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Sulfur Accumulation and Atmospherically Deposited Sulfate

in the Lake States

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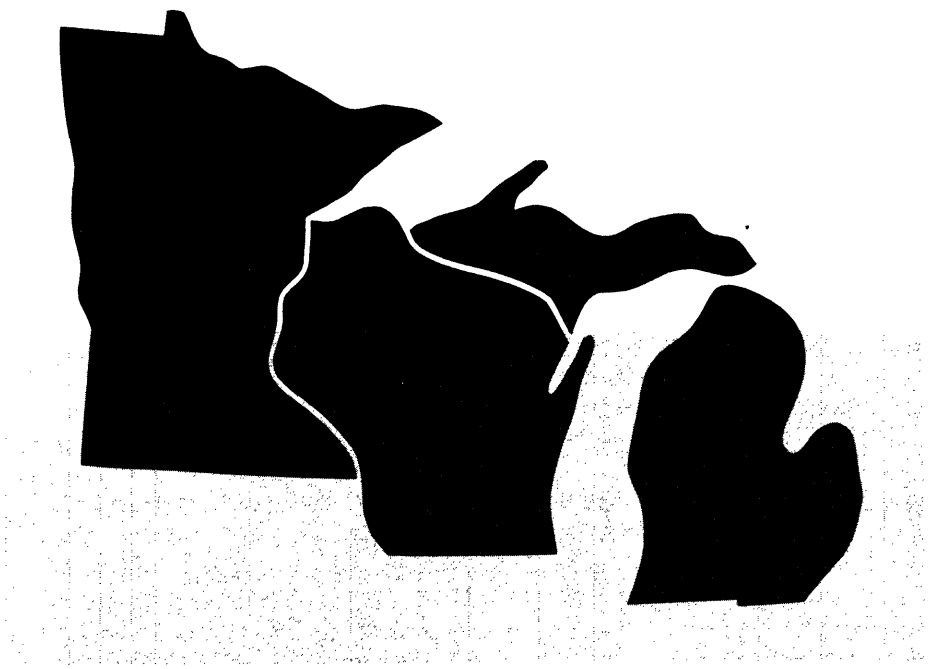

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Sulfur Accumulation and Atmospherically Deposited Sulfate in the Lake States

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Based on data from the U.S. National Atmospheric Deposition Program (NADP), a gradient is present in sulfate deposited by precipitation (atmospheric wet deposition) from northwestern Minnesota to southeastern Michigan (Harris and Verry 1985, Nichols and Verry 1985, Glass and Loucks 1986, Nichols and McRoberts 1986). The average pH of precipitation (1979-1982) along this gradient declines from 5.3 to 4.3, with a corresponding increase in sulfate deposition (from 3.4 to 8.5 kg S ha^{-1} yr^{-1}) (Glass and Loucks 1986). Glass and Loucks (1986) and Nichols and McRoberts (1986) found a relationship between the chemistries of precipitation and surface water in weakly-buffered lakes in north-central Wisconsin and northern Michigan. Although there is strong interest in mechanisms by which forested watersheds modify sulfur (S) input to surface waters, few studies have examined the mass of S in soils in relation to wet atmospheric deposition of sulfate.

Sulfur from atmospheric deposition can accumulate in forest soils and biomass by a number of processes, including: sulfate adsorption (Johnson 1984, Fuller *et al.* 1985); microbial immobilization (Johnson 1984, David *et al.* 1987, Swank *et al.* 1984, David and Mitchell 1987); and vegetative uptake (Johnson 1984, David *et al.* 1987). Sulfate adsorption capacities for soils north of the limit of Wisconsin glaciation are apparently low (Bloom and Grigal 1985, Rochelle *et al.* 1987). Vegetation is also thought to be a minor sink for sulfate (Johnson 1984), and net microbial immobilization has been difficult to quantify under field conditions (Swank *et al.* 1984, David and Mitchell 1987). David *et al.* (1988) found that forest floor and upper mineral soil (25 cm) S concentrations reflected a geographical gradient in wet sulfate deposition. Plots were grouped by five zones across Minnesota, Wisconsin, and Michigan. After S concentrations were adjusted for nitrogen (N) levels, higher concentrations were observed in eastern than in western zones (David *et al.* 1988).

Grigal and Ohmann (1989) examined concentrations of other elements in the forest floor samples used by David *et al.* (1988). They observed that calcium, magnesium, potassium, sodium, and phosphorus decreased in concentration from west to east, and that lead and cadmium increased. The trends were consistent with atmospheric deposition of the former group from western soil-derived sources and the latter elements from eastern anthropogenic sources.

In addition to the potential effects of sulfate deposition on surface waters, there is increasing interest in the potential effects of acidic deposition on forest growth. This report is part of a larger research project initiated in the northern Lake States to examine possible relationships between the radial growth of trees and the S content of woody tissue and soils across an established gradient of sulfate deposition. The primary hypothesis to be tested in this project is that the gradient of sulfate deposition is reflected in the amount of accumulated S in the forest floor-soil system and in tree tissue, and is related to differences in radial increment of trees on inventory plots. The secondary hypothesis we tested is that the mass of forest floor and mineral soil S correlates positively with the sulfate deposition gradient in wet precipitation (NADP) from northwestern Minnesota to southeastern Michigan.

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METHODS

Detailed information on sampling and analysis can be found in David *et al.* (1988), which used the same samples to evaluate soil S concentration gradients. Relationships of S, carbon (C), and N concentrations as affected by atmospheric deposition and vegetation were detailed in that work, but that report did not examine the mass of those elements within the soil. A brief summary of the methods from that work is given below. Additional information on soil mapping units can be found in Ohmann *et al.* (1989).

Plot Selection

The Lake States were divided into five geographical zones to evaluate our hypotheses (fig. 1). The divisions roughly corresponded to the 0.3, 0.7, 1.3, and 2.6 kg S ha^{-1} yr^{-1} isolines of the acid sulfate deposition gradient, where acid sulfate is that deposited in association with hydrogen concentrations of more than 13 μeq L^{-1} (Nichols and Verry 1985, Verry and Harris 1988). Forest inventory plots established by the Forest Inventory and Analysis (FIA) unit of the North Central Forest Experiment Station were screened to identify a subpopulation of plots having a limited range of initial tree densities, ages, and site indices. An attempt was made to balance the 169 sample plots across the zones among each of five vegetation types. Cover types, with number of plots in parentheses, were balsam fir (*Abies balsamea* (L.) Mill.) (24), jack pine (*Pinus banksiana* Lamb.) (39), red pine (*Pinus resinosa* Ait.) (27), aspen (*Populus tremuloides* Michx.) (38), and sugar maple (*Acer saccharum* Marsh.) (41).

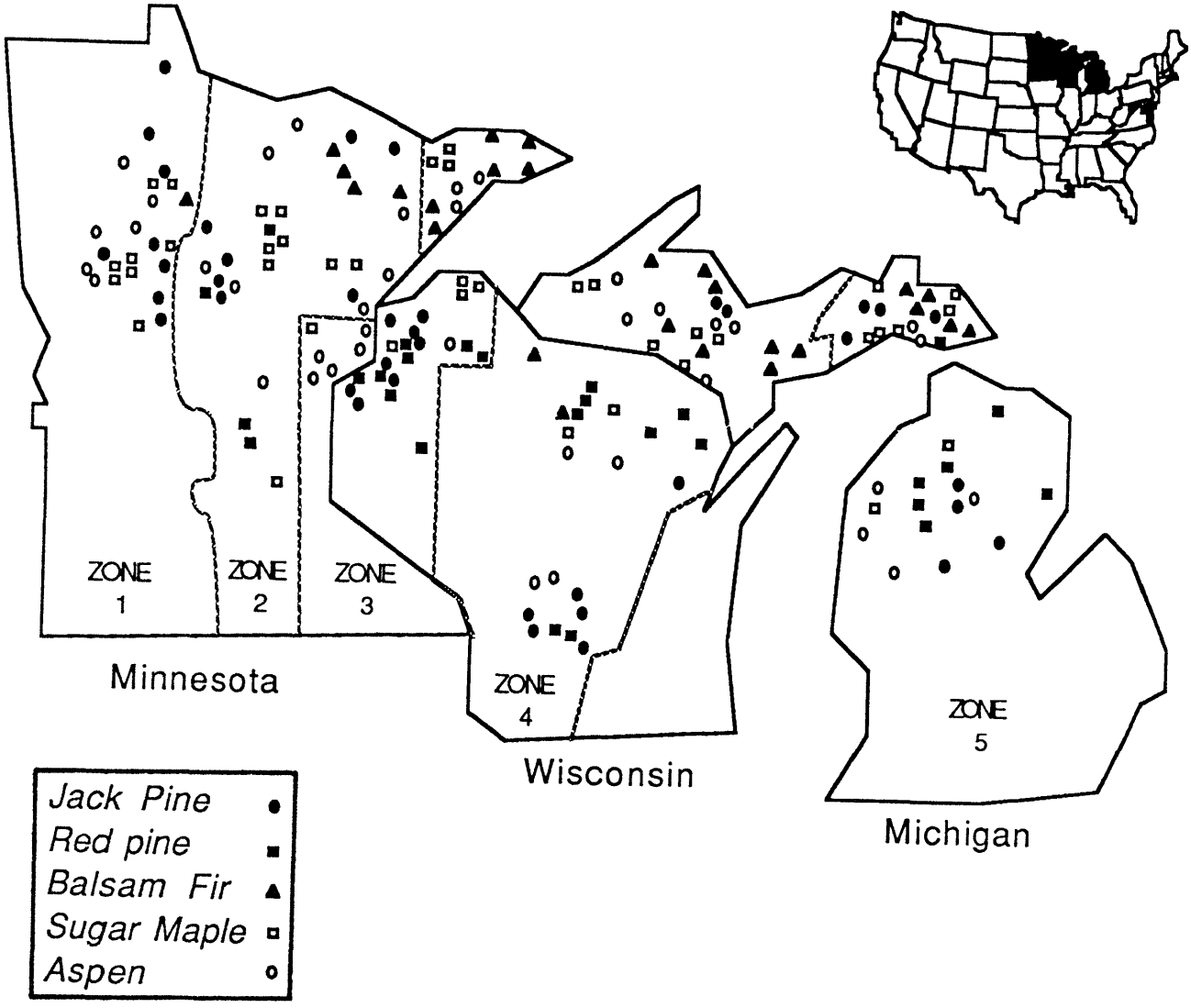

Figure 1.—*Location of plots and deposition zones across the Lake States acidic deposition gradient.*

Soil Sampling and Laboratory Analyses

Forest floor and mineral soil samples were collected within each plot and analyzed for total S and N. In each plot, five sample trees were selected, and three forest floor (using a stainless steel 12 cm diameter ring) and upper mineral soil (to 25 cm) samples were collected at 45, 135, and 225° azimuths, 1.5 m from the stem of each sample tree. Samples were bulked by sample tree and analyzed for total S using a LECO SC-132 automated analyzer (David *et al.* 1989) and total N by semi-micro Kjeldahl (Bremner and Mulvaney 1982). Over 1,800 composite soil samples were analyzed for S and N. National Bureau of Standards and in-house standards were used as checks, with duplicates run on 20 percent of the samples. Relative standard deviations for duplicate analyses averaged 11 and 6 percent for mineral soil and forest floor total S, respectively, and 4 percent for Kjeldahl N.

To examine soil extractable sulfate on a subset of the plots, three cover types were selected (jack pine, maple, and aspen) for which 15 randomly chosen plots were sampled. The plots were distributed with three replicates among each of the five zones; therefore, 45 plots were examined with 9 in each zone. Mineral soil (0-25 cm) was composited from the five samples previously used on each plot. Soil used for this compositing was dried at 105°C. Sulfate was determined by three extractions with 0.016 M sodium phosphate, following the procedure of Cappo *et al.* (1987). To examine potential sulfate adsorption, a 20 mg L^{-1} $MgSO_4$ solution was added to each sample (Cappo *et al.* 1987). This represents a much greater amount of sulfate than in throughfall and soil solutions at the present time, and should provide a relative index of sulfate adsorption capacities among the soils.

Soil Mass Estimation

Forest floor and mineral soil mass were calculated to determine the content of S and N. Forest floor mass was determined by the mean weight of the triplicate samples collected at each sample tree after drying at 65°C. Mineral soil bulk density was determined by the excavation method (Howard and Singer 1981) at two soil depth increments (0 to 12.5 cm and 12.5 to 25 cm). Rock material <20 mm diameter was determined in the laboratory after sieving. Material >20 mm was estimated in the field. Soil mass was determined using the rock estimates and bulk densities. We calculated a mass per unit area of S and N for forest floor and mineral soil from bulk density, concentration, and thickness data for both layers. Based on contour mapping (technique discussed in detail below), forest floor mass increased from east to west, and mineral soil mass from north to south. Both statistical models were weak, however, indicating no strong geographic relationships.

Atmospheric Wet Deposition Estimates

Deposition for each plot was determined by estimating precipitation quantity (30-year normal values) and separately estimating sulfate concentration from 1983 NADP values (Shifley 1988). NADP values from 1983 were used because a complete data set was available. Although sulfate deposition has been decreasing in this region, we were interested in the gradient and not in the absolute amount in a given year; therefore, use of the 1983 data alone was considered reasonable for estimating the gradient, and we realize that deposition varies greatly from year to year because of both precipitation amount and concentration. The use of 30-year precipitation data should have removed some of the variation from the former source. Dry deposition was not accounted for in our analysis due to a lack of data. An assumption was made that dry sulfate deposition was proportional to wet deposition, and that wet deposition can be used as a surrogate for total sulfate deposition (Nichols and McRoberts 1986).

RESULTS AND DISCUSSION

Contour Mapping

Empirical response surface models (statistically based) were developed to generate contour maps for atmospheric sulfate deposition and mass of S in both forest floor and mineral soils (fig. 2). The models were designed to determine if the contours for atmospheric sulfate were oriented in the same direction as the contours for S in the soil. For atmospheric sulfate deposition, a second-order model was developed (after careful evaluation and rejection of first-order and various other models):

$$\text{Sulfate} = b_0 + b_1\text{LAT} + b_2\text{LONG} + b_3\text{LONG}^2 + b_4\text{LAT}^2 + b_5\text{LAT} \times \text{LONG}$$

where the latitude (LAT) and longitude (LONG) are the independent variables of the models, and b_0 to b_5 are estimated regression coefficients. The overall model was significant ($P < 0.0001$ and $R^2 = 95\%$).

For both mass of S in the forest floor and mineral soil, first-order response surface models were developed. Mass of N was included in the models because it was highly correlated with S in both layers. The form of the model used was:

$$T = b_0 + b_1TN + b_2LAT + b_3LONG$$

where TS is mass of S in the layer, TN is mass of N in the layer, and b_0 to b_3 are the estimated regression coefficients. Both forest floor and mineral soil models were found to be significant for mass of S (forest floor: $P < 0.0001$ and $R^2=96\%$; mineral soil: $P < 0.0001$ and $R^2=87\%$). The estimated regression coefficients for mass of N were also significant (forest floor: $P < 0.0001$; mineral soil: $P < 0.0001$), and given that TN was in the models, the estimated regression coefficients for LAT and LONG were also significant (forest floor: $P < 0.001$; mineral soil: $P < 0.01$). Contour maps were generated by setting the mass of N for each layer at the mean for the layer across the entire region, because N showed no trends among the zones.

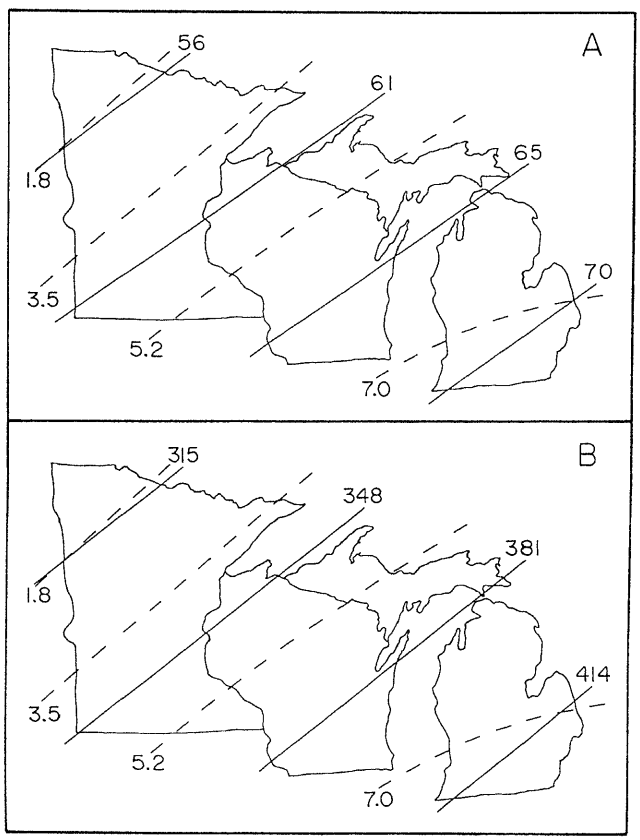

Figure 2.—*Contour maps of estimated wet sulfate deposition (dashed line, expressed as kg S ha^{-1} yr^{-1}) along with mass of S in forest floor (A) and mineral soil, 0-25 cm depth (B) (solid lines, kg S ha^{-1}) across the northern Lake States.*

Atmospheric Sulfate Deposition

Sulfate deposition levels ranged from 1.8 to 7.0 kg S ha^{-1} yr^{-1} across the Lake States based on the empirical response surface models developed to generate contour maps (fig. 2). As would be expected, this was similar to the gradient observed by Harris and Verry (1985) and Glass and Loucks (1986) who also used NADP data.

Soil Nitrogen and Sulfur

Mass of N in the forest floor and mineral soil showed no trends with zone (table 1). Zone 1 had the highest mass of this element in the mineral soil, whereas zone 5 had the highest mass in the forest floor. In evaluating the distribution of soil S across the gradient, mass of N was included in the model to account for the close relationship between S and N in soils. This relationship is expected because both are primarily found in organic forms in most soils and correlate strongly with each other (David *et al.* 1984). Sulfur and N in soil organic matter are affected by both climatic and vegetation factors. Inclusion of N in the models should help eliminate some of the variation in S related to climate and vegetation. Differences in levels of adjusted S mass can then be attributed to other unknown or hypothesized causes.

For both forest floor and mineral soil, contour maps of the distribution of S mass increased from northwest to southeast in the same manner as sulfate deposition (expressed as S) (fig. 2). Atmospheric deposition of sulfate is a possible explanation for the pattern of S found in the soils. David *et al.* (1988), using concentration data from the same soils, found increasing S concentrations when plots were

Table 1.—*Mass of N in forest floor and mineral soils (0- to 25-cm depth) by zone across the northern Lake States (kg N ha^{-1})*

Zone	Forest floor	Mineral soil
1	487	2,681
2	622	2,660
3	540	2,378
4	418	2,532
5	657	2,210

grouped by zones across the deposition gradient. Because many other factors affect estimates of soil S besides concentration, and because this analysis is based on individual plot data rather than on plot means, we feel that the similar results obtained by these two different analytical approaches lends considerable support to our conclusion.

The difference in mass of S of the mineral soil from northwestern Minnesota to southeastern Michigan was approximately 100 kg S ha^{-1}. The corresponding 1983 wet deposition input increased by about 5 kg S ha^{-1} yr^{-1}. Therefore, 20 years of wet deposition could account for an increase of this magnitude, if most accumulated in the upper mineral soil. Sulfate entering the system would likely be retained in the upper mineral horizons, because O horizons have little ability to adsorb sulfate. Uptake and litter returns could then add sulfate to the forest floor in an organic form (David *et al.* 1987), resulting in the observed increase; however, as discussed below, little sulfate was found in the soils, suggesting tree uptake and microbial immobilization were important retention processes.

Barrow *et al.* (1969) found in various regions of Australia that soil sulfate adsorption capacity (but not mass of S) was related to rainfall and parent material. They hypothesized that the positive sulfate relationship to increasing rainfall was due to greater reactive aluminum in soils where more rainfall occurred. Soils formed from basic parent material also adsorbed more than soils derived from acid parent material. In this study, differences in rainfall and parent material may have affected mass of soil S by partially regulating the potential for sulfate adsorption. Also, various parent materials could release different amounts of S from mineral weathering reactions; however, exchangeable calcium and magnesium in the 0-25 cm mineral soil depth showed no consistent patterns among zones, although potassium did increase from west to east (unpublished data). We would expect exchangeable calcium and magnesium to be good indicators of differences in soil chemistry of this upper soil depth. Rainfall varied from 60 cm in zone 1 to 80 cm in zone 5, and was partially reflected in more Alfisols in zone 1 and more Spodosols in zone 5 (Grigal and Ohmann 1989). Because we examined only the upper mineral soil (top 25 cm), however, differences in soil chemistry reflected by orders should not have affected our conclusions regarding mass of soil S.

Sulfate and Potential Adsorption

Phosphate-extractable sulfate levels were very low for all zones and vegetation types, and showed no trends across the gradient (table 2). Addition of a 20 mg S L^{-1} sulfate solution indicated negative adsorption in all but 3 of the 45 samples, with mean values less than zero. Taken together, these data indicate that the 0- to 25-cm soil depth sampled had little ability to retain sulfate, with present concentrations of sulfate representing <3 percent of total S. Higher levels of sulfate deposition would not be retained in these soils at the studied depth (0- to 25-cm depth) by sulfate adsorption, based on the negative adsorption results. These soils had little sulfate compared with Spodosol or Ultisol Bt, Bh, or Bs horizons, which often have considerable adsorbed sulfate (e.g., 50-100 mg S kg^{-1}) and the capacity to adsorb additional amounts (Johnson and Todd 1983, Fuller *et al.* 1985). It is possible that deeper soil horizons in these plots could have greater sulfate levels as well as adsorption capacities.

CONCLUSIONS

The increase in mass of S in forest floors and mineral soils of 169 forested plots across the northern Lake States suggests that patterns of sulfate deposition are reflected in terrestrial ecosystems and supports

Table 2.—*Phosphate extractable sulfate and net adsorption of a 20 mg sulfate-S L^{-1} solution in mineral soils (0-25 cm depth) by zone (n=9) and vegetation type (n=15) across the northern Lake States. Standard error of the mean in parenthesis.*

Zone	Sulfate		Adsorption	
	- - - - - - - mg S kg^{-1} - - - - - - -			
1	2.8	(0.4)	-6.9	(1.4)
2	3.2	(0.6)	-8.6	(2.8)
3	3.9	(0.8)	-7.4	(2.4)
4	3.9	(0.8)	-11.0	(2.7)
5	2.8	(0.5)	-8.7	(2.4)
Vegetation Type				
Jack pine	2.9	(0.4)	-6.6	(1.5)
Maple	3.7	(0.5)	-10.2	(2.0)
Aspen	3.2	(0.5)	-8.7	(1.8)

our hypothesis. The sulfate in these layers is apparently retained as organic S, because little adsorbed sulfate was found in any of the soils. Further work is needed to examine whether this pattern of soil S and N, reflecting deposition, is related to patterns of forest growth and yield.

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Characterizes the mass of soil sulfur (adjusted for nitrogen), and atmospherically deposited sulfate along an acid precipitation gradient from Minnesota to Michigan. The relationship of these variables, presented graphically through contour mapping, suggests that patterns of atmospheric wet sulfate deposition are reflected in soil sulfur pools.

KEY WORDS: Forest soils, sulfate adsorption, contour mapping, acidic deposition gradient, soil sulfur pools.