Soil-solution chemistry in black locust, pine/mixed-hardwoods and oak/hickory forest stands in the southern Appalachians, U.S.A.

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ABSTRACT


Soil-solution chemistry was measured over a 15-month period in three forest stands of contrasting nitrogen mineralization and nitrification rates in the southern Appalachians of North Carolina, U.S.A., using porous-cup lysimeters. In a black-locust-dominated stand, soil solution NO₃-N was 3.73 and 5.04 mg l⁻¹ at 30- and 60-cm depth respectively, and dissolved organic N (DON) was 0.718 and 0.582 mg l⁻¹ respectively. Values at 30 and 60 cm for a pine/mixed-hardwood stand were 0.032 and 0.058 mg l⁻¹ NO₃-N, and 0.201 and 0.168 mg l⁻¹ DON (values are means over the whole duration of the study). At both depths, soil solution conductivity, pH, Ca, Mg, K and PO₄-P were higher in black locust than in pine/mixed-hardwoods, and there were no differences in soil solution Na. In an oak/hickory stand, soil solution NO₃-N at 30-cm depth was 0.008 mg l⁻¹, and DON was 0.357 mg l⁻¹. At 30-cm depth, soil-solution conductivity, Ca, Mg and PO₄-P were higher in black locust than in oak/hickory, with no differences in pH, K and Na; DON, pH and K were higher in oak/hickory than in pine/mixed-hardwoods. In the oak/hickory and pine/mixed-hardwoods forest stands, with relatively lower soil N turnover rates, DON was a major portion of soil solution N.

INTRODUCTION

Increased soil-nitrate leaching is a frequent response to disturbance in terrestrial ecosystems. Several investigators have studied factors determining the magnitude of soil-nitrate leaching following disturbance in temperate ecosystems (e.g., Likens et al., 1969; Vitousek et al., 1979, 1981, 1982; Vitousek and Matson, 1984). Nitrate leaching is accompanied by cation leaching.

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(Likens et al., 1969; Vitousek, 1984). In terrestrial ecosystems, generally less than 10% of the soil organic N pool is mineralized annually (Keeney, 1982) and thus susceptible to leaching. Leaching of organic N can also be quantitatively important (Swank and Waide, 1980; Sollins and McCorison, 1981; Sollins et al., 1981).

The influence of N$_2$-fixing trees on elevated soil solution N concentration, and on other aspects of soil-solution chemistry, has been reported by Binkley et al. (1982) and by Van Miegroet and Cole (1984, 1985), in temperate ecosystems of North America. In this paper, we report soil-solution chemistry in two forest stands located in an early successional watershed, and in another stand in a mixed-hardwood forest watershed, at the Coweeta Hydrologic Laboratory, in the southern Appalachians of North Carolina (U.S.A.). Within the early successional watershed, areas dominated by black locust (*Robinia pseudo-acacia* L.), a leguminous, N$_2$-fixing tree, were compared with areas of pine/mixed-hardwoods to assess the influence of black locust on soil-solution chemistry.

Areas with black locust had high N inputs from symbiotic N$_2$ fixation, which has been documented for this tree in another watershed at Coweeta (Boring and Swank, 1984), and high N content in annual litterfall (White, 1986; White et al., 1988). Results of earlier studies showed that nitrification rates were higher in black-locust soil (36.0 mg kg$^{-1}$ 30 days$^{-1}$) than in pine-mixed hardwoods soil (27 mg mg$^{-1}$ 30 days$^{-1}$); nitrification was much lower in the oak/hickory forest stand of the adjacent watershed (2.04 mg kg$^{-1}$ 30 days$^{-1}$; values averaged for one sampling season (Montagnini, 1985; Montagnini et al., 1986, 1989)). The objective of the present study was to compare soil-solution chemistry (mineral and organic N, pH, conductivity, Ca, Mg, K, Na and PO$_4$-P) between these sites with different vegetation and contrasting soil nitrifying activity.

**STUDY SITE**

The study was conducted at the 2185-ha Coweeta Hydrologic Laboratory (35°N lat., 83°W long.), in the Blue Ridge Province of the southern Appalachian Mountains of North Carolina, U.S.A. Annual precipitation varies from 1800 mm at lower elevations to 2500 mm on the upper slopes. Precipitation is rather evenly distributed throughout the year, and the mean annual temperature is 13°C (Swank, 1986). Annual NO$_3$-N inputs in bulk precipitation average 2.9 kg/ha (means over a 10-year period, 1973–1982, at watershed 18, adjacent and with same aspect as the watersheds in this study; Swank and Waide, 1988).

The successional watershed was an 8.86-ha north-facing catchment that had been left to natural revegetation since 1968. When this study was conducted, vegetation consisted of dense black-locust stands on 73% of the watershed,
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and pine/mixed-hardwoods and mesic mixed-hardwoods, with low densities of black locust, on the remaining 12 and 15% of the area, respectively.

The mixed forest on the adjacent 61.1-ha north-facing watershed was dominated by oak (*Quercus* spp.) and hickory (*Carya* spp.), with mountain laurel (*Kalmia latifolia* L.) and rose-bay rhododendron (*Rhododendron maximum* L.) as the most important understory species (Day and Monk, 1974). This forest had been undisturbed since 1924 (Swank and Douglass, 1977).

The three forest stands were on Ultisols (Orthic Acrisols in the F.A.O. system), of the Saluda series, Evard-Cowee gravelly loams (members of the family of Typic Hapludults) on the slopes, and Sawnooke gravelly loams (members of the family of Humic Hapludults; U.S. Soil Taxonomy) on the lower elevations (Swank, unpublished data, 1985). Textural analysis of A$_1$ horizons at four elevations from stream banks to ridges showed similar sandy loams (Montagnini, 1985). Detailed data on soil chemical characteristics and soil N mineralization and nitrification rates are presented in Montagnini et al. (1986, 1989, 1990).

METHODS

The soil solution was sampled at the same sites where soil N mineralization, nitrification and inorganic- and organic-N pools were measured, as part of studies on factors controlling nitrification and soil N accumulation (Montagnini et al., 1986, 1989). The soil solution was sampled with porous-cup lysimeters (Hansen and Harris, 1975) at three elevations from stream banks to ridge tops, at nine sampling points in both a black-locust and a pine/mixed-hardwood stand in the successional watershed. Depth of samplers in black locust and pine/mixed-hardwoods was 30 cm (below the main rooting zone) and 60 cm (bottom of the mineral soil). In the oak/hickory forest, three collectors were installed at three sampling points at 30-cm depth. A tension of $-20$ kPa, approximating that of soil water at field capacity, was created with a hand vacuum pump. Collectors were installed in May 1983 and sampled 2-weekly from September 1983 until December 1984. Samples were expelled into acid-washed polypropylene bottles by positive pressure from a hand pump.

Phenyl mercuric acetate (PMA) at a rate of 0.5 ml/l was added to all solution samples as a preservative. PMA was prepared by dissolving 0.1 g of phenyl mercuric acetate in 15 ml of dioxane and completing volume to 100 ml with deionized water. Samples were kept at $4^\circ$C until analysis. NH$_4$-N and NO$_3$-N were analyzed with a Technicon Auto-Analyzer (Anonymous, 1970). Total Kjeldahl Nitrogen (TKN) was analyzed by acid digestion in a heater block followed by colorimetric determination of NH$_4$-N in the digests with a Technicon Auto-Analyzer (Anonymous 1977a,b). Soil-solution samples were not filtered before Kjeldahl digestion, as they had passed through the 1.2-$\mu$m
pore size of the ceramic cups. Dissolved organic nitrogen (DON) was calculated as the difference between TKN and NH$_4$-N.

The conductivity was measured with a Hach conductivity meter (City State of MFG, Loveland, Colorado, U.S.A.) calibrated with a 1000 mg/l solution of sodium chloride (NaCl). The pH was measured with a glass electrode and an Orion 701-A Ion Analyzer (Orion Research, Cambridge, Massachusetts, U.S.A.). Cations (Ca, Mg, K, Na) and PO$_4$-P were analyzed in a sub-set of samples (two collections in October 1984). Cations were measured with a Perkin Elmer 5000 Atomic Absorption Spectrophotometer (Perkin Elmer, Norwalk, Connecticut, U.S.A.) and PO$_4$-P was measured by the Strickland and Parsons (1972) colorimetric test, using a Spectronic 700 spectrophotometer (Bausch and Lomb, Rochester, New York, U.S.A.). Certified standards (Water Pollution Quality Control, Nutrient Samples, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio, U.S.A.) of low (<1 conductivity

<table>
<thead>
<tr>
<th>Depth (cm)</th>
<th>Pine/mixed-hardwoods</th>
<th>Black locust</th>
<th>Oak/hickory</th>
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</thead>
<tbody>
<tr>
<td>NO$_3$-N (mg/l)</td>
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<td></td>
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<tr>
<td>30</td>
<td>0.032 (0.01)$^b$</td>
<td>3.73 (0.25)$^a$</td>
<td>0.008 (0.007)$^b$</td>
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<td>60</td>
<td>0.058 (0.02)$^b$</td>
<td>5.04 (0.33)$^a$</td>
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<tr>
<td>DON (mg/l)</td>
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<tr>
<td>30</td>
<td>0.201 (0.03)$^c$</td>
<td>0.718 (0.05)$^a$</td>
<td>0.357 (0.04)$^b$</td>
</tr>
<tr>
<td>60</td>
<td>0.168 (0.03)$^b$</td>
<td>0.582 (0.07)$^a$</td>
<td>–</td>
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<tr>
<td>pH</td>
<td>6.14 (0.01)$^b$</td>
<td>6.28 (0.03)$^a$</td>
<td>6.27 (0.05)$^a$</td>
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<td>6.04 (0.03)$^b$</td>
<td>6.18 (0.03)$^a$</td>
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<td>conductivity (µS/cm)</td>
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<td>30</td>
<td>14.3 (1.2)$^b$</td>
<td>52.4 (3.9)$^a$</td>
<td>15.08 (1.4)$^b$</td>
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<td>60</td>
<td>11.4 (0.45)$^b$</td>
<td>54.37 (4.4)$^a$</td>
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<tr>
<td>Ca (mg/l)</td>
<td>1.2 (0.2)$^b$</td>
<td>7.4 (0.8)$^a$</td>
<td>1.1 (0.3)$^b$</td>
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<tr>
<td>60</td>
<td>1.26 (0.1)$^b$</td>
<td>7.0 (1.5)$^a$</td>
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<tr>
<td>Mg (mg/l)</td>
<td>0.87 (0.2)$^b$</td>
<td>4.4 (0.4)$^a$</td>
<td>1.1 (0.3)$^b$</td>
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<td>60</td>
<td>0.52 (0.04)$^b$</td>
<td>6.0 (1.8)$^a$</td>
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<tr>
<td>K (mg/l)</td>
<td>0.27 (0.05)$^b$</td>
<td>3.59 (0.97)$^a$</td>
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<td>0.74 (0.29)$^a$</td>
<td>1.62 (0.19)$^a$</td>
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<tr>
<td>Na (mg/l)</td>
<td>0.49 (0.03)$^a$</td>
<td>0.48 (0.03)$^a$</td>
<td>0.51 (0.03)$^a$</td>
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<tr>
<td>60</td>
<td>0.40 (0.03)$^a$</td>
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<tr>
<td>PO$_4$-P (mg/l)</td>
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<td>30</td>
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<td>60</td>
<td>0.007 (0.003)$^a$</td>
<td>0.015 (0.003)$^a$</td>
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</table>

$^1$ Values are means for the whole duration of the study. Means with non-matching superscript letters indicate significant differences ($P<0.001$) between sites (not between depths). Cations and PO$_4$-P were measured on a subset of samples from two collections in October 1984.
mg/l) and high (>10 mg/l) NH₄-N and NO₃-N and low (<1 mg/l) and TKN and PO₄-P were run with each set of determinations. Statistical analyses were done with the means and GLM procedures of SAS (Helwig and Council, 1979).

RESULTS

NH₄-N was undetectable in the soil solution in all samples from the three forest stands; therefore, the dissolved organic nitrogen (DON) equaled the TKN values. NO₃-N, DON, pH, conductivity, Ca, Mg, K and PO₄-P were higher in black-locust soil solution than in pine/mixed-hardwoods, at both 30- and 60-cm depth, and there were no differences in Na (Table 1). NO₃-N concentrations were higher at 60 cm than at 30 cm for black locust (statistics not shown).

Fig. 1 Soil-solution nitrate and dissolved organic nitrogen (DON) for black locust, pine/mixed-hardwoods and oak/hickory (monthly means from September 1983 to December 1984). NO₃-N values for oak/hickory were too low to show in the figure.
At 30 cm, NO$_3$-N, DON, Ca, Mg, PO$_4$-P and conductivity were higher in black locust than in oak/hickory, with no differences in pH, K and Na, while DON, pH and K were higher in oak/hickory than in pine/mixed-hardwoods (Table 1).

In black locust, soil-solution NO$_3$-N concentrations at both 30- and 60-cm depths peaked in October and November 1983, then declined through the winter months with an additional peak in May (Fig. 1). High concentrations (> 7 mg/l) were again observed in November and December 1984. Low NO$_3$-N concentrations in pine/mixed-hardwoods and oak/hickory prevented detection of seasonal changes in concentrations. No clear or consistent seasonal trends of DON soil solution concentrations were apparent in either of the three stands (Fig. 1).

**DISCUSSION**

*Influence of black locust on soil-solution nitrate concentrations*

Greater NO$_3$-N concentrations in black-locust soil solution suggest that this area of the successional watershed was a potentially important source of NO$_3$-N to the saturated zones of the catchment. As greater concentrations were found at 60- than at 30-cm depth in black locust, apparently anion exchange capacity was low and little NO$_3$-N was retained at exchange sites at that depth; high nitrate concentrations at 60 cm may also result from nitrification taking place between 30- and 60-cm soil depth. Concentrations of NO$_3$-N in the soil solution at 60-cm depth were 87 times higher in black locust than in pine/mixed-hardwoods. Since black locust constituted about 70% of the basal area of the successional watershed, areas dominated by this tree were the main source of NO$_3$-N to groundwater.

At 30-cm depth, soil solution NO$_3$-N concentration was greater in black locust than in either pine/mixed-hardwoods or oak/hickory. Increased NO$_3$-N soil-solution concentrations under N$_2$-fixing trees have been reported elsewhere. For example, Binkley et al. (1982) found that soil-solution NO$_3$-N concentrations were 6.2 times higher in a younger ecosystem dominated by red alder (*Alnus rubra* Bong.) and Douglas fir (*Pseudotsuga menziesii* (Mirb.) Franco), than in an older ecosystem dominated by western hemlock (*Tsuga heterophylla* (Raf.) Sarg.), Douglas fir, and western cedar (*Thuja plicata* Donn.), in coastal British Columbia, Canada. Greater NO$_3$-N concentrations in the soil solution under the younger ecosystem were probably a result of N fixation by red alder. Van Miegroet and Cole (1984) also found that NO$_3$-N concentrations in the soil solution were greater in a red-alder ecosystem than in an adjacent Douglas-fir ecosystem located in the Cascade Mountains, Washington, U.S.A.; concentrations under red alder periodically exceeded 10
mg/l, which is close to the concentrations reported here for black locust at Coweeta.

The seasonal pattern of NO$_3$-N concentration in soil solution is the result of the interaction of nitrification, plant and microbial uptake, denitrification and leaching. Concentrations at 30- and 60-cm depth were least during the winter months, possibly due to limited nitrifying activity, and they were also less in July, which is the time when plant uptake rates are greater. Peaks in NO$_3$-N concentrations in the soil solution in October and November suggest that NO$_3$-N production was still occurring in autumn while uptake by vegetation decreased. The NO$_3$-N peak in May suggests that nitrification in the soil started early in spring, while uptake by vegetation was low, resulting in a high NO$_3$-N content in the soil solution. A periodic variation of nutrient levels in the root zone is the general case, with a minimum in early autumn and a maximum in the spring (Wiklander, 1974).

*Soil solution cation, H$^+$ and PO$_4$-P concentrations*

In addition to greater NO$_3$-N, black-locust soil solution had higher conductivity, pH, Ca, Mg and PO$_4$-P than pine/mixed-hardwoods at both 30- and 60-cm depth. Consistent with the findings at Coweeta, Binkley et al. (1982) reported that conductivity, and NO$_3$-N, Ca, Mg and K concentrations, were higher in the soil solution in the ecosystem dominated by an N$_2$-fixing tree (alder). However, unlike the results at Coweeta, the pH of the mineral soil leachate was lower in the alder-dominated ecosystem. Van Miegroet and Cole (1984, 1985) also reported that subsurface solutions were more acid under red alder than under Douglas fir; the acidification of the solution coincided with intensive nitrification under red alder. They estimated that the actual amount of H$^+$ in the soil solution was less than calculated from nitrification, indicating partial buffering of the soil solution against acidification. The oxidation of NH$_4$-N to NO$_3$-N leads to the release of H$^+$ that can acidify the soil, the soil solution, or both. The extent to which acidification proceeds depends on the rate of H$^+$ release relative to neutralization. Processes that can counteract the acidifying effects of nitrification include the uptake of NO$_3$-N, high decomposition rates, adsorption of H$^+$ at soil-exchange sites (Binkley, 1986) and denitrification. The sensitivity to pH changes in soils depends on cation exchange capacity and Ca saturation (Reuss and Johnson, 1986). Possibly, the acidifying effects of elevated nitrification in the black-locust soil were neutralized due to its high base saturation of 47.3%, and high Ca, 73.5 mg/100 g (data from 0–15 cm depth; cation exchange capacity was calculated as sum of bases plus exchangeable hydrogen; cations were extracted with double acid solution of 0.025N H$_2$SO$_4$ and 0.05N HCl; Montagnini et al., 1986).

With generally greater concentrations in the soil solution, areas with black locust had greater potential for leaching of Ca, Mg, K, Na and PO$_4$-P from the
soil column, than areas with pine/mixed-hardwoods. Binkley et al. (1982) and Van Miegroet and Cole (1984) also reported that cation leaching was greater in the ecosystems dominated by red alder. Increased cation leaching in the areas dominated by the N$_2$-fixing trees was related to the presence of large amounts of NO$_3$-N in the soil solution. Vitousek (1984) reported a large increase of cation losses following disturbance of a mixed forest in southern Indiana. This increase was related to an increase of NO$_3$-N production and loss, and the results tended to support a model that suggests that anion and cation leaching through soils is controlled by the supply and mobility of ions (Johnson and Cole, 1980).

**Soil-solution dissolved organic-N concentrations**

Dissolved organic-N concentrations at 30-cm depth were about three times greater in black locust than in pine/mixed-hardwoods, and two times higher than in oak/hickory (Table 1). However, in black locust, dissolved organic-N concentrations at 30- and 60-cm depth were 5-8 times less than those of NO$_3$-N (Table 1), and NO$_3$-N was the major form of N leaching from these stands. Binkley et al. (1982) measured DON on a few test samples in the soil solution in a red-alder stand, and found that organic N accounted for 25–65% of the total (mineral + organic) N.

Soil N mineralization and nitrification rates, and soil NO$_3$-N, NH$_4$-N and TKN concentrations in black locust, pine/mixed-hardwoods and oak/hickory were reported by Montagnini (1985), and Montagnini et al. (1986, 1989, 1990). Nitrogen turnover rates, calculated as the proportion of N mineralized/total soil N, for a six-month growing-season (May–October) were calculated as 3.48, 1.83 and 0.23% of total soil N for black locust, pine/mixed-hardwoods and oak/hickory, respectively (Montagnini, 1985). In pine/mixed-hardwoods and oak/hickory, DON concentrations in the soil solution at 30-cm depth were relatively greater than those of NO$_3$-N: six times higher in pine/mixed-hardwoods, and 44 times higher in oak/hickory. Therefore, in these two forest stands where N turnover was relatively smaller, leaching losses of N in dissolved organic forms had greater importance than those in mineral forms. In another oak/hickory forest at Coweeta, Qualls (1988) found that the average annual DON output from the forest floor was 31% of the input in solid litterfall, and that over 95% of total dissolved organic matter was removed as the water percolated through the soil profile, leaving the ecosystem in groundwater. Our results suggest that, in soils with low nitrification rates, DON leaching may have a relative larger contribution to total soil N leaching.

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