeneity within the Tuscarora. Using a GIS database was quite successful at targeting potentially impaired streams based on small differences in bedrock sandstone geology. Stream chemistry results paired with data collected by highly experienced volunteer anglers in small headwater streams allowed us to assess wide regions rapidly, reliably, and very inexpensively.

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