Kershaw, K. A., and J. W. Millbank, 1970, Nitrogen Metabolism in Lichens. II: The Partition of Cephalodial-Fixed Nitrogen Between the Mycobiont and Phycobionts of *Peltigera aphtbosa*, *New Pbytol.*, 69: 75-79.

Masse, L., 1966, Etude comparée des teneurs en azoté total des lichens et de leur substrat: les espèces à gonidies Cyanophycées, *C. R. Hebd. Séances, Ser. D, Sci. Natur. (Paris)*, 263: 781-784.

Millbank, J. W., 1972, Nitrogen Metabolism in Lichens. IV: The Nitrogenase Activity of the *Nostoc* Phycobiont in *Peltigera canina*, *New Pbytol.*, 71: 1-10.

——, and K. A. Kershaw, 1970, Nitrogen Metabolism in Lichens. III. Nitrogen Fixation by Internal Cephalodia in *Lobaria pulmonaria*, *New Pbytol.*, 69: 595-597.

——, and K. A. Kershaw, 1969, Nitrogen Metabolism in Lichens. I. Nitrogen Fixation in the Cephalodia of *Peltigera aphtbosa*, *New Pbytol.*, 68: 721-729.

Schell, D. M., and V. Alexander, 1973, Nitrogen Fixation in Arctic Coastal Tundra in Relation to Vegetation and Micro-Relief, *Arctic*, 26: 130-137.

——, and V. Alexander, 1970, Improved Incubation and Gas Sampling Techniques for Nitrogen Fixation Studies, *Limnol. Oceanogr.* 15: 961-962.

Schollhorn, R., and R. H. Burris, 1966, Study of Intermediates in Nitrogen Fixation, *Fed. Proc.*, 24: 710.

Stewart, W. D. P., 1966, *Nitrogen Fixation in Plants*, The Athlone Press, University of London, London.

——, G. P. Fitzgerald, and R. H. Burris, 1967, *In situ* Studies on N_2 Fixation Using the Acetylene Reduction Technique, *Proc. Nat. Acad. Sci. U. S. A.*, 58: 2071-2078.

EFFECTS OF FOREST FIRES ON ATMOSPHERIC LOADS OF SOLUBLE NUTRIENTS

in Mineral Cycling in Southeastern Ecosystems
Edited by F.G. Howell, J.B. Gentry, & M.H. Smith
Pub. by Technical Information Center, Office of Public Affairs
U.S. Energy Research and Development Administration
1975

WILLIAM M. LEWIS, JR.
Department of E.P.O. Biology, University of Colorado, Boulder, Colorado

ABSTRACT

Combustion of litter in pine forests was reproduced under controlled conditions by enclosing fire and smoke in an airtight chamber sufficiently large to prevent oxygen starvation. A known proportion of the air was pumped out of the chamber after the fire and passed through triplicate water columns designed to extract water-soluble substances released by the fire. Combustion of light litter did not produce significant amounts of airborne cations or sulfur compounds but did produce significant amounts of soluble organic compounds and inorganic nitrogen compounds. Mean nitrogen content of unburned litter was 0.95%. About one-third of this, 72 kg/ha, was released by fire. Although the bulk of the nitrogen was not recoverable as fixed inorganic nitrogen, significant amounts of nitrite and ammonia were present in the combustion products. The amounts of nitrite were unexpectedly high, and nitrate was not produced at all. Total release of nitrite and ammonia from these light litter fires was approximately equal to two-thirds of the yearly input of fixed nitrogen in rain. The implications of these findings for the atmospheric links in the nitrogen cycle are discussed.

Fire is a potent environmental catalyst capable of abruptly altering the distribution and flux of nutrients in grasslands and forests. The significance of fire in mineral cycling is actually dual, since combustion can be expected to affect the flow of nutrients across ecosystem boundaries as well as between ecosystem compartments. Both inter- and intrasystem effects are of great ecological interest, but the focus of this paper is on the transfer of materials across ecosystem boundaries.

Fire promotes the movement of nutrients across ecosystem boundaries by three principal mechanisms. (1) Fire destroys the structural matrix of organic matter so that salts can be leached in large amounts from the litter and can pass into aquatic systems via runoff, and to a lesser extent into groundwater. (2) Fire produces ash, which is moved more readily by wind than unburned litter, and

simultaneously opens the understory to wind. (3) Fire produces volatile and fine particulate material that can be returned to terrestrial or aquatic systems by rain or dry fallout. Loss of nutrients in water or wind can be considerable or slight depending on the conditions of combustion. For example, great increases in solubility of ions in litter will in some cases be offset by low runoff or high soil adsorption capacities. Factors that control the output of volatile and fine particulate material due to fire are much less obvious, as is the general significance of fire in the atmospheric links of various nutrient cycles. The experimental work described here was formulated to help clarify the role of fire in promoting the atmospheric transport of nutrients.

There is, of course, a large body of information dealing with the combustion products of fossil fuels, and some of this information is relevant to this study. Much air-pollution study is focussed on substances that are actually or potentially hazardous to human health. Since the point of interest here is instead the transport of materials that are potentially of general ecological significance, the scope of the investigation can be simplified in several ways. First, materials that are not soluble in water will be considered nutritionally irrelevant on the supposition that they are not readily returned to the soil and are quickly diluted to insignificance by the atmosphere, despite the possibility that they may be sufficiently concentrated at the site of a fire to constitute a short-term human health hazard. For example, hydrocarbons are produced both by controlled (i.e., industrial, domestic) combustion (Butcher and Charlson, 1972) and by combustion of agricultural and forest materials (Darley et al., 1966; Gerstle and Kemnitz, 1967; Fritschen, Bovee, and Buethner, 1970). Since most of these compounds are highly insoluble, they are more likely to be photochemically degraded than scrubbed out by rain. Similarly, much emphasis has been directed toward carbon monoxide as a combustion product, but CO is not likely to perturb normal carbon cycling. Although CO is produced by combustion in amounts sufficient to create a local hazard, its general abundance is certain to be much lower than that of CO_2 because it is converted to CO_2 at a steady rate in air (Dimitriades and Whisman, 1971) and probably at soil surfaces as well (Inman, Ingersoll, and Levy, 1971).

Substances of direct nutritional significance which could be liberated by open fires include the major inorganic salts, fixed nitrogen compounds, and soluble organic matter. The mechanisms of release include true volatilization and particulate emission. This study attempts to quantify the total output of soluble substances from litter fires by both mechanisms. The only litter type considered here is that of a mature longleaf pine (*Pinus palustris* Mill.) forest; it should be emphasized that the general combustion properties of other litter types may be considerably different. Some tree species, including longleaf and other pines as well as eucalyptus species, produce an especially combustible litter that apparently evolved as an adaptive mechanism favoring fire, which confers a competitive advantage on these species (Mutch, 1970). Other litter types may

burn more slowly and give off different amounts of volatile and particulate materials.

METHODS

Experimental fires were ignited inside an airtight combustion chamber made of Plexiglas (1.8 by 1.3 by 1.3 m). The walls of the chamber were provided with gas bladders to accommodate the expansion of air during combustion. After combustion and a brief settling period (5 to 10 min), air from the chamber was pumped at a known rate (1 m^3/hr) through a series of three glass extraction columns containing 5 liters each of distilled water. The gas bladders on the chamber collapsed as a predetermined portion of the volatile and fine particulate materials was pumped from the combustion chamber. The water from each of the three extraction columns was then analyzed separately. The efficiency of extraction for each substance was computed from the decrease in its concentration between columns. Retention of materials on chamber walls was assumed to be insignificant.

The conditions of combustion were fixed in that the chamber was closed to outside air currents and the fuels were not sloped. Convection currents caused by the rapid heating of air circulated oxygen over the flame at what was considered to be a realistic rate of airflow for calm weather. Oxygen was, of course, consumed by the flame, but the amount of fuel was always small compared to the total air capacity of the chamber. The amount of fuel was adjusted so that the decrease in dry weight caused by combustion did not exceed 30 g. Calorimetric energy values for pine straw may vary slightly between species, but they average very near 5000 cal/g (Hough, 1969). Thus each fire produced at most 150 kcal of heat. Complete combustion of average biological hydrocarbons (glucose) produces heat at a rate of 114 kcal per mole of O_2 consumed. The amount of oxygen required to burn 30 g of pine straw at STP is that in 29.5 liters of air, which is equivalent at 25°C to 0.15 m^3 of air. Since the capacity of the chamber plus bladders is almost 20 times this figure, oxygen starvation, other than that which would ordinarily occur in the deeper, more poorly ventilated portions of the litter, is not likely.

All chemical determinations on the water from the extraction columns were matched by control runs during which the chamber was flushed of smoke, resealed, and partially emptied into the gas train in a manner analogous to the experimental procedure except that there was no fire. Values reported here are the differences between these control values and the fire treatments, unless otherwise indicated.

Water analysis was initiated immediately after extraction. All samples were filtered onto glass fiber paper that had been ignited in a muffle furnace to remove organics and nitrogen compounds. The samples were analyzed for pH, conductance, Ca^{2+}, Mg^{2+}, K^+, Na^+, SO_4^{2-}, PO_4^{3-}, silicate, NO_3^-, NO_2^-, NH_4^+, and

absorbance spectrum (200 to 900 nm). Cations were measured by atomic absorption, sulfate by the barium turbidometric method (Golterman and Clymo, 1969), and phosphate by an ascorbic acid–molybdate method (Murphy and Riley, 1962). Silicate tests were done by the method of Armstrong and Butler (1962) on unfiltered samples. Nitrate was determined as nitrite after reduction in a cadmium–copper couple (Wood, Armstrong, and Richards, 1967). Ammonia analysis followed a phenolhypochlorite method (Solorzano, 1969). Absorbances were measured in a spectrophotometer with a 10-cm cell.

The composition of burned and unburned litter samples was determined by arc spectrograph for the first 14 elements shown in Table 1, by Kjeldahl digestion for nitrogen, and by sulfur analysis for total sulfur following the method of Jones and Isaac (1972). Dry weights were determined by desiccation in a forced-draft oven (80°C).

TABLE 1

COMPOSITION OF LITTER SAMPLES FROM THE STUDY AREA*

Fraction of dry weight, ppm									
Na	Sr	Ba	B	Al	Mo	Mn	Fe	Cu	Zn
71	15	18	9	1700	8	283	510	9	28

Fraction of dry weight, %					
Ca	Mg	K	P	N	S
0.36	0.23	†	0.10	0.95	0.08

*Each value is the mean of nine determinations.
†Below detection limit.

Litter samples were taken from a mature (~30-year-old) stand of South Carolina longleaf pine. The litter in the collection area was composed almost exclusively of pine needles in various stages of decomposition. The litter was readily separable from a matted duff over the mineral soil. The water content of the litter averaged 20.5% (SD, 8.1%). The dry weight of litter in the collection area was 2.2 kg/m^2 (SD, 0.30 kg/m^2).

The principal set of experiments was conducted on intact soil–litter blocks that were transferred from the field site to the combustion chamber. The blocks were carefully removed after an incision had been made around a square of litter surface measuring about 15 by 15 cm. Exact measurements of block size were made after combustion. Whenever sampling followed a heavy rain, the blocks were allowed to dry in the laboratory for from 1 to 4 days. At the time of an

experiment, a soil–litter block was placed in the center of the chamber and ignited at one point on its surface.

RESULTS AND DISCUSSION

The average composition of the dry litter is indicated in Table 1, and the percent change in its composition due to combustion is shown in Fig. 1. The uppermost needles were completely reduced to ash during combustion, but deeper portions of the litter, which were both wetter and less adequately ventilated, burned incompletely. Reduction of litter weight by combustion averaged 38.5% for the soil–litter blocks. Reliable figures for reduction in weight of litter caused by prescribed fire under field conditions range between 75% (Sweeney and Biswell, 1961) and 26% (Wells, 1971) for pine forests. Percentages may be considerably higher for wildfires. Prescribed winter fire in a pine forest near the site of litter collection reduced the litter weight by 33%

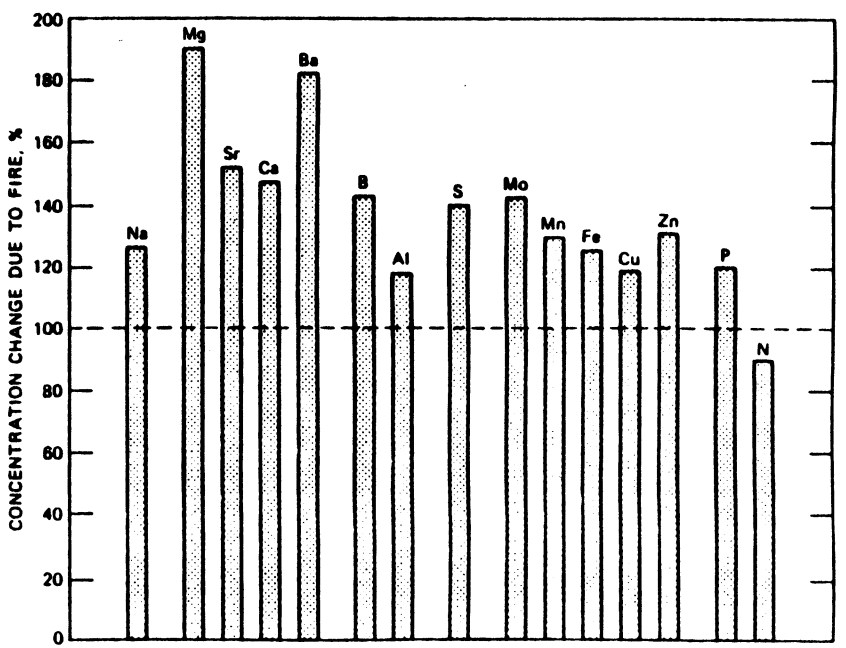

Fig. 1 Changes in elemental composition of the litter due to an experimental fire consuming approximately one-third of the litter. Change is expressed as the ratio of the postfire concentration to the prefire concentration of the elements times 100 (%).

(Lewis, 1974). The reduction in litter weight under experimental conditions therefore conforms with the reduction anticipated for light fires under field conditions.

Figure 1 gives no evidence of gross volatile loss for any element except nitrogen. Apparent concentrations of magnesium and barium are greater than anticipated, probably because of methodological inaccuracies. Pairwise statistical comparison of change in nitrogen with changes in other elements indicates that the decrease in nitrogen concentration due to fire is significant at $\alpha = 0.05$ (nonparametric sign test, $n = 9$, Sokal and Rohlf, 1969). Other elements are concentrated in the postfire litter by an amount approximately equal to the inverse of litter weight loss due to burning. Thus it is clear that the only elements volatilized in amounts that are large compared with the amounts present in litter are C, H, O, and N. Volatile release of small amounts of salts or release of small amounts of soluble compounds attached to particulates cannot be deduced from the litter-composition data but should be detectable in the water extractions.

The effect of combustion products on the pH and conductance of water in the extraction columns is shown in Table 2. The use of three columns proved unnecessary since the extraction of soluble substances was essentially complete

TABLE 2

EXTRACTION DATA AND EFFECT OF COMBUSTION PRODUCTS ON pH AND CONDUCTANCE OF WATER IN EXTRACTION COLUMNS*

	Treatment		Control	
	Col. 1	Col. 2	Col. 1	Col. 2
Ca^{2+}, ppb	8	8	0	8
Mg^{2+}, ppb	12	10	9	9
Na^{2+}, ppb	17	10	7	39
K^{+}, ppb	31	10	19	10
SO_4^{2-}, ppb	380	144	252	116
PO_4^{3-}, ppb	113	37	77	3
Silicate, ppb	80	150	40	100
pH	4.64	5.29	5.46	6.02
CV† for pH, %	1.1	1.0	2.2	1.7
Conductance, μmho/cm	13.38	4.17	3.06	2.08
CV† for conductance, %	9.6	13.7	13.9	10.0

*The amount of air pumped from chamber into columns was 1 m^3; all columns contained 5 liters of water.

†Coefficient of variation.

in the first two columns. Table 2 shows that combustion products markedly lowered the pH of the first treatment column. This effect is attributable to CO_2 produced by combustion and to inorganic acids. The pH of the first control column is also depressed below that of the second control column because of the presence of soluble substances, primarily CO_2, in untreated air, but the effect is much less pronounced than in the treatment columns. Conductance follows the same patterns. Initial conductance of the distilled water was 1.3 to 1.6 μmho/cm.

Major Cations, Sulfate, Phosphate, and Silicate

The extraction data on major cations, sulfate, orthophosphate, and reactive silicate are summarized in Table 2. There is no statistical difference in the concentration of these substances between treatments and controls.

Given the detection limits of the analytical techniques, the amount of litter burned, and the percentage of volatile materials that were passed through the extraction columns, we can calculate the maximum amount of each of the major cations that could have been produced without showing up in Table 2. For calcium, an output of 38 ppm Ca^{2+} from the burned litter is the detection threshold. This is 1.1% of the calcium available in the litter (Table 1). Thus, if inorganic calcium was released in volatile or fine particulate form, it did not exceed 38 ppm of the burned material or 1.1% of the calcium available in the litter. Comparable figures for magnesium are 5 ppm (0.2%), and for sodium, 6 ppm (8.4%). The exact amount of potassium in the litter is known only to be less than 100 ppm. The amounts in fresh litter are ordinarily higher than this, but potassium is leached rapidly from litter (Gosz, Likens, and Bormann, 1973). For present purposes the amount of potassium can be conservatively approximated as 80 ppm. The escape of potassium to air must be less than 24 ppm or, using the approximation, 30% of the available potassium.

The complete absence of detectable levels of cations is somewhat surprising. Measurable cation output has been reported in at least one account of low-temperature combustion (Allen, 1964). Allen gives evidence that measurable amounts of all major cations are lost in smoke from heather fires burning at temperatures that would be within the same general range expected in the fires of my study (550 to 650°C). Since Allen's fires were much more confined than the pine-litter fires described here, he may have included some of the larger particulate material that was allowed to settle in my study. The losses reported by Allen for Ca^{2+} (0.1%) and K^{+} (1.4%) would have gone undetected in the pine-litter study, but a release of Mg^{2+} equivalent to that observed by him (0.4%) should have been detected. The exact conditions of combustion may prove to be important.

It can be shown from the data at hand that amounts of major cations released by light litter fires cannot be significant in comparison with the amounts of ions normally present in rain. The amount of ionic calcium in

continental rain is approximately 0.25 to 0.75 ppm (Gorham, 1961; Gambell and Fisher, 1966; Wells, Whigham, and Lieth, 1972), hence the amount delivered in rain over a year in the South Carolina area averages about 6 kg ha^{-1} $year^{-1}$. This approximation is confirmed by measurements near the study site for the year 1969, during which calcium input by rain was 6.3 kg ha^{-1} $year^{-1}$ (Polisini, Boyd, and Didgeon, 1970). Thus the amount of calcium delivered in rain over a year is about seven times the maximum amount that could have been liberated in the experimental fires. Additional normal delivery of calcium in fallout renders this estimate even more conservative. For magnesium the annual rain input is only about 10% as much as for calcium, or 0.6 kg ha^{-1} $year^{-1}$ (Polisini et al. found 0.9 kg ha^{-1} $year^{-1}$). This is six times the maximum possible release due to light fire. Sodium input is highly variable according to proximity of the sea, but it can be approximated as 0.5 ppm, or 6.0 kg ha^{-1} $year^{-1}$ (Polisini et al. found 3.7 kg ha^{-1} $year^{-1}$). This is 44 times the maximum possible release of sodium. Potassium concentration in rain is roughly 0.2 ppm, which amounts to 2.0 kg ha^{-1} $year^{-1}$ (Polisini et al. found 3.0 kg ha^{-1} $year^{-1}$). This is four times the maximum amount that could have been released under the experimental conditions of this study. Since the annual input of all major cations in rain is considerably above the maximum possible release due to the litter fires, fires of this type are not likely to produce ecologically significant amounts of atmospheric cations.

The small amount of detectable sulfate in the extraction is not surprising considering the rather small amounts of sulfur in pine litter (Table 1). Combustion may have produced some SO_2, which would not necessarily have been detected by the analytical method used. There was an excess of sulfate in the treatments, but the amounts are not quite statistically separable from the controls. If further study validates the amounts reported in Table 2, the total yield of SO_4^{2-} due to fire would be about 20 mg/m^2 or 0.20 kg/ha for conditions similar to the experimental ones. This is far below the annual rain input, which is near 25 kg ha^{-1} $year^{-1}$, or two orders of magnitude greater (Gambell and Fisher, 1966). Amounts such as those recovered from the treatments are not likely to be significant considering the industrial output of sulfur and the amount of sulfur in rain (Johnson, Reynolds, and Likens, 1972).

The presence of detectable orthophosphate is in apparent agreement with the findings of Allen (1964), who reported loss of phosphorus in heather fires. The present data indicate that the amount of phosphorus lost as phosphate is about 0.96 kg/ha, but this figure is not statistically significant. If this proves to be a good estimate, release of phosphorus by litter fires may be ecologically interesting. Very small amounts of phosphorus are delivered in rain, hence any source of atmospheric phosphorus could significantly increase the input from this source. Annual phosphorus delivery in rain, reported by Wells, Whigham, and Lieth, (1972), is 0.28 kg ha^{-1} $year^{-1}$ and, by Polisini, Boyd, and Didgeon (1970), is 0.29 kg ha^{-1} $year^{-1}$. Hence a release of the type obtained in this study

could be equivalent to a 3- to 4-year input by rain. Phosphorous may, of course, have been released in other forms, such as organic complexes, which would not have been detected by the ascorbic acid–molybdate test, and any output by such mechanisms would augment the ecological significance of phosphorus release.

Volatilization of silicate was not expected at all, but it was considered possible that particulate material from fires might give up silicate in measurable amounts. This did not prove to be the case, as indicated in Table 2. The amount of soluble reactive silicate released in fires is no doubt insignificant in view of the concentrations of this substance in surface water and interstitial groundwater.

Nitrogen Compounds

The total amounts of nitrate, nitrite, and ammonia produced by the litter fires are indicated in Table 3. The extraction efficiency for all these compounds was quite high. Averages of 74% of the ammonia, 86% of the nitrite, and 84% of the nitrate were found in the first extraction column.

Combustion of litter under field conditions associated with prescribed burning of pine forests is known to release large amounts of nitrogen, ordinarily comprising some one-fourth to one-half of the total nitrogen in the litter, or 100 to 300 kg/ha of nitrogen (Knight, 1964; Wells, 1971). Knight (1966) has also shown by use of a muffle furnace that volatile loss of nitrogen begins at about 300°C and increases to about 60% at 700°C. It has been generally assumed, largely because of lack of contrary evidence, that most of the nitrogen is released as N_2. DeBell and Ralston (1970), looking for nitrate and ammonia in smoke from pine litter burned in the laboratory, found a small amount of NO_x (0.3%

TABLE 3

TOTAL YIELD OF INORGANIC FIXED NITROGEN FROM COMBUSTION OF PINE LITTER*

	NH_4^+–N	NO_2^-–N	NO_3^-–N	Total N (fixed inorganic)
Kg released/ha†	0.27	1.20	0.00	1.47
% burned litter	0.0032	0.0144	0.0000	0.0176
% burned litter N	0.33	1.50	0.00	1.83
CV,‡ %	19	27		18

*All values are significantly different from controls at $\alpha = 0.05$ (nonparametric signs test), except nitrate.

†The yield per hectare is computed on the basis of 2.2 kg/m^2 of litter and 38.5% combustion.

‡The coefficient of variation (CV) indicates the experimental variability of release.

of nitrogen released) and no ammonia. Fixed nitrogen was therefore considered to be an insignificant by-product of fires.

The results of the present study differ in several important respects from those of DeBell and Ralston. Substantial ammonia was routinely detected in the treatment runs. It seems likely that the ammonia was volatilized at relatively low temperatures in the upper mineral soil or duff, where it would not decompose in the flame, and subsequently escaped into the atmosphere. This could not have happened in the DeBell and Ralston experiments since uniform fuels rather than the soil–litter complex were used. The large amounts of nitrite in the extraction water were also unexpected. Since nitrite and nitrate are lumped by the analytical methods used by DeBell and Ralston, no comparison is possible. That nitrite is, in fact, the principal soluble nitrogen byproduct of the experimental fires in my study is interesting in view of the scarcity of information on nitrite in rain. It is probably possible for nitrite to be converted to nitrate in air (Georgii, 1963).

The nitrate and nitrite released by the fire must be to a large degree derived from the volatile nitrogen oxides known to be produced in varying amounts by the combustion of organic matter. Of the three major oxides (N_2O, NO, NO_2), nitrous oxide (N_2O) is not likely to be involved in nitrate and nitrite production because it is quite inert even in the atmosphere (Robinson and Robbins, 1970).

Both NO and NO_2 are probably produced by litter fires although the relative amounts are not known. The NO produces NO_2 in air at a rate that is markedly dependent on the amount of NO present (Hardison, 1970). Nitrogen dioxide then combines with water in an autoredox reaction that produces equal amounts of nitric and nitrous acids (Hutchinson, 1954). If fixed nitrogen were produced by this mechanism during the experimental fires, we would expect nitrate as well as nitrite to occur in the leach water. Since nitrite was recovered in great amounts and nitrate not at all, it appears that either a more complex set of reactions, leading to nitrite accumulation, occurs in the tubes or that other mechanisms of nitrogen release are involved.

The behavior of the nitrogen oxides in air would presumably be quite different from that in the extraction tubes, although some of the oxides would undoubtedly be scrubbed out by rain. Since the dominant photochemical reactions of the oxides all lead ultimately to the formation of nitrate, nitrite, or ammonia, the nitrogen recovered in the experiments (Table 3) is assumed to be destined for biological use. It is possible that, with the exception of the ammonia, some or all of this fixed nitrogen is "new" in the sense that it may be derived from combination of N_2 with O_2 in the flame rather than from the organic matter itself.

The fixed nitrogen recovered from the litter fire is of ecological significance in view of the limiting effect of nitrogen in many habitats. Although values vary considerably, the average input of ammonia, nitrate, and nitrite in rain in rural areas is very likely to be less than 10 kg ha^{-1} $year^{-1}$ as nitrogen (Eriksson, 1952). Survey values for the continental United States indicate that the average is, in fact, considerably lower. The data given by Junge (1958) suggest a rainfall input of NH_4–N of about 0.2 kg ha^{-1} $year^{-1}$ in the South Carolina region and of NO_3^-–N plus NO_2^-–N of 0.6 kg ha^{-1} $year^{-1}$, for a total of about 0.8 kg ha^{-1} $year^{-1}$. The data summarized by Wells, Whigham, and Leith (1971) suggest a somewhat higher figure, perhaps nearer 2.0 kg ha^{-1} $year^{-1}$, and the value reported by Polisini, Boyd, and Didgeon (1970) is still higher, 5.7 kg ha^{-1} $year^{-1}$. Given the intermediate value of 2.0 kg ha^{-1} $year^{-1}$, the total amount of nitrogen lost to the atmosphere in the experimental litter fires is approximately equivalent to a 40-year rain input of nitrogen. The amount of fixed nitrogen, which is a small portion of the total released in these fires, is equivalent to about two-thirds of the annual rain input.

Because field fires consume more fuel and burn hotter than the experimental fires, it is not unreasonable to expect volatile output of fixed nitrogen to reach 10 times the amount reported here in some cases. Forest fires must therefore be considered a significant element in producing regional and probably global supplies of fixed nitrogen in the atmosphere, but it hardly seems possible from the data at hand that fires can be the dominant atmospheric source of these compounds.

Soluble Hydrocarbons

The water from the first extraction column in the treatment series always showed a marked light absorbance at short wavelengths, principally in the near ultraviolet range. It was concluded that the compounds responsible for this effect must be highly soluble since the effect was barely detectable in the second column of the series. The absorbance spectra of the water from the first treatment and first control columns are shown in Fig. 2. The only potential cause for the absorbance other than organic matter is nitrite. Laboratory tests with solutions of 100 ppb NO_2^- gave an absorbance due to nitrite of 0.021 at 300 nm (10-cm cell). Considering the concentrations of nitrite present in the first treatment column, we would predict an average absorbance of 0.032 at 300 nm, but the observed absorbance is actually about triple this amount (Fig. 2). It is evident from these data that organic matter is responsible for most of the absorbance in the water of the first treatment column.

The organic compounds causing absorbance have not yet been identified, but they are probably of low molecular weight since the larger compounds known to be produced by combustion of plant matter (e.g., terpenoids) are for the most part insoluble. The compounds produced during combustion may prove to be insignificant in comparison with the amounts of organics routinely released by plants (Went, 1960), or they may be significant as carriers of limiting nutrients, such as phosphorus or nitrogen.

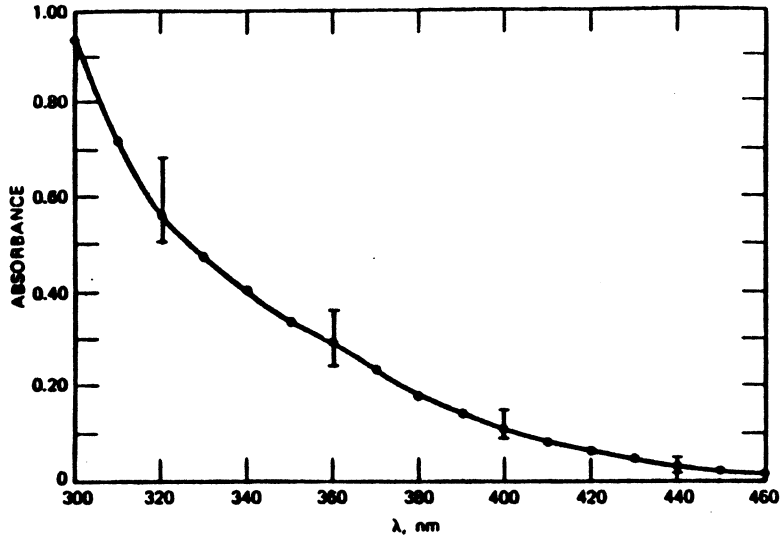

Fig. 2 Absorbance spectra (10-cm cell) of water from the first treatment extraction columns. The range of values is indicated for selected points along the curve (N = 4). Absorbance of control columns over the same range was effectively zero (<0.05).

CONCLUSIONS

Fires of the type described here are not significant ecological sources of major cations or sulfate in air. The atmospheric links of the nitrogen cycle and possibly of the phosphorous cycle as well are affected by open burning of forest materials, however. Thus forest fires may be a prehistoric and modern source of atmospheric nutrients. Although the delivery of nutrients in rain over a year is, in general, far exceeded by the total inventory of nutrients in the standing crop, the steady supply via rainfall can, over long time spans, play an important role in determining the nutrient inventory of the standing crop. Since the mobility of numerous nutrients is being radically changed by man, it is presently of great interest to determine which nutrient supply factors are most important in both natural and altered systems, and fire would seem to deserve more consideration in this context.

ACKNOWLEDGMENT

The research reported here was supported by U. S. Atomic Energy Commission contract AT(38-1)-819 and was conducted at the Savannah River Ecology Laboratory, Aiken, S. C.

REFERENCES

Allen, S. E., 1964, Chemical Aspects of Heather Burning, *J. Appl. Ecol.*, 1: 347-367.

Armstrong, F. A. J., and E. I. Butler, 1962, Chemical Changes in the Sea Water off Plymouth During 1960, *J. Mar. Biol. Ass. U.K.*, 42: 253-258.

Butcher, S. S., and R. J. Charlson, 1972, *An Introduction to Air Chemistry*, Academic Press, Inc., New York.

Darley, E. F., F. R. Burleson, E. H. Mateer, J. T. Middleton, and V. P. Osterli, 1966, Contribution of Burning of Agricultural Wastes to Photochemical Air Pollution, *J. Air Pollut. Contr. Ass.*, 11: 685-690.

DeBell, D. S., and C. W. Ralston, 1970, Release of Nitrogen by Burning Light Forest Fuels, *Soil Sci. Soc. Amer., Proc.*, 34: 936-938.

Dimitriades, B., and M. Whisman, 1971, Carbon Monoxide in Lower Atmosphere Reactions, *Environ. Sci. Technol.*, 5: 219-222.

Eriksson, E., 1952, Composition of Atmospheric Precipitation. I. Nitrogen Compounds, *Tellus*, 3: 215-232.

Fritschen, L., H. Bovee, and K. Buethner, 1970, Slash Fire and Atmospheric Pollution, Research Paper PNW-97, Pacific Northwest Forest and Range Experiment Station, Forest Service, U. S. Department of Agriculture.

Gambell, A. W., and D. W. Fisher, 1966, Chemical Composition of Rainfall in Eastern North Carolina and Southeastern Virginia, Water-Supply Paper 1535-K, U. S. Geological Survey.

Georgii, H. W., 1963, Oxides of Nitrogen and Ammonia in the Atmosphere, *J. Geophys. Res.*, 68: 3963-3971.

Gerstle, R. W., and D. A. Kemnitz, 1967, Atmospheric Emissions from Open Burning, *J. Air Pollut. Contr. Ass.*, 17: 324-327.

Golterman, H. L., and R. S. Clymo, (Eds.), 1969, *Methods for Chemical Analysis of Fresh Waters*, International Biological Program Handbook No. 8, Blackwell Scientific Publications, Oxford.

Gorham, E., 1961, Factors Influencing Supply of Major Ions to Inland Waters, with Special Reference to the Atmosphere, *Geol. Soc. Amer., Bull.*, 72: 795-840.

Gosz, J. R., G. E. Likens, and F. H. Bormann, 1973, Nutrient Release from Decomposing Leaf and Branch Litter in the Hubbard Brook Forest, New Hampshire, *Ecol. Monogr.*, 43: 173-191.

Hardison, L. C., 1970, Techniques for Controlling the Oxides of Nitrogen, *J. Air Pollut. Contr. Ass.*, 20: 377-382.

Hough, W. A., 1969, Caloric Value of Some Forest Fuels of the Southern United States, Research Note SE-120, Southeastern Forest Experiment Station, Forest Service, U. S. Department of Agriculture.

Hutchinson, G. E., 1954, The Biochemistry of the Terrestrial Atmosphere, in *The Earth as a Planet*, The Solar System Series, Vol. 2, G. P. Kuiper (Ed.), pp. 371-433, University of Chicago Press, Chicago.

Inman, R. E., R. B. Ingersoll, and E. A. Levy, 1971, Soil: A Natural Sink for Carbon Monoxide, *Science*, 172: 1229-1231.

Johnson, N. M., R. C. Reynolds, and G. E. Likens, 1972, Atmospheric Sulfur: Its Effect on the Chemical Weathering of New England, *Science*, 177: 514-516.

Jones, J. B., and R. A. Isaac, 1972, Determination of Sulfur in Plant Material with a Leco Sulfur Analyzer, *J. Agr. Food Chem.*, 20: 1292-1294.

Junge, C. E., 1958, The Distribution of Ammonia and Nitrate in Rain Water over the United States, *Trans. Amer. Geophys. Union*, 39: 241-248.

Knight, H. A. W., 1966, Loss of Nitrogen from the Forest Floor by Burning, *Forest. Chron.*, 42: 149-152.

—, 1964, Some Effects of Slash Burning and Clearcut Logging on Soil Properties and Initial Tree Growth, Ph. D. Thesis, University of Washington, Seattle.

Lewis, W. M., Jr., 1974, Effects of Fire on Nutrient Movement in a South Carolina Pine Forest, *Ecology*, 55: 1120-1127.

Murphy, J., and J. P. Riley, 1962, A Modified Single Solution Method for the Determination of Phosphate in Natural Waters, *Anal. Chim. Acta*, 27: 31-36.

Mutch, R. W., 1970, Wildland Fires and Ecosystems—A Hypothesis, *Ecology*, 51: 1046-1051.

Polisini, J. M., C. E. Boyd, and B. Didgeon, 1970, Nutrient Limiting Factors in an Oligotrophic South Carolina Pond, *Oikos*, 21: 344-347.

Robinson, E. and R. C. Robbins, 1970, Gaseous Nitrogen Compound Pollutants from Urban and Natural Sources, *J. Air Pollut. Contr. Ass.*, 20: 303-306.

Solorzano, L., 1969, Determination of Ammonia in Natural Waters by the Phenolhypochlorite Method, *Limnol. Oceanogr.*, 14: 799-801.

Sokal, R. R., and F. J. Rohlf, 1969, *Biometry*, the Principals and Practice of Statistics in Biological Research, W. H. Freeman and Company, San Francisco.

Sweeney, J. R., and H. H. Biswell, 1961, Quantitative Studies of the Removal of Litter and Duff by Fire Under Controlled Conditions, *Ecology*, 42: 572-575.

Wells, C. G., 1971, Effects of Prescribed Burning on Soil Chemical Properties and Nutrient Availability, Prescribed Burning Symposium Proceedings, pp. 86-97, Southeastern Forest Experiment Station, Asheville, N. C., Forest Service, U. S. Department of Agriculture.

Wells, C. G., D. Whigham, and H. Lieth, 1972, Investigation of Mineral Nutrient Cycling in an Upland Piedmont Forest, *J. Elisha Mitchell Sci. Soc.*, 88: 66-78.

Went, F. W., 1960, Blue Hazes in the Atmosphere, *Nature*, 187: 641-643.

Wood, E. D., F. A. J. Armstrong, and F. A. Richards, 1967, Determination of Nitrate in Sea Water by Cadmium–Copper Reduction to Nitrite, *J. Mar. Biol. Ass. U.K.*, 47: 23-31.

CATION FLUX IN HARDWOOD AND WHITE PINE WATERSHEDS

G. RONNIE BEST* and CARL D. MONK†
*Department of Botany and †Institute of Ecology,
University of Georgia, Athens, Georgia

ABSTRACT

The nutrient content of precipitation input, throughfall, litter flow through, soil percolation, and stream discharge was measured in a hardwood and in a white pine watershed. Amounts of water passing through various levels of the forest ecosystems changed markedly from input to output, and leaching of cations from vegetation exhibited pronounced seasonal changes. Leaching of potassium, calcium, and magnesium was least during dormant winter months but increased with commencement of spring growth. Most potassium was leached from the leaves before leaf fall, but most calcium and magnesium losses occurred after leaf fall. A reduction of sodium in throughfall during the summer months was evident in white pines. The total leachate loss from vegetation was greatest for potassium and least for sodium; magnesium and calcium losses were intermediate. Once the water became streamflow discharge, the cation load was similar to its original input level, giving evidence of the ability of the ecosystem to minimize external loss while maintaining a large internal flux.

The two major sources of cation input to a terrestrial first-order watershed ecosystem are (1) atmospheric input and (2) weathering of bedrock material. Atmospheric input may enter the system in the form of snow, sleet, rain, hail, or dry precipitation. When we consider nutrient cycles, we assume that any loss from a stable ecosystem which is not re-supplied by atmospheric input is restocked by rock weathering (Johnson et al., 1968). Rock weathering releases some elements that become bound on exchangeable sites in secondary minerals and others that are made available to the ecosystem in the form of soluble ions.

Atmospheric input of most cations shows seasonal, or slightly seasonal, variations. The seasonal aspect of input derives from the release, in the form of dust, of the free cations by agricultural practices; this yields concentrations high in the summer and low in the winter (Gambell and Fisher, 1966; Fisher, 1968).