AN INVESTIGATION INTO THE CHLORIDE ION CONCENTRATIONS OF FOUR BROOKS WITHIN BLACK ROCK FOREST OVER A SIX MONTH PERIOD, AS AN INTEGRATOR OF CHEMICAL CONCENTRATION INCREASES OF ACID DEPOSITION

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DEDICATION

All of my work at LDEO and Black Rock Forest as well as this paper, I dedicate to my wife, Barbara, and two daughters, Kirsten and Janine, without whose loving cooperation, consideration, and invaluable help and support, I would not have been able to complete all of my endeavors. I also dedicate these efforts to the generosity of the Bristol-Meyers Squibb Foundation who underwrote my visiting scholar status in Columbia's Summer Research Program.

ABSTRACT

Fossil fuel combustion and increased use of commercial fertilizers have increased carbon dioxide and nitrate emissions substantially. However, fluxes in atmospheric and oceanic reservoirs have not fully reflected these perturbations in the global carbon and nitrogen cycles. It is posited that this discrepancy or "missing sink" could be the result of an interaction of these two cycles in terrestrial ecosystems. Some of the missing carbon and nitrogen may be sequestered in the biota and soils of temperate forests. Black Rock Forest (BRF) lies in a zone which is typical of the global variations and offers an important opportunity to study the net changes in the carbon cycle via nitrogen budget investigations. In order to accurately estimate integrated budgets of important nutrients, chemical concentration increases resulting from evapotranspiration must be accounted for. This research explores the concentration of fluvial chloride ions which can then be compared to precipitation concentrations. Since chloride ions should be unaffected by local BRF soils and biota, it will be an excellent integrator of chemical concentration increases.

Stream samples from four brooks within separate BRF catchments had been collected over a six month period, corresponding to National Acid Deposition Program efforts at a station on the nearby West Point Military Academy. After pH and nitrate measurements, they were sealed and refrigerated. Prior to making chloride measurements, I had to vacuum filter each sample. The measuring device then had to be carefully calibrated. Following stream sample measurements and data entry, ppm concentrations were derived from application of slope and intercept of a calibration curve of standard chloride concentrations.

INTRODUCTION

Human perturbations of the carbon and nitrogen cycles have been widely discussed. The human consequences of ever-increasing fossil fuel combustion and use of commercial fertilizers have led the most reluctant to recognize the problems under various titles, such as greenhouse effects, acid-rain and eutrophication. However strong these anthropogenic perturbations are at present, they are projected to continue to increase. In order to feed an ever increasing population which demands higher standards of living, fertilizer production is expected to grow by about 10% per year and fossil fuel combustion by about 3%. It is clear that intentional and inadvertent additions of carbon and nitrogen oxides to global cycles by human activities pose serious environmental implications for the future development of civilization. It would be prudent to analyze the impact of our activities.

Carbon and nitrogen move in complicated pathways through the environment that are crucial to and interactive with every aspect of the global ecosystem. Atmospheric and oceanic studies of carbon and nitrogen oxides have been extensive in a variety of disciplines. However, Schlessinger (1991) estimates that about one-third of all carbon dioxide now being produced is not even accounted for by studies of atmospheric and oceanic reservoirs. This amounts to 2.2×10^{15} g of carbon. Terrestrial sinks, including biota (Simpson, 1976) and soils (Harrison, 1994), could account for the entire amount that is missing. Harrison describes a possible "greening of the terrestrial biosphere" whereby the unaccounted for carbon undergoes long term storage as a result of increased carbon dioxide fertilization and nitrogen deposition stimulation. Precipitation and "dry" fallout are the dominant inputs in the nitrogen budget of a forest. On the output side, the primary transport out of a forest occurs via streams. Therefore it is important that accurate empirical data on the chemistry of both precipitation and surface water be obtained, in order to better understand the processes of broad interest.

Since the greatest amount of uncertainty in regard to the global cycles of carbon and nitrogen remains in terrestrial ecosystems, it is appropriate to investigate these budgets in a representative forest. Black Rock Forest is a logical site to analyze the effects of these fluxes. It is adjacent to the West Point Military Academy, where one of 200 National Acid Deposition Program (NADP) stations is located. Weekly composite precipitation samples have been collected every Tuesday since 1979 and analyzed for relevant chemical parameters at the Central Analytic Laboratory by the Illinois State Water Survey at the University of Illinois. Precipitation data is therefore available for more than a decade.

In addition, tree girth measurements at BRF have been made since mid-1930, making available a long term measure of carbon flux in the above ground biota. Also, the forest lies in a zone that is impacted by carbon and nitrogen fluxes, which may alter the net storage of carbon. BRF soils are for the most part thin, in addition, and changes in the net storage of carbon would have been diluted to a lesser extent. Lastly, the low permeability of the crystalline rocks that underlie the entire site avoids any possible ground storage and exchange with surface water, that could highly complicate the measurement of chemical budgets.

Since nitrate is being traced in solution, both in precipitation and run-off, concentration by evapotranspiration must be accounted for and this can be done by tracing chloride concentrations. Since chlorides play a minimal role in the biota (Swank and Waide, 1988), the bedrock cannot act as a source and chlorides are not available in the soil, and local road salting has little impact on the drainage basins being studied, chloride concentrations will be an excellent integrator of chemical concentration increases. NADP makes chloride concentrations available for precipitation. The chloride concentrations in the stream samples should therefore reflect the amount-weighted mean concentration of chlorides in precipitation, as increased by evapotranspiration.

SITE DESCRIPTION

Black Rock Forest is owned by a not for profit corporation which leases the property to a consortium of educational institutions. A 3,600 acre hilly woodland, it is located a few miles west of the Hudson River, in southwestern Orange County, N.Y. It lies in the belt of rocky hills known as the Hudson Highlands, part of the Reading Prong, a body of crystalline rocks extending from New England southward through New Jersey. There are two physiological divisions, the Highland and the Northern Slope.

The Highland division comprises almost two-thirds of the forest. It is a rolling plateau-like region and includes Aleck Meadow Reservoir, drained by Black Rock Brook through Black Rock Hollow, and Glycerine Hollow, drained by Cascade Brook. Canterbury Brook and Mineral Spring Brook also have their sources here. Canterbury and Black Rock flow northwest, while Mineral Spring flows southwest and Cascade drains to the South. These are separated by numerous small, stony knolls and occasional cliffs, with large blocks of talus at the bases of the steeper hills. The remainder of the forest is in the Northern Slope, with uniform rises. At the lower levels, rough, stony slopes give way to a more gently sloped glacial till, pushed in from the northwest. Black Rock Brook and Canterbury Brook have cut deep V-shaped ravines through deep till and penetrated a few feet into the underlying bedrock, as they have passed through the area.

The forest is presently comprised of mixed hardwood species, with a few stands of pine and scattered hemlock in the hollows. Early settlement consisted of self sustaining farming, with less than 100 acres cultivated. The Continental Army used the Old Continental Road which crosses the forest from north to south. The land is dotted by the remnants of charcoal pits, used to supply local brick factories, and the area has been clear cut often, but has not been subject to any major cutting for almost 100 years. (Hardesty)

METHODOLOGY

Dr. W. Schuster, forest director, and/or J. Brady, chief forester, collected samples from Black Rock Brook, Mineral Spring Brook, Cascade Brook, Canterbury Brook, and BRF precipitation, every Tuesday morning, following the NADP schedule, from January 4, 1994 on. These were brought back to the forest office. The pH was determined with a hand held meter. The nitrate concentration was determined with a Lamotte field kit coloridometer. These were then refrigerated in tightly closed high-density plastic bottles. I filtered the January-July samples, using a hand vacuum pump at low, 20-30 psi, pressure through .45 filter paper in a millipore funnel, into new high-density plastic bottles.

The instrument that I used to determine the chloride concentrations was a Buchler-Cotlove Chloridometer, which performed the titration automatically. Repipettes were used to deliver 0.5 ml of a 50 ppm spike and 0.4 ml of reagent (3.2 ml con. HNO_3 , 50 ml glacial acetic acid in a 500 ml volumetric flask, then filled with DDW). Two to three drops of gel (6.2 g of dry powder, consisting of 6.0 g of gelatin, 1.0 g of Thymol Blue, and 1.0 g of Thymol, mixed in 1.0 liter of hot DDW, heated while swirled until clear, then refrigerated in glass) were added. 4.5 ml of the sample were lastly carefully pipetted into the vial mixture. The small vial containing this recipe was then placed on the chloridometer so that a constant electrical current could pass through it by way of two silver electrodes. Silver ions were generated at the sacrificial anode. These reacted with chloride ions to form an insoluble milky white precipitate of silver chloride that was held in suspension by the gel. Silver ions were generated at a fixed rate and so consumed chloride ions at a fixed rated. The end point was detected as a rapid rise in current amperometrically by a pair of silver-sensing electrodes. This current rise was detected by a microswitch and the circuit was broken. Therefore, the number of coulombs of current passed was directly proportional to the chloride ions in solution, and so also to the duration of the constant current. The time elapsed was measured automatically. (Froelich)

Before any samples were run, all electrodes were cleaned and the electrodes then reconditioned by running several titrations of the same standard until results agreed. The vial and electrodes were always rinsed with distilled water between measurements. At the beginning of each run of samples, a set of standard chloride solutions were run in order to calibrate the chloridometer. Following data entry of the standards, a scatter plot was created and a linear curve fit was applied. The resulting linear equation was applied to the stream sample titration times so as to convert the latter to ppm concentrations. Between each triplicate run on stream samples in random order, a 10 ppm standard chloride sample was run in order to detect any drift by the chloridometer.

RESULTS

Following the filtration of the first four samples of Black Rock Brook, evidence of an algae bloom was apparent on the filter paper and the bottom of the original bottles. A second set of bottles was then ordered, as initially I was to have refilled the original bottles after rinsing them with about 20 ml of the filtrate, but this could not remove the algae at the bottom. Evidence of algae bloom reappeared in the last three Black Rock Brook samples, out of thirty, and again in the last seven samples of Cascade Brook. Since algae will alter concentrations of nutrient ions other than chloride, future plans to more accurately determine nitrate and other ion concentrations at LDEO on these samples may have to be abandoned.

An examination of the 10 ppm standard times showed a slight downward drift that is insignificant according to an expert (Chillrud, S.).

An examination of my data by an expert (Chillrud, S.) revealed that all titration curves and stream sample times were reliable and well within the minimally acceptable 5% range. Unfortunately, NADP precipitation data was not available at the time of printing and therefore no comparison of chloride concentrations could be made. This will be done at a later date.

The first six Black Rock Brook samples showed significantly higher chloride concentrations, 5X to 9X, than the other streams.

Dr. Schuster's investigation of pH and nitrates demonstrated significantly acid conditions in precipitation samples while pH measurements of stream samples were significantly higher and showed an increase through the year, especially after "leaf flush". The situation with regard to nitrate concentrations is the reverse. Precipitation showed significant levels of nitrate, while stream samples were consistently lower with a decline through the year, again especially after "leaf flush", until negligible. Only Canterbury Brook, which flows through heavy glacial till, showed somewhat lower pH's and measurable nitrates.

DISCUSSION

Although a final analysis of my chloride data is pending, during the "shakedown" of the equipment and mock procedural runs, precipitation samples were run. These showed chloride concentrations on the order of 1 ppm. According to Chillrud, this is a likely condition at BRF, where precipitation chloride concentrations should be on the order of 0.1 to 20 ppm, depending on the source, continental or marine. If this is the case, then a two-fold to three-fold increase was present. This agrees with Coweeta data where chloride was also used as a reference ion (Swank and Waide) and understandably different from the inland Hubbard study where bedrock sources of chloride were suspected (Likens).

A more problematic situation occurs with regard to the first six Black Rock samples' excessive chloride concentrations. These samples may have been improperly collected. Further testing may reveal the source of the additional chloride. For example, unusual bromide concentrations could reveal if road salt contamination were the problem.

According to Dr. Schuster, BRF is approaching climax and no significant removal of materials from the forest has occurred in decades. Such a point was described by Vitousek and Reiners (1975) as mature, where production equals respiration. As biomass stabilizes, the storage capacity for nutrients approaches a steady state and outputs equal inputs. Rice and Pancholy (1977) came to the same conclusion regarding nitrates in climax forests, from a very different direction, namely analysis of energy flows and fluxes at root hairs. Nitrate concentrations should be relatively high and constant as opposed to a successional forest ecosystem's watersheds where nitrates would be distinctly seasonal and low. Something very different is happening in BRF which warrants further investigation. BRF nitrate data is supported by the Hubbard (Likens) and Coweeta (Swank and Waide) investigations.

Perhaps the "beta factor" needs reinvestigation, even though Schlesinger (1991) could find little or no support for it. Waring (1985) and Reuss (1986) suggested that nitrates in acid rain could fertilize forests, especially where the soil is nitrogen-limited, and BRF has very thin soils. The exception is in the Canterbury Brook catchment where there is a thicker glacial till, and indeed nitrates do wash out in that watershed, albeit at a very low level. Waring also observes that below ground stores of nitrogen represent 92-96% of the forest reservoir. With Harrison (1994), it is suggested that terrestrial investigations should consider soil biota and chemistry as well as above ground biomass. Acid rain is partially neutralized by a forest canopy and throughfall is normally higher in pH than precipitation (Reuss), so the decrease in pH is to be expected. It is the fate of the nitrate that poses the most curious problem.

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