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Evidence for Potential Impact of Acid Deposition on Some Surface Waters of Extreme South Central Indiana in the Hoosier National Forest

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Introduction

Water quality evaluation of ponds in Perry and Crawford Counties of southern Indiana during fish population assessment revealed the possibility of impact from acidic precipitation. The low alkalinity concentrations found had not been previously reported for Indiana surface waters. Since several of the ponds had alkalinities within the known "sensitive" (6) range for impact from acid deposition, microcosm experiments using simulated acid rain (SAR) from a representative pond were completed to assess the potential for impact.

Simulation of ecosystem stress due to increasing acidic input was attempted in microcosm experiments using water treated with SAR and water with sediment treated with SAR. The models simulated water basins where one-third of the volume was replaced by acidic precipitation in the form of SAR having pH levels of 5.6, 4.5, 4.0 and 3.5. The characteristics evaluated with addition of SAR included alkalinity, conductivity, and pH.

The major objectives of this study were to classify a representative assemblage of south-central Indiana ponds and lakes for potential susceptibility to acid precipitation and to assess potential changes of those waters when treated with addition of acid precipitation in laboratory microcosm experiments.

Study Area

Ponds and lakes surveyed for susceptibility are located in the Hoosier National Forest of extreme south-central Indiana, from near the Ohio River in Perry County northward to central Crawford County. They are all man-made impoundments that receive runoff water from adjacent drainage areas and are situated in a variety of topographic locations from hilltops to hillsides and lowlands.

Oriole Pond, where water and substrate was collected for microcosm experiments, is located near State Route 66 in Perry County about 5 mi. north of the Ohio River. When sampled in 1985, the pond had an estimated surface area of 1.1 hec., a maximum depth of about 5 m, and an average depth of about 2.8 m. Oriole Pond water and substrate was used in microcosm experiments since it is a representative aquatic system in the survey area. In addition, the soils and basic geologic characteristics appear to be the type that could be conducive to surface water quality changes from acid precipitation. The soil in the pond vicinity was Typic Fragindalfs, fine silty, mixed and mesic (7). This soil is commonly known as Zanesville Silt Loam belonging to the Zanesville series of classification. It developed in silty loess, 18 to 48 in. thick, over material weathered from acid sandstone, siltstone and shale known to have a low buffering capacity.

Methods and Materials

Oriole Pond water samples and bottom sediment were collected in September from the pond surface at a point near the shoreline in about 0.5 m of water. Clean glass containers were used to transport the samples to the laboratory where they were stored at room temperature in opaque boxes until experiments were initiated.

In the laboratory, microcosm experiments were conducted in two groups with the following experimental conditions:

- 1. Pond water alone with four treatment levels of SAR: pH 5.6, 4.5, 4.0, and 3.5
- Pond water and sediment with four treatment levels of SAR: pH 5.6, 4.5, 4.0, and 3.5

Four replicate microcosms were used at each pH treatment level of SAR for the two groups resulting in a total of 32 microcosms; 16 with pond water alone and 16 with pond water and sediment.

Each of the 32 microcosms consisted of 250 ml of pond water placed in a clean 950 ml wide-mouth glass jar. In addition, 16 microcosms received 20 ml of substrate sediment. The four microcosm replicates for each SAR test level were aligned on a large table in the laboratory directly beneath a florescent fixture with two 48-in. cool-white tubes. Each microcosm was covered with a double layer of colorless translucent plastic to minimize evaporation. The photoperiod cycle used was 12 hr. of light followed by 12 hr. of darkness. All microcosms were established on December 19, 1985. They were left undisturbed until SAR experiments were initiated on February 7, 1986. This allowed a time period for establishment of water-sediment equilibruim and clearing of turbidity in microcosms. Water in all microcosms was clear and observed to be essentially colorless at the start of SAR experiments. The laboratory temperature ranged from 18 to 24 C over the total period from establishment of microcosms through SAR treatment and testing.

Stock SAR solutions were prepared using concentrated reagent grade sulfuric acid diluted with double-distilled water to pH 5.6, 4.5, 4.0 and 3.5. They were stored in glass bottles in the refrigerator prior to use. All pH determinations were made using a model 265 Instrumentation Laboratory pH meter read to the nearest 0.1 pH unit. Meter readings were temperature corrected and standardized using a pH 4.0 buffer solution.

Total alkalinity concentration of water was determined in field sampling and the laboratory using the standard titrametric procedure outlined in Standard Methods for the Analysis of Water and Wastewater (1). All field collections of water were from just beneath the surface in the middle of the lake or pond using a clear 300 ml glass stoppered bottle. Conductivity was measured using a model 33 Yellow Springs Instrument conductivity meter with temperature correction.

At the start of the SAR experiments on February 7, 100 ml of water was withdrawn from each microcosm using a clear syringe. The water was tested to establish the beginning levels of alkalinity, conductivity and pH. Next, 75 ml of SAR was added to each microcosm at appropriate pH levels using a clean syringe. Thus, each microcosm received SAR in a 1:2 ratio representative of a theorethical model where one-third of the volume was renewed by addition of stimulated rainfall to each microcosm system. Tests for alkalinity, conductivity, and pH were completed the day after SAR was added to each microcosm.

Results and Discussion

Field Survey of Surface Waters

A total of 21 ponds and lakes in Perry and Crawford counties were surveyed during June or July of 1983-86 (Table 1). Sizes of these impoundments range from 0.1 to 1.1 hectares. Classification of the lakes into two general categories was completed

| Name/Class* | County Crawford | Legal Description | | | | |
|------------------|--------------------|---|--|--|--|--|
| Atkinson | | NW 1/4, SW 1/4, Sec 7, T 3 S, R 1 E | | | | |
| Deer | Perry | NW 1/4, NE 1/4, Sec 3, T 7 S, R 2 W | | | | |
| Derby* | Perry | NW 1/4, NE 1/4, Sec 6, T 6 S, R 1 W | | | | |
| Deuchars | Crawford | NW 1/4, NW 1/4, Sec 20, T 4 S, R 1 E | | | | |
| Gatchel* | Perry | E central, NE 1/4, Sec 29, T 5 S, R 2 W | | | | |
| Gerber* | Perry | NW 1/4, SE 1/4, Sec 27, T 6 S, R 2 W | | | | |
| German Ridge | Perry | N central, NE 1/4, NE 1/4, Sec 35, T 6 S, R 2 W | | | | |
| Harding* | Perry | SE 1/4, SW 1/4, Sec 6, T 6 S, R 1 W | | | | |
| Helwig Hollow* | Perry | N central, SW 1/4, Sec 27, T 6 S, R 2 W | | | | |
| Hemlock* | Crawford | SE 1/4, NE 1/4, Sec 8, T 3 S, R 1 W | | | | |
| Middle Deer* | Perry | NW corner, SE 1/4, NE 1/4, Sec 4, T 6 S, R 2 W | | | | |
| Oriole | Perry | SE 1/4, NW 1/4, Sec 11, T 4 S, R 1 W | | | | |
| Popcorn* | Crawford | SE corner, SW 1/4, NE 1/4, Sec 20, T 4 S, R 1 E | | | | |
| Range | Perry | W central, NE 1/4, Sec 20, T 5 S, R 2 W | | | | |
| Spring | Crawford | Center, NE 1/4, NE 1/4, Sec 30, T 3 S, R 1 E | | | | |
| Timberlake* | Perry | SE 1/4, NE 1/4, Sec 18, T 6 S, R 2 W | | | | |
| Triumph* | Perry | NE 1/4, NW 1/4, Sec 9, T 4 S, R 2 W | | | | |
| West Fork "A" | Crawford | SE corner, NW 1/4, SW 1/4, Sec 22, T 3 S, R 1 W | | | | |
| Wheatley* | Perry | SW corner, SE 1/4, SE 1/4, Sec 17, T 5 S, R 2 W | | | | |
| Whispering Pines | Crawford | Center, SW 1/4, NE 1/4, Sec 9, T 3 S, R 2 W | | | | |
| Unnamed | Perry | NW corner, NE 1/4, SW 1/4, Sec 2, T 4 S, R 2 W | | | | |

TABLE 1. The names, classification, and locations of 21 ponds and lakes surveyed in the Hoosier National Forest in Perry and Crawford Counties, Indiana.

* Ponds and lakes classified as sensitive to acid precipitation had measured total alkalinities equal or less than 10 mg/1. Additional information is available in unpublished Final Project Reports by Mc Comish (2,3,4) and Mc Comish and Kiley (5) on deposit in Braken Library at Ball State University.

on the basis of total alkalinity measurements which ranged from 6 to 128 mg/l. According to Omernik and Kinney (6) "it is generally agreed that waters of total alkalinity >200 ueq/l (> 10 mg/l) are relatively insensitive to acidic deposition." A total of 11 of the lakes and ponds sampled were classified as "sensitive (≤ 10 mg/l)", having total alkalinity values ranging from 6-10 mg/l with the mean at 7 mg/l (SD \pm 2). The remaining 10 lakes and ponds were in the insensitive range (> 10 mg/l) with alkalinity values from 13-128 mg/l with the mean at 39 mg/l (SD \pm 39). The survey data show over half (11 of 21) of the ponds and lakes classified as potentially sensitive to acid precipitation.

The high percentage of sample ponds and lakes in the sensitive classification appears representative of the impounded surface waters (natural lentic systems of any size are nonexistant) of the Hoosier National Forest area in Perry and Crawford Counties. This conclusion is justified on the basis of the variety of topographic locations and the wide distribution of the impoundments sampled within the defined area. A future comprehensive sample of south-central Indiana surface waters may provide a more exact estimate of the pond and lake numbers, locations, and degree of sensitivity to acidic deposition.

Microcosm Comparison Before SAR Treatment

The total alkalinity, conductivity and pH of microcosms with water alone were compared to those with water and sediment just prior to SAR treatment on February 7. Great differences were found in the characteristics evaluated using a *t*-test of means. The mean total alkalinity of water alone was 59.2 mg/l (SD \pm 2.5) compared to water with sediment at 0.9 mg/l (SD \pm 0.8) (Significant at P < 0.001). The mean pH of water alone was 7.9 (SD \pm 0.1) compared to water with sediment at 5.7 $(SD \pm 0.2)$ (Significant at P < 0.001). The difference in conductivities of the two microcosms was not as great with the mean at 97.6 (SD \pm 0.7) for water alone and 104.2 (SD \pm 3.4) for water with sediment (Significant at P < 0.001).

These data indicate that the substrate material was responsible for significantly lowering both total alkalinity and pH while slightly increasing conductivity. The exact mechanisms involved are unknown but thought related to the acid sandstone, siltstone and shale predominant in soils of the area (7). As expected, these data reveal the importance of the lake basin, with inherent geologic and edaphic characteristics, in determining the nature of water quality components of surface water.

Pond Water Alone Microcosm Experiment

Microcosms with water only were treated with SAR at levels of pH 5.6, 4.5, 4.0, and 3.5 (Table 2). Since the pH of rain is naturally about 5.6, it was considered

TABLE 2. Comparison of selected water quality characteristics for experimental microcosms with water alone and water with substrate sediment after SAR treatments.

| | SAR pH Treatment Levels | | | | | | | | |
|------------------------------|-------------------------|-----|-------|-----|-------|-----|-------|-----|--|
| Microcosm/ Characteristic | 5.6 | | 4.5 | | 4.0 | | 3.5 | | |
| | Mean | SD | Mean | SD | Mean | sD | Mean | SD | |
| Water Alone: | | | | | | | | | |
| Total Alkalinity (mg/l) | 44.4 | 4.3 | 40.8 | 1.6 | 35.2* | 4.4 | 26.3* | 1.0 | |
| Conductivity (Micromohs) | 69.0 | 7.9 | 59.8* | 4.0 | 61.8* | 2.2 | 64.3 | 2.6 | |
| pH | 8.0 | 0.2 | 7.8 | 0.2 | 7.6* | 0.8 | 7.7* | 0.8 | |
| Water With Sediment: | | | | | | | | | |
| Total Alkalinity (mg/l) | 0.7 | 0.8 | 1.4 | 0.9 | 0.6 | 0.5 | 0.2 | 0.0 | |
| Conductivity (Micromohs) | 82.8 | 7.5 | 70.3* | 9.2 | 80.5 | 3.1 | 76.5 | 1.7 | |
| pH | 5.9 | 0.3 | 5.8 | 0.5 | 6.3 | 1.6 | 5.1* | 1.0 | |

* Indicates t-test of mean significantly different (P < 0.05) compared with SAR pH 5.6.

the baseline impact on water quality components. Therefore, SAR at pH 5.6 was used as a basis of comparison of measured changes. Total alkalinity ranged from 44.4 mg/l at SAR 5.6 to a low of 26.3 mg/l at SAR 3.5. The total alkalinity level at SAR 5.6 compared to both SAR 4.0 and 3.5 was significantly (P < 0.05) different. Conductivity change was less clear and more minor with SAR 5.6 at 69 micromohs compared to 60-64 at other SAR treatment levels. Differences in conductivity were significant comparing SAR 5.6 with SAR 4.5 and 4.0 (P < 0.05) but not significant with SAR 3.5. The comparison of pH revealed a gradual decreasing trend from 8.0 at SAR 5.6 to 7.7 at SAR 3.5. Comparison of SAR treatment levels with SAR 5.6 revealed significant (P < 0.05) differences at SAR 4.0 and 3.5.

The addition of SAR to microcosms results in a clear decrease of both total alkalinity and pH. Total alkalinity change from the level found with normal rainfall (SAR 5.6) resulted in a mean 8% lower at SAR 4.5 (Not Significant), 21% lower at SAR 4.0 (Significant at P < 0.05) and 41% lower at SAR 3.5 (Significant at P < 0.05). The change in pH from that in normal rainfall was less dramatic ranging from a 0.2 pH unit decrease at SAR 4.5 (Not Significant) to 0.4 and 0.3 pH units at SAR 4.0 and 3.5, respectively (Significant at P < 0.05). The addition of acid in the form of SAR had a progressive effect on buffering with the greatest effect at the lowest pH (3.5). Conductivity appeared to be reduced but results were less definitive than for total alkalinity and pH.

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This experiment revealed that the water was significantly impacted with the addition of SAR especially at pH 4.0 and 3.5. The buffering capacity of the water was very limited, therefore it had little ability to accept the SAR without a resultant major change in basic chemical character.

Pond Water With Sediment Microcosm Experiment

Microcosms with water and sediment were treated with SAR at levels of pH 5.6, 4.5, 4.0, and 3.5 (Table 2) in exactly the same way as the water alone microcosm experiment, again using pH 5.6 as the basis of comparison. Mean measured total alkalinities ranged from 0.7 mg/l at SAR 5.6 to a low of 0.2 mg/l at SAR 3.5 with no significant differences regardless of SAR treatment level. Measured conductivity change was minor with SAR 5.6 at 83 micromohs compared to 70-81 at other SAR treatment levels. Differences in conductivity were significant comparing SAR 5.6 with SAR 4.5 (P < 0.05) but not significant with SAR 4.0 or 3.5. Comparison of pH revealed minor differences in computed means with 5.9 at SAR 5.6 and 5.1-6.3 at other SAR treatment levels. The only level of pH SAR treatment significantly different from SAR 5.6 was 3.5 (P < 0.05).

The addition of SAR to microcosms did not result in any clear pattern of impact. Changes in total alkalinity values of the water with sediment present were judged to be too low for accurate measurement with the method used. This is suggested when examining standard deviation (SD) values which were at or near computed means in all except one case. It should also be noted that total alkalinity was essentially at trace levels of detection in all of the microcosms. Conductivity differences were too small to demonstrate any significant differences (excepting SAR 4.5) although all three SAR treatment levels had computed means slightly below that estimated for SAR 5.6. Observations of pH change were also small with significance only at the most acid treatment level (3.5).

Results of this experiment were inconclusive due at least in part to the inability to precisely measure change in total alkalinity and pH with the methods used at the low existing levels of these characteristics. Future evaluations should consider these limitations of measurement by using more sensitive methods.

Conclusions

Over half of 21 ponds and lakes surveyed in Perry and Crawford Counties of extreme south-central Indiana were found to have summer total alkalinity concentrations in the sensitive range for impact from acidic depositions (n = 11). A comparison of experimental microcosms with water alone to microcosms with water and sediment revealed sediment in the pond water significantly lowered alkalinity and pH and elevated conductivity. These changes were judged due to edaphic and geologic effects inherent to surface waters in this region of Indiana. Microcosm experiments with water alone treated with SAR at pH 4.5, 4.0, and 3.5 revealed significant impact over that experienced with SAR at pH 5.6, the normal pH for rainwater. Changes observed were an 8-41% lower total alkalinity, a decrease of pH from 0.3-0.4 units, and lowered conductivity from 7-9 umhos. Microcosm experiments with water and sediment had smaller and less conclusive changes than those found for water alone because only trace levels of total alkalinity were found and pH was already at or below about six. Conductivity of the microcosms with water and sediment appeared to be little changed after treatment with SAR. More sensitive methods should be employed to evaluate changes of water quality characteristics such as those found in microcosms with water and sediment.

These results confirm that some surface waters in Perry and Crawford Counties

are sensitive to acidic loading. Future comprehensive field sampling may reveal the exact extent of the potentially sensitive surface waters but the current survey indicates over half may be involved.

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