Environmental Pollution **74** (1991) 325–343

Combined Use of Open-Air and Indoor Fumigation Systems to Study Effects of SO_2 on Leaching Processes in Scots Pine Litter

P. A. Wookey*

Institute of Environmental and Biological Sciences, Division of Biological Sciences, University of Lancaster, Bailrigg, Lancaster LA1 4YQ, UK

&

P. Ineson

Merlewood Research Station, Institute of Terrestrial Ecology, Grange-over-Sands, Cumbria LA11 6JU, UK

(Received 13 November 1990; revised version received 28 April 1991; accepted 30 April 1991)

ABSTRACT

*Both an open-air fumigation system and a laboratory-based system were used to expose decomposing Scots pine (*Pinus sylvestris *L.) needles to controlled concentrations of SO_2 (arithmetic mean ≤ 48 nl litre^{-1}) during a period, in total, of 301 days. The experimental design involved reciprocal litter transplants from 'clean' to 'polluted' air and vice versa, using the two fumigation systems. The objectives were (1) to observe the effects of SO_2 on leachate and litter chemistry, (2) to assess whether pollution-induced changes are reversible in clean air, and (3) to test the suitability of small-scale fumigation chambers (litter microcosms) compared with open-air systems in soil studies.*

Through the formation of SO_4^{2-} ions, dry-deposited SO_2 exhibited a marked capacity to remove 'base' cations (Ca^{2+}, Mg^{2+} and K^+) from decomposing pine needles, and also to acidify litter leachates (as indicated by proton fluxes from the litter). When litter was transferred from polluted air (48 nl litre^{-1} SO_2, in the open-air system) to either clean or

* Present address: Merlewood Research Station, Institute of Terrestrial Ecology, Grange-over-Sands, Cumbria LA11 6JU, UK.

Environ. Pollut. 0269-7491/91/$03.50

polluted air in the laboratory, the effects of prior exposure to SO_2 on leachate composition were still evident even after 86 days: the role of base cation depletion within the litter, caused by SO_4^{2-} -induced leaching, is discussed.

Data for SO_4^{2-} fluxes in leachates collected from the small-scale chambers indicated that dry deposition velocities for SO_2 were not anomalously high within this fumigation system. It is therefore concluded that microcosm studies can provide information complementary to the open-air fumigation approach in soils research.

INTRODUCTION

Dry deposition of SO_2 has been implicated as a major factor contributing to the acidification of soils and freshwater systems in Europe (van Breemen *et al.*, 1984; Paces, 1985), and there is now a wealth of data emphasizing the quantitative significance of dry deposition, relative to wet ('acid rain'), over considerable areas closer to emissions sources (Moss, 1978; UK Review Group on Acid Rain, 1987; Williams *et al.*, 1989). Indeed, the United Kingdom Review Group on Acid Rain (1987) has stated that, in broad terms, dry deposition may exceed wet in those regions where atmospheric SO_2 concentrations exceed 3·8 nl litre^{-1}. The data of EMEP (1984), and Williams *et al.* (1989), provide clear evidence that this concentration has been exceeded over much of central Europe (mainly in Germany, The Netherlands and western regions of Czechoslovakia) and central and eastern England.

Unfortunately, the major significance of dry-deposition fluxes to terrestrial ecosystems has not prompted an equivalent research effort. There have thus been few attempts to determine, in controlled experiments, whether the dry deposition of pollutant gases (notably SO_2 and NO_2) directly to litter and soils could have a significant ecological impact. Experiments are needed, none the less, in order to better understand the relationship between specific concentrations of atmospheric SO_2, deposition fluxes, and the associated acidification reactions.

Dry-deposited SO_2 has a greater capacity to cause acidification than an equivalent input of wet-deposited sulphur (as sulphate) in acid rain. This arises because inputs of gaseous SO_2 to terrestrial or freshwater ecosystems carry no neutralizing capacity, this being in contrast to the situation with wet-deposited SO_4^{2-}. The sulphate component of acid rain is balanced not only by H^+, but also by 'base' cations such as Ca^{2+} and K^+ (EMEP, 1984; Lindberg *et al.*, 1986). The presence of NH_4^+ ions in rainfall, though contributing to neutralization, may ultimately represent an

input of acidity to soil systems upon oxidation to NO_3^- (van Breemen *et al.*, 1984).

Fluxes of SO_2 to forested ecosystems remain a subject of intense debate. Particular attention has focussed on canopy interactions, and the relative significance of foliar leaching and dry deposition to the sulphur content of canopy throughfall (Lindberg & Garten, 1988; Gay & Murphy, 1989; Puckett, 1990). The major significance of dry deposition to forest canopies, both to external plant surfaces and via the stomata, does not, however, indicate that dry-deposited SO_2 has only limited impacts on forest soils; indeed, Garland and Branson (1977) stressed that much of the sulphur dry-deposited to canopies 'must eventually reach the forest floor as sulphate'.

The research described in this paper relates specifically to the effects of dry-deposited SO_2 on chemical events occurring in Scots pine (*Pinus sylvestris* L.) litter. In this study, decomposing pine needles were exposed to controlled SO_2 concentrations, first in an open-air and then subsequently in a laboratory-based fumigation. The results of the open-air experiment are described in full elsewhere (Wookey *et al.*, 1991; Wookey & Ineson, in press), although they are outlined briefly here because they are of central importance for the interpretation of the laboratory studies.

In the open-air experiment decomposition processes—both biotic (performed by decomposer organisms) and abiotic (aqueous leaching processes involving ion exchange reactions)—were altered by exposure to SO_2 concentrations (arithmetic mean values of 15 nl litre^{-1} the lowest concentrations tested) similar to those known to occur over substantial areas of industrialized Europe (see Martin, 1980; Lefohn & Mohnen, 1986; Ling & Ashmore, 1987). The most notable observations included a marked reduction in microbial respiration (an index of catabolic processes), greater acidification of decomposing pine needles and an increased leaching loss of the divalent cations Ca^{2+} and Mg^{2+} in association with higher SO_2 concentrations. The leaching of divalent cations occurred in response to enhanced SO_4^{2-} leaching.

The very marked effects of SO_2 on decomposition processes, as demonstrated in the open-air fumigation experiment, prompted a laboratory-based fumigation study which sought: (1) to complement the open-air studies by providing information on *cumulative* fluxes of SO_4^{2-}, H^+, Ca^{2+}, Mg^{2+} and K^+ from pine litter over time (the open-air studies described above only provide instantaneous measurements of fluxes); (2) to evaluate the changes in chemical composition of leachates when litter was moved from 'polluted' to 'clean' air; and (3) to indicate whether the kinds of results obtained during open-air studies could also be obtained under artificial conditions in the laboratory. Open-air fumigation systems are

costly to build and maintain, and few such systems exist; the possibility of using smaller-scale, and considerably less complex, laboratory-based systems to complement results from open-air studies is therefore attractive.

In the study described here these questions were considered by collecting pine litter from the open-air fumigation system after 215 days of exposure to either ambient ('control') air, or air to which additional SO_2 had been added ('polluted'). Each of these two litter samples was then subdivided and subsequently exposed to either charcoal-filtered air or to artificially polluted air—with similar arithmetic mean SO_2 concentrations to the open-air 'polluted' treatment—in a laboratory-based fumigation system.

MATERIALS AND METHODS

Open-air fumigation of Scots pine needle litter

A full technical description of the open-air fumigation system can be found in McLeod *et al.* (1991). The system was designed, constructed and maintained by staff of the Central Electricity Research Laboratory (now the National Power Technology and Environmental Centre (NPTEC), Leatherhead, UK, and was sited at the Institute of Horticultural Research, Littlehampton, Sussex. The system consisted of four field plots, one receiving ambient SO_2 exposure (generally less than 10 nl litre^{-1} as an annual mean). The remaining three plots contained dispersion pipework to allow enrichment of the atmosphere immediately above them with SO_2.

Scots pine (*Pinus sylvestris* L.) litter, for use in the open-air fumigation, was collected from the litter (L) layer of the forest floor in a 32-year-old stand at Gisburn Forest, Lancashire (G.R. SD 750588). This was then air-dried prior to transportation and placement at the open-air site (see Wookey *et al.*, 1991 for full details of procedures). The pine litter was exposed to the four contrasting SO_2 regimes for a period of 215 days in total.

Litter collected from the open-air site was analyzed for rates of CO_2 release (microbial respiration) (Wookey *et al.*, 1991), chemistry of leachates, and needle calcium, magnesium, potassium and nitrogen contents (Wookey & Ineson, in press).

Transfer of *Pinus sylvestris* litter from the open-air fumigation experiment to the laboratory-based fumigation system

The first litter set was removed from the ambient (control) plot and had been exposed to a mean SO_2 concentration of 7 nl litre^{-1}. The other set

came from the plot with the highest arithmetic mean concentration of SO_2, 48 nl litre^{-1}.

Each of the two litter samples was used to prepare six 'microcosm chambers' (Fig. 1), based on the design of Anderson and Ineson (1982). Six chambers thus contained pine needles from the ambient open-air plot, and six contained needles from the 48 nl litre^{-1} SO_2 plot. The microcosm chambers were designed to allow decomposition processes to be studied under carefully controlled environmental conditions. Such chambers proved appropriate both for SO_2 fumigation work, and also the examination of leachate solutions, without causing undue disturbance of the decomposing litter. The microcosm system also enabled experimental treatments to be replicated.

Fresh litter was used for the microcosms, although the equivalent oven-dry weights—estimated by drying subsamples of litter and then applying the appropriate conversion factor—ranged from 1·46 to 1·94 g per microcosm. Once filled with litter, each of the microcosm chambers was thoroughly moistened with a 100 ml aliquot of deionized water, which was then allowed to drain away, before being connected to the laboratory-based fumigation system (described in full in Wookey *et al.*, 1991).

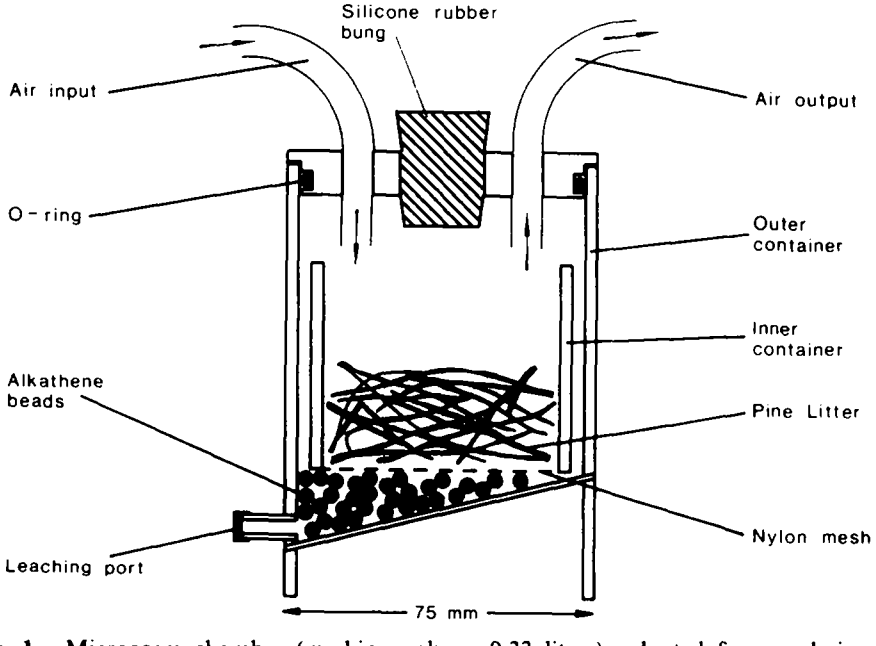

Fig. 1. Microcosm chamber (working volume 0·33 litres), adapted from a design by Anderson and Ineson (1982), and constructed principally from clear perspex sheet and cylinders. Twelve such microcosm chambers were used for the laboratory-based fumigation. During fumigation the leaching port remained sealed.

TABLE 1
Outline of the SO_2 Concentrations to which *P. sylvestris* Needles were exposed in the Open-Air Fumigation and Subsequently the Laboratory System

Treatment identity	*Abbreviation*	*No. of replicate microcosms*	*SO_2 concentration (nl litre^{-1})*	
			For 215 days in open-air fumigation	*For 86 days in laboratory based system*
Control–control	CC	3	7	2
Control–polluted	CP	3	7	47[a]
Polluted–control	PC	3	48	2
Polluted–polluted	PP	3	48	47[a]

[a] In the laboratory system the SO_2 supply was switched *off* for 19% of the time (for the collection of leachates, and for other analyses). The SO_2 concentration quoted here is the arithmetic mean value only for the period during which the SO_2 supply was *on* (70 out of 86 days). When the value is recalculated to show mean SO_2 concentration during the complete 86 day period the figure becomes 38 nl litre^{-1}.

Table 1 provides a summary of the SO_2 regimes, both in the open-air fumigation system and in the laboratory-based system, to which the Scots pine litter was exposed. Of the six microcosms containing litter exposed to 7 nl litre^{-1} SO_2 in the open air, three were subsequently placed in the 'SO_2-free' (control) airstream (corresponding to treatment 'CC'), the other three were exposed to an airstream containing a mean of 47 nl litre^{-1} SO_2 (treatment 'CP'). Of the six microcosms containing litter exposed to 48 nl litre^{-1} SO_2 in the open air, three were placed in the SO_2-free airstream (treatment 'PC'), and the other three were exposed to 47 nl litre^{-1} SO_2 (treatment 'PP').

The laboratory-based fumigation system

The air supply entering the laboratory-based fumigation system (5·2 litre min^{-1} of outside air) was filtered through activated charcoal (8/12 mesh), contained within a column, 445 mm long and 65 mm diameter, and subsequently humidified by bubbling through deionized water. The airstream was then split into 13, and SO_2 was added to the six 'polluted' airstreams to give the desired concentration (Wookey *et al.*, 1991). Of the seven 'SO_2-free' airstreams, one was passed through an empty 'reference' microcosm chamber in order to provide a 'blank' for analytical purposes.

All 13 microcosms were housed within an incubator (15·8 °C) and air-

flow rates through each of them were maintained at *c.* 0·4 litre min^{-1}. A Meloy Model SA 185-2 flame photometric detection sulphur analyzer (Meloy Laboratories Inc., Springfield, VA) was used to measure SO_2 concentrations of air entering each microcosm chamber. This was calibrated using sulphur hexafluoride (SF_6) in air (BOC Special Gases, London) at a concentration of 85 nl $litre^{-1}$.

Sulphur dioxide concentrations for the laboratory-based system (see Table 1) were monitored at the *input* to the microcosms, since this was the sampling point at which effective control could best be exerted. In view of the small volume of the microcosm chambers (0·33 litre working volume), the authors consider that input concentrations were appropriate, although with larger chambers, in which the air is also well mixed, it is generally accepted that *output* concentrations are most representative of conditions within the chamber (Koziol, 1980; Unsworth & Mansfield, 1980).

The laboratory-based component of the SO_2 fumigation commenced two days after the litter microcosms were established and lasted exactly 12 weeks thereafter; leachates were collected for chemical analyses every two weeks. During leachate collection each microcosm in turn was disconnected from the fumigation system, the silicone bung removed from the lid (Fig. 1) and the litter then flooded with 100 ml of deionized water. The resulting leachates were removed via the leaching port and retained for chemical analyses. SO_4^{2-} was analyzed by chemically suppressed ion chromatography (Dionex), H^+ (pH) using a combination electrode, Ca^{2+} and Mg^{2+} by atomic absorption spectrophotometry, K^+ by flame emission spectrophotometry, and NH_4^+-N using an auto-analyzer (Berthelot reaction). Fluxes of ions from the litter were expressed as μ-equivalents leached g^{-1} litter. Analyses were confined to litter leachates only and did not include an examination of the litter material itself.

During the course of the fumigation, the needles in the microcosms were occasionally moistened with small and equal-measured aliquots of deionized water, to prevent excessive drying. SO_2 concentrations were, as far as possible, held constant, this being in marked contrast to the situation in the open-air fumigation where the large temporal fluctuations in SO_2 concentrations better represented the situation in the polluted environment (McLeod *et al.*, 1985). SO_2 concentrations during the laboratory-based fumigation were, as far as possible, monitored daily and adjusted when necessary.

RESULTS AND DISCUSSION

Results are presented graphically in Figs 2–4. Statistical significance of the data was assessed by means of one way analysis of variance and

Tukey's comparison of means test for each sampling occasion. The leachate compositions for day zero have been taken from results for the second sampling date (11 July 1986) of the open-air experiment (see Wookey & Ineson, in press).

Figures 2 and 3 show SO_4^{2-} leaching from the pine needles during the laboratory-based fumigation. At day zero, two days before the SO_2 was switched on, the quantity of SO_4^{2-} leached from needles previously exposed to 48 nl litre^{-1} SO_2 in the open-air amounted to four times as much as was leached from needles exposed to 7 nl litre^{-1} SO_2 (ambient air). However, 14 days after the start of fumigation (day 16) sulphate release from 'CP' needles had risen sharply to match that of the 'PP' needles. Subsequently, leaching was high from all the microcosms exposed to 47 nl litre^{-1} SO_2 in the laboratory-based system.

If not immobilized by microorganisms, SO_2 deposited to leaf litter and soils will ultimately oxidize to SO_4^{2-} under moist conditions (Lockyer

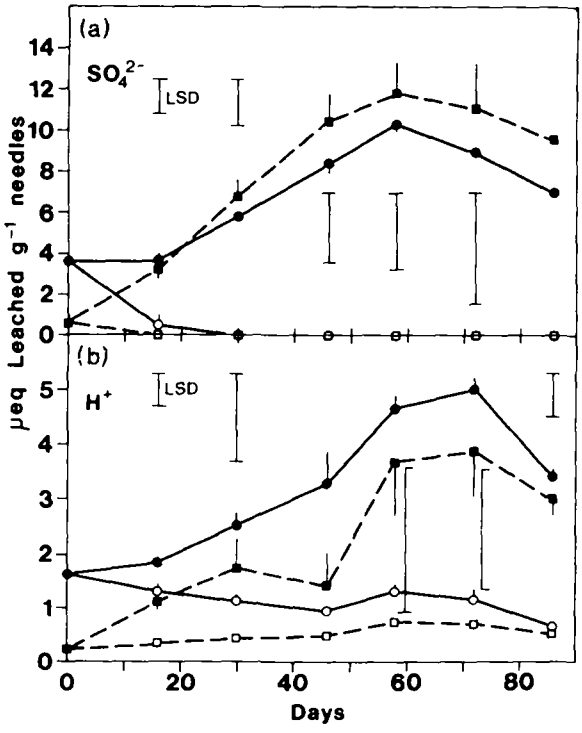

Fig. 2. Leachate composition of *P. sylvestris* needles (μ-equivalents leached g^{-1} needles) plotted against time (days) since the beginning of the laboratory-based fumigation experiment. Means (± 1 standard error) are joined by lines. Statistical significance indicated by least significant difference (LSD), Tukey's comparison of means test ($P < 0{\cdot}05$). Treatments: CC, □; CP, ■; PC ○; PP, ●.

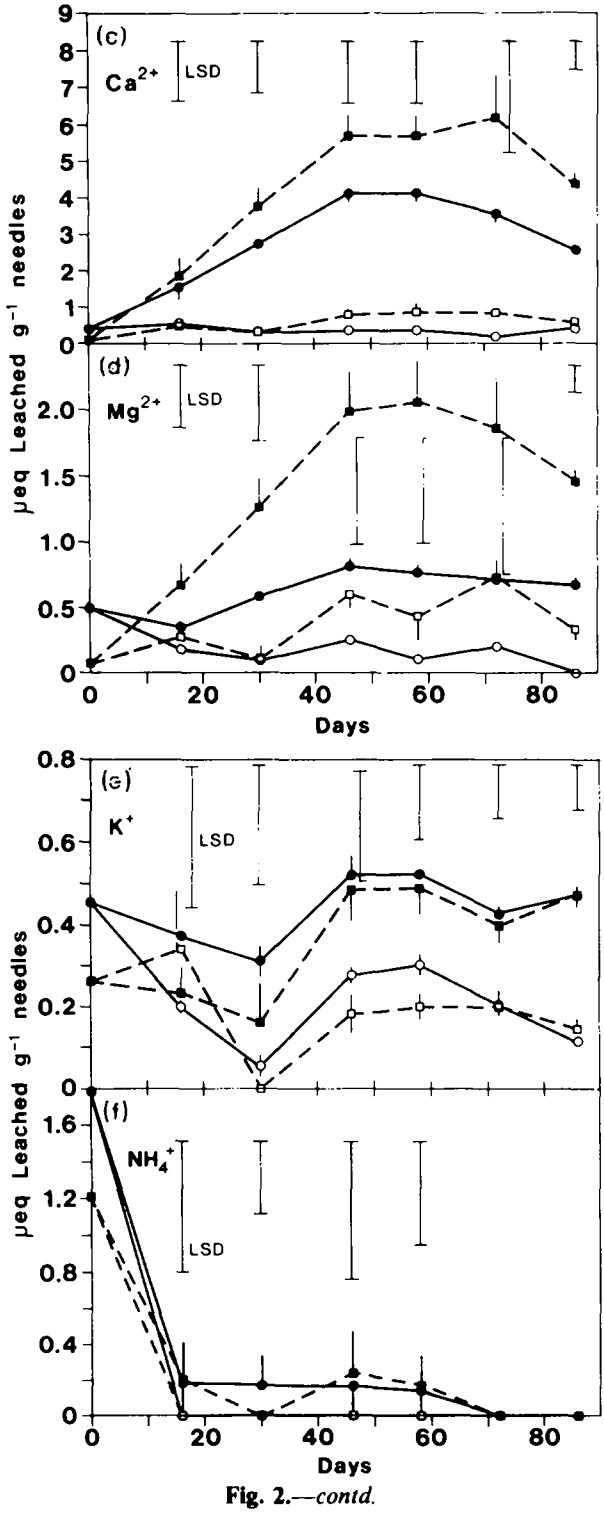
(c)
Ca^{2+}
LSD
(d)
Mg^{2+}
LSD
µeq Leached g^{-1} needles
Days
(e)
K^+
LSD
(f)
NH_4^+
LSD
µeq Leached g^{-1} needles
Days

Fig. 2.—*contd.*

et al., 1978; Lettl, 1984). Chemical transformations leading to sulphate formation in aqueous phase have been considered by Brimblecombe (1978), Davies (1979), Babich and Stotzky (1980) and Cape (1984). The subsequent fate of SO_4^{2-} ions, originating from both wet and dry deposition from the atmosphere, is of central importance in understanding acidification reactions both in soils and in freshwater ecosystems (Tamm, 1976; Krug & Frink, 1983; Abrahamsen, 1984; Johnson & Reuss, 1984; Morrison, 1984; Reuss *et al.*, 1987).

No sulphate (or rather quantities below the analytical detection limit of 1·1 μ-equivalents g^{-1} litter) was leached from pine needles exposed to

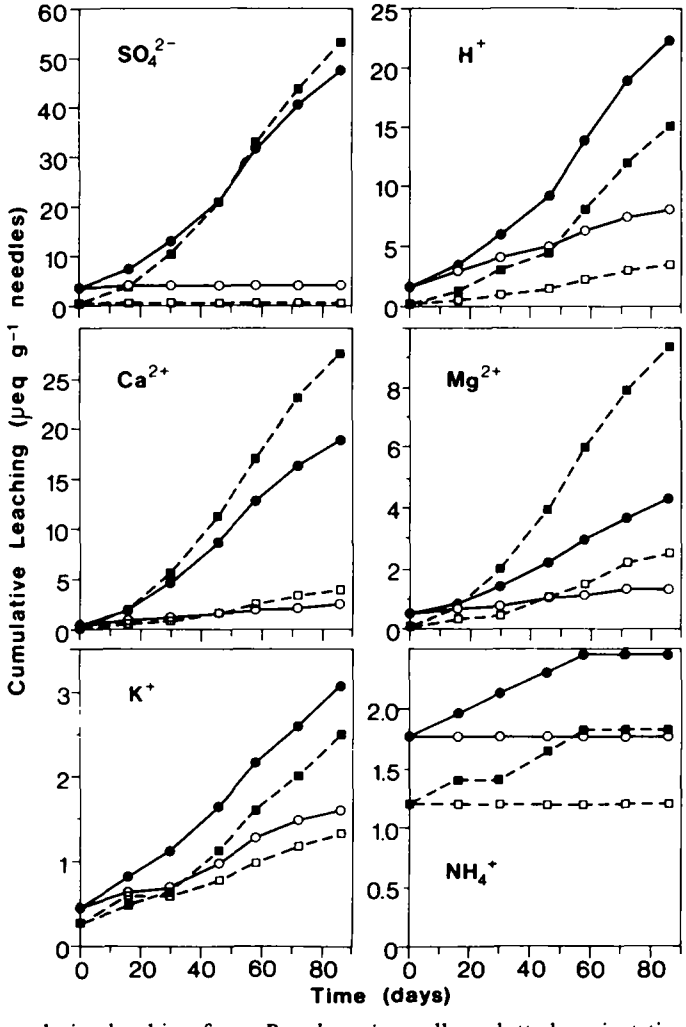

Fig. 3. Cumulative leaching from *P. sylvestris* needles, plotted against time (days) since the beginning of the laboratory experiment. Treatments as for Fig. 2.

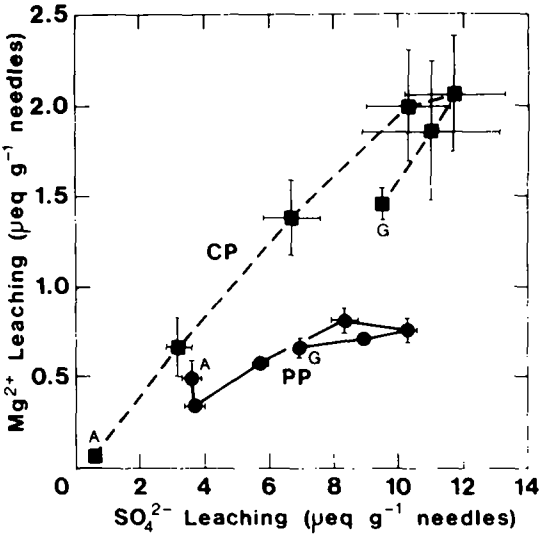

Fig. 4. Mg^{2+} leaching plotted against SO_4^{2-} leaching for CP (■); and PP (●) treatments. Means (± 1 standard error) are joined by lines. The points marked 'A' show leachate composition at the start of the laboratory-based fumigation, while those marked 'G' show the final values.

'SO_2-free' air (actually 2 nl litre ^{1} SO_2) in the laboratory system, with the exception of the PC needles which still lost a small amount of residual SO_4^{2-} up to day 16. These results suggest that microbial mineralization of organically bound sulphur in the pine needles did not contribute significantly to leachate SO_4^{2-} fluxes during the course of this experiment.

The general increase in SO_4^{2-} leaching from needles exposed to 47 nl litre^{-1} SO_2 in the laboratory (CP and PP) compared with needles exposed to 48 nl litre^{-1} in the open-air fumigation (leaching on day 0 for PC and PP needles) may be explained by the contrasting nature of environmental regimes and sampling procedures in the open air and in the microcosm chambers. Needles exposed to SO_2 in the open will have been 'leached' naturally by rainfall, which much of the dry-deposited sulphur present on the needle surfaces prior to any rainfall event presumably being removed in the percolating rainwater. Thus, in the open air the amount of SO_4^{2-} leached from the needles at any particular time will be a function not only of the recent deposition flux but also of the time elapsed since the last rainfall event. Since the sampling dates for the open-air fumigation were not chosen with respect to rainfall, the amounts of SO_4^{2-} leached from the needles therefore indicate *relative* differences between SO_2 regimes only, and do not represent absolute fluxes to the needles, being valid only for a particular moment in time.

The laboratory system contrasted in two ways with the open-air system. First, needles in microcosm chambers were not exposed to rain-washing events. Needles were moistened regularly between leachate collections with small aliquots of deionised water (to prevent excessive drying), but this treatment was considered insufficient, relative to a rainfall event, to wash a significant amount of SO_4^{2-} from the needle surfaces (quantities of deionized water were selected to avoid accumulation of excess liquid at the base of microcosms). Thus, in the laboratory, the surfaces of needles exposed to SO_2 will have been in contact with contrasting absolute concentrations and temporal patterns of SO_4^{2-} relative to needles exposed in the open air. Only the fortnightly leaching with deionized water could have simulated the type of SO_4^{2-} removal associated with a rainfall event. The second major difference concerns the fact that values for SO_4^{2} leaching obtained from the laboratory fumigation represented SO_4^{2} production over the whole of the time period which had elapsed since the previous leaching. It is therefore possible that leachate sulphate fluxes from the litter could provide an indication of the dry-deposition fluxes of SO_2, although the possibility of microbial mineralization of organically bound sulphur in the litter contributing to the leachate SO_4^{2-} should not be overlooked.

The oxidation of SO_2 to SO_4^{2-}—the mobile anion of a strong acid (Reuss *et al.*, 1987)—can be expected to have profound implications for a number of chemical reactions occurring at litter surfaces, and also lower down a soil profile. The generation of SO_4^{2-} will tend to promote acidification reactions by encouraging the formation of H^+ ions (protons) to maintain charge balance (Nyborg, 1978; van Breemen *et al.*, 1984; Paces, 1985). These protons can then enter into exchange reactions with cations held on negatively charged sites in litter layers of mineral soil. 'Base' cations such as Ca^{2+}, Mg^{2+}, Na^+ or K^+, or the 'acid' cations Al^{3+}, which are electrostatically bound to organic or mineral particles, can thus be released into solution and made available for leaching. This provides a means for buffering H^+ ions associated with anions in solution: the existence of such cation exchange processes can be clearly demonstrated in the present study by comparing the results for sulphate leaching, expressed on a charge equivalence basis, with those for the leaching of base cations, and also protons.

Sulphate present in litter leachates was not entirely balanced in charge by an equivalent formation of protons. Indeed, proton formation balanced less than half the SO_4^{2-}, the remainder of the positive charge being provided principally by the cations Ca^{2+}, Mg^{2+}, K^+ and NH_4^+ (Figs 2 and 3).

Leaching rates of the divalent cations during the laboratory-based fumigation reflected not only the SO_2 concentration of the air but also

the 'pool size' of the element in question. On an equivalence basis, Ca^{2+} was the most significant cation. If the calcium content of the needles, after 215 days of exposure to 7 nl litre^{-1} SO_2 in the open air, was the same as that of needles exposed to 48 nl litre^{-1} then the subsequent laboratory treatment may have been expected to yield magnitudes to Ca_2^+ leaching in proportion to SO_4^{2-} leaching. Clearly the response pattern was different, with PP needles losing 31% less calcium than the CP needles by the end of the laboratory-based fumigation (Fig. 3). These results are readily explained by the observation (Wookey & Ineson, in press) that exposure to 48 nl litre^{-1} SO_2 for 156 days in the open air resulted in a reduction in needle calcium contents (Table 2: Ca, Mg and K contents of litter). At the start of the laboratory-based fumigation the PP needles probably (see footnote to Table 2) contained a more heavily depleted calcium pool than the CP needles, thereby leading to a lower availability of Ca^{2+} for SO_4^{2-} mediated leaching. Further support for the hypothesis is provided by comparing calcium leaching (Figs 2(c) and 3) from the CC and PC needles.

Data for Mg^{2+} leaching during the laboratory-based part of this experiment showed the same patterns as Ca^{2+}, except that the cation depletion effect was even more clearly evident (Figs 2(d) and 4, and also Table 2). The cumulative leaching of Mg^{2+} from the CP needles after 86 days in the laboratory system amounted to 115% more than that leached from the PP needles (Fig. 3); this pattern is further highlighted by plotting Mg^{2+} leaching from CP and PP needles against SO_4^{2-} (Fig. 4). Magnesium

TABLE 2

Element Analyses (% dry weight) for Litter Bag Samples Collected After 156 Days of Exposure in the Open-Air Fumigation Experiment. Means of six replicate Samples are given. Differences between SO_2 Treatments Statistically Significant ($P < 0.01$) for All Elements

Treatment	*Element*		
	Ca	*Mg*	*K*
Ambient SO_2 (8 nl litre^{-1})	0·312 (0·11)[a]	0·058 (0·002)	0·106 (0·007)
High SO_2 (50 nl litre^{-1})	0·140 (0·004)	0·031 (0·001)	0·077 (0·003)

[a]Standard error in parentheses.

Note: Values given here refer to litter composition 59 days prior to collection date of litter for use in the laboratory-based fumigation study (litter bag samples collected after 215 days were used for microbiological studies and could not, therefore, be analyzed in the same way; see Wookey *et al.* (1991)).

loss from the PC needles was very low over the course of the experiment and reached 'zero' (below the analytical detection limit of 0·1 μ-equivalents g^{-1} litter) after 86 days.

The same type of leaching pattern was not found for K^+ compared with Ca^{2+} or Mg^{2+} (Figs 2(e) and 3): the data for K^+ show no sign that leachable potassium reserves were appreciably depleted in litter exposed to 48 nl $litre^{-1}$ SO_2 in the open-air compared to the 7 nl $litre^{-1}$ control. This is in direct contrast with the actual results of needle analyses (Table 2) which show a statistically significant reduction in potassium content of litter exposed to 50 nl $litre^{-1}$ SO_2 compared with the control (8 nl $litre^{-1}$ SO_2). It should be emphasized, however, that the litter analyses of the open-air fumigation were performed after 156 days of exposure, rather than after 215 days, and the K content of the needles may have changed appreciably during the intervening 59 days.

Ammonium leaching rates were very low in the laboratory-based system (Figs 2(f) and 3) and rapidly declined to below the detection limit (0·43 μ-equivalents g^{-1} litter) in all of the microcosm chambers exposed to clean air (CC and PC). Conversely, small quantities of NH_4^+ were still detected until day 72 in leachates removed from some, but not all, of the 'polluted' chambers (this resulted in mean values lower than the analytical detection limit and not significantly different from zero; $P > 0{\cdot}05$). It is likely that charcoal filtration of the air entering the laboratory system removed a substantial proportion of the gaseous ammonia present in ambient air (Dueck, 1990) and this, in turn, may have limited both the dry deposition of NH_3 to pine litter and the subsequent formation of NH_4^+. Such a mechanism could also explain the very marked reduction in NH_4^+ leaching when litter was transferred from the open-air (Fig. 2(f) 'Time 0') to the laboratory-based system. It is of interest that NH_4^+ leaching could be detected only from microcosms exposed to 47 nl $litre^{-1}$ SO_2 in the laboratory, and these results may indicate that the acidification of polluted litter (see below) enhanced the deposition of residual NH_3 still present in the airstream after filtration. The data are consistent with the phenomenon of co-deposition of SO_2 and NH_3 (McLeod *et al.*, 1990), although the lack of statistically significant differences between treatments in this study, together with leaching rate close to (or below) the analytical detection limits, places restrictions on this interpretation.

Base cation and ammonium leaching was insufficient to completely buffer the SO_4^{2-} present in leachates and, as expected, protons provided the remainder of the charge balance. Leachate analyses indicated that needle material exposed to 47 nl $litre^{-1}$ SO_2 in the laboratory system was acidified compared with needles exposed to SO_2-free air. The close association between proton formation and the degree of base cation (calcium

and magnesium) depletion of the needles is clearly indicated by the results (Figs 2 and 3). Needles exposed to 48 nl litre^{-1} SO_2 in the open–air initially leached more H^+ ions (had a lower pH; values ranging from a pH of 4·0 to 4·4) than needles exposed to ambient air (pH 5·0–5·3). This was attributed to enhanced SO_4^{2-} formation in the needles exposed to higher SO_2 concentrations. When needles were taken from an open-air environment containing 48 nl litre^{-1} SO_2 and then placed into an airstream containing 47 nl litre^{-1} SO_2 in the laboratory system, the formation of protons remained high, due both to high SO_4^{2-} concentrations occurring as a consequence of SO_2 deposition, and also the high degree of cation depletion resulting in a low SO_4^{2-} buffering capacity.

The results for CP needles were quite different and can be explained on consideration of the higher base status of the needles before the laboratory-based component of SO_2 exposure. In spite of higher SO_4^{2-} leaching from the CP needles compared with the PP needles, there was actually less H^+ ion formation in the former, probably because more of the SO_4^{2-} was balanced by cation leaching, especially of Ca^{2+} (Fig. 3). Needles exposed to SO_2-free air in the laboratory system support this hypothesis since, although SO_4^{2-} leaching quickly dropped to undetectable amounts from the PC needles, these needles still leached more H^+ ions than the CC needles, even after 86 days, indicating that their buffering capacity was lower than the CC needles.

The use of small microcosm chambers within a laboratory-based fumigation system enabled fluxes of ions in leachates to be assessed regularly, and the results to be related to specific concentrations of gaseous SO_2 under carefully controlled conditions. The laboratory-based system can therefore be used to provide high-resolution data which can supplement results from open-air studies. It is important to recognize, however, that the artificial environmental conditions within the microcosm chambers may have resulted in unrealistic deposition fluxes of SO_2 to the litter. This was tested by estimating the deposition velocity (V_g) of SO_2 to the pine litter on the basis of SO_4^{2-} fluxes (see Wookey (1988) for details of methods).

Estimates of V_g ranged from 1·2 to 1·3 mm s^{-1}, these values probably representing an upper limit, and this compares favourably with values reported for a range of soils, coniferous forest canopies, and for a senescent cereal crop (Lockyer *et al.*, 1978; Fowler 1980, 1985). Ineson (1983) measured V_g to the litter layer of a recently felled *P. sylvestris* stand and found values ranging from 2 to 2·5 mm s^{-1}. V_g values did not, therefore, seem to be unusually high within the laboratory-based system: viewed in conjunction with the data on cation leaching from the litter, they provide a very striking indication of the capacity of dry-deposited SO_2 to bring about chemical changes.

CONCLUSIONS

Both the open-air and the laboratory-based fumigation studies illustrated the marked capacity for dry-deposited SO_2 to alter the nature of chemical reactions within decomposing *P. sylvestris* litter. Exposure to arithmetic mean SO_2 concentrations of 47 nl litre^{-1} for 70 days (out of 86 days), using the microcosm chamber system, enabled cumulative fluxes of SO_4^{2-}, H^+, NH_4^+ and base cations within the leachates to be assessed. Sulphate formation—in response to the dry deposition of SO_2—provided the mobile anions, and associated protons, to initiate cation exchange reactions within the litter: in this way Ca^{2+}, Mg^{2+} and K^+ were made available for removal by leaching. More than half of the negative charge associated with SO_4^{2-} leaching was balanced by Ca^{2+} plus Mg^{2+}.

Reciprocal litter transplants, using the two fumigation systems, indicated that pollution-induced changes in leachate chemistry were not immediately reversible in clean air. Leachates collected from litter previously exposed to 48 nl litre^{-1} SO_2 for 215 days in the open-air, and then subsequently to 2 nl litre^{-1} in the microcosm system ('PC' treatment), showed evidence of base cation depletion (particularly Ca^{2+} and Mg^{2+}) during the open-air fumigation. The leachates also remained slightly acidified (compared with the CC controls) for much of the 'clean air' exposure (86 days) even though SO_4^{2-} fluxes rapidly declined to below the analytical detection limit. Leachates collected from the PP (polluted–polluted) treatment provided particularly striking evidence of base cation depletion associated with SO_4^{2-} leaching.

Estimates of the deposition velocity (V_g) of SO_2 to litter within the microcosm system (1·2–1·3 mm s^{-1}) gave values well within the range reported by other workers, and it is concluded that microcosm studies can provide a valid supplement to the open-air fumigation approach. Laboratory-based microcosm systems cannot reproduce, however, the complex fluctuations in air pollutant concentrations and environmental conditions encountered in the open-air: and for this reason they should not be considered a complete replacement for open-air fumigation systems.

ACKNOWLEDGEMENTS

The authors thank the Natural Environment Research Council for funding this research. P.I. would also like to acknowledge the support of the Department of the Environment,. The open-air fumigation was conducted at the Central Electricity Research Laboratories (now National Power Technology and Environmental Centre) system at Littlehampton,

and the authors are particularly grateful to Dr A. R. McLeod for enabling them to work at the site. Thanks are due to the staff of the Analytical Chemistry Section at Merlewood Research Station, whose assistance made this study possible. The microcosm chambers were constructed by Peter Williams and Philip Smith at Lancaster University.

REFERENCES

Abrahamsen, G. (1984). Effects of acidic deposition on forest soil and vegetation. *Philosophical Transactions of the Royal Society of London (B)*, **305**, 369–82.

Anderson, J. M. & Ineson, P. (1982). A soil microcosm system and its application to measurement of respiration and nutrient leaching. *Soil Biol. & Biochem.*, **14**, 415–16.

Babich, H. & Stotzky, G. (1980). Environmental factors that influence the toxicity of heavy metal and gaseous pollutants to micro-organisms. *CRC Critical Rev. in Microbiol.*, **8**, 99–145.

van Breemen, N., Driscoll, C. T. & Mulder, J. (1984). Acidic deposition and internal proton sources in acidification of soils and waters. *Nature*, **307**, 599–604.

Brimblecombe, P. (1978). 'Dew' as a sink for sulphur dioxide. *Tellus*, **30**, 151–7.

Cape, J. N. (1984). The importance of solution equilibria in studying the effect of sulphite on plants. *Environ. Poll. (series A)*, **34**, 259–74.

Davies, T. D. (1979). Dissolved sulphur dioxide and sulphate in urban and rural precipitation (Norfolk, UK). *Atmospheric Environment*, **13**, 1275–85.

Dueck, T. A. (1990). Effects of ammonia and sulphur dioxide on the survival and growth of *Calluna vulgaris* (L.) Hull seedlings. *Functional Ecology*, **4**, 109–16.

EMEP (Co-operative Programme for Monitoring and Evaluation of the Long-Range Transmission of Air Pollutants in Europe) (1984). Summary report from the Chemical Co-ordinating Centre for the second phase of EMEP. Norwegian Institute for Air Research, Royal Norwegian Council for Scientific and Industrial Research. EMEP/CCC-Report 2/84.

Fowler, D. (1980). Removal of sulphur and nitrogen compounds from the atmosphere in rain and by dry deposition. In *Ecological Impact of Acid Precipitation*, ed. D. Drablos & A. Tollan. SNSF-Project, Oslo, pp. 22–32.

Fowler, D. (1985). Deposition of SO_2 onto plant canopies. In *Sulphur Dioxide and Vegetation: Physiology, Ecology and Policy Issues*, ed. W. E. Winner, H. A. Mooney & R. A. Goldstein. Stanford University Press, Stanford, CA, pp. 389–402.

Garland, J. A. & Branson, J. R. (1977). The deposition of sulphur dioxide to a pine forest assessed by a radioactive tracer method. *Tellus*, **29**, 445–54.

Gay, D. W. & Murphy, C. E. Jr (1989). Measurement of the deposition and fate of sulfur-dioxide-35 in a pine plantation. *J. Environ. Quality*, **18**, 337–44.

Ineson, P. (1983). *The effect of airborne sulphur pollutants upon decomposition and nutrient release in forest soils.* PhD thesis, University of Liverpool, UK.

Johnson, D. W. & Reuss, J. O. (1984). Soil-mediated effects of atmospherically deposited sulphur and nitrogen. *Philosophical Transactions of the Royal Society of London (B)*, **305**, 383–92.

Koziol, M. J. (1980). Monitoring gas concentrations in pollutant exposure systems: Defining exposure concentrations. *J. Experimental Botany*, **31**, 1413–23.

Krug, E. C. & Frink, C. R. (1983). Acid rain on acid soil: A new perspective. *Science*, **221**, 520–5.

Lefohn, A. S. & Mohnen, V. A. (1986). The characterization of ozone, sulfur dioxide, and nitrogen dioxide for selected monitoring sites in the Federal Republic of Germany. *J. Air Pollution Control Assoc.*, **36**, 1329–37.

Lettl, A. (1984). The effect of atmospheric SO_2 pollution in the microflora of forest soils. *Folia Microbiologica*, **29**, 455–75.

Lindberg, S. E. & Garten, C. T., Jr (1988). Sources of sulphur in forest canopy throughfall. *Nature (London)*, **336**, 148–51.

Lindberg, S. E., Lovett, G. M., Richter, D. D. & Johnson, D. W. (1986). Atmospheric deposition and canopy interactions of major ions in a forest. *Science*, **231**, 141–5.

Ling, K. A. & Ashmore, M. R. (1987). Acid rain and trees—An appraisal of the evidence for damage to native tree species by air pollution and acid precipitation in the United Kingdom. Report commissioned by the Nature Conservancy Council. Focus on Nature Conservation, 19. Nature Conservancy Council. Peterborough, UK.

Lockyer, D. R., Cowling, D. W. & Fenlon, J. S. (1978). Laboratory measurements of dry deposition of sulphur dioxide on to several soils from England and Wales. *J. Sci. Food & Agric.*, **29**, 739–46.

McLeod, A. R., Fackrell, J. E. & Alexander, K. (1985). Open-air fumigation of field crops: Criteria and design for a new experimental system. *Atmospheric Environment*, **19**, 1639–49.

McLeod, A. R., Holland, M. R., Shaw, P. J. A., Sutherland, P. M. Darrall, N. M. & Skeffington, R. A. (1990). Enhancement of nitrogen deposition to forest trees exposed to SO_2. *Nature (London)*, **347**, 277–9.

McLeod, A. R., Roberts, T. M., Alexander, K. & Cribb, D. M. (1991). The yield of winter cereals exposed to sulphur dioxide under field conditions. *Agriculture, Ecosystems and Environment*, **33**, 193–213.

Martin, A. (1980). Sulphur in air and deposited from air and rain over Great Britain and Ireland. *Environ. Poll. (series B)*, **1**, 177–93.

Morrison, I. K. (1984). Acid rain. A review of the literature on acid deposition effects in forest ecosystems. *Forestry Abstracts*, **45**, 483–506.

Moss, M. R. (1978). Sources of sulfur in the environment; the global sulfur cycle. In *Sulfur in the Environment. Part 1: The Atmospheric Cycle*, ed. J. O. Nriagu. John Wiley, Chichester, pp. 23–50.

Nyborg, M. (1978). Sulfur pollution and soils. In *Sulfur in the Environment—Part II: Ecological Impacts*, ed. J. O. Nriagu. John Wiley, New York, pp. 359–90.

Paces, T. (1985). Sources of acidification in central Europe estimated from elemental budgets in small basins. *Nature (London)*, **315**, 31–6.

Puckett, L. J. (1990). Estimates of ion sources in deciduous and coniferous throughfall. *Atmospheric Environment*, **24A**, 545–55.

Reuss, J. O. & Johnson, D. W. (1986). *Acid Deposition and the Acidification of Soils and Waters*. Springer Verlag, New York.

Reuss, J. O., Cosby, B. J. & Wright, R. F. (1987). Chemical processes governing soil and water acidification. *Nature (London)*, **329**, 27–32.

Tamm, C. O. (1976). Acid precipitation: Biological effects in soil and on forest vegetation. *Ambio*, **5**, 235–8.

United Kingdom Review Group on Acid Rain (1987). *Acid Deposition in the United Kingdom, 1981–1985*. Warren Spring Laboratory, Department of Trade and Industry, Stevenage.

Unsworth, M. H. & Mansfield, T. A. (1980). Critical aspects of chamber design for fumigation experiments on grasses. *Environ. Poll. (Series A)*, **23**, 115–20.

Williams, M. L., Atkins, D. H. F., Bower, J. S., Campbell, G. W., Irwin, J. G. & Simpson, D. (1989). *A preliminary assessment of the air pollution climate of the UK*. Warren Spring Laboratory report LR 723 (AP), Warren Spring Laboratory, Department of Trade and Industry, Stevenage.

Wookey, P. A. (1988). *Effects of dry deposited sulphur dioxide on the decomposition of forest litter*. PhD thesis, University of Lancaster, UK.

Wookey, P. A. & Ineson, P. (in press). Chemical changes in decomposing forest litter in response to atmospheric sulphur dioxide. *J. Soil Sci.*

Wookey, P. A., Ineson, P. & Mansfield, T. A. (1991). Effects of atmospheric sulphur dioxide on microbial activity in decomposing forest litter. *Agriculture, Ecosystems and Environment*, **33**, 263–80.