Decadal Changes in Potassium, Calcium, and Magnesium in a Deciduous Forest Soil

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Decadal changes in soil exchangeable K^+, Ca^{2+}, and Mg^{2+} concentrations and contents from 1972 to 2004 in eight intensively monitored plots on Walker Branch Watershed were compared with estimates of increments or decrements in vegetation and detritus. The results from these eight plots compared favorably with those from a more extensive set from 24 soil sampling plots sampled in 1972 and 2004. Increases in exchangeable K^+ were noted between 1972 and 1982, but few changes were noted between 1982 and 2004 despite significant increments in vegetation and detritus and significant potential losses by leaching. Total K contents of soils in the 0- to 60-cm sampling depth were very large and a slight amount of weathering could have replenished the K^+ lost from exchanges sites. With one notable exception, exchangeable Ca^{2+} and Mg^{2+} concentrations and contents decreased continuously during the sampling period. Decreases in exchangeable Ca^{2+} could be attributed mostly to increments in biomass and detritus, whereas decreases in exchangeable Mg^{2+} could not and were attributed to leaching. The major exception to these patterns was in the case of exchangeable Ca^{2+}, where significant increases were noted in one plot and attributed to Ca release from the decomposition of Ca-rich coarse woody debris from oak (*Quercus* spp.) mortality. With minor exceptions, soils and changes in soils among the eight intensively sampled core plots were similar to those in a more extensive set of plots distributed across the watershed. This study shows that averaging among plots can mask significant and important spatial patterns in soil change that must be taken into account in assessing long-term trends.

Abbreviations: CWD, coarse woody debris; DBH, diameter at breast height.

Case studies of long-term soil change are becoming more common in the literature and are adding substantially to our knowledge about this important subject (Bailey et al., 2005; Falkenggren-Grerup and Eriksson, 1990; Falkenggren-Grerup and Tyler, 1992; Hallbacken and Tamm, 1986; Johnson et al., 1988, 1994; Johnson and Todd, 1990; Knoepp and Swank, 1994; Richter et al., 1994; Richter and Markewitz, 2001; Trettin et al., 1999). In polluted regions of the world, atmospheric deposition may play a major role in causing soil acidification and decreases in exchangeable K^+, Ca^{2+}, and Mg^{2+} (Falkenggren-Grerup and Eriksson, 1990; Hallbacken and Tamm, 1986; Johnson and Todd, 1990). Uptake and accumulation in tree biomass can also be a significant cause of soil change, especially when the site is occupied by species with high Ca concentrations in their biomass (Alban, 1982; Johnson et al., 1988; Johnson and Todd, 1990; Richter and Markewitz, 2001; Trettin et al., 1999). It is important to quantify the effects of uptake and atmospheric deposition to the extent possible before making a judgment as to which factor is most responsible for the observed changes (Johnson, 2005).

Soils within eight core plots on Walker Branch Watershed have now been sampled four times in the last three decades, and we have attempted to reconcile the observed changes with estimates of uptake, atmospheric deposition, and leaching (Johnson et al., 1988; Johnson and Todd, 1990; Trettin et al., 1999). In the second sampling, we reported that exchangeable Ca^{2+} and Mg^{2+} in several core plots had declined during the period 1972 to 1982 (Johnson et al., 1988). Nutrient budget analyses at that time suggested that the declines in exchangeable Ca^{2+} content could be approximately accounted for by Ca accumulation in tree biomass while the declines in exchangeable Mg^{2+} could not, and we speculated that the latter changes were due to leaching. Both increases and decreases in exchangeable K^+ were noted in various plots with no clear overall trend.

In a later study, we measured leaching in selected plots and verified that biomass Ca increment exceeded leaching in plots where exchangeable Ca^{2+} declined (Johnson and Todd, 1990). We could neither confirm not refute the hypothesis that the declines in exchangeable Mg^{2+} were due to leaching, however, because leaching was extremely variable due to the high variability in soil sulfate retention (Johnson and Todd, 1990). Trettin et al. (1999) reported continued declines in soil exchangeable Ca^{2+} and Mg^{2+} in the third sampling in 1993 and once again attributed most of the Ca^{2+} decline to sequestration in trees and most of the Mg^{2+} decline to leaching. They also noted that decreases in exchangeable Ca^{2+} were less than what would be expected from increments in biomass in some

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plots, suggesting that deep rooting was supplementing Ca^{2+} supplies. Trettin et al. (1999) did not report the results for K^{+}.

In this study, we sampled soils in the eight core plots on Walker Branch Watershed for the fourth time in 2004 and the remainder of the 24 soil sampling plots originally established in 1972 for the second time. The results of the C and N changes in soils and vegetation of these plots have been recently reported (Johnson et al., 2007). The objectives of the current study were threefold: (i) to compare changes in soil exchangeable K^{+}, Ca^{2+}, and Mg^{2+} from 1972 to 2004 in the eight core plots with those in the 24 plots originally established for the soil sampling database; (ii) to assess whether the trends seen between 1972 and 1993 continued into 2004; and (iii) to reconcile soil changes (if any) with estimates of above-soil K, Ca, and Mg sequestration in biomass and detritus. We hypothesized that:

1. The eight core plots are representative of the more extensive soil sampling plots established in 1972;
2. The changes reported by Trettin et al. (1999) for the third sampling in 1993 would continue to 2004; and
3. As in the past, changes in exchangeable Ca^{2+} but not Mg^{2+} can be attributed to sequestration in above-soil biomass and detritus.

MATERIALS AND METHODS

Site

Walker Branch Watershed is located on Chestnut Ridge within the Department of Energy's Oak Ridge Reservation near Oak Ridge, TN. The watershed is at approximately 300- to 350-m elevation, has 14.5°C mean annual temperature, and approximately 135-cm average annual precipitation, of which 43 to 48% is estimated to be lost as evapotranspiration (Henderson et al., 1978; Johnson and Van Hook, 1989; Johnson et al., 1988). The watershed is underlain by Knox group dolomite with several different formations occurring within the study area. Soils are mostly Ultisols (primarily Typic Paleudults) on geomorphically more stable upland interfluves and Inceptisols on steep slopes and alluvium. The upland residual soils are developed from deep (up to 30 m) saprolite and saprolitic material, although areas of ancient and modern alluvium and colluvium of different ages also occur within the watershed boundary (Lietzke 1994).

Before World War II, land use on the 97.5-ha watershed consisted of a mix of forest, sustenance agriculture, and open woodland grazing. After the federal government acquired it in 1942, the watershed was allowed to return to a forested state and has not been disturbed since except by a fire in 1967 and by the invasion of insects such as the southern pine beetle (*Dendroctonus frontalis* Zimmermann). Major forest types originally identified by Grigal and Goldstein (1971) were characterized predominately as upland hardwoods (*Quercus* spp., *Acer rubrum* L., *Carya* spp.) with stands dominated by chestnut oak (*Q. prinus* L.) and some intermixing of pine (*Pinus echineta* Mill. and *P. virginiana* Mill.) on ridges and old fields. Mesic coves and riparian zones are mainly yellow poplar (*Lirodendron tulipifera* L.) and American beech (*Fagus grandifolia* Ehrh.). Major changes in vegetation have taken place in many of these forest types, and some (in particular the pine type) no longer retain their original characteristics.

Field Sampling

In 1967, 298 vegetation inventory plots were established on the Walker Branch Watershed as per the protocol of Grigal and Goldstein (1971) and Harris et al. (1973). A nested set of three circular concentric plots (0.004, 0.04, and 0.08 ha) was established at each of the 298 plot locations. The diameter at breast height (DBH, 1.37 m) of trees of 1.5- to 9-cm diameter was measured within the smallest (0.004-ha) plot, the DBH of trees of 9- to 24-cm diameter was measured in the next smallest (0.04-ha) plot, and the DBH of trees >24 cm was measured in the largest plot.

As part of the original study, 24 of the 298 inventory plots were selected in 1972 to represent the major soil and forest types (pine, yellow poplar, oak–hickory, and chestnut oak) for forest floor and soil sampling (Henderson et al., 1978). Within each of these 24 soil sampling plots, a 12- by 12-m square grid was established and monumented with metal stakes for long-term forest floor and soil sampling. Beginning in 1972, the forest floor and soils were sampled in the spring from six randomly selected 1-m^2 subplots within each 12- by 12-m soil sampling grid (Henderson and Harris, 1975; Henderson et al., 1978). In each subplot, all wood >2.5 cm in diameter was collected within 1 m^2. After woody material was removed, a 0.25-m^2 ring was used to define the area in which wood <2.5 cm and O1 and O2 horizons were collected. In the subsequent (1982, 1993, and 2004) samplings, we followed the protocol of the original study, O1 litter defined as recognizable by species (equivalent to Oi) and O2 as more highly decomposed (equivalent to Oe plus Oa). After removal of the forest floor, one soil core was taken in the center of each 1-m^2 sub-subplot with a 5-cm-diameter bucket auger in depth increments of 15 cm to a final depth of 60 cm. Unfortunately, only the 0- to 15-

Table 1. Basic soil and vegetation characteristics of the eight intensively sampled study plots.

Plot	Geomorphic setting	Soil series	Classification	Slope position	Slope	Aspect	Dominant species (current/original)
					%	°	
179	saprolite	Fullerton silt loam	Typic Paleudult	upper slope near ridge top	15	280	chestnut oak/chestnut oak
107	saprolite	Fullerton cherty silt loam	Typic Paleudult	secondary ridge top	5.5	355	oak–hickory/oak–hickory
237	saprolite	Fullerton silt loam	Typic Paleudult	midslope, slight depression	16	135	chestnut oak, white oak/chestnut oak
98	cove	Claiborn cherty silt loam	Humic Paleudult	toe	10	130	yellow poplar, white oak/yellow poplar
281	cove	Claiborn silt loam	Humic Paleudult	toe	24	65	yellow poplar/yellow poplar
26	doline–saprolite	Fullerton silt loam	Typic Paleudult	midslope	5	260	yellow poplar/shortleaf pine
42	colluvium	Fullerton silt loam	Typic Paleudult	ridge top	13.5	160	red oak, chestnut oak, white oak/ oak–hickory
91	chert bed	Bodine cherty silt loam	Typic Paleudult	secondary narrow ridge top	12.5	110	oak–hickory/oak–hickory

and 45- to 60-cm samples were kept in this original sampling. The soil sampling plots were relocated in 2004 and sampled according to the same procedures (D.E. Todd being present at both samplings), except that all soil depths were collected, analyzed, and archived in sealed glass bottles from the 2004 sampling.

In later years (1982 and 1993), a subset of eight of the soil sampling plots (hereafter referred to as the *core plots*) was identified as representative of the various forest types, soil types, and geomorphic settings for more intensive temporal sampling. This subset of core plots has served as the basis for assessing long-term changes in soil chemical properties and nutrient cycling (Johnson et al., 1988; Trettin et al., 1999). Table 1 provides a brief summary of the geomorphic setting, soil series and classification, slope, aspect, landscape position, and both original and current (2004) dominant vegetation composition. Three plots (179, 107, and 237) occur on soils formed from saprolite weathered from dolomite. They are characterized by a silt loam surface overlying a clay loam argillic horizon. Vegetation on these plots was dominated by chestnut oak with lesser amounts of hickory (Plot 107) and white oak (Plot 237), and species composition changed little during the sampling period. Two of the plots (98 and 281) occur in cove positions near the base of slopes. Soils are derived from parent materials derived from colluvium from upper slope positions and are enriched in organic matter and nutrients from upslope deposits. Vegetation in these plots is dominated by yellow poplar with lesser amounts of white oak in Plot 98, and species composition changed little during the sampling period. Plot 26 is derived from saprolite weathered from dolomite and lies on the side of a doline (a collapse structure similar to a sinkhole but without an open swallow hole). Vegetation on this plot changed substantially during the sampling period from shortleaf pine to yellow poplar dominance. Plot 42 is derived from upper slope colluvial soils from dolomite. Vegetation in this plot changed from oak–hickory to predominantly oak, with substantial mortality of both hickory and chestnut oak during the sampling period. Plot 91 is characteristic of soils formed on chert beds and has a substantial (30–60%) chert component. Vegetation in this plot was dominated by oak and hickory and did not change substantially during the sampling period.

Forest floor and soils were sampled in the core plots in 1982, 1993, and 2004 as described above and soil samples from all depths were analyzed and archived for future analysis in an oven-dried state in sealed glass bottles.

Laboratory Preparation and Analysis

Twigs, bark, and leaves were separated from Oi and Oe + Oa samples before drying. Subsamples of wood, woody litter, and O horizon samples were oven dried to constant weight at 100°C while soil samples were dried at 60°C. Litter samples were crushed and sieved at 2 mm to separate rocks from the Oe + Oa material. Litter samples were processed by grinding in a Tecator Cyclotec sample mill (FOSS North America, Eden Prairie, MN) and stored in glass containers until extraction and analysis. Subsamples of vegetation and litter components were analyzed for K, Ca, and Mg at A&L Agricultural Laboratories, Modesto, CA. At A&L, K, Ca, and Mg in vegetation and litter were analyzed by inductively coupled plasma emission spectroscopy (ICP) after microwave digestion using a HNO_3–H_2O_2 digestion mixture.

Soil samples were crushed and sieved at 2 mm to separate the soil from the coarse fraction. All soils, including archived samples from 1972, 1982, and 1993, were analyzed for exchangeable Ca^{2+}, Mg^{2+}, and K^+ (10 g soil in 50 mL of 1 mol L^{-1} NH_4OAc followed by ICP analyses) at A&L Agricultural Laboratories. Ten percent blind duplicate samples were included in the analysis. Only the results from the current (2005) analysis were used in this comparison of laboratory bias. Some older samples had been depleted to <1 g by previous analyses, resulting in complete analyses in 23 of 24 possible comparisons in the 0- to 15-cm depth and 19 of 24 in the 45- to 60-cm depth for the 1972 to 2004 data set.

Biomass and Nutrient Content Calculations

Changes in biomass (live, standing dead, and downed and dead) were estimated from measurements of DBH on 0.04-ha nested plots (Johnson and Van Hook 1989) using allometric equations established by Harris et al. (1973). Vegetation nutrient contents were estimated from these mass data and nutrient concentrations obtained by destructive sampling on Walker Branch Watershed (Henderson et al., 1978) and the Chestnut Ridge whole-tree harvest site (Johnson et al., 1982). For standing dead and downed and dead biomass (coarse woody debris, CWD), DBH measurements from the previous inventory were used to estimate biomass. More detailed descriptions of these procedures are found in the above publications.

Forest floor nutrient contents were estimated from dry mass measurements and nutrient analysis by horizon. Soil nutrient contents were estimated using current nutrient analysis of both 2004 and archived soil samples combined with bulk density and coarse fragment data from previous samplings (Johnson et al., 1988; Trettin et al., 1999)

Statistical Analyses

For watershed-level changes in soil exchangeable K^+, Ca^{2+}, and Mg^{2+}, the concentration changes in the individual soil plots between 1972 and 2004 were analyzed using unpaired Student's *t*-tests (Microsoft Excel) because the individual soil samplings could not be co-located. Changes in the grand average of all soil plots were analyzed using paired Student's *t*-tests on the average values for each plot using Microsoft Excel. Paired *t*-tests were used in the latter analysis because the averages by plot were co-located in the same plots.

For changes in concentrations in the core plots, the effects of plot, year, and depth on soil concentrations in the eight core plots were analyzed using PROC GLM in SAS software (Version 9.1 for Windows, SAS Institute, Cary, NC). Statistical analyses of vegetation, forest floor, soil, and ecosystem K, Ca, and Mg contents were conducted using plot as a replicate because only one estimate of tree K, Ca, and Mg content was available per plot. The effects of plot and year on ecosystem contents were analyzed by using PROC GLM in SAS software, and pairwise comparisons of K, Ca, and Mg contents of various ecosystem components were conducted using least significant differences (Carmer and Swanson, 1973). Statistical significance was determined at $\alpha = 0.05$.

RESULTS AND DISCUSSION

Watershed-Level Changes in Soil Exchangeable Potassium, Calcium, and Magnesium, 1972 to 2004

The changes in soil exchangeable K^+, Ca^{2+}, and Mg^{2+} in the A (0–15 cm) and Bt (45–60 cm) horizons in the original soil plots and in the eight core plots between 1972 and 2004 are depicted in Fig. 1 and the grand averages (averages of all plot averages) are given in Table 2. The changes in exchangeable K^+ were fairly consistent across the watershed, with increases in most plots, especially in the surface depths. In the 0- to 15-cm

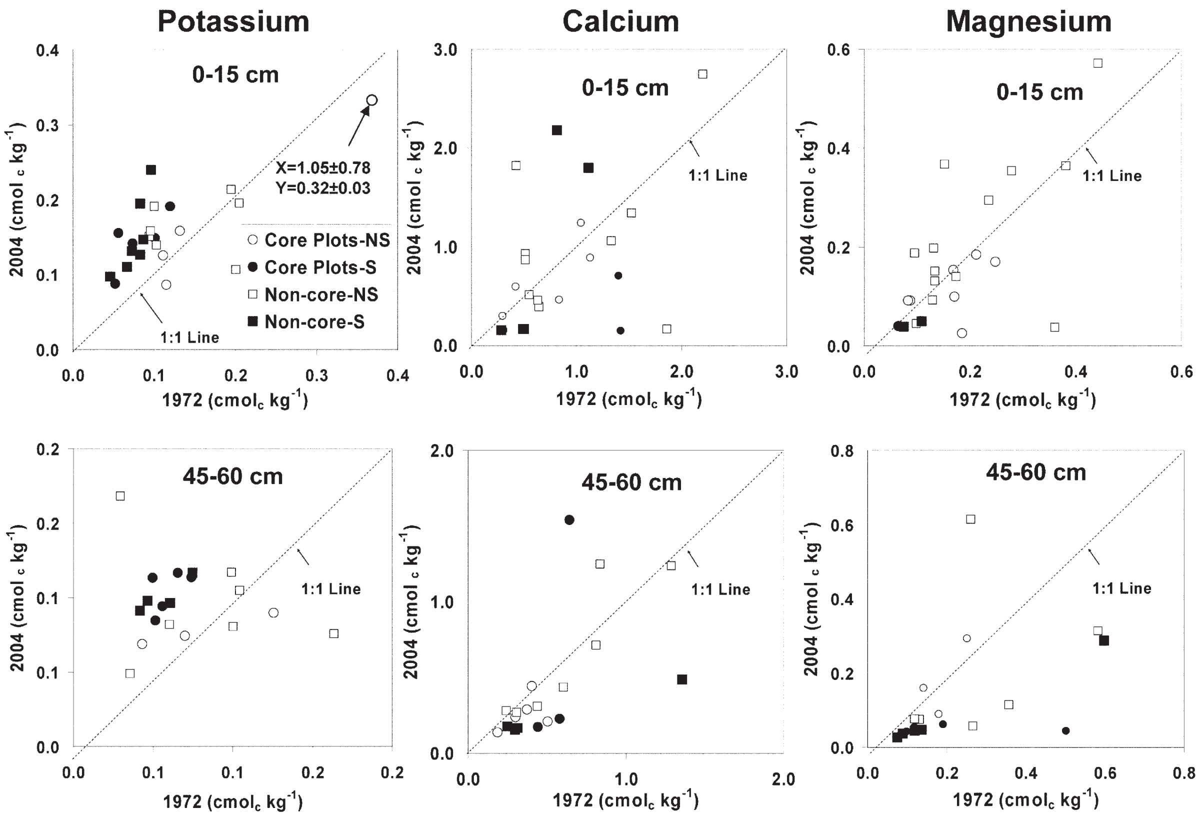

Fig. 1. Scatter plots of soil exchangeable K^+, Ca^{2+}, and Mg^{2+}concentrations in the A (0–15 cm) and Bt (45–60 cm) horizons in the original, noncore plots and the eight core plots in 1972 (*x* axis) and 2004 (*y* axis). Points falling above the 1:1 line indicate an increase, points falling below the 1:1 line indicate a decrease. Values for the eight core plots are shown as circles, values for the noncore plots are shown as squares. Solid symbols (S) indicate statistically significant differences, unpaired Student's *t*-test for the individual plots and paired *t*-tests for the averages among all plots ($P \le 0.05$); hollow symbols (NS) indicate no significant difference.

Table 2. Grand average (average of all plot averages) values for exchangeable K^+, Ca^{2+}, and Mg^{2+} in 1972 and 2004 among all plots and among the intensive core plots. Probability values for differences between all plots and intensive core plots for each year (*P* values, plots) and probability values for significant changes with time (*P* values, year) are given (Student's *t*-test).

Nutrient and depth	1972	2004	*P* values, year
	——— $cmol_c\ kg^{-1}$ ———		
K^+ (0–15 cm)			
All plots	0.15 ± 0.04	0.16 ± 0.01	0.37
Core plots	0.10 ± 0.01	0.14 ± 0.01	0.01
P values, plots	0.13	0.12	
K^+ (45–60 cm)			
All plots	0.07 ± 0.01	0.10 ± 0.01	0.01
Core plots	0.07 ± 0.01	0.09 ± 0.01	0.02
P values, plots	0.37	0.40	
Ca^{2+} (0–15 cm)			
All plots	0.88 ± 0.11	0.84 ± 0.15	0.38
Core plots	0.86 ± 0.17	0.56 ± 0.13	0.07
P values, plots	0.45	0.09	
Ca^{2+} (45–60 cm)			
All plots	0.54 ± 0.08	0.46 ± 0.10	0.17
Core plots	0.43 ± 0.05	0.41 ± 0.17	0.44
P values, plots	0.13	0.39	
Mg^{2+} (0–15 cm)			
All plots	0.18 ± 0.02	0.17 ± 0.03	0.29
Core plots	0.15 ± 0.02	0.11 ± 0.02	0.03
P values, plots	0.19	0.05	
Mg^{2+} (45–60 cm)			
All plots	0.23 ± 0.04	0.13 ± 0.03	0.01
Core plots	0.22 ± 0.05	0.10 ± 0.03	0.04
P values, plots	0.44	0.25	

depth, 10 of 23 soil plots analyzed and four of the eight core plots showed significant ($P < 0.05$, Student's *t*-test) increases in exchangeable K^+ concentrations between 1972 and 2004. The grand averages of exchangeable K^+ in the 23 soil plots and eight core plots did not differ significantly in either 1972 or 2004, but the changes between 1972 and 2004 did differ: there was a significant increase in the eight core plots, but no significant change in the average of the 23 soil plots. The lack of significant change in the 23 soil plots in the 0- to 15-cm depth was due to a significant outlier value (Fig. 1). The value of this outlier for 1972 was five times greater than any other value for that year and well beyond the range defined for extreme outliers ($x > Q3 + 3IQR$, where x = the value, Q3 = the third quartile, and IQR = interquartile range, Q3–Q1). The 2004 value for that same point was 60% higher than any other value for that year, and qualified as a mild outlier ($x > Q3 + 1.5IQR$) (Renze, 2007). If this outlier is removed, the difference between the grand average values of exchangeable K^+ for 1972 (0.10 ± 0.01) and 2004 (0.15 ± 0.01) is highly significant ($P < 0.001$) for the entire data set as well as the eight core plots.

In the 45- to 60-cm depth, eight of the 19 soil plots analyzed and five of the eight core plots showed significant increases in exchangeable K^+. The grand averages of exchangeable K^+ of the 19 soil plots did not differ significantly from the grand average of the eight core plots in either 1972 or 2004, and the increases between 1972 and 2004 were significant in both cases.

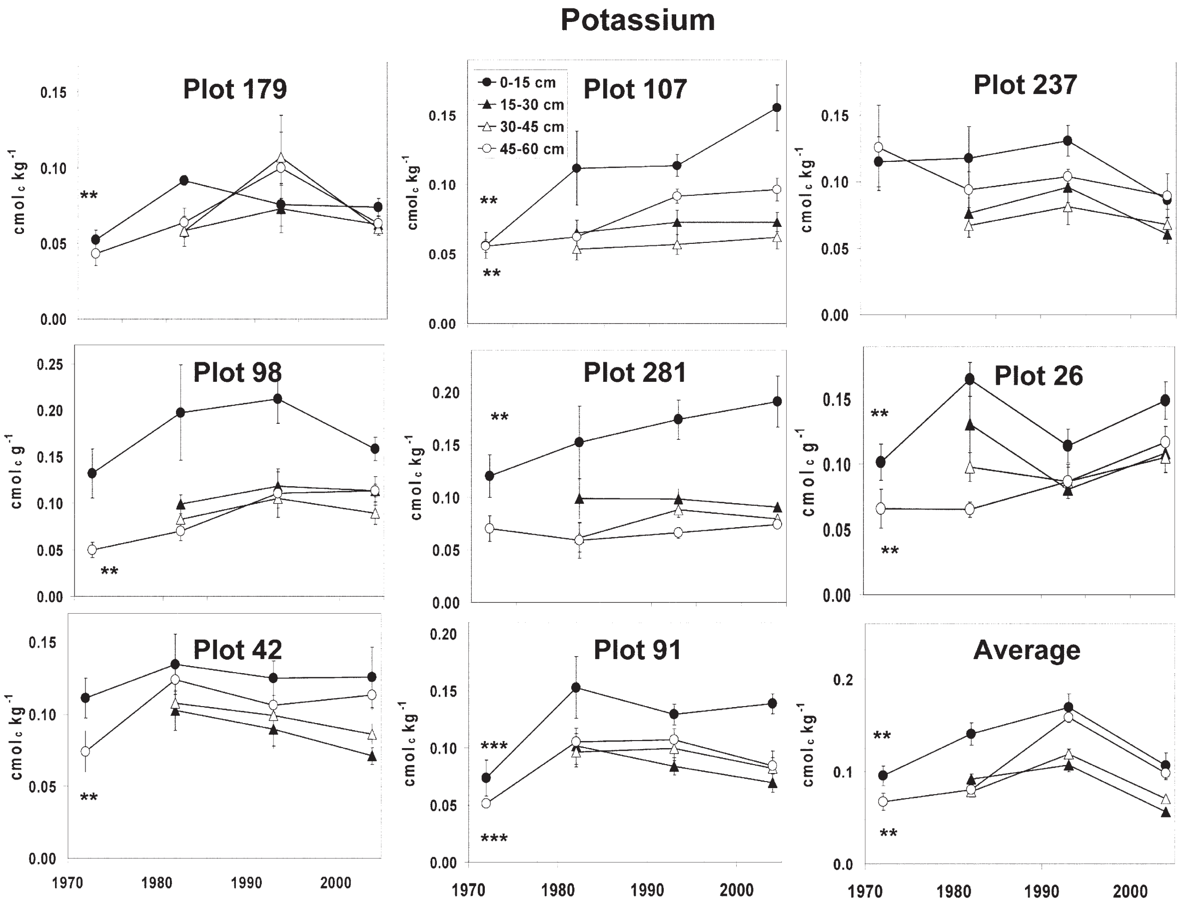

Fig. 2. Changes in soil exchangeable K^+ concentrations between 1972 and 2004 in the eight core plots. The panel labeled *average* shows the average values of all plots, using the plot average for each year. Standard errors are shown. Asterisks indicate significant differences between 1972 and 2004 analyses (0–15- and 45–60-cm depths only, unpaired Student's *t*-test, * $P \leq 0.05$, ** $P \leq 0.01$).

The changes in exchangeable Ca^{2+} were highly variable across the watershed, with both increases and decreases. In the 0- to 15-cm depth, two of 23 soil plots showed significant increases and six showed significant decreases in exchangeable Ca^{2+} between 1972 and 2004. Among the eight core plots, two showed significant decreases in exchangeable Ca^{2+} between 1972 and 2004 in the 0- to 15-cm depth. The grand averages of exchangeable $Ca^{2+}$of the 23 soil plots did not differ significantly from the grand average of the eight core plots in either 1972 or 2004 in the 0- to 15-cm depth, and the changes between 1972 and 2004 were not significant in either case. In the 45- to 60-cm depth, seven of 19 soil plots showed significant decreases in exchangeable Ca^{2+} and one plot showed a significant increase in exchangeable Ca^{2+}. Among the eight core plots, two showed significant decreases and one (the same one as in the larger database) showed a significant increase in exchangeable Ca^{2+}. The grand averages of exchangeable Ca^{2+} of the 23 soil plots did not differ significantly from the grand average of the eight core plots in either 1972 or 2004 in the 45- to 60-cm depth, and the average changes between 1972 and 2004 were not significant in either case.

Changes in exchangeable Mg^{2+} across the watershed were consistently negative. In the 0- to 15-cm depth, five of the 23 soil plots analyzed and three of the eight core plots showed significant decreases in exchangeable Mg^{2+} between 1972 and 2004. The grand averages of exchangeable $Mg^{2+}$of the 23 soil plots did not differ significantly from the grand average of the eight core plots in 1972, but the value for the core plots was significantly lower in 2004 (Table 2). The changes between 1972 and 2004 in the 0- to 15-cm depth were not significant among the 23 soil plots but were significant among the eight core plots. In the 45- to 60-cm depth, 10 of 19 soil plots and three of the eight core plots showed significant decreases in exchangeable Mg^{2+}. The grand averages of exchangeable Mg^{2+} of the 19 soil plots did not differ significantly from the grand average of the eight core plots in either 1972 or 2004 in the 0- to 15-cm depth, and the changes between 1972 and 2004 were significant in both cases.

Changes in Soil Exchangeable Potassium, Calcium, and Magnesium in Core Plots, 1982 to 2004

Changes in exchangeable K^+, Ca^{2+}, and Mg^{2+} in the eight core plots are shown in Fig. 2 to 4 and ANOVA analyses are given in Tables 3 and 4. Table 3 provides analyses of the effects of year and depth within each plot, and Table 4 gives analyses of the overall changes among all plots, depths, and years. Measurements in the intervening years (1982 and 1993) between 1972 and 2004 in the core plots indicated that the observed increases in exchangeable K^+ occurred primarily between 1972 and 1982, with little further change thereafter in most cases. Statistical analyses of the 1982 to 2004 data set (including all depths) showed that the effects of year were significant for exchangeable K^+ in only two core plots (26 and 237; Table 3). The changes in

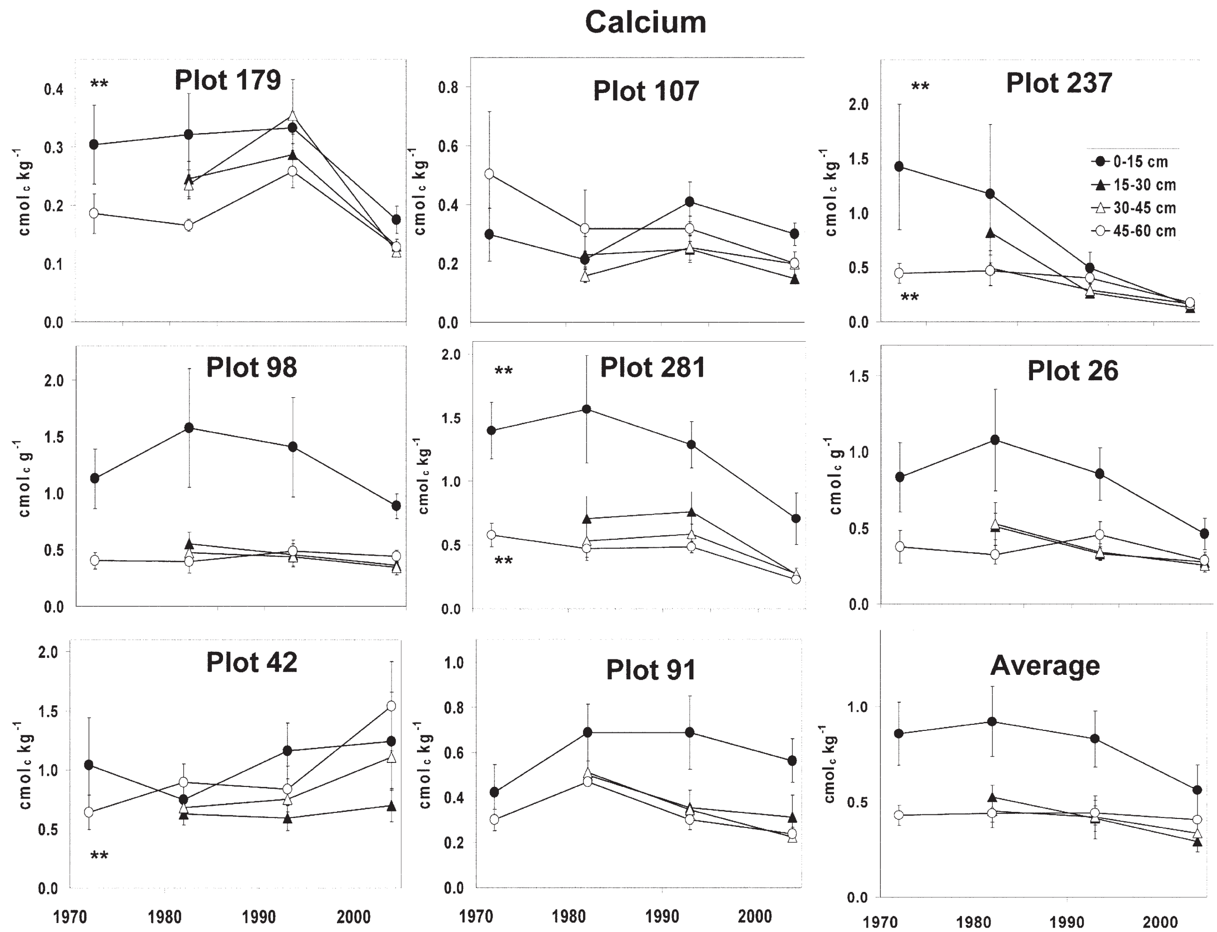

Fig. 3. Changes in soil exchangeable Ca^{2+} concentrations between 1972 and 2004 in the eight core plots. The panel labeled *average* shows the average values of all plots, using the plot average for each year. Standard errors are shown. Asterisks indicate significant differences in 1972 and 2004 analyses (0–15- and 45–60-cm depths only, unpaired Student's *t*-test, * $P \leq 0.05$).

exchangeable K^+ in these two plots were not in the same direction, however: in Plot 26, exchangeable K^+ fluctuated with time in the surface depths and showed an increase in the 45- to 60-cm depth, whereas in Plot 237 exchangeable K^+ showed a decrease between 1993 and 2004 at all depths. The average change in exchangeable K^+ among all plots was not statistically significant (Table 4).

The effects of year on exchangeable Ca^{2+} were significant in seven of the eight core plots (all but Plot 98; Table 3) as well as the average of all plots (Table 4). The changes in exchangeable Ca^{2+} were negative except for Plot 42. The increase in exchangeable Ca^{2+} in Plot 42 no doubt contributed substantially to the significance of the plot × year interaction term (Table 4).

The effects of year on exchangeable Mg^{2+} were significant in six of the eight core plots (Table 3, Fig. 4) as well as the average of all plots (Table 4). Exchangeable Mg^{2+} decreased in all cases where the effects of year were statistically significant (Fig. 4).

Changes in Ecosystem Potassium, Calcium, and Magnesium Contents in Core Plots, 1982 to 2004

The average K contents of live trees, standing dead trees, O horizon, total above-soil materials (live trees + standing dead trees + downed logs + O horizon), and total ecosystem in the core plots changed significantly during the 22-yr sampling period (1982–2004) but the changes in CWD K content and soil exchangeable K^+ contents did not (Fig. 5A, Table 5). The average above-soil K increment (49 ± 20 kg ha^{-1}) equaled 26% of the average soil exchangeable K^+ content in 1982 (190 ± 17 kg ha^{-1}). Estimates of net leaching fluxes of K^+ (atmospheric deposition minus leaching) extrapolated across a period of 22 yr from the 1983 to 1986 collection period (Johnson and Todd, 1990) averaged 74 ± 19 kg ha^{-1}, or 39% of exchangeable K^+, in 1982. Despite the apparent pressures on soil exchangeable K^+ pools from the aboveground increment plus leaching (averaging 123 kg ha^{-1} or 65% of soil exchangeable K^+ content in 1982), average net changes in exchangeable K^+ contents between 1982 and 2004 were small (–6 ± 9 kg ha^{-1}) and nonsignificant. Soil total K pools (18440 ± 970 kg ha^{-1}) measured in 1982 were nearly two orders of magnitude greater than exchangeable pools and thus a very low rate of weathering could have replenished any withdrawals of K^+ from the exchangeable pools (Fig. 5A).

The average Ca contents of live trees, standing dead trees, O horizon, total above-soil materials, and total ecosystem in the core plots changed significantly during the sampling period but the average changes in downed trees and soil exchangeable Ca^{2+} did not (Fig. 5B, Table 5). The average above-soil Ca increment of 497 ± 138 kg ha^{-1} equaled 86% of the exchangeable Ca^{2+} in 1982 (577 ± 92 kg ha^{-1}). Average net leaching fluxes of Ca^{2+} (58 ± 46 kg ha^{-1}) were much smaller, equaling only 10% of exchangeable Ca^{2+} in 1982. The average net change in soil exchangeable Ca^{2+} content between 1982 and 2004 (–178 ± 114 kg ha^{-1} or 31% of the 1982 content) was much smaller

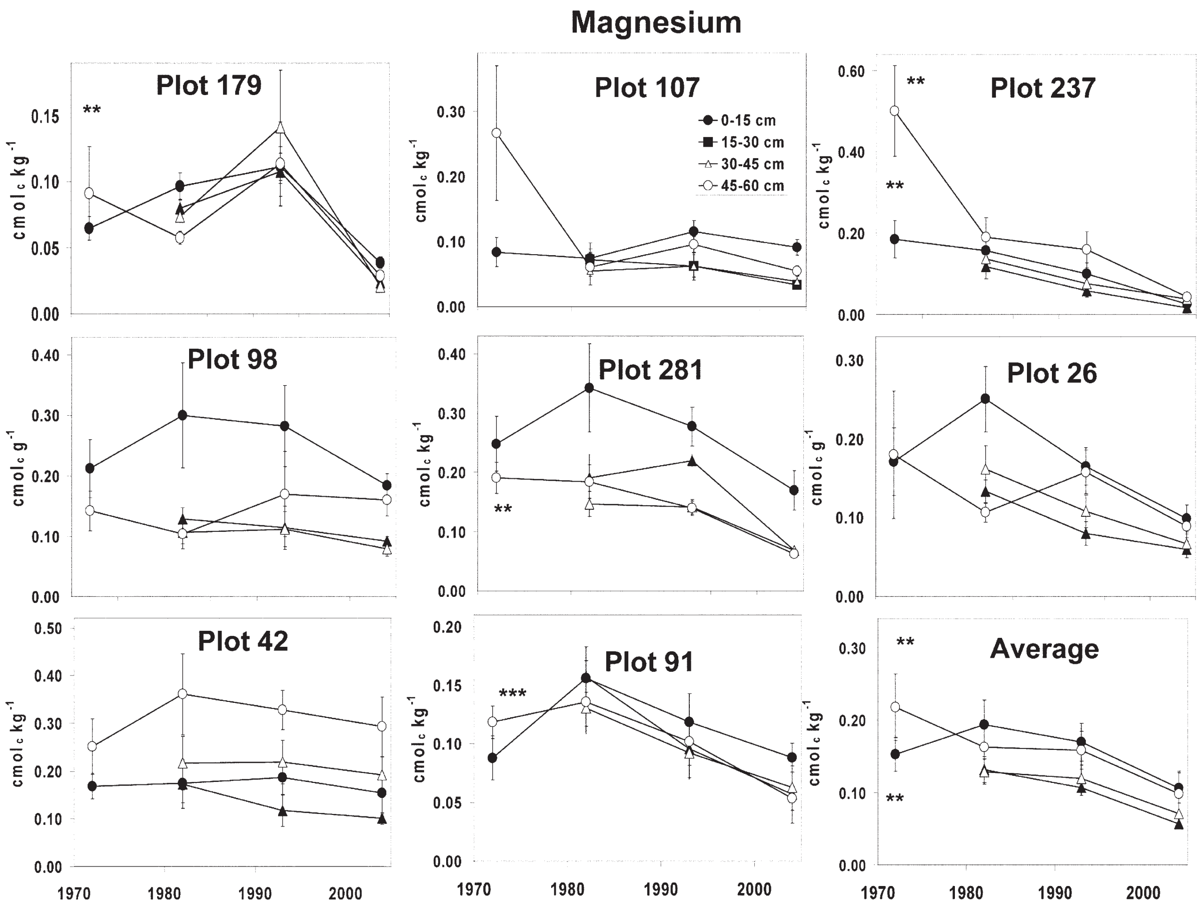

Fig. 4. Changes in soil exchangeable Mg^{2+} concentrations between 1972 and 2004 in the eight core plots. The panel labeled *average* shows the average values of all plots, using the plot average for each year. Standard errors are shown. Asterisks indicate significant differences in 1972 and 2004 analyses (0–15- and 45–60-cm depths only, unpaired Student's *t*-test, * $P \leq 0.05$, ** $P \leq 0.01$).

than the above-soil increment plus leaching (555 kg ha^{-1}) and not statistically significant. Total soil Ca pools were small: the above-soil increment plus leaching equaled 26% of total soil Ca in 1982 (2110 ± 220 kg ha^{-1}). Thus, weathering from the top 60 cm of the soil would not appear to be a probable source for replenishing Ca^{2+} removed from exchange sites. As hypothesized by Trettin et al. (1999), deep rooting into dolomite bedrock may have provided Ca in some cases where bedrock is relatively close to the surface; on ridge tops, however, bedrock can be as much as 30 m below the surface. Another source in some cases (i.e., Plot 42) may be the decomposition of Ca-rich CWD. This possibility is discussed in detail below.

The average Mg contents of live trees, standing dead trees, O horizon, total above-soil material, and soil exchange sites in the core plots changed significantly during the sampling period but the changes in downed tree and total ecosystem Mg did not (Fig. 5C, Table 5). The average above-soil Mg increment of 18 ± 4 kg ha^{-1} equaled only 19% of the soil exchangeable Mg^{2+} content in 1982 (94 ± 15 kg ha^{-1}). Estimates of net fluxes of Mg^{2+} (100 ± 25 kg ha^{-1}) are much greater than the net above-soil increment and are approximately equal to exchangeable Mg^{2+} in 1982. Average net changes in the soil exchangeable Mg^{2+} contents between 1982 and 2004 (–44 ± 9 kg ha^{-1}) were statistically significant but less than the net above-soil increment plus net leaching (118 kg ha^{-1}), suggesting either deep rooting or weathering from surface soils as sources for the replenishment of exchangeable Mg^{2+}. Average soil total Mg in the top 60 cm (5990 ± 440 kg ha^{-1}) was large relative to exchangeable Mg^{2+} (Fig. 5C).

Tests of Hypotheses

Hypothesis 1 (the eight core plots are representative of the more extensive soil sampling plots established in 1972) was supported by the comparisons of the average values of exchangeable K^+, Ca^{2+}, and Mg^{2+} in all the soil plots with those in the core plots. Of the 24 possible comparisons (12 comparisons of 1972 and 2004 concentrations and 12 comparisons of changes with time), only three showed significant differences between the soil and core plot averages. In one case (changes in K^+ in the 0–15-cm depth), the difference between the two averages was due to a significant outlier; without the outlier, the changes with time in the soil plots would be statistically significant, as was found for the core plots.

Hypothesis 2 (the changes reported by Trettin et al. [1999] for the third sampling in 1993 would continue to 2004) was supported in part by the results of this study: with one notable exception, the declines in exchangeable Ca^{2+} and Mg^{2+} noted in the 1972 to 1993 samplings generally continued into 2004. (Recall that Trettin et al. [1999] did not report on exchangeable K^+.) The one major exception to this was Plot 42, where exchangeable Ca^{2+} (but not Mg^{2+} or K^+) increased with time. We hypothesize that this was due to the decomposition of Ca-rich CWD from chestnut oak mortality in that case. The estimated Ca increase in CWD from downed trees in this plot

Table 3. Analysis of variance probabilities for changes in soil concentrations of K^+, Ca^{2+}, and Mg^{2+} in the individual core plots between 1982 and 2004.

Source	df	K^+		Ca^{2+}		Mg^{2+}	
		F ratio	*P*	*F* ratio	*P*	*F* ratio	*P*
Plot 26							
Year	2	5.058	0.010	5.822	0.005	16.182	<0.001
Depth	3	9.287	<0.001	9.542	<0.001	7.898	0.000
Year × depth	6	2.219	0.054	1.261	0.290	2.726	0.021
Plot 42							
Year	2	1.532	0.225	3.611	0.034	0.969	0.386
Depth	3	4.587	0.006	2.544	0.065	9.853	<0.001
Year × depth	6	0.218	0.970	0.633	0.703	0.127	0.993
Plot 91							
Year	2	2.862	0.066	5.088	0.010	13.587	<0.001
Depth	3	13.373	<0.001	8.029	<0.001	0.950	0.423
Year × depth	6	0.591	0.736	0.252	0.956	0.171	0.984
Plot 98							
Year	2	1.569	0.218	1.766	0.181	1.123	0.333
Depth	3	14.765	<0.001	14.255	<0.001	8.800	<0.001
Year × depth	6	0.771	0.596	0.716	0.638	0.721	0.635
Plot 107							
Year	2	4.244	0.019	4.470	0.015	3.703	0.030
Depth	3	20.242	<0.001	3.424	0.022	4.389	0.007
Year × depth	5	1.029	0.415	1.290	0.275	0.860	0.529
Plot 179							
Year	2	2.643	0.081	35.278	<0.001	25.361	<0.001
Depth	3	0.900	0.447	3.209	0.030	0.377	0.770
Year × depth	6	1.212	0.315	1.181	0.331	0.567	0.755
Plot 237							
Year	2	5.532	0.006	8.103	0.001	17.410	<0.001
Depth	3	6.788	0.001	1.232	0.306	2.973	0.039
Year × depth	6	0.566	0.755	0.810	0.566	0.474	0.825
Plot 281							
Year	2	0.886	0.418	9.513	<0.001	17.433	<0.001
Depth	3	22.278	<0.001	15.026	<0.001	13.177	<0.001
Year × depth	6	0.371	0.894	0.801	0.573	0.759	0.605

was very large (751 kg ha^{-1}; Table 6) due to mortality and tree fall of Ca-rich chestnut oak, and some of the Ca contained in the woody tissues of this species could well have entered the soil during decomposition and accounted for the observed increase in exchangeable Ca^{2+} (493 kg ha^{-1}). The inventory method used to calculate downed trees does not allow us to determine the degree to which this CWD has decomposed since it entered the latter category; however, we note that decomposition of CWD on and near Walker Branch proceeds at a relatively rapid rate. For example, we found that >85% of the CWD left behind after clear-cut logging in a nearby site with similar soils and vegetation had decomposed during a period of 15 yr (Johnson and Todd, 1998). The Ca released during the decomposition of the logging residues was fully accounted for by significant increases in exchangeable Ca^{2+} during the same time period. The K and Mg losses during decomposition of the logging residues were not large enough to have caused significant changes in soil exchangeable K^+ or Mg^{2+}, however, and no changes were found. The situation in Plot 42 is analogous to the logging residue study except that the residue was in the form of tree mortality in the latter case.

Hypothesis 3 (changes in exchangeable Ca^{2+} but not Mg^{2+} can be attributed to sequestration in above-soil biomass and detritus) was partially supported by the results of this study. Despite the pressure from the above-soil increment, and the fact that changes in soil exchangeable Ca^{2+} concentrations were significant in seven out of the eight core plots (Table 3) and among all core plots (Table 4), the average changes in soil exchangeable Ca^{2+} content were not statistically significant. The lack of significance in the average exchangeable Ca^{2+} content was specifically due to the anomalous increase in Plot 42. The value for the change in exchangeable Ca^{2+} content for Plot 42 does not qualify as a statistical outlier, but it is certainly anomalous, being the only positive value. If Plot 42 is omitted from the data set, the decreases in exchangeable Ca^{2+} content would average −274 ± 6 kg ha^{-1} and the changes would be significant ($P = 0.001$).

The average change in soil exchangeable Mg^{2+} content was statistically significant and consistently in the negative direction, including in Plot 42 (Table 6). As in the past, the available nutrient budget data suggest that, on average, the decreases in soil exchangeable Mg^{2+} content can be attributed primarily to leaching, with a smaller contribution from sequestration in vegetation and detritus. The variability among individual plots is very high, however: above-soil Mg sequestration in two individual plots (98 and 107) equaled or exceeded the decreases in soil exchangeable Mg^{2+} content (Table 6). Estimated Mg^{2+} leaching rates were considerably greater than above-soil Mg sequestration rates in three of the four plots in which leaching was estimated. As was the case for Ca, however, there is a significant anomaly: Plot 107, where net Mg^{2+} leaching was very low because of a very high degree of sulfate retention in the soil, thereby reducing the mobile anion component that must be present for cation leaching (Johnson and Todd, 1990). As in the case of Ca in Plot 42, this seemingly anomalous result is a real and explainable one, not simply noise in the data.

Another factor in the exchangeable Mg^{2+} decrease could be reduced atmospheric deposition. Records from the National Atmospheric Deposition Program site on Walker Branch show statistically significant declines in wet deposition of Mg^{2+} between 1981 and 2005 (Fig. 6). There was also a decline in wet deposition of Ca^{2+} but it was not statistically significant. There was no trend in wet deposition of K^+.

Although we attribute the changes in exchangeable Ca^{2+} and Mg^{2+} to different causes (primarily vegetation uptake for Ca and leaching for Mg), the changes in the soil contents of these two nutrients are generally correlated. This

Table 4. Analysis of variance results for changes in soil exchangeable K^+, Ca^{2+}, and Mg^{2+} in the eight intensively sampled core plots for the period 1982 to 2004, including all depths.

Source	df	K^+		Ca^{2+}		Mg^{2+}	
		F ratio	*P*	*F* ratio	*P*	*F* ratio	*P*
Plot	7	11.08	<0.001	27.30	<0.001	28.39	<0.001
Depth	3	64.14	<0.001	30.23	<0.001	16.65	<0.001
Year	2	1.08	0.341	11.30	<0.001	40.77	<0.001
Plot × year	14	2.50	0.019	4.27	<0.001	2.06	0.013
Depth × year	6	1.68	0.124	1.96	0.069	0.69	0.660

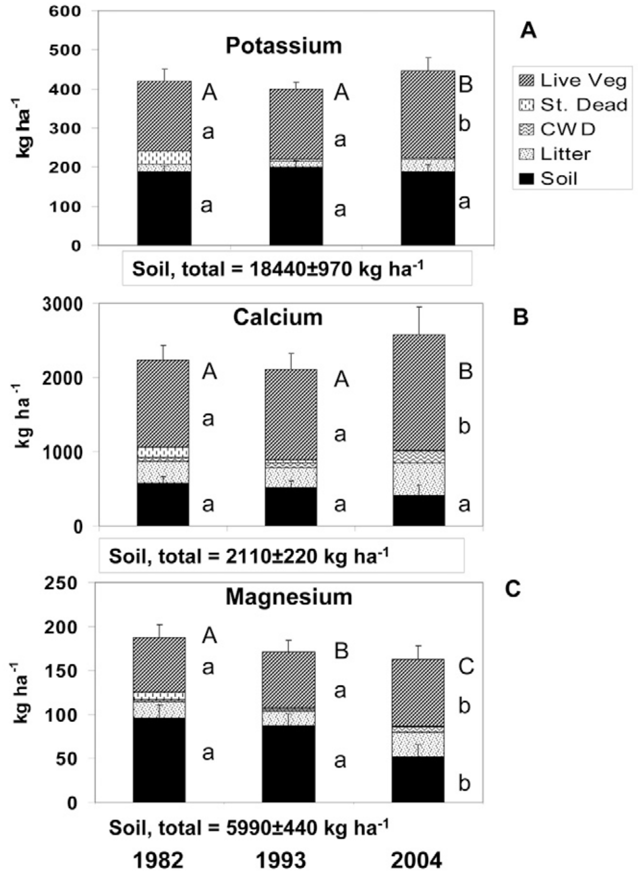

Fig. 5. Average (A) K^+, (B) Ca^{2+}, and (C) Mg^{2+} contents in live vegetation, standing dead vegetation, downed trees (coarse woody debris, CWD), O horizon litter, and soil exchange sites in the core plots with time between 1982 and 2004. Standard deviations for soil exchangeable and total ecosystem contents are shown. Total soil contents measured in 1982 are shown below each figure. Bars with the same lowercase letters are not significantly different ($P < 0.05$) in soil exchangeable and live tree contents with time; bars with the same uppercase letters are not significantly differenct in total above-soil contents (live vegetation + standing dead vegetation + down trees + O horizons) with time.

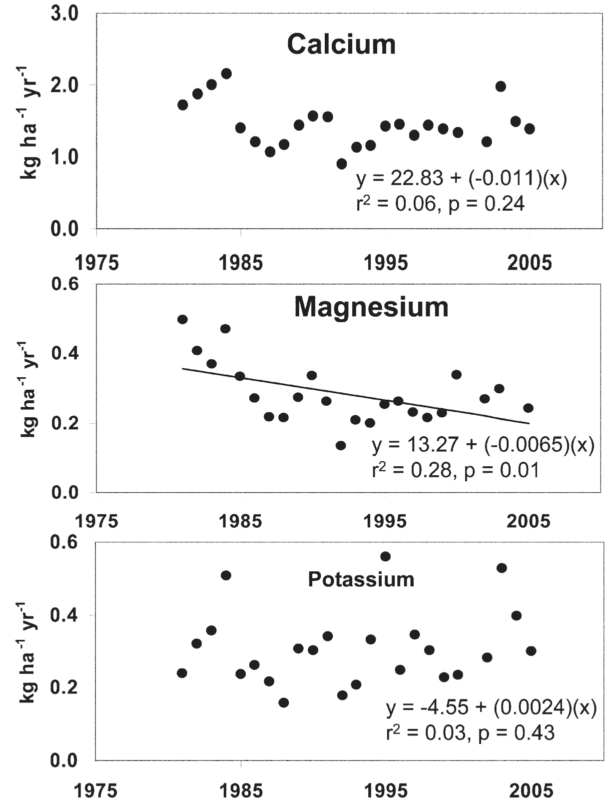

Fig. 6. Wet deposition of Ca^{2+}, Mg^{2+}, and K^+ on Walker Branch Watershed, 1982 to 2005. (source: National Atmospheric Deposition Program Office, Illinois State Water Survey, Champaign).

is shown in Fig. 7, which plots changes in exchangeable Ca^{2+} and Mg^{2+}against one another. Leaving Plot 42 aside, Fig. 7 shows that (i) the declines in exchangeable Ca^{2+} and Mg^{2+} are highly correlated ($r^2 = 0.82$, $P = 0.003$), and (ii) the changes were greatest in soils with initially higher contents.

The examples of Ca in Plot 42 and Mg in Plot 107 raise the issue of averaging as a means of characterizing biogeochemical pools and processes. Recent studies have documented the importance of understanding the roles of "hot spots" and "hot moments" in soils, whereby plant roots can forage in nutrient-rich sites and abandon them when they are depleted (McClain et al., 2003; Schimel and Bennett, 2004). Such a strategy allows plants to "mine" soils for N that would otherwise be denied to them by microbial competition away from the hot spots. Averaging or bulking soils masks this important feature and thereby obfuscates our understanding of its importance. Similarly, averaging the changes in individual plots or individual cores within plots in this study masks real variability in soil changes and the reasons for such changes. Thus, to say that average soil exchangeable Ca^{2+} content did not change on Walker Branch Watershed during the sampling period is not to say that no changes in soil exchangeable Ca^{2+} content occurred on the watershed. Had we bulked within or among plots, we would have reached very different and erroneous conclusions about soil changes in this site.

Table 5. Analysis of variance values for average changes in ecosystem K^+, Ca^{2+}, and Mg^{2+} contents between 1982 and 2004.

Source	df	K^+		Ca^{2+}		Mg^{2+}	
		F ratio	*P*	*F* ratio	*P*	*F* ratio	*P*
Live vegetation							
Plot	7	12.95	<0.001	19.23	0.003	18.65	<0.001
Year	3	6.52	0.010	8.75	<0.001	15.30	<0.001
Standing dead trees							
Plot	7	1.00	0.471	0.75	0.636	0.97	0.490
Year	2	5.16	0.021	7.70	0.006	9.47	0.003
Downed trees							
Plot	7	3.04	0.036	3.79	0.016	3.02	0.037
Year	2	2.47	0.120	1.25	0.309	1.63	0.230
O horizon							
Plot	7	2.02	0.125	5.34	0.004	6.88	0.001
Year	2	8.42	0.004	8.96	0.003	13.84	0.005
Total above soil							
Plot	7	13.41	<0.001	27.64	<0.001	19.58	<0.001
Year	2	9.45	0.003	16.77	<0.001	32.78	<0.001
Soil							
Plot	7	7.41	<0.001	7.15	<0.001	16.63	<0.001
Year	2	2.62	0.108	2.05	0.153	15.46	<0.001
Total ecosystem							
Plot	7	6.93	<0.001	15.79	<0.001	12.06	<0.001
Year	2	3.32	0.066	4.48	0.031	3.11	0.076

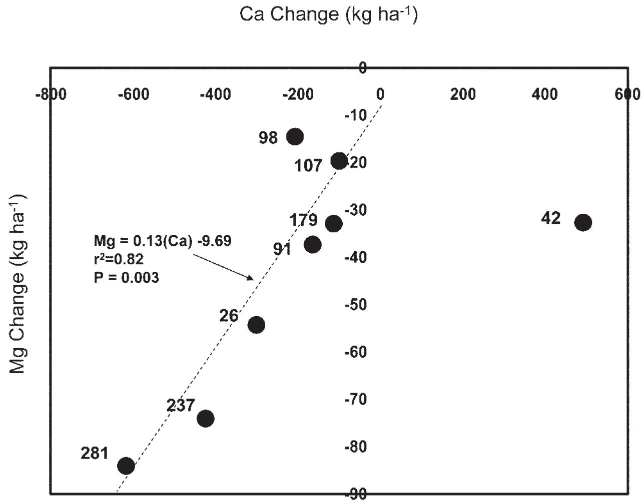

Fig. 7. Changes in soil exchangeable Ca^{2+} contents plotted against changes in exchangeable Mg^{2+} contents in the core plots. The dotted line shows the regression of soil Mg^{2+} against Ca^{2+} contents for all but Plot 42.

SUMMARY AND CONCLUSIONS

1. The eight core plots sampled intensively during the last 32 yr for changes in soil nutrients are, with minor exception, representative of soils from a larger subset of 24 soil sampling plots distributed across Walker Branch Watershed and sampled twice during this interval.
2. With one exception, the declines in soil exchangeable Ca^{2+} and Mg^{2+} concentrations noted in previous studies from the eight core plots (Johnson et al., 1988; Trettin et al., 1999) continued into the fourth sampling in 2004. The major exception to these patterns was in the case of exchangeable Ca^{2+}, where significant increases in concentration were noted and attributed to Ca release from decomposing CWD in one plot.
3. As noted in past studies, sequestration in above-soil material (live and dead trees plus detritus components) appeared to be the greatest factor causing declines in exchangeable Ca^{2+} content, whereas leaching appeared to be the greatest factor causing declines in exchangeable Mg^{2+} content. There were, however, important exceptions to this general pattern in specific plots.

This study shows that soil sampling at long intervals can mask important temporal variations, and that averaging or bulking among or within plots can mask significant and important spatial patterns in soil change. The variations in soil changes on Walker Branch Watershed—both spatial and temporal—are real and informative, and should not be treated simply as statistical noise.

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Table 6. Net changes in the K^+, Ca^{2+}, and Mg^{2+} contents in live trees, standing dead trees, downed trees, O horizon, total above-soil (AS) increment (live trees + standing dead trees + down trees + O horizon), soil exchange sites, and the total ecosystem in the core plots between 1982 and 2004. Also shown are extrapolated estimates of atmospheric deposition minus leaching from data collected from selected plots by Johnson and Todd (1990). Standard errors are shown for averages of all plots.

Component	Net change								
	Plot 26	Plot 42	Plot 91	Plot 98	Plot 107	Plot 179	Plot 237	Plot 281	Avg. ± SE
	kg ha^{-1}								
	$K^{\pm}$								
Live trees	−10	46	9	58	169	33	37	19	45 ± 19
Standing dead trees	−21	−14	−38	−9	−43	−13	−5	−9	−19 ± 5
Downed trees	10	71	7	5	4	0	−1	−5	11 ± 9
O horizon	12	−9	27	8	24	0	32	14	14 ± 5
Total AS	−25	93	5	61	154	20	63	20	49 ± 20
Soil exchange sites	22	−40	−31	21	−14	−5	−25	28	−6 ± 9
Total ecosystem	−3	53	−27	82	140	14	38	47	43 ± 18
Deposition – leaching	−84			−105	21	−126			−74 ± 23
	$Ca^{2\pm}$								
Live trees	134	151	151	528	1214	423	484	43	391 ± 134
Standing dead trees	−71	−107	−321	−72	−318	−80	−45	−68	−135 ± 41
Downed trees	31	751	41	34	29	−25	−21	−34	101 ± 94
O horizon	165	−115	268	318	328	−3	123	137	153 ± 55
Total AS	260	581	140	808	1252	315	541	79	497 ± 138
Soil exchange sites	−299	493	−163	−207	−100	−112	−614	−422	−178 ± 114
Total ecosystem	−39	1174	−23	601	1153	203	−73	−344	332 ± 205
Deposition – leaching	−189			−21	105	−126			−58 ± 46
	$Mg^{2\pm}$								
Live trees	9	13	−1	15	31	15	17	7	13 ± 3
Standing dead trees	−4	−7	−18	−2	−15	−4	−2	−7	−7 ± 2
Downed trees	5	23	2	1	2	−1	−2	−2	4 ± 3
O horizon	14	−8	13	6	15	7	16	12	9 ± 3
Total AS	18	21	−4	21	33	17	28	10	18 ± 4
Soil exchange sites	−54	−33	−37	−15	−20	−33	−84	−74	−44 ± 9
Total ecosystem	−36	−12	−41	6	13	−16	−56	−64	−26 ± 10
Deposition – leaching	−105			−168	0	−126			−100 ± 25

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