DOE UMBRELLA CONTRACT - SUMMARY REPORT 1989

1. Surface - Atmosphere exchange of NO, NO_2, O_3, NH_3

2. Open-top chamber studies of O_3 and acid effects on Norway spruce and Beech

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Review of Air Pollution Effects

Research 1988-1989

SUMMARY REPORT OF WORK AT ITE, EDINBURGH

This summary includes work in two different projects.

1. Surface-atmosphere exchange of NO, NO_2, O_3 and NH_3.
2. Open-top chamber studies of effects of O_3 and acid mist on Norway Spruce and Beech.

1. Surface-atmosphere exchange of NO, NO_2, O_3 and NH_3.

The work during the year includes (i) field measurements of NO, NO_2, O_3 and NH_3 exchange over moorland, heather and more recently cereal crops, (ii) an analysis of nitrogen and sulphur deposition on forest, (iii) dry deposition modelling in the UK and (v) preparation for the first European experiment in Eurotrac (BIATEX).

The field measurements of NO_2 over moorland and unimproved grassland show consistently small deposition rates which are frequently smaller than the rate of NO release into the atmosphere. Deposition velocities are generally in the range 0.1 to 4 mm s^{-1} with median values of around 1 mm s^{-1}, and fluxes of typically 20 to 50 ng NO_2 $m^{-2}s^{-1}$. Fluxes of NO are in the range 2 to 50 ng NO_2 (equivalent) $m^{-2}s^{-1}$. The absorption of NO_2 at the ground when measured by micrometeorological methods is often confounded by a reversible adsorption at the surface giving rise to upward fluxes when NO_2 concentrations are decreasing and vice versa. Ammonia is deposited on moorland and unimproved grassland at rates controlled entirely by atmospheric transfer, and except during very dry weather these surfaces may be considered perfect sinks for ammonia. For cereal fieds the ammonia exchange is more complex, and even for cereals which have not been fertilized with urea or aqueous ammonia and are not senescent, significant upward fluxes have been observed. The net exchange of ammonia over cereal fields over a season remains unclear but it seems likely to be a net source.

Measurements of surface/atmosphere exchange

NO, NO_2, O_3

During the year the flux-gradient system for measurements of NO, NO_2 and O_3 exchange has been reconstructed to include a constant reference monitor. In this way the effects of changing ambient concentration during the measurements can be followed while a separate gas analyser is dedicated to the determination of vertical profiles. We have also used a rapid response NO_2 detector (10s) for the profile measurements to reduce the equilibration time between successive sampling levels.

Following these instrumental changes the system has been used at three field sites.

<u>Bush - 28th February 1989</u>

Location: Bush Estate, Penicuik, Midlothian. National grid Reference NT245640.

Table 1.

BUSH RUN 1

Conditions

Thin, broken snow cover, surface damp. Snow melting rapidly.

Concentrations (ppbV)

NO_2	NO	SO_2	O_3
2.0	0.5	0.5	18

Wind

W. 8-9 m s^{-1}

u_*=0.677 m s^{-1}

z_0=0.006 m d=0.11 m

Temperature

2-3 °C

	Vmax (m s^{-1})	Vg (m s^{-1})	r_a (s m^{-1})	r_b (s m^{-1})	r_c (s m^{-1})
NO_2	0.037	-0.010	18.5	8.2	73.3
O_3	0.038	0.003	18.5	8.1	306.4
SO_2	0.036	0.056	18.5	9.4	-10.0

Table 1 (Cont)

BUSH RUN 2

Conditions

Patchy snow cover, melting rapidly. Small amounts of standing water.

Concentrations (ppbV)

NO_2	NO	SO_2	O_3
6.0	1.0	0.5	15

Wind

W. 7-8 m s^{-1}

u_*=0.476 m s^{-1}

z_o=0.005 m   d=0.10 m

Temperature

2-3 ^oC

	Vmax (m s^{-1})	Vg (m s^{-1})	r_a (s m^{-1})	r_b (s m^{-1})	r_c (s m^{-1})
NO_2	0.027	-0.008	27.1	10.2	87.7
O_3	0.027	0.004	27.1	10.1	212.8
SO_2	0.026	0.029	27.1	11.8	-4.4

Table 1 (Cont)

BUSH RUN 3

Conditions

Snow melted completely. Large amount of standing water on the field.

Concentrations (ppbV)

NO_2	NO	SO_2	O_3
10.0	1.5	1.0	12

Wind

W. 7-8 m s^{-1}

u_*=0.456 m s^{-1}

z_o=0.008 m d=0.05 m

Temperature

2-3 ^oC

	Vmax (m s^{-1})	Vg (m s^{-1})	r_a (s m^{-1})	r_b (s m^{-1})	r_c (s m^{-1})
NO_2	0.027	0.001	25.8	11.8	962.4
O_3	0.027	0.006	25.8	11.7	129.2
SO_2	0.025	0.037	25.8	13.6	-12.4

Description: A permanent pasture (canopy height 0.05-0.15 m) of perennial ryegrass mixture containing 25% clover extending to approximately 6 ha. From the measurement site at the eastern corner of the field the land rises to the NNW, W and SW at a slope of approximately 1 in 20. Fetch to the NNW and W is 200-250 m, to the SW 100-150 m.

Local Sources: The A702 Biggar-Edinburgh road borders the north-western edge of the site (500 m from the measurement position) and an unclassified road runs along the north-eastern margin. The city of Edinburgh (pop. 420,000) lies 13 km to the north and the town of Penicuik (pop. 17,500) 3 km to the south. Various research institutes lie to the north-east and south-east at a distance of 200 to 1000 m.

Objectives: To study trace gas exchange over a melting snow pack. It was expected that sulphur dioxide would be rapidly deposited to the wet surface irrespective of the proportion of snow cover. Ozone was expected to display an increase in deposition rate as the snow melted to expose the underlying vegetation. Nitrogen dioxide was thought to exchange more slowly than the other trace gas species.

Observations: During the first two runs (each run represents the mean of 3, 20 minute flux/gradient measurements) nitrogen dioxide was emitted from the surface at a rate of 25-30% of Vmax. As the ambient concentration rose (from 2/6 ppb to 10 ppb) emission ceased and deposition, at a very slow rate, began. The canopy resistance to ozone deposition decreased as the snow melted. It is thought this reflects the uncovering of the vegetation during snow-melt allowing uptake of ozone. Sulphur dioxide was deposited at the maximum rate permitted by the aerodynamic characteristics of the boundary-layer. This is almost certainly due to dissolution of sulphur dioxide into the water present on the vegetation and on the surface of the melting snow. Ammonia was also deposited onto the melting snow pack at rates close to the maximum, so that this surface was a perfect sink for SO_2 and NH_3 but a rather poor absorber of both NO_2 and O_3.

Wether Law - 21st February 1989

Location: Wether Law, nr Longformacus, Duns. National Grid Reference NT652609.

Description: A remote upland site, altitude 400 m, the vegetation being predominantly heather of height 0.3 - 0.4 m. The site provides fetches of 700 to 800 m in S, SW and W directions with a very slight upward incline to the SW.

Local Sources: The nearest habitation within the sector of the fetch is the village of Lauder (pop. 800) which lies 17 km to the SW. An unclassified road runs along the north-eastern edge of the site.

Objectives: The purpose of this study was to determine trace gas exchange at a site remote from pollution sources, representative of the upland areas of the United Kingdom. The exchange rates of nitrogen dioxide and ozone were investigated.

Observations: During both runs, each of which are hourly means of 3, 20 minute flux-gradient estimates, nitrogen dioxide was emitted from this site at a rate 30-50% of that permitted by Vmax. Ambient concentrations did not vary so that it was not possible to show whether emission ceased at higher

Table 2

VETHER LAV RUN 1

Conditions

Dry, overcast sky. Canopy dry throughout. Ground frozen but thawing rapidly.

Concentrations (ppbV)

NO_2	NO	SO_2	O_3
4.0	0.1	n/a	16

Wind

V. 5-6 m s^{-1}

u_*=0.527 m s^{-1}

z_o=0.022 m   d=0.26 m

Temperature

0-1 °C

	Vmax (m s^{-1})	Vg (m s^{-1})	r_a (s m^{-1})	r_b (s m^{-1})	r_c (s m^{-1})
NO_2	0.032	-0.017	17.7	58.8	27.6
O_3	0.032	0.003	17.7	13.4	302.2

Table 2 (Contd)

WETHER LAW RUN 2

Conditions

Canopy dry. Ground fully thawed and surface slightly damp.

Concentrations (ppbV)

NO_2	NO	SO_2	O_3
4.0	0.3	n/a	15

Wind

W. 5–6 m s^{-1}

u_*=0.537 m s^{-1}

z_0=0.025 m   d=0.25 m

Temperature

2–3 ^oC

	Vmax (m s^{-1})	Vg (m s^{-1})	r_a (s m^{-1})	r_b (s m^{-1})	r_c (s m^{-1})
NO_2	0.033	-0.010	16.8	13.8	69.4
O_3	0.033	0.006	16.8	13.6	136.3

concentrations. Ozone was deposited at a rate controlled mainly by canopy resistance. The decline in canopy resistance from Run one to Run two is an indication of increased chemical affinity of the heather for O_3 as temperatures increased, but at such low air temperatures we do not believe that this reflects stomatal uptake. The Bowen ratio energy balance system was not available for this experiment, so that water flux measurements were not available.

Howmuir - 8th/9th June 1989

Location: Howmuir Farm, Biel, near Dunbar, East Lothian. National Grid Reference NT614769.

Description: A crop of spring barley (cv. Camargue), canopy height 0.41-0.49 m in a level field of approximately 14 ha. From the measurement site along the southern edge of the field the minimum fetch is 300 m to NNW, increasing to 400 m to ENE and 500 m to W.

Local Sources: The A1 Edinburgh-London trunk road runs east-west approximately 350 m north of the northern boundary of the field. Dunbar (pop. 6000) lies 6 km to the west and the village of East Linton (pop. 1200) is 2.5 km to the east.

Objectives: To determine trace gas fluxes to a commercially grown cereal crop, representative of arable land in the United Kingdom. Nitrogen dioxide, ozone and sulphur dioxide were studied at this site and a comparison between day and night-time exchange processes was possible using a Bowen-Ratio system to determine Km in calm conditions.

Table 3

HOWMUIR RUN 1

Conditions

16:00 GMT. Dry, sunny. Canopy dry.

Concentrations (ppbV)

NO_2	NO	SO_2	O_3
4.0	0.9	0.4	45

Wind

WNW. 5-6 m s^{-1}

u_*=0.700 m s^{-1}

z_o=0.05 m d=0.50 m

Temperature

22 °C

	Vmax (m s^{-1})	Vg (m s^{-1})	r_a (s m^{-1})	r_b (s m^{-1})	r_c (s m^{-1})
NO_2	0.042	0.013	10.4	13.3	55.8
O_3	0.043	0.004	10.4	13.1	206.0
SO_2	0.039	0.038	10.4	15.2	0.6

Table 3 (Cont)

BOWMUIR RUN 2

Conditions

23:00 GMT. Fine, dry.
Canopy dry.

Concentrations (ppbV)

NO_2	NO	SO_2	O_3
0.1	0.2	3.0	32

Wind

Variable. 1 m s^{-1}

u_*=0.057 m s^{-1}

z_o=0.05 m   d=0.50 m

Temperature

11 °C

	Vmax (m s^{-1})	Vg (m s^{-1})	r_a (s m^{-1})	r_b (s m^{-1})	r_c (s m^{-1})
NO_2	0.005	0.003	128.2	89.3	160.8
O_3	0.005	0.001	128.2	88.3	951.0
SO_2	0.004	0.003	128.2	102.5	92.8

Observations: Nitrogen dioxide was observed to be deposited at a rate controlled by stomatal resistance. However, this deposition occurred at low ambient concentrations which, at the other sites, resulted in emission. Ozone also displayed evidence of control by stomatal resistance, but the resistance to ozone transfer was considerably larger than that for nitrogen dioxide. During daylight, sulphur dioxide was deposited at the maximum possible rate, suggesting that uptake was directly onto surfaces and not soley via stomata. An increase in canopy resistance was observed at night, but deposition continued at 75% of Vmax. Two other visits to this site during June provided flux gradient data which are currently being analysed. However, the NO_2 fluxes appear to be small (as for the moorland and unimproved grassland) but they represent deposition rather than emission.

Throughout these measurements Bowen ratio energy balance instrumentation was used to provide latent and sensible heat partitioning from which the canopy resistance to water vapour loss was determined.

The use of such a system with the trace gas flux measurements makes it possible to investigate stomatal control in gas fluxes.

EUROTRAC

All of the short series of measurements during the spring of 1989 form part of the preparation for the 1 month of measurements in September as a part of the Eurotrac Biotex experiment.

In this the UK as host for the experiment provides the site for the initial experiment.

The site selected is a large flat permanent grass field in the middle of the Halvergate marshes 10 km from the east coast north of Great Yarmouth in Norfolk, which provides 2 km of flat grassland in most directions. At the site, a consortium of research groups from Europe will attempt to measure NO, NO_2, PAN, HNO_3, NH_3, O_3 and SO_2 fluxes by a range of methods. The methods include flux gradient technique for all of the gases, cuvette systems for NO, NO_2, SO_2 AND O_3 and eddy correlation methods for total sulphur, NO_2 and O_3. The groups who will participate include:

ITE, Edinburgh	NH_3, NO, NO_2, O_3, SO_2 flux/gradient (+ NO_2 eddy correlation)
Harwell, Oxfordshire	PAN, HNO_3, H_2O_2 flux/gradient
Fraunhafer Institute FRG (Garmisch Partenkirchen)	NO, NO_2, O_3, cuvette and flux/gradient
T.N.O. Delft Netherlands	NO_2 and O_3 eddy correlation
	NH_3, PAN, O_3, NO and NO_2 flux/gradient
IMI Stockholm, Sweden	NO, NO_2, SO_2, cuvette
Institute of Atmospheric Physics, Hungary	NO, NO_2, O_3 flux/gradient

The experiment is due to begin on the 4th September and with the scale of measurement systems a substantial body of data on these trace gases will be provided for a relatively simple site. It will therefore provide a good test of methods and should show which process exert primary control over exchange rates for each trace gas. The experiment has attracted considerable interest from other groups and we have agreed to visits by Spanish and US scientists but with 18 people already involved we are reluctant to allow the experiment to expand further. As this is the first of these experiments we wish to concentrate on the main task of obtaining high quality flux measurements using at least two methods from the 5 groups.

HNO_3, NO, NO_2 and NH_3 fluxes over grassland

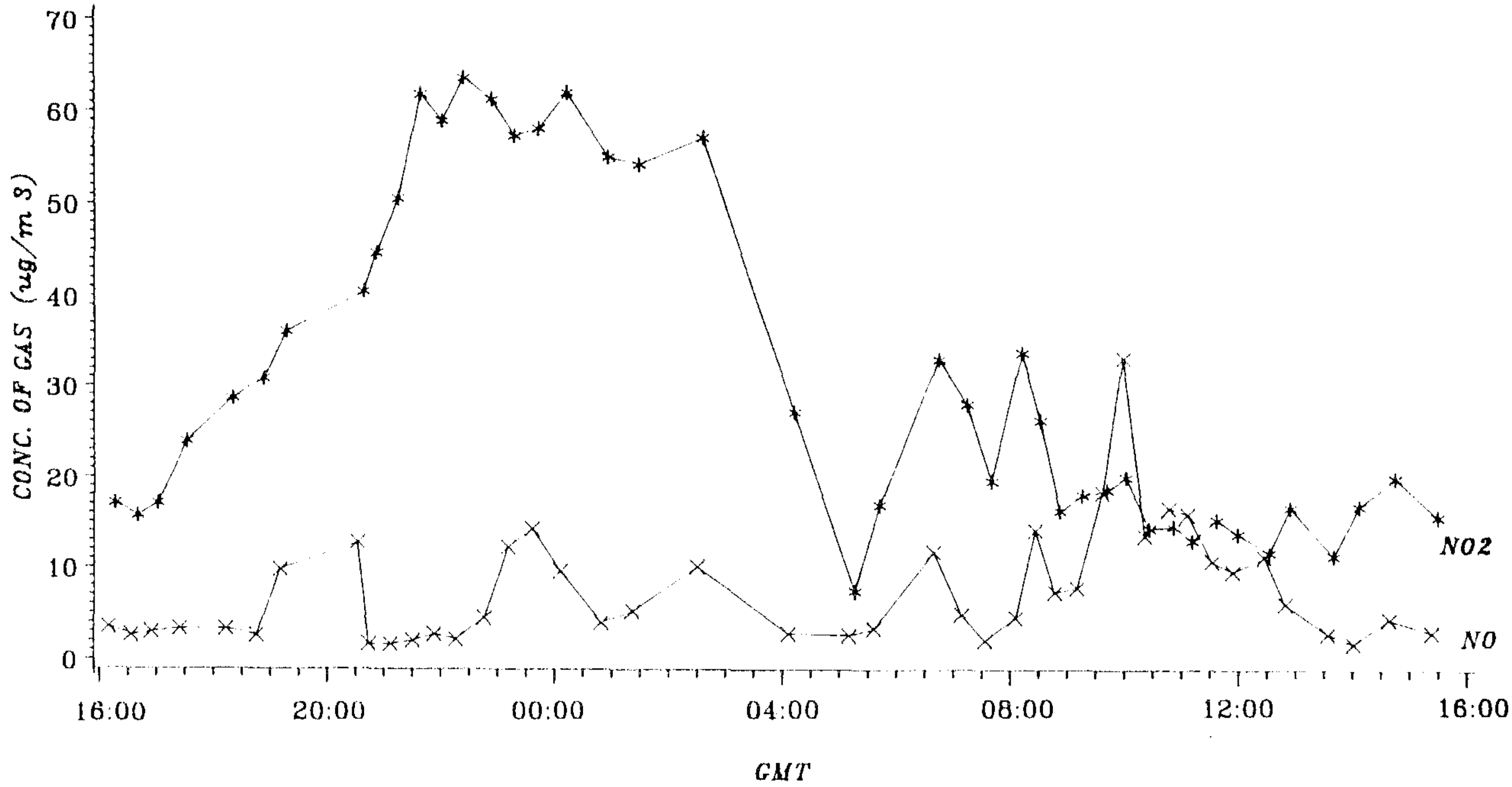
The joint ITE/Harwell field campaign results at Cambridge in Autumn 1987 have now been analysed. They show that the field, which is unimproved grassland, and an SSSI with >40 species present, is a perfect sink for ammonia and nitric acid. Annual inputs of N to this site through dry deposition exceed 40 kg N ha^{-1}. With wet deposition the total input is in the region 50 kg N ha^{-1} per year. It is not known whether at this site the nitrogen inputs are sufficient to influence species composition but sites in this area are incorporated in a study of species composition changes of natural plant communities by ITE for the NCC.

The fluxes of NO and NO_2 at this site showed very interesting trends with time.

RESULTS

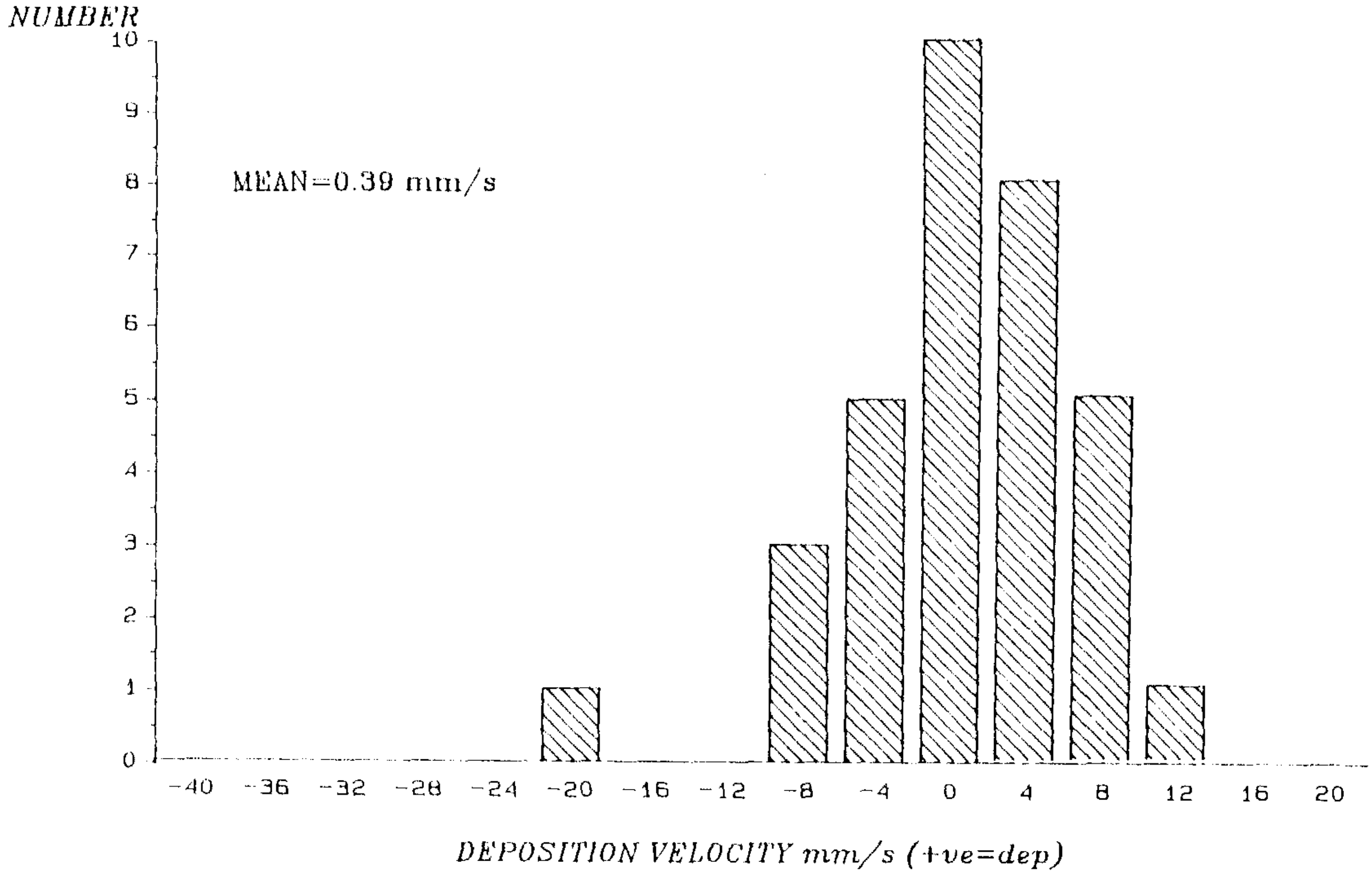
The measurements began at 1600 GMT on 12th August in bright sunny conditions, and continued through the night with initially clear skies, and continued through the night with initially clear skies, dewfall, but moderate

CONCENTRATION AT 1.73M FOR NO AND NO2



Huntingdon NOX Experiment
12–13 August 1987

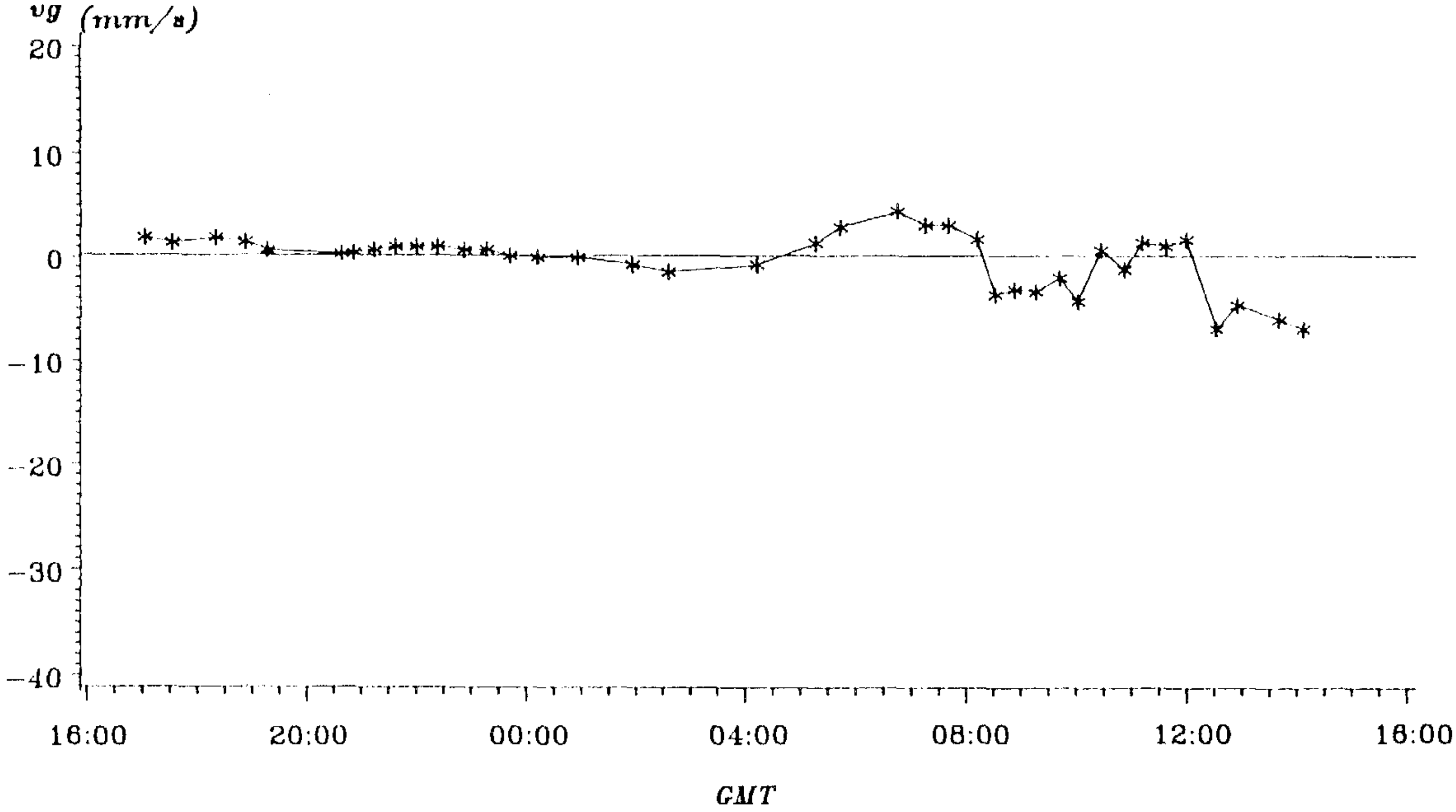
DEPOSITION VELOCITY FOR NO2



(2) *Huntingdon NOX Experiment*
12–13 August 1987

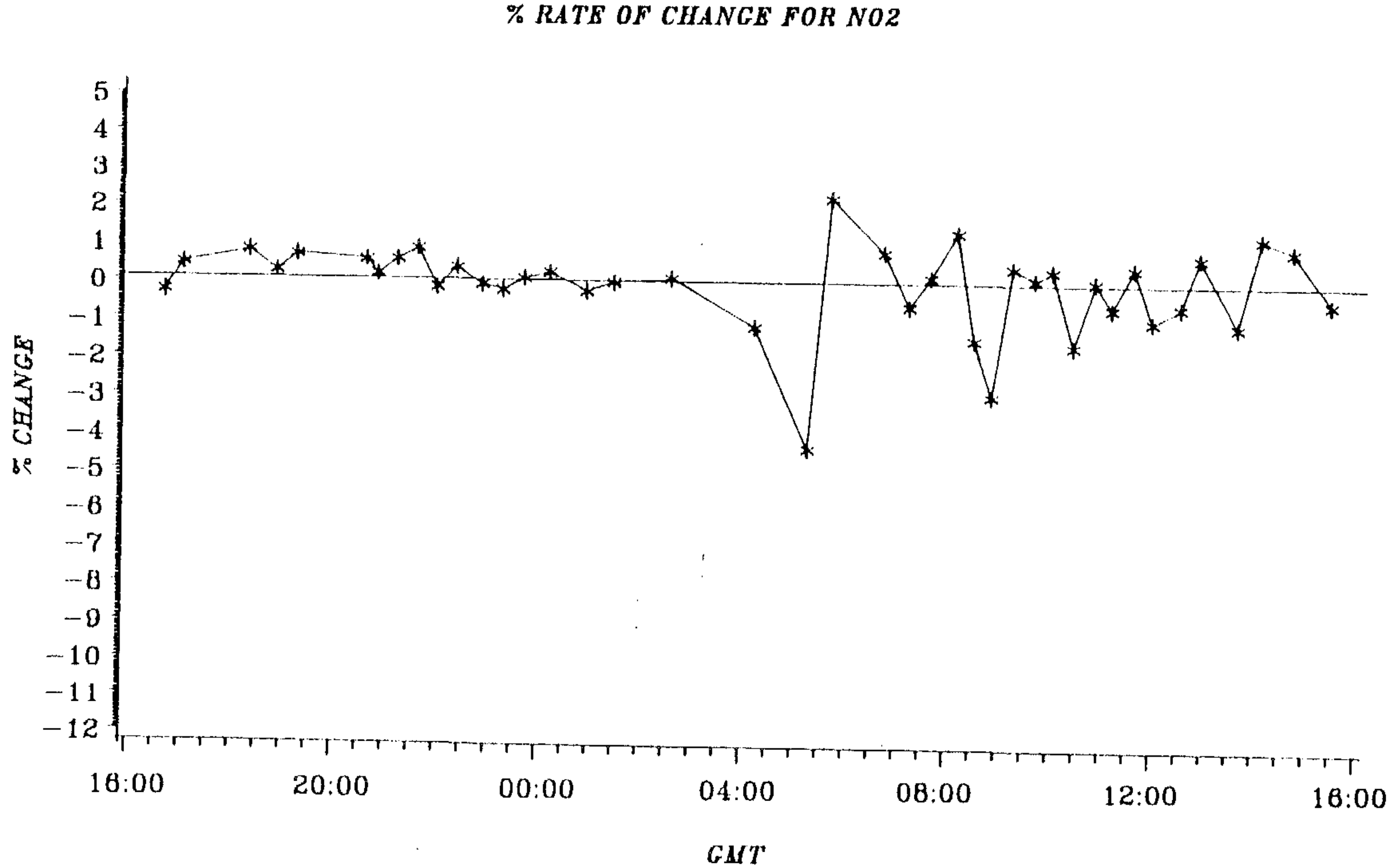
DEPOSITION VELOCITY Vs TIME

5 POINT RUNNING MEAN FOR NO2



(A) *Huntingdon NOX Experiment*
12–13 August 1987

% RATE OF CHANGE IN CONCENTRATION Vs TIME



(5) *Huntingdon NOX Experiment*
12–13 August 1987

windspeeds. By 0300 a layer of stratus covered the sky and the dew evaporated, until by 0730 the surface was dry. Measurements continued until 1600 on 13th August when it started to rain.

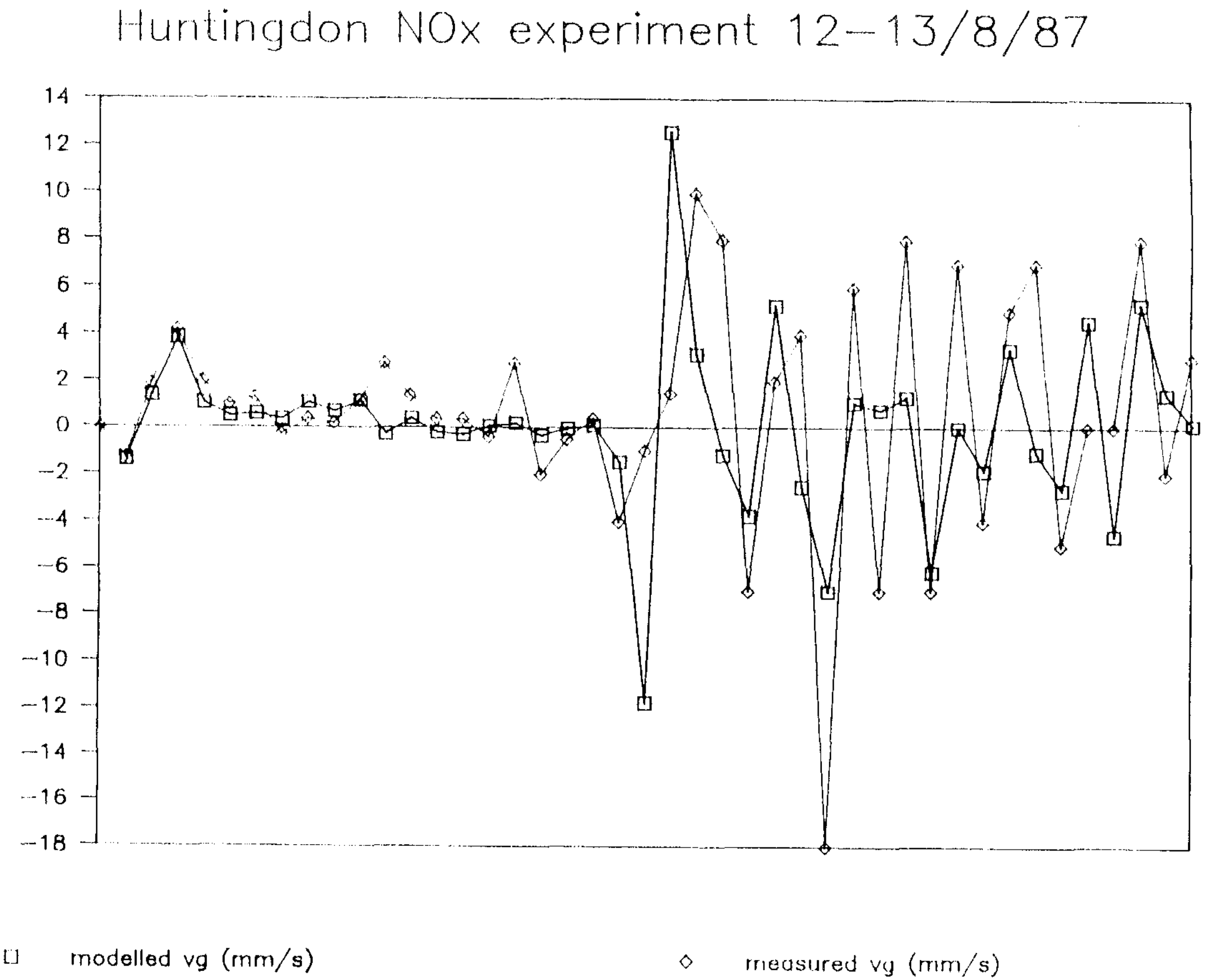
Over the 24 hours the 46 periods of measurement (each between 20 and 30 minutes) provided an approximately normal distribution of vg (fig. 2), with a mean value of 0.39 mm/s, an emission maximum of 20 mm/s, and a deposition maximum of 12 mm/s. During this period the air concentrations of NO_2 at the site varied from 7 to 63 ug NO_2/m^3.

Deposition velocity for NO_2 shows marked variations with time during the experiment. When concentrations are increasing NO_2 is deposited at rates between 0.5 and 4 mm/s; while concentrations are falling NO_2 appears to be emitted by the surface. These features are illustrated by comparing the deposition velocity (fig. 4) and the rate of exchange of concentration (fig. 5).

The divergence in flux, Fa, resulting from advection is one source of the apparent upward and downard fluxes:

$$Fa = \int_{z1}^{z2} U.d(NO_2)dx\ dz$$

where z1 and z2 are the heights of the surface, and at which the flux is measured, respectively, u is windspeed and $d(NO_2)/dx$ is the horizontal gradient in NO_2 concentration. Simplifying, by taking a mean windspeed between z1 and z2: $Fa = u.d(NO_2)/dx.(z1-z2)$. During the period 1700 GMT to


Huntingdon NOx experiment 12–13/8/87
14
12
10
8
6
4
2
0
−2
−4
−6
−8
−10
−12
−14
−16
−18
modelled vg (mm/s)
measured vg (mm/s)

2200 on 12th August the advection error in the measured vertical flux is only 5%. Similarly, during the period when NO_2 concentrations fell sharply, the error is only 15%.

It appears likely that the variability in the measured flux results from reversible storage of NO_2 on the surfaces of the vegetation, and that this masks a small net NO_2 uptake which occurs over the whole period, and is seen when concentrations remain constant. If the quantity of NO_2 absorbed is taken to be proportional to the logarithm of NO_2 partial pressure, then changes may be modelled, assuming rapid equilibrium at the surface. The comparison between measured deposition velocity and that modelled on the basis of reversible sorption is shown in fig. 6. The underlying deposition velocity for NO_2 is small, certainly smaller than 1 mm/s during these measurements.

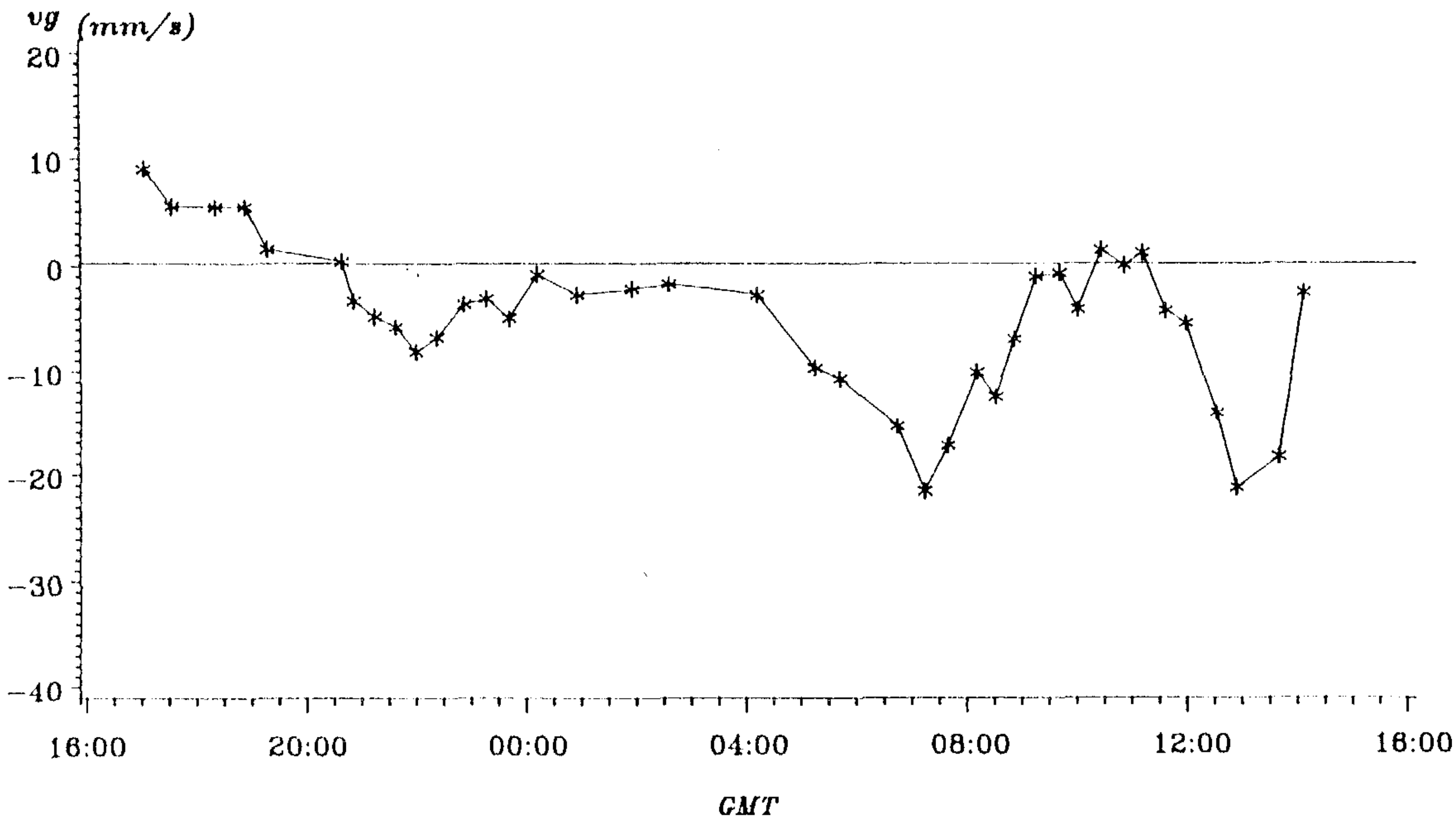
NITRIC OXIDE

Fluxes of nitric oxide were both up and downwards but over the 24 hours the average flux was upwards, at 20 $ng/m^2/s$. The concept of deposition velocity is of doubtful value for soil emissions, but for consistency with the NO_2 data vg has been plotted (fig. 7). The variation over the 24 hours is not closely related to atmospheric conditions, and may be more closely coupled to soil processes.

The net flux of nitrogen as NO or NO_2 at this site is away from the ground, amounting to 0.7 mg N/m^2 over the 24 hours. These measurements are consistent with those of Johannson, and imply that vegetation is a very poor

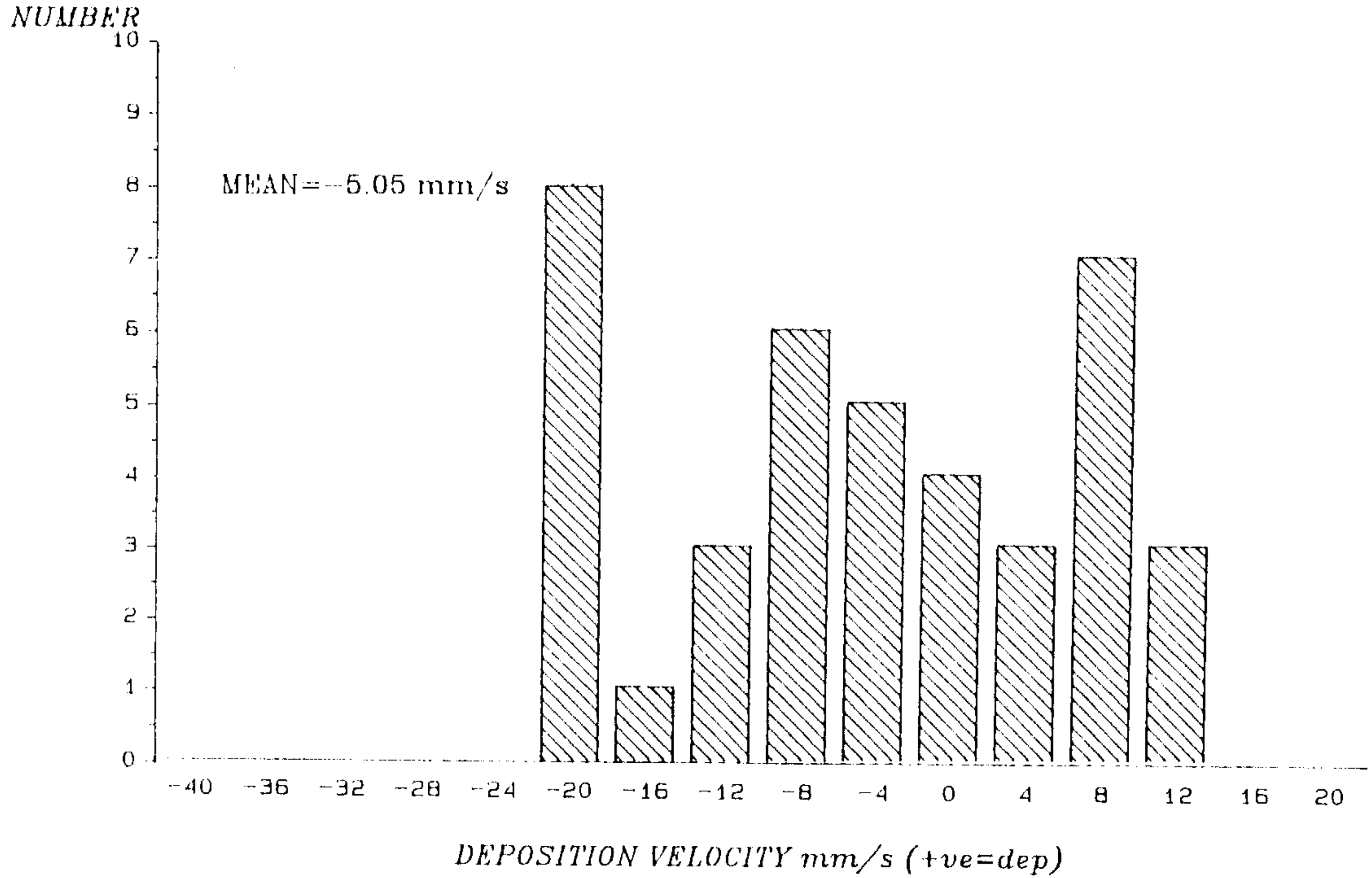
DEPOSITION VELOCITY Vs TIME

5 POINT RUNNING MEAN FOR NO



(7) *Huntingdon NOX Experiment*
12–13 August 1987

DEPOSITION VELOCITY FOR NO



⑤ *Huntingdon NOX Experiment*
12–13 August 1987

sink for NO_2. As a consequence, the atmospheric lifetime of NO_2 is longer than has previously been assumed, and is almost entirely controlled by chemical processes.

Surface/Atmosphere Exchange of Gaseous Ammonia

Atmospheric ammonia gas is of major importance because of its effects on atmospheric chemistry and on ecosystems, when deposited. Yet little is known about its exchange between the two systems. This project uses micrometeorological methods to assess source and sink land uses and to examine the mechanisms and rate limiters of exchange. Emphasis is made on natural ecosystems as information here is sparse. Concentration monitoring also made will allow total doses to be calculated.

The aerodynamic gradient method isused and results interpreted according to usual resistance analogy theory, giving deposition velocities (Vg), and canopy resistances (Rc). However, this assumes surface concentration of the gas (Xs) to be zero, which may well be false. Interpretation is therefore also made via a surface concentration estimate (X[Zo']), which accounts for the atmospheric resistances to transfer (Ra, Rb). Sampling involves parallel measurement of windspeed, temperature and ammonia with height above a uniform land surface. A filter pack system measures ammonia. Particulate ammonium is removed with a 1µm pore size PTFE filter, then an acid Whatman 42 filter captures ammonia gas. Minimising blank contamination and lab. deposition to samples is essential so filters are precleaned in an ultrasonic bath and clean air chambers used for all lab. work.

Moorlands and natural grasslands are areas noted as being sensitive to ammonia deposition. Two moorland sites have been studied: Great Dun Fell, Cumbria @ 2500 ft) and Fala Moor, Lothian (@ 1000 ft). Both sites gave deposition at rates limited by atmospheric turbulence, which for these site roughnesses and wind conditions were Vg = 2.5 cm s^{-1}. Correspondingly, both Rc and X[Zo'] approximated to zero and absorbtion must be by leaf surfaces. Measurements of the effect of surface drying show a possible but small Rc may develop.

Two natural grassland sites have been studied: Brampton Racecourse S.S.S.I., Huntington, a species rich (neutral/calcareous) alluvial meadow, and a recently harrowed calcareous meadow at Harwell. At the former deposition was again limited by turbulence, with results here of Vg = 1-2 cm s^{-1}, however at Harwell a considerable surface resistance was seen (c. 100 s m^{-1}) and deposition ranged over Vg = 0.1-1 cm s^{-1}. Deposition even at low air concentrations suggested the Rc interpretation to be more appropriate than X[Zo']. This probably relates to the high leaf surface pH from the disturbed soil, which would reduce ammonium solubility.

These results may be compared to exchange over a fertilised grass crop, nearing anthesis, at Bush, Edinburgh, which gave a clear emission pattern. Within crop profiles identified the crop itself as the source, with emission increasing with temperature, and reducing with surface wetness. Here X[Zo'] is appropriate and describes the theoretical minimum emission potential. If this is substomatally driven the actual potential would be greater. Measurements of stomatal resistance have yet to be worked up. For the measurement period (10-20^{o}C, wet/dry) X[Zo'] = 0.2 ug m^{-3}).

Much of the concern about ammonia relates to forests, yet virtually no flux measurements have been made, since a number of theoretical constraints operate to make concentration gradients here very small. Measurements were however attempted at Dunslair Heights, Peebles, over mixed conifer forest and, while lacking in precision as expected, especially as air concentrations were low (c. 0.05-0.4 ug m^{-3}), they gave results consistent with turbulence limiting deposition to leaf surfaces. As the roughness of the forest is great the maximum rates wee large, at 4-9 cm s^{-1} over the period of measurement.

Surface/Atmosphere Exchange of Ammonia

Interest

- role in SO_2 scavenging by water
- acidifying suseptible soils
- increased N supply in N limiting systems
  (heathland changes, forest health)

Specific aims

- identify source and sink land uses of NH_3 particularly sinks (natural vegetation) as less information
- examine rate limitors of exchange and mechanisms
- quantify doses by relating rates to ambient concentrations

The following 5 tables list the measurements of ammonia deposition over 5 contrasting surfaces - 2 moorland sites, lowland grass, calcareous grass and a forest. All with the exception of calcareous grass showing the surface to behave as a perfect sink.

Table 4

Ammonia fluxes over Eriophorum/Calluna Moor

Fala Moor, Midlothian

24-25/5/88, soil pH = 3.9, surface watertable, *Sphagnum* abundant.
L > |80|, Zo = 2.7-3.3cm

Time (GMT)	U[1m] ms^{-1}	Vmax $cm\ s^{-1}$	T[Zo'] °C	X[1m] μgm^{-3}	Flux [NH_3] $ng\ m^{-2}\ s^{-1}$	Vg $cm\ s^{-1}$	r_c sm^{-1}	X[Zo'] μgm^{-3}	Surface
1445* 1645	5.0	4.2	13.4	0.49	10.3	2.1	23.5	0.25	Dry
1710 1900	4.9	4.1	10.6	1.15	64.3	5.6	-6.4	-0.42	Dry
0415 0625	4.2	3.4	4.7	0.62	29.2	4.7	-8.5	-0.25	Wet
0700 0900	5.8	4.8	12.7	0.69	37.3	5.4	-2.5	-0.07	Partly Wet
0930 1130	5.7	5.2	17.3	0.59	25.8	4.4	3.4	0.08	Drying
1200* 1400	6.5	5.4	19.5	0.51	7.5	1.5	49.0	0.37	Dry
1430 1715	5.8	4.9	17.6	0.45	17.0	3.6	7.7	0.14	Dry
1755 1955	1.8	3.4	10.5	0.55	15.6	2.9	5.2	0.09	Partly Wet
Mean(6)				0.675	31.53	4.67	-0.2		

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Table 5

Great Dun Fell, Moorhouse N.N.R., Cumbria
Soil pH = 3.9, Zo = 0.7-0.9cm

Date	Time GMT	U[1m] cms^{-1}	Vmax cms^{-1}	L m	T[Zo^{1}] °C	X[1m] μgm^{-3}	Flux[NH_3] $ngm^{-2}\ s^{-1}$	Vg cms^{-1}	r_c sm^{-1}	X[Zo^{1}] μgm^{-3}	Surface
27/5/87	1250* 1500	4.1	2.7	–	–	1.24	64.5	5.2	-18.4	-1.18	Partly wet
	1630 1910	(4.1)	(2.7)	–	–	1.21	35.1	2.9	- 3.0	-0.11	Partly wet
29/3/88	1730* 1910	4.9	2.7	NS	2.2	0.81	19.0	2.4	5.4	0.10	Wet
	1955 2220	3.5	2.0	NS	0.7	0.47	7.2	1.5	14.6	0.10	Wet
30/3/88	1010 1235	4.6	2.6	-120	2.8	0.61	14.6	2.4	3.3	0.07	Melting snow
	1330 1530	5.8	3.4	-112	6.0	1.02	32.7	3.2	1.3	0.08	Wet
	1700 1840	4.4	2.0	-124	2.8	0.68	12.7	1.9	4.3	0.11	Wet
	1925 2210	3.3	1.8	NS	-0.1	0.12	0.8	0.7	93.2	0.07	Wet
21/4/88	1045 1245	3.9	3.0	-24.3	14.2	0.67	17.2	2.6	5.4	0.17	Partly wet
	1330* 1530	2.9	1.9	-11.3	14.1	0.49	4.5	0.9	56.1	0.32	Partly wet

Table 6

Ammonia fluxes over unimproved alluvial grassland

Brampton Racecourse S.S.S.I., Huntingdon, Cambridgeshire
11-13/8/1987 neutral-calcareous, Zo = 1-2cm, T = 15-20°C

Time GMT	U[1m] ms^{-1}	Vmax $cm\ s^{-1}$	X[1m] μgm^{-3}	Flux NH_3 $ng\ m^{-2}\ s^{-1}$	Vg $cm\ s^{-1}$	r_c sm^{-1}	X[Zo'] μgm^{-3}	Surface
1120 1350	3.0	1.9	1.92	38.8	2.0	- 2.6	-0.10	Partly wet
1445 1540	2.7	1.7	1.49	19.9	1.3	15.5	0.31	Dry
0925* 1105	3.6	2.0	2.22	58.7	2.6	-11.6	-0.69	Wet
1600 1800	1.6	1.4	1.84	15.6	0.8	46.3	0.81	Dry
1835 2025	1.0	1.5	3.44	56.6	1.6	- 5.3	-0.52	Dry
2130 0035	2.0	1.3	2.20	34.9	1.6	-15.4	-0.62	Dew forming
0130* 0500	1.9	1.4	2.11	49.8	2.4	-29.0	-1.67	Dew
0940 1140	3.3	2.2	1.26	8.6	0.6	115.8	1.01	Wet
1225 1425	3.6	2.2	1.34	23.2	1.6	19.7	0.49	Wet
Mean(9)		1.67	1.98	34.01	1.72			Mean $\frac{Vg}{Vmax}$ =1.03

Table 7

Harrowed calcareous grassland, Harwell, Oxfordshire

16-17/3/1988, soil pH = 8.4, Zo = 0.3-0.6cm

Time (GMT)	U[1m] ms^{-1}	Vmax $cm\ s^{-1}$	L m	T[Zo'] °C	X[1m] $\mu g m^{-3}$	Flux [NH_3] $\mu g m^{-2}\ s^{-1}$	Vg $cm\ s^{-1}$	r_c sm^{-1}	X[Zo']	Surface
1000 1200	4.59	2.11	-93	10.2	2.97 ±0.17	22.0 ±15.8	0.74 ±0.53	87.5	1.92 ±0.62	Partly wet
1300 1445	4.84	2.30	-261	10.3	3.71 ±0.27	28.5 ±26.3	0.77 ±0.71	86.6	2.47 ±0.96	Drying
1535* 1645	4.04	1.61	NS	7.6	3.21 ±0.69	34.0 ±51.0	1.06 ±1.61	32.1	1.09 ±2.68	Dry
1735 0820	1.07	0.52	NS	4.2	0.33 ±0.00	0.23 ±0.11	0.07 ±0.03	1291	0.29 ±0.02	Wet
1015 1655	2.37	1.31	15.7	9.7	0.25 ±0.13	1.1 ±7.6	0.44 ±3.06	154	0.17 ±0.49	Dry
1800 0915	1.01	1.59	NS	3.5	0.12 ±0.04	0.12 ±2.81	0.10 ±2.40	916	0.11 ±0.15	Partly wet

Table 8 **Dunslair Heights, Glentress Forest, Peebles**

Dry deposition fluxes of gaseous ammonia and particulate/aerosol ammonium

12-17/11/1988, winds S-W, 4-7°C, L > |200|, z_0 = 0.16 - 0.32m

AMMONIA Errors are 95% confidence limits

Date Time (GMT)	U[1m] ms^{-1}	V_{max} $cm\ s^{-1}$	$X[\overline{z-d}]$ μgm^{-3}	$F[NH_3]$ $ngm^{-2}s^{-1}$	V_g[1m] cms^{-1}	r_c sm^{-1}	Canopy
12 1130 1335	3.4	8.3	0.12 ± 0.05	14.4 ± 122	16.7 ± 153	-6.1	Dry
12 1415 1630	5.0	9.0	0.11 -	9.9 max.	-	-	Partly wet
14 1255 1600	4.8	7.3	0.43 ± 0.06	27.7 ± 103	8.19 ± 31.7	-1.5	Wet
15 1110 1355	4.1	6.4	0.06 ± 0.02	3.8 max.	-	-	Wet
15 1445 1640	2.3	4.2	0.13 ± 0.61	0.8 ± 527	0.66 ± 423	129	Wet
16 1115 1350	2.7	4.8	0.13 ± 0.05	1.0 ± 59	0.80 ± 48.4	104	Wet
17 1305 1630	2.1	4.1	0.06 ± 0.04	- 13.1 ± 29.1	-	-	In cloud Wet
Mean (4)	3.29	5.69	0.17	11.0	6.55	- 2.3	$\frac{V_g}{V_m}$ =1.15
AMMONIUM							
12 1130 1630	4.3	-	0.32 ± 0.03	10.9 ± 94	3.75 ± 22.8	-	Partly wet
14 1255 1600	4.8	-	0.46 ± 0.09	2.1 ± 147	0.48 ± 32.7	-	Wet
15 1110 1640	3.4	-	1.22 ± 0.05	18.7 ± 55.9	1.65 ± 4.96	-	Wet
16 1115 1350	2.7	-	3.26 ± 0.13	9.1 ± 146	0.28 ± 4.54	-	Wet
17 1350 1605	2.1	-	0.43 ± 0.06	7.9 ± 59.2	0.16 ± 16.3	-	Wet
Mean (5)	3.45	-	1.09	9.74	0.39	-	$\frac{V_g}{V_m(NH_3)}$ =0.16

Method: micrometeorology

- large ground area measured
- net interaction with atmosphere
- does not disturb canopy

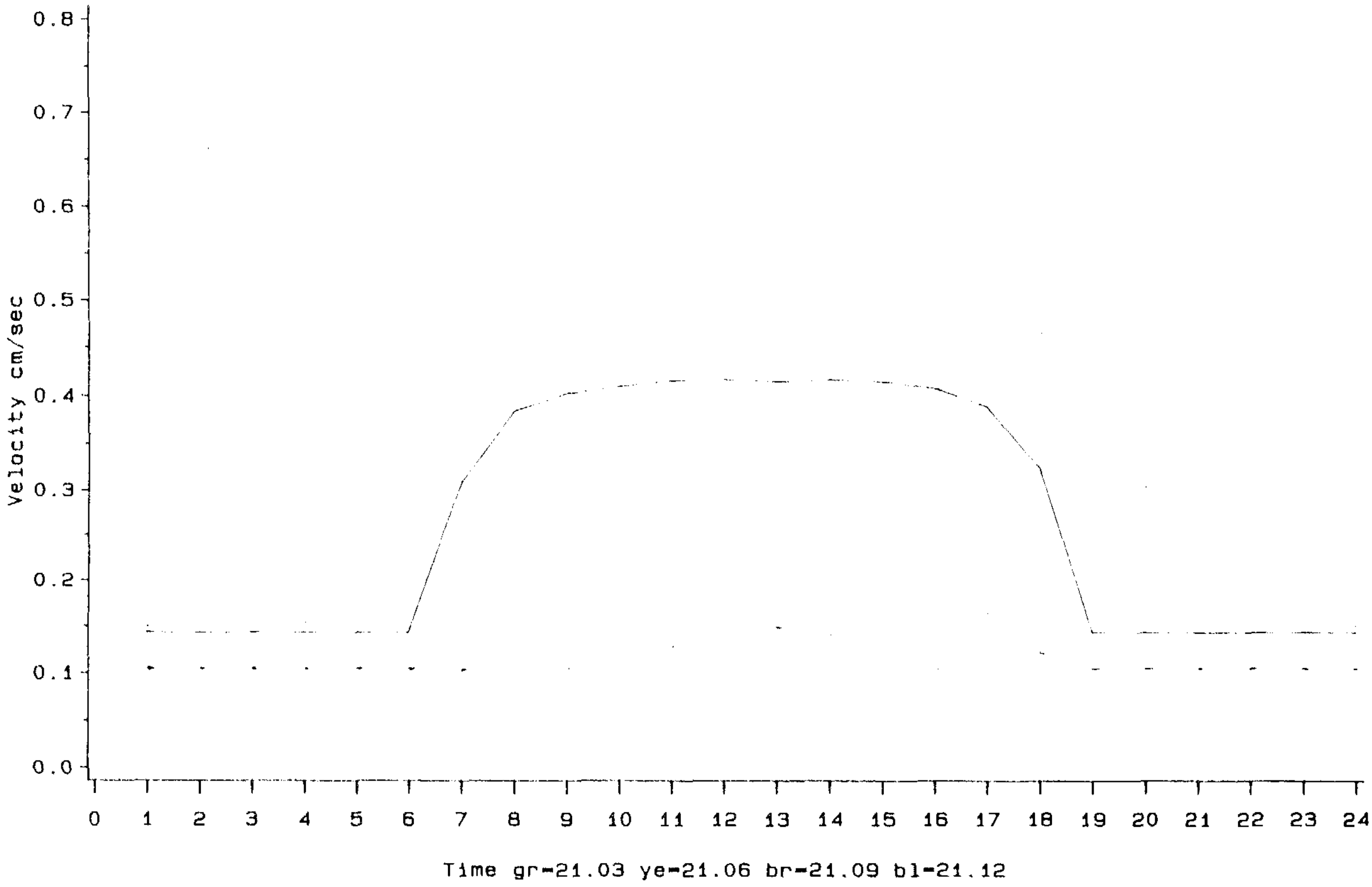
Aerodynamic gradient method - permits large detection times needed.

Dry deposition in the UK

The existing maps of SO_2 dry deposition provided the review group on acid-rain were produced by selecting appropriate deposition velocities for 5 UK land classes and applying these to the modelled SO_2 concentration field. There are two major defects with this approach, first the concentration field used was calculated using a long range transport model for SO_2, which contains a deposition velocity as an important variable. Second, the land classification data was crude and each 20 x 20 km grid square was constrained to be just one of the land uses.

To improve on the earlier map we have used the measured SO_2 concentration field supplied by the Warren Spring Laboratory and interpolated on a 20 x 20 km grid. Second, we have calculated the percentage land use occupied by each of the land classes in each 20 x 20 km grid square and modelled SO_2 dry deposition. The model uses 1 hour time steps and for each grid square and each land class it calculates bulk canopy conductance for SO_2 from time of day, Julian date and temperature. The cuticular conductances are set as constant from literature values and diurnal profiles for each of the land

Diurnal cycle in deposition velocity of grass



(10) SO2-FLUX FROM APRIL 87 to MARCH 88

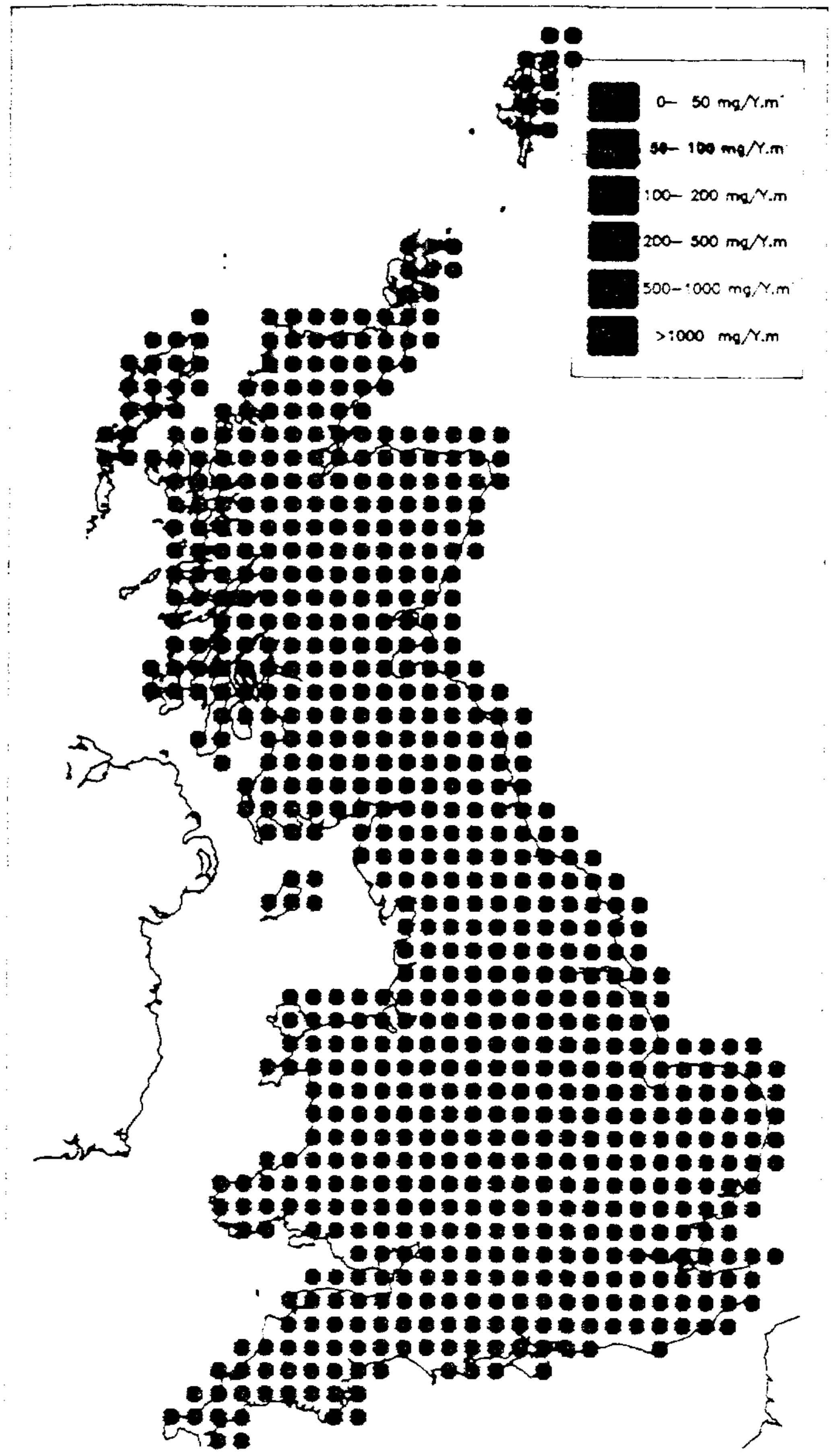


TABLE A1

AMBIENT 03,NO,NO2 and SO2 MEANS AND MAXIMA (ppbV) for 1988

CY = calendar year, SM = summer.

POLLUTANT	CY Mean	CY Max	SM Mean	SM Max	CY Data Capt
03 (M.Labs)	27	89	30	89	97%
NO (M.Labs)	1	62	0.7	19	95%
NO2 (M.Labs)	5.5	43	4.5	39	95%
NO2 (Scintrex)	5.8	43	4.6	38	88%
NO2 (AA)	5.8	40	4.8	30	47%
NO2 (Diff. Tubes)	6.0	-	-	-	-
SO2 (M.Labs)	2.2	50	1.9	50	90%

classes have been compared with published deposition velocity-time profiles. The results are then summed for all grid squares and land classes to provide monthly or annual deposition. The result is shown in figure and leads to a much smaller SO_2 dry deposition estimate for the UK (1.8×10^5 tonnes SO_2 per year). A paper describing the method and results is in preparation and the results will be incorporated in the next report of the review group on acid rain.

2. Open-top chamber studies of effects of O_3 and acid mist on Norway spruce and beech

O_3

In the first experiment in 1988, Beech and Norway spruce seedlings which had been grown from seed in charcoal filtered air in a glasshouse were subject to the following treatment:

Charcoal filtered air (CF)	- 2 chambers -	each	with	50 Norway	spruce +	50 beech
Ambient (see table 1)	"	"	"	"	"	"
CF + episodes to 100 ppbV O_3	"	"	"	"	"	"
CF + " " 140 ppbV O_3	"	"	"	"	"	"
CF + " " 140 ppbV O_3 + acid mist	2 chambers			"	"	"

Episodes of O_3 were generated from pure oxygen and metered into the charcoal filtered outlet from the fan-filter unit whenever air temperatures in the chamber exceed 15°C <u>and</u> global short wave radiation exceeds 400 Wm^{-2}. Using these criteria the cumulative total during 1988 was 211 hours in the period

June-September. The duration of individual episodes varied between 2 and 8 hours but averaged 6.3 hours for the 33 days. These exposures were designed to produce an episode regime similar to that at low or moderate altidude sites in Bavaria or the Black Forest. In this way they differ from high altitude sites (eg Schauiusland), where in episode conditions elevated O_3 concentrations may persist continuously for several days.

The acid mist treatment was included to simulate the moderate altitude site which experienced polluted cloud water twice each week as well as frequent O_3 episodes. The composition of the acid mist spray was H_2SO_4 + NH_4NO_3 at a pH of 2.5. The mixture had been shown in earlier work (autumn 1987 to induce damage to Red spruce.

Acid Mist

In a separate group of 12 open-top chambers the observations of extensive damage to Red spruce from the Autumn 1987 experiment was followed up by an experiment to show which ion or combination of ions caused the damage. Norway spruce was included to show the relative responses of Norway spruce and Red spruce. The treatments were all applied in charcoal filtered air in chambers with lids to exclude rain. The spray system provided droplets with a number mean radius of about 40 um which were applied at a precipitation equivalent rate of 3 mm h^{-1}. Each application provided 2 mm of solution to the plants and was just enough to cause drip from the foliage.

The treatments were as in Table 9.

Table 9

	Solutions		pH	$[H^+]$/mM	$[NH_4^+]$/mM	$[NO_3^-]$/mM	$[SO_4^=]$/mM
	$H_2SO_4+NH_4NO_3$		2.5	3.2	1.6	1.6	1.6
	$(NH_4)_2SO_4$		5.6	-	3.2	-	1.6
	NH_4NO_3		5.6	-	1.6	1.6	-
1988	H_2SO_4	a)	2.5	3.2	-	-	1.6
	H_2SO_4	b)	3.0	1.0	-	-	0.5
	HNO_3		2.5	3.2	-	3.2	-
	H_2O (control)		5.6	-	-	-	-

RESULTS

The Beech and Norway spruce were subject to a range of physiological and growth analysis measurements during and following treatment.

1. Growth measurements

Plant height measurements throughout the treatment period showed no treatment differences. At harvest during December 1988 Norway spruce plants from all ozone treatments showed similar amounts of growth and with similar partitioning into foliage stress and roots (Table 9b). The large numbers of plants used allowed us to detect quite small treatment differences (< 10%) but no treatments effects were detected. Such results are similar to many published responses of conifers in the first year of ozone treatment. We therefore allocated a block of plants for the second years experiment to show

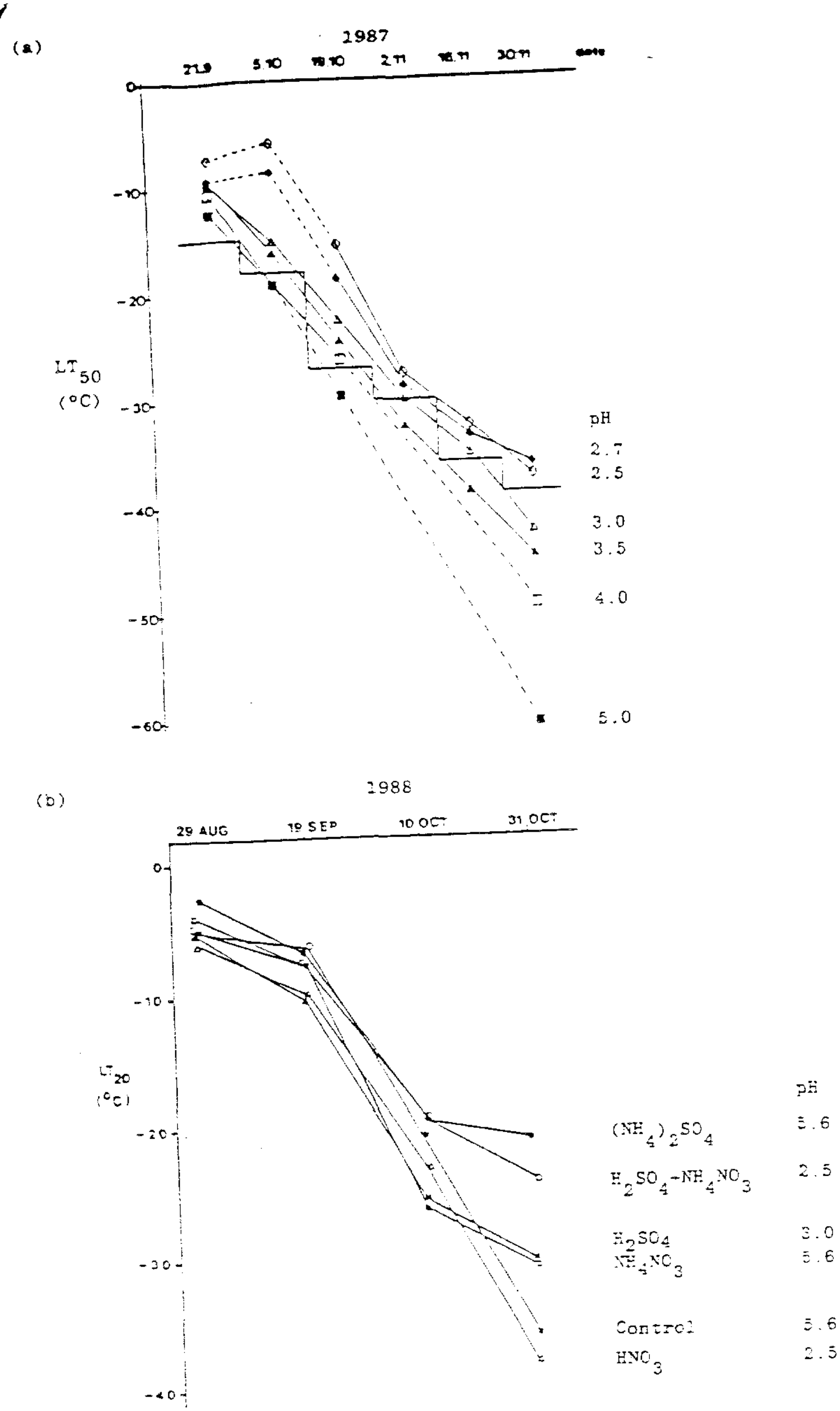


Figure 11. Development of shoot frost hardiness in red spruce seedlings receiving different acid mist treatments.

LT_{50} = temperature killing 50% of shoots; LT_{20} = temperature killing 20% of shoots.

VARIABLE	N	MEAN	STANDARD DEVIATION	C.V	STD ERROR OF MEAN
CHAMBER=1					
STEM	10	0.21609430	0.03266116	15.114	0.01032837
NEEDLE	10	0.36890689	0.03386250	9.179	0.01070826
TOTAL	10	0.58500120	0.02782124	4.756	0.00879785
CHAMBER=2					
STEM	10	0.23261099	0.02644554	11.369	0.00836281
NEEDLE	10	0.37118042	0.02919889	7.866	0.00923350
TOTAL	10	0.60379141	0.03521672	5.833	0.01113650
CHAMBER=3					
STEM	9	0.20182472	0.02159823	10.701	0.00719941
NEEDLE	9	0.36561877	0.04363809	11.935	0.01454603
TOTAL	9	0.56744349	0.03872733	6.825	0.01290911
CHAMBER=4					
STEM	10	0.21701521	0.02235740	10.302	0.00707003
NEEDLE	10	0.35330905	0.03189872	9.029	0.01008726
TOTAL	10	0.57032426	0.02743568	4.811	0.00867592
CHAMBER=5					
STEM	10	0.21951574	0.04062014	18.505	0.01284528
NEEDLE	10	0.37577661	0.04088449	10.880	0.01292881
TOTAL	10	0.59529234	0.02055005	3.452	0.00649850
CHAMBER=6					
STEM	8	0.22307339	0.04527963	20.298	0.01600877
NEEDLE	8	0.36873693	0.04220200	11.445	0.01492066
TOTAL	8	0.59181033	0.02971312	5.021	0.01050517
CHAMBER=7					
STEM	9	0.20948325	0.03215849	15.351	0.01071950
NEEDLE	9	0.36716237	0.02983715	8.126	0.00994572
TOTAL	9	0.57664563	0.03112169	5.397	0.01037390
CHAMBER=8					
STEM	9	0.24350403	0.04267083	17.524	0.01422361
NEEDLE	9	0.33696428	0.10907319	32.369	0.03635773
TOTAL	9	0.58046830	0.08602480	14.820	0.02867493
CHAMBER=9					
STEM	10	0.24598187	0.02968773	12.069	0.00938809
NEEDLE	10	0.36383693	0.02047091	5.626	0.00647347
TOTAL	10	0.60981880	0.02367047	3.882	0.00748526

VARIABLE	N	MEAN	STANDARD DEVIATION	C.V.	STD ERROR OF MEAN
CHAMBER=10 (140)					
STEM	9	0.23001818	0.03780321	16.435	0.01260107
NEEDLE	9	0.39432640	0.05159740	13.085	0.01719913
TOTAL	9	0.62434458	0.05823207	9.327	0.01941069
CHAMBER=11 (100)					
STEM	10	0.23665540	0.04371482	18.472	0.01382384
NEEDLE	10	0.35568050	0.03147367	8.849	0.00995285
TOTAL	10	0.59233589	0.03657881	6.175	0.01156723
CHAMBER=12 (open)					
STEM	3	0.22645669	0.01460607	6.450	0.00843282
NEEDLE	3	0.36047841	0.02633883	7.307	0.01520673
TOTAL	3	0.58693510	0.02755407	4.695	0.01590835

OBS	PLANT	N1	S1	N2	S2	DIAM	STEM	NEEDLE	TOTAL	CHAMBER
1	1	2.987	6.404	8.152	4.116	9.000	0.190036	0.376379	0.566416	1
2	2	2.415	8.596	9.000	5.931	12.770	0.228625	0.346928	0.575553	1
3	3	3.220	8.511	13.269	6.764	11.140	0.212945	0.417737	0.630683	1
4	4	4.126	8.253	12.323	4.641	9.900	0.158164	0.419964	0.578128	1
5	5	2.000	5.374	6.594	3.742	8.335	0.211293	0.372332	0.583625	1
6	6	3.091	11.283	11.107	9.296	13.140	0.267303	0.319378	0.586681	1
7	7	2.404	8.487	8.599	5.973	9.875	0.234576	0.337706	0.572281	1
8	8	2.872	10.276	13.322	9.254	11.895	0.259042	0.372915	0.631956	1
9	9	3.482	7.680	10.428	5.287	11.275	0.196711	0.387990	0.584701	1
10	10	2.425	9.855	9.016	5.399	9.580	0.202248	0.337741	0.539989	1
11	11	2.327	8.620	10.369	7.582	10.150	0.262371	0.358814	0.621185	2
12	12	1.644	7.472	9.171	5.792	12.455	0.240542	0.380871	0.621413	2
13	13	4.549	10.690	12.660	7.032	13.275	0.201311	0.362429	0.563740	2
14	14	2.299	7.354	8.165	6.315	11.115	0.261675	0.338333	0.600008	2
15	15	2.894	9.243	8.796	4.966	11.745	0.191745	0.339627	0.531372	2
16	16	3.432	8.664	12.288	7.142	11.800	0.226543	0.389774	0.616317	2
17	17	3.097	6.760	11.665	6.045	11.805	0.219284	0.423151	0.642435	2
18	18	2.342	8.255	12.127	7.272	11.755	0.242432	0.404287	0.646720	2
19	19	2.435	11.488	11.906	9.400	12.740	0.266826	0.337960	0.604786	2
20	20	2.100	6.223	7.643	4.331	9.195	0.213381	0.376558	0.589939	2
21	21	3.293	10.067	9.606	5.545	10.020	0.194486	0.336923	0.531409	3
22	22	.	.	.	.	11.500	.	.	.	3
23	23	3.946	9.429	11.625	5.151	7.295	0.170840	0.385559	0.556399	3
24	24	3.593	7.056	14.470	5.523	10.930	0.180243	0.472228	0.652470	3
25	25	3.149	9.643	10.251	6.899	9.640	0.230412	0.342362	0.572774	3
26	26	4.393	13.790	13.748	9.240	13.285	0.224430	0.333924	0.558354	3
27	27	4.546	12.317	14.200	8.212	10.750	0.209090	0.361553	0.570643	3
28	28	2.225	1.612	9.087	5.478	9.200	0.224490	0.372388	0.596877	3
29	29	1.946	4.200	4.447	2.374	9.035	0.183080	0.342947	0.526028	3
30	30	3.716	11.400	11.311	6.580	13.775	0.199352	0.342685	0.542037	3
31	31	4.451	9.453	14.326	6.235	11.165	0.180908	0.415668	0.596576	4
32	32	2.013	5.186	7.932	4.586	9.580	0.232591	0.402292	0.634884	4
33	33	2.867	7.650	8.215	5.222	9.935	0.218001	0.342949	0.560950	4
34	34	3.000	7.092	8.275	4.939	10.470	0.211920	0.355059	0.566978	4
35	35	4.324	8.200	9.458	4.806	11.335	0.179409	0.353069	0.532477	4
36	36	2.225	6.748	7.176	4.492	10.990	0.217625	0.347658	0.565283	4
37	37	1.457	4.500	4.519	3.284	8.540	0.238663	0.328416	0.567078	4
38	38	4.084	9.804	10.461	7.115	10.470	0.226131	0.332475	0.558607	4
39	39	2.189	8.886	7.948	6.273	9.155	0.247984	0.314200	0.562184	4
40	40	3.565	8.294	9.162	5.823	9.350	0.216920	0.341305	0.558225	4
41	41	4.176	8.922	13.582	5.154	9.830	0.161902	0.426651	0.588553	5
42	42	2.459	9.930	10.106	7.932	12.130	0.260690	0.332139	0.592829	5
43	43	4.904	10.300	12.505	5.979	10.590	0.177482	0.371200	0.548682	5
44	44	1.832	6.486	6.797	4.742	8.290	0.238807	0.342297	0.581105	5
45	45	1.959	6.429	8.511	4.921	9.110	0.225527	0.390055	0.615582	5
46	46	2.970	10.478	12.184	9.066	10.830	0.261283	0.351144	0.612427	5
47	47	3.324	8.687	12.731	5.579	8.985	0.183998	0.419874	0.603872	5
48	48	3.645	7.806	12.659	5.216	11.440	0.177863	0.431665	0.609527	5
49	49	3.711	9.747	13.100	8.247	11.360	0.236949	0.376383	0.613331	5
50	50	2.365	10.910	10.169	8.700	12.125	0.270657	0.316358	0.587015	5
51	51	2.864	10.284	10.222	8.229	10.020	0.260420	0.323491	0.583911	6
52	52	4.049	7.841	12.039	5.120	8.280	0.176254	0.414438	0.590692	6
53	53	.	.	.	.	10.540	.	.	.	6
54	54	2.730	11.107	11.377	8.854	12.210	0.259892	0.333950	0.593842	6
55	55	3.542	6.208	10.700	3.820	8.750	0.157396	0.440874	0.598269	6

OBS	PLANT	N1	S1	N2	S2	DIAM	STEM	NEEDLE	TOTAL	CHAMBER
56	56	4.370	9.989	12.426	6.668	11.48	0.199324	0.371447	0.570771	6
57	57	.	.	.	.	11.54	.	.	.	6
58	58	0.340	7.993	8.692	6.963	11.10	0.290270	0.362348	0.652618	6
59	59	1.282	7.314	6.207	4.219	9.65	0.221796	0.326306	0.548102	6
60	60	2.165	7.792	9.299	5.407	9.72	0.219235	0.377043	0.596278	6
61	61	5.015	12.804	15.078	8.249	12.28	0.200481	0.366451	0.566932	7
62	62	3.254	12.112	12.456	8.097	12.40	0.225424	0.346780	0.572204	7
63	63	4.420	8.518	11.355	4.618	8.76	0.159732	0.392757	0.552489	7
64	64	2.079	7.850	9.015	6.260	9.82	0.248373	0.357681	0.606055	7
65	65	3.858	9.425	10.403	5.463	11.62	0.187416	0.356890	0.544307	7
66	66	2.429	10.785	10.796	7.903	12.95	0.247642	0.338295	0.585937	7
67	67	5.375	13.026	16.044	7.053	13.08	0.169960	0.386621	0.556581	7
68	68	3.927	12.048	19.080	9.726	16.80	0.217190	0.426074	0.643264	7
69	69	.	.	8.257	5.284	10.04	.	.	.	7
70	70	3.103	10.055	10.002	6.884	11.12	0.229131	0.332912	0.562042	7
71	71	4.561	12.314	1.526	7.957	12.74	0.301882	0.057895	0.359777	8
72	72	4.033	14.211	14.556	12.630	13.50	0.278010	0.320405	0.598415	8
73	73	4.429	11.071	17.999	9.637	10.56	0.223410	0.417262	0.640671	8
74	74	3.620	13.148	17.439	9.860	11.98	0.223750	0.395738	0.619489	8
75	75	2.111	6.663	7.927	6.310	8.81	0.274217	0.344487	0.618704	8
76	76	3.825	12.711	14.200	9.533	14.47	0.236733	0.352629	0.589362	8
77	77	.	.	.	.	10.34	.	.	.	8
78	78	1.002	4.400	5.363	4.115	8.40	0.276546	0.360417	0.636962	8
79	79	6.059	11.408	16.287	6.703	9.35	0.165682	0.402576	0.568258	8
80	80	3.722	9.956	12.800	7.094	10.72	0.211307	0.381270	0.592577	8
81	81	3.259	8.121	10.438	6.042	9.51	0.216870	0.374659	0.591529	9
82	82	2.607	6.516	7.900	4.060	9.73	0.192572	0.374709	0.567282	9
83	83	2.553	8.168	10.529	7.620	9.37	0.263942	0.364704	0.628646	9
84	84	2.244	7.889	9.353	8.222	9.76	0.296737	0.337556	0.634293	9
85	85	2.539	8.053	9.080	6.841	11.24	0.258024	0.342474	0.600498	9
86	86	1.943	7.580	8.536	6.738	10.55	0.271726	0.344235	0.615962	9
87	87	2.977	10.650	11.500	7.592	8.87	0.232036	0.351478	0.583514	9
88	88	1.900	6.757	8.058	5.653	10.10	0.252727	0.360247	0.612974	9
89	89	2.150	7.050	10.099	6.300	13.25	0.246103	0.394508	0.640611	9
90	90	4.450	10.246	15.346	8.927	14.20	0.229080	0.393800	0.622880	9
91	91	1.781	5.993	7.820	5.203	9.34	0.250180	0.376016	0.626196	10
92	92	3.419	10.002	11.094	8.377	10.22	0.254682	0.337286	0.591968	10
93	93	0.679	7.135	15.160	6.548	10.48	0.221801	0.513515	0.735316	10
94	94	3.444	9.331	13.010	5.266	8.26	0.167435	0.413659	0.581094	10
95	95	.	.	.	.	10.67	.	.	.	10
96	96	2.352	6.591	12.059	8.898	10.04	0.297592	0.403311	0.700903	10
97	97	4.206	9.123	13.887	7.144	10.37	0.207916	0.404162	0.612078	10
98	98	3.511	12.393	14.959	10.284	10.26	0.249933	0.363550	0.613483	10
99	99	3.378	9.926	13.139	7.478	11.64	0.220453	0.387341	0.607795	10
100	100	2.977	6.502	7.379	4.219	8.71	0.200171	0.350097	0.550268	10
101	101	2.354	8.440	9.905	6.199	12.48	0.230463	0.368243	0.598706	11
102	102	5.400	15.818	15.931	8.398	11.56	0.184381	0.349771	0.534152	11
103	103	2.960	9.758	10.716	7.751	11.84	0.248549	0.343627	0.592176	11
104	104	3.339	6.069	9.268	4.921	8.30	0.208543	0.392762	0.601305	11
105	105	3.100	10.048	13.433	7.100	10.19	0.210801	0.398830	0.609632	11
106	106	2.035	6.804	6.278	3.511	8.68	0.188480	0.337020	0.525499	11
107	107	1.239	6.300	5.743	5.703	8.89	0.300395	0.302502	0.602897	11
108	108	3.650	8.465	12.357	7.000	9.16	0.222420	0.392635	0.615055	11
109	109	1.166	4.690	5.600	5.194	9.81	0.311952	0.336336	0.648288	11
110	110	2.850	11.965	12.277	9.547	11.38	0.260569	0.335080	0.595649	11

OBS	PLANT	N1	S1	N2	S2	DIAM	STEM	NEEDLE	TOTAL	CHAMBER
111	111	3.042	8.438	10.952	6.088	10.81	0.213464	0.384011	0.597475	12
112	112	.	.	.	.	.	.	.	.	12
113	113	.	.	.	.	.	.	.	.	12
114	114	.	.	.	.	.	.	.	.	12
115	115	3.223	12.310	11.607	7.818	10.66	0.223640	0.332027	0.555667	12
116	116	.	.	.	.	.	.	.	.	12
117	117	.	.	.	.	.	.	.	.	12
118	118	.	.	.	.	.	.	.	.	12
119	119	.	.	.	.	.	.	.	.	12
120	120	2.906	9.269	11.339	7.518	9.07	0.242266	0.365397	0.607663	12

ANALYSIS OF VARIANCE PROCEDURE

CLASS LEVEL INFORMATION

CLASS	LEVELS	VALUES
TREAT	5	100 140 140+mist ambient clean
REP	2	2 3

NUMBER OF OBSERVATIONS IN DATA SET = 120

NOTE: ALL DEPENDENT VARIABLES ARE CONSISTENT WITH RESPECT TO THE PRESENCE OR ABSENCE OF MISSING VALUES. HOWEVER, ONLY 107 OBSERVATIONS CAN BE USED IN THIS ANALYSIS.

ANALYSIS OF VARIANCE PROCEDURE

TUKEY'S STUDENTIZED RANGE (HSD) TEST FOR VARIABLE: TOTAL
NOTE: THIS TEST CONTROLS THE TYPE I EXPERIMENTWISE ERROR RATE

ALPHA=0.05 CONFIDENCE=0.95 DF=102 MSE=.0017098
CRITICAL VALUE OF STUDENTIZED RANGE=3.928

COMPARISONS SIGNIFICANT AT THE 0.05 LEVEL ARE INDICATED BY '***'

TREAT COMPARISON	SIMULTANEOUS LOWER CONFIDENCE LIMIT	DIFFERENCE BETWEEN MEANS	SIMULTANEOUS UPPER CONFIDENCE LIMIT
140 - 140+mist	-0.03140	0.00648	0.04436
140 - 100	-0.01421	0.02413	0.06247
140 - clean	-0.01146	0.02562	0.06271
140 - ambient	-0.00701	0.02806	0.06314
140+mist - 140	-0.04436	-0.00648	0.03140
140+mist - 100	-0.01914	0.01765	0.05444
140+mist - clean	-0.01633	0.01915	0.05462
140+mist - ambient	-0.01179	0.02158	0.05496
100 - 140	-0.06247	-0.02413	0.01421
100 - 140+mist	-0.05444	-0.01765	0.01914
100 - clean	-0.03447	0.00149	0.03746
100 - ambient	-0.02996	0.00393	0.03783
clean - 140	-0.06271	-0.02562	0.01146
clean - 140+mist	-0.05462	-0.01915	0.01633
clean - 100	-0.03746	-0.00149	0.03447
clean - ambient	-0.03003	0.00244	0.03491
ambient - 140	-0.06314	-0.02806	0.00701
ambient - 140+mist	-0.05496	-0.02158	0.01179
ambient - 100	-0.03783	-0.00393	0.02996
ambient - clean	-0.03491	-0.00244	0.03003

ANALYSIS OF VARIANCE PROCEDURE

TUKEY'S STUDENTIZED RANGE (HSD) TEST FOR VARIABLE: NEEDLE
NOTE: THIS TEST CONTROLS THE TYPE I EXPERIMENTWISE ERROR RATE

ALPHA=0.05 CONFIDENCE=0.95 DF=102 MSE=.0021401
CRITICAL VALUE OF STUDENTIZED RANGE=3.928

COMPARISONS SIGNIFICANT AT THE 0.05 LEVEL ARE INDICATED BY '***'

TREAT COMPARISON	SIMULTANEOUS LOWER CONFIDENCE LIMIT	DIFFERENCE BETWEEN MEANS	SIMULTANEOUS UPPER CONFIDENCE LIMIT
140 - 140+mist	-0.02990	0.01248	0.05486
140 - ambient	-0.02025	0.01899	0.05824
140 - 100	-0.02173	0.02117	0.06406
140 - clean	-0.01389	0.02759	0.06908
140+mist - 140	-0.05486	-0.01248	0.02990
140+mist - ambient	-0.03083	0.00651	0.04386
140+mist - 100	-0.03247	0.00869	0.04985
140+mist - clean	-0.02458	0.01512	0.05481
ambient - 140	-0.05824	-0.01899	0.02025
ambient - 140+mist	-0.04386	-0.00651	0.03083
ambient - 100	-0.03575	0.00217	0.04009
ambient - clean	-0.02772	0.00860	0.04493
100 - 140	-0.06406	-0.02117	0.02173
100 - 140+mist	-0.04985	-0.00869	0.03247
100 - ambient	-0.04009	-0.00217	0.03575
100 - clean	-0.03381	0.00643	0.04667
clean - 140	-0.06908	-0.02759	0.01389
clean - 140+mist	-0.05481	-0.01512	0.02458
clean - ambient	-0.04493	-0.00860	0.02772
clean - 100	-0.04667	-0.00643	0.03381

ANALYSIS OF VARIANCE PROCEDURE

TUKEY'S STUDENTIZED RANGE (HSD) TEST FOR VARIABLE: STEM
NOTE: THIS TEST CONTROLS THE TYPE I EXPERIMENTWISE ERROR RATE

ALPHA=0.05 CONFIDENCE=0.95 DF=102 MSE=.0012592
CRITICAL VALUE OF STUDENTIZED RANGE=3.928

COMPARISONS SIGNIFICANT AT THE 0.05 LEVEL ARE INDICATED BY '***'

TREAT COMPARISON	SIMULTANEOUS LOWER CONFIDENCE LIMIT	DIFFERENCE BETWEEN MEANS	SIMULTANEOUS UPPER CONFIDENCE LIMIT
140+mist - clean	-0.026418	0.004028	0.034475
140+mist - 140	-0.026510	0.005999	0.038508
140+mist - 100	-0.022606	0.008964	0.040535
140+mist - ambient	-0.013574	0.015070	0.043714
clean - 140+mist	-0.034475	-0.004028	0.026418
clean - 140	-0.029853	0.001970	0.033793
clean - 100	-0.025928	0.004936	0.035800
clean - ambient	-0.016821	0.011042	0.038904
140 - 140+mist	-0.038508	-0.005999	0.026510
140 - clean	0.033793	-0.001970	0.029853
140 - 100	-0.029934	0.002966	0.035866
140 - ambient	-0.021031	0.009071	0.039174
100 - 140+mist	-0.040535	-0.008964	0.022606
100 - clean	-0.035800	-0.004936	0.025928
100 - 140	-0.035866	-0.002966	0.029934
100 - ambient	-0.022981	0.006106	0.035192
ambient - 140+mist	-0.043714	-0.015070	0.013574
ambient - clean	-0.038904	-0.011042	0.016821
ambient - 140	-0.039174	-0.009071	0.021031
ambient - 100	-0.035192	-0.006106	0.022981

ANALYSIS OF VARIANCE PROCEDURE

DEPENDENT VARIABLE: TOTAL

SOURCE	DF	SUM OF SQUARES	MEAN SQUARE	F VALUE	PR > F	R-SQUARE	C.V.
MODEL	4	0.01307798	0.00326949	1.91	0.1141	0.069759	7.0005
ERROR	102	0.17439629	0.00170977		ROOT MSE		TOTAL MEAN
CORRECTED TOTAL	106	0.18747427			0.04134934		0.59066397

SOURCE	DF	ANOVA SS	F VALUE	PR > F
TREAT	4	0.01307798	1.91	0.1141
REP	1	0.00727574	4.26	0.0417
TREAT*REP	-1	0.00000000	.	.

TESTS OF HYPOTHESES USING THE ANOVA MS FOR TREAT*REP AS AN ERROR TERM

SOURCE	DF	ANOVA SS	F VALUE	PR > F
TREAT	4	0.01307798	.	.

ANALYSIS OF VARIANCE PROCEDURE

DEPENDENT VARIABLE: NEEDLE

SOURCE	DF	SUM OF SQUARES	MEAN SQUARE	F VALUE	PR > F	R-SQUARE	C.V.
MODEL	4	0.00823515	0.00205879	0.96	0.4318	0.036354	12.6615
ERROR	102	0.21829427	0.00214014		ROOT MSE		NEEDLE MEAN
CORRECTED TOTAL	106	0.22652942			0.04626165		0.36537272

SOURCE	DF	ANOVA SS	F VALUE	PR > F
TREAT	4	0.00823515	0.96	0.4318
REP	1	0.00326841	1.53	0.2194
TREAT*REP	-1	0.00000000	.	.

TESTS OF HYPOTHESES USING THE ANOVA MS FOR TREAT*REP AS AN ERROR TERM

SOURCE	DF	ANOVA SS	F VALUE	PR > F
TREAT	4	0.00823515	.	.

ANALYSIS OF VARIANCE PROCEDURE

DEPENDENT VARIABLE: STEM

SOURCE	DF	SUM OF SQUARES	MEAN SQUARE	F VALUE	PR > F	R-SQUARE	C.V.
MODEL	4	0.00313087	0.00078272	0.62	0.6481	0.023797	15.7506
ERROR	102	0.12843434	0.00125916		ROOT MSE		STEM MEAN
CORRECTED TOTAL	106	0.13156521			0.03548465		0.22529125

SOURCE	DF	ANOVA SS	F VALUE	PR > F
TREAT	4	0.00313087	0.62	0.6481
REP	1	0.00079118	0.63	0.4298
TREAT*REP	-1	0.00000000	.	.

TESTS OF HYPOTHESES USING THE ANOVA MS FOR TREAT*REP AS AN ERROR TERM

SOURCE	DF	ANOVA SS	F VALUE	PR > F
TREAT	4	0.00313087	.	.

whether the second year produces larger treatment differences (> 10%), as has been shown by others. The Beech was subject to extensive aphid attack during the mid summer of 1988 which seriously confounded growth analysis and for this reason has not been tabulated.

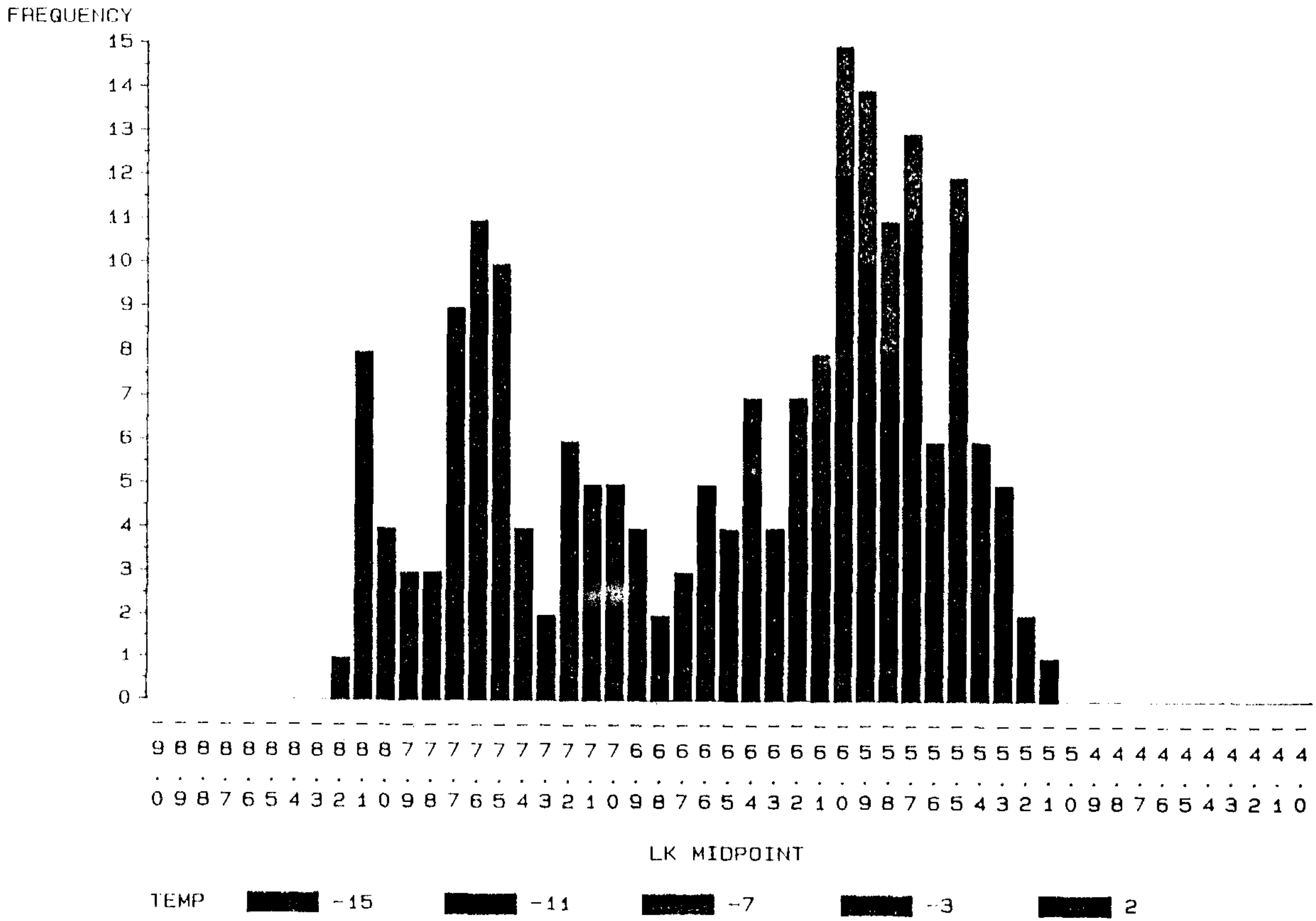
Unlike visible injury Red spruce which showed marked visible injury responses to acid mist at pH's in the range 2.5 to 3.5, the Norway spruce showed no foliar lesions in any of the treatments tabled. In the Ozone 'episode' chambers the only treatments to show visible injury were the O_3 at 140 ppbv + acid mist. In these chambers by the end of the experiment a third of all plants showed > 20% needle necrosis (34 plants out of 100) both true replicate chambers showing the same response, Table 10, even though individual treatments of O_3 at 140 ppbV or acid mist H_2SO_4 + NH_4NO_3 at pH 2.5 produced no significant visible injury.

NORWAY SPRUCE FROST-HARDINESS RESPONSE TO ACID MIST

The earlier work on Red spruce showed clear effects of acid mist on frost hardiness (Fig. 11). The 1988 experiment separated the major ions to identify the ion or ionic combination responsible for the response using both Red spruce and Norway spruce seedlings. The method used to deduce frost hardiness closely follows that developed for Red spruce and is based on electrolyte leakage. The method has been shown to quantify the needle mortality resulting from freezing treatment, the entire population of shoots taken from the freezing tests at 6 temperatures evenly spaced over 10^{o} above and below the killing temperature fall into two distinct populations, one with large electrolyte leakage rates, the needles from which quickly turn brown while the other with small electrolyte leakage rates do not quickly turn brown, Figure 12.

Histogram of log(k) values

SPECIES=Norway spruce



The critical value for electrolyte leakage separating these populations is used to determine the killing temperatures and can be shown to have a consistent value for the species throughout the experiment.

The testing of seedlings was done on 5 occasions during the autumn of 1988 from 29 August onwards. The lethal temperature for 20% shoot death (LT_{20}) at the first harvest 29 August (prior to the frost hardening period) was -4^{o}C and did not differ significantly between treatments. With time the frost hardiness gradually increased and by harvest 3 the frost hardiness (LT_{20}) ranged from -8^{o}C for the pH 2.5 mixture (H^{+}, SO_4^{2-}, NO_3^{-}, NH_4^{+}) and the $(NH_4)_2SO_4$ to -22^{o}C for the control (deionized water) by the harvest on 7th November the treatments were again significantly different. The LT_{20} of the H^{+}, SO_4^{2-}, NH_4^{+}, NO_3^{-} mixture at pH 2.5 was -10^{o}C while the control and HNO_3 (at pH 2.5) and NH_4NO_3 was -28^{o}C. The results are summarized in Table 5.

While the frost hardiness responses to acid mist are smaller for Norway spruce than Red spruce they are broadly similar. The general pattern identifies the SO_4^{2-} as that must consistently associated with the decreased frost hardiness and NO_3^{-} as the least important. On the 7th November harvest the Nitric Acid treatment was one of the least frost hardy but on all other sample dates (and on all sample dates for Red spruce) the HNO_3 treatments are the most frost hardy with the exception of the control.

Table 11

Frost hardiness of Norway spruce following acid mist treatment, values in the table are LT_{20} temperatures.

Date 1988		29.8	19.9	10.10	7.11	
H_2SO_4 NH_4NO_3 (pH 2.5)		-4	-4	-8	-19	**
H_2SO_4	pH 3.0*	-4	-4	-16	-27	
$(NH_4)_2$ SO_4	pH 5.0	-4	-4	-8	-24	*
NH_4NO_3	pH 5.0	-4	-4	-13	-28	
HNO_3	pH 2.5	-4	-4	-16	-13	*
'Control'						
deionized		-4	-4	-22	-27	

+After two weeks of initial H_2SO_4 at pH 2.5 all plants were badly damaged and were replaced, and H_2SO_4 concentrations reduced by a factor of 3.

Table 12

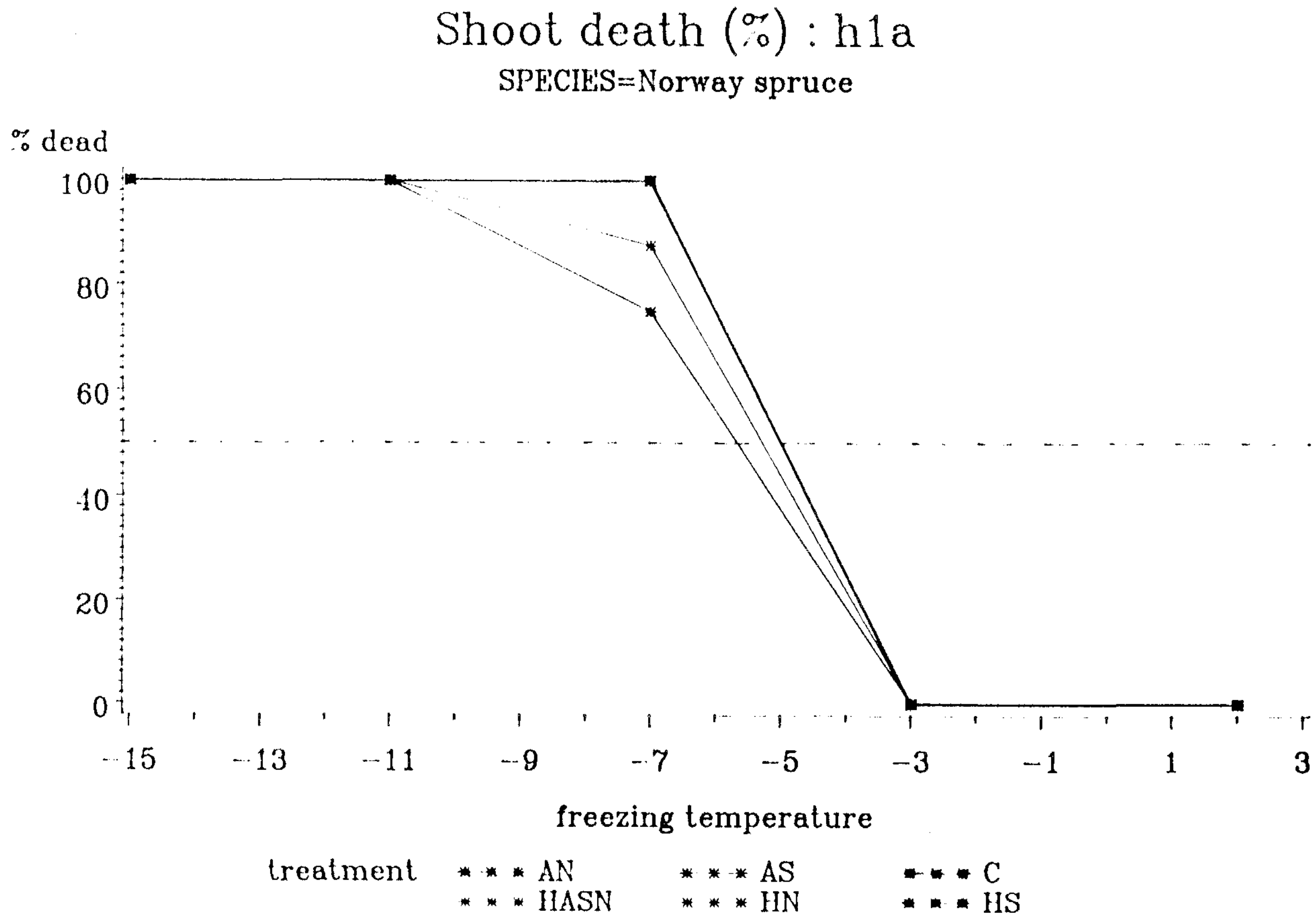
Frost hardiness of Norway spruce following ozone and acid mist treatment.

	Lethal temperature °C for LT_{100} needle death (LT_{100})
Charcoal filtered air	-34
Ambient	-33
CF + 100 ppbV O_3 (207h)	-34
CF + 140 ppbV O_3 (207h)	-28 *
CF + 140 ppbv O_3 (207h) + acid mist (pH 2.5)	-29 *

Figures 13, 14 and 15 show the variation of % of dead needles with freezing temperature (within the programmable freezing cabinet which is used to simulate air frosts). Figure 13 shows the results on the frost harvest, prior to frost hardening and Figures 14 and 15 show the results on the 10th October and 7th November.

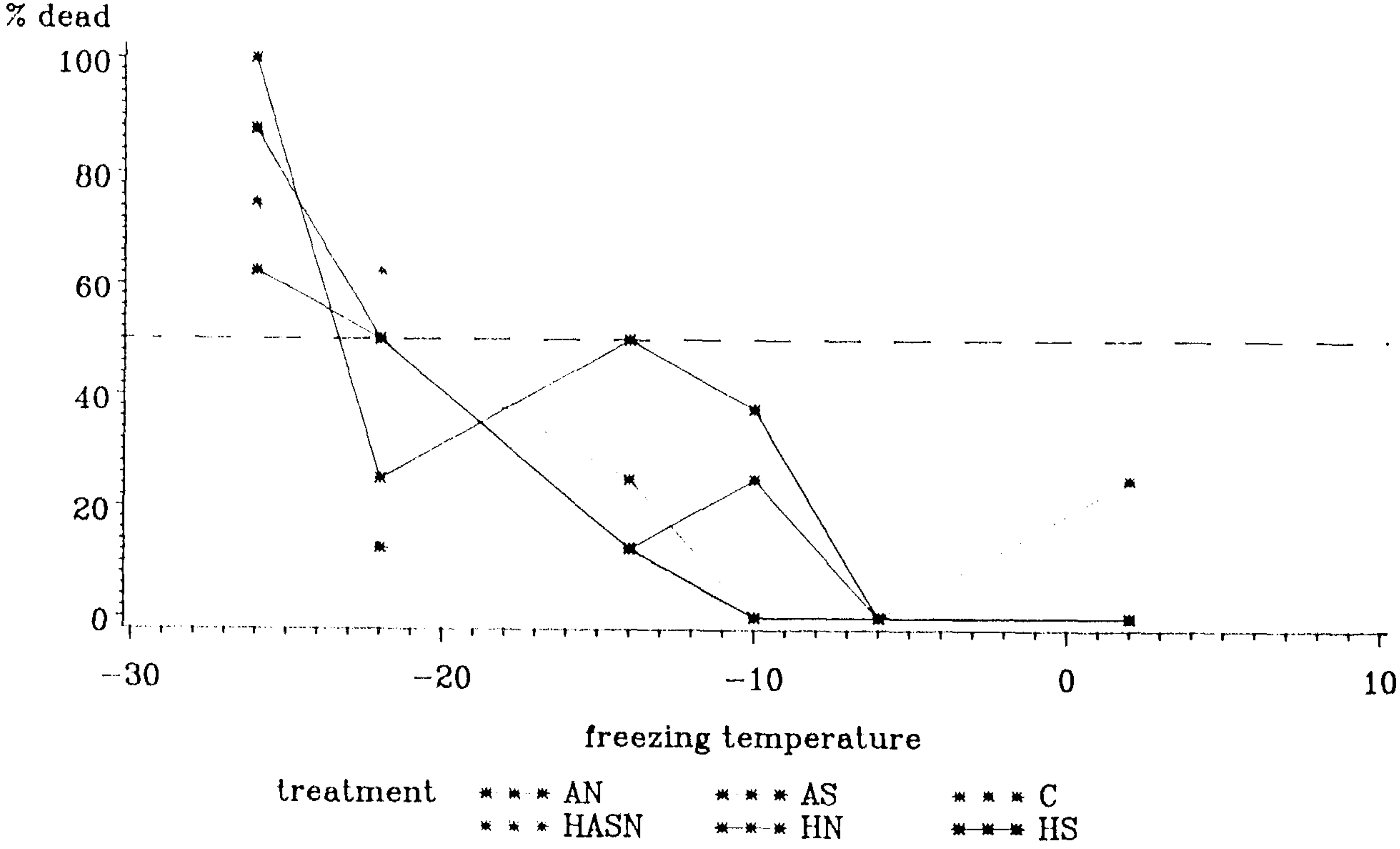
The responses of the O_3 and O_3 + acid mist treatments to frost were also tested to investigate the relative effects of O_3 acid mist.

Table 12 shows the LT_{50} temperatures for the 5 treatments at the 7th November harvest. The only two treatments which differed significantly from the control were the 140 ppbV O_3 and the 140 ppbV O_3 + acid mist, and these two treatments showed a similar effect. They were about 5°C less frost hardy than the control (or ambient or 100 ppbV O_3 treatments).

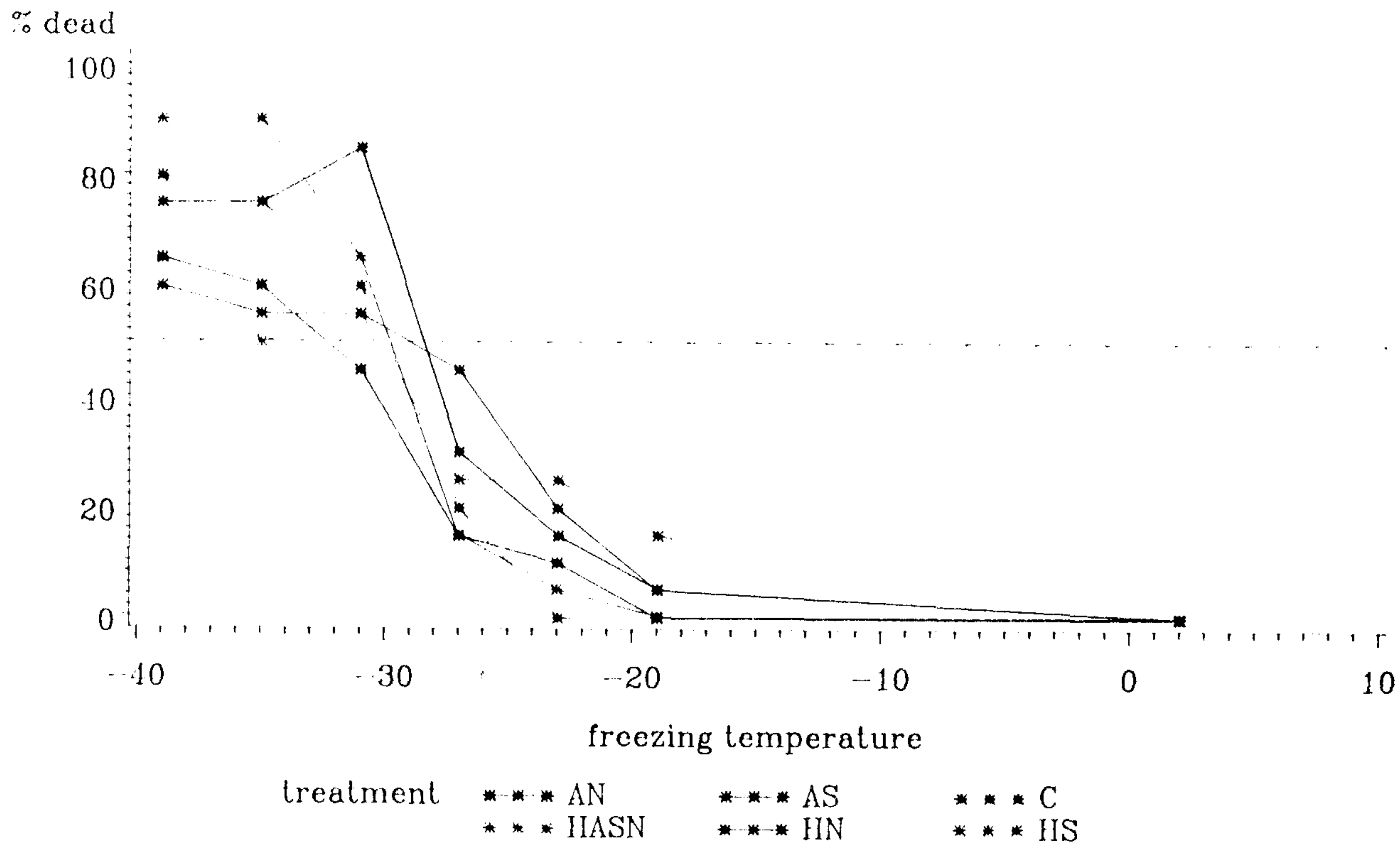

Shoot death (%) : h1a
SPECIES=Norway spruce
% dead
100
80
60
40
20
0
-15
-13
-11
-9
-7
-5
-3
-1
1
3
freezing temperature
treatment
AN
AS
C
HASN
HN
HS

Shoot death (%) : h3a

SPECIES=Norway spruce



Shoot death (%) : h5a



EXPERIMENTAL TREATMENTS 1989

Ozone

Charcoal filtered air (CF)	2	chambers	Norway	spruce	Beech
Ambient	2	"	"	"	"
CF + episodes of O_3 to 100 ppbV	2	"	"	"	"
CF + episodes of O_3 to 140 ppbV	2	"	"	"	"
CF + episodes of O_3 to 140 ppbV + acid mist	2	"	"	"	"

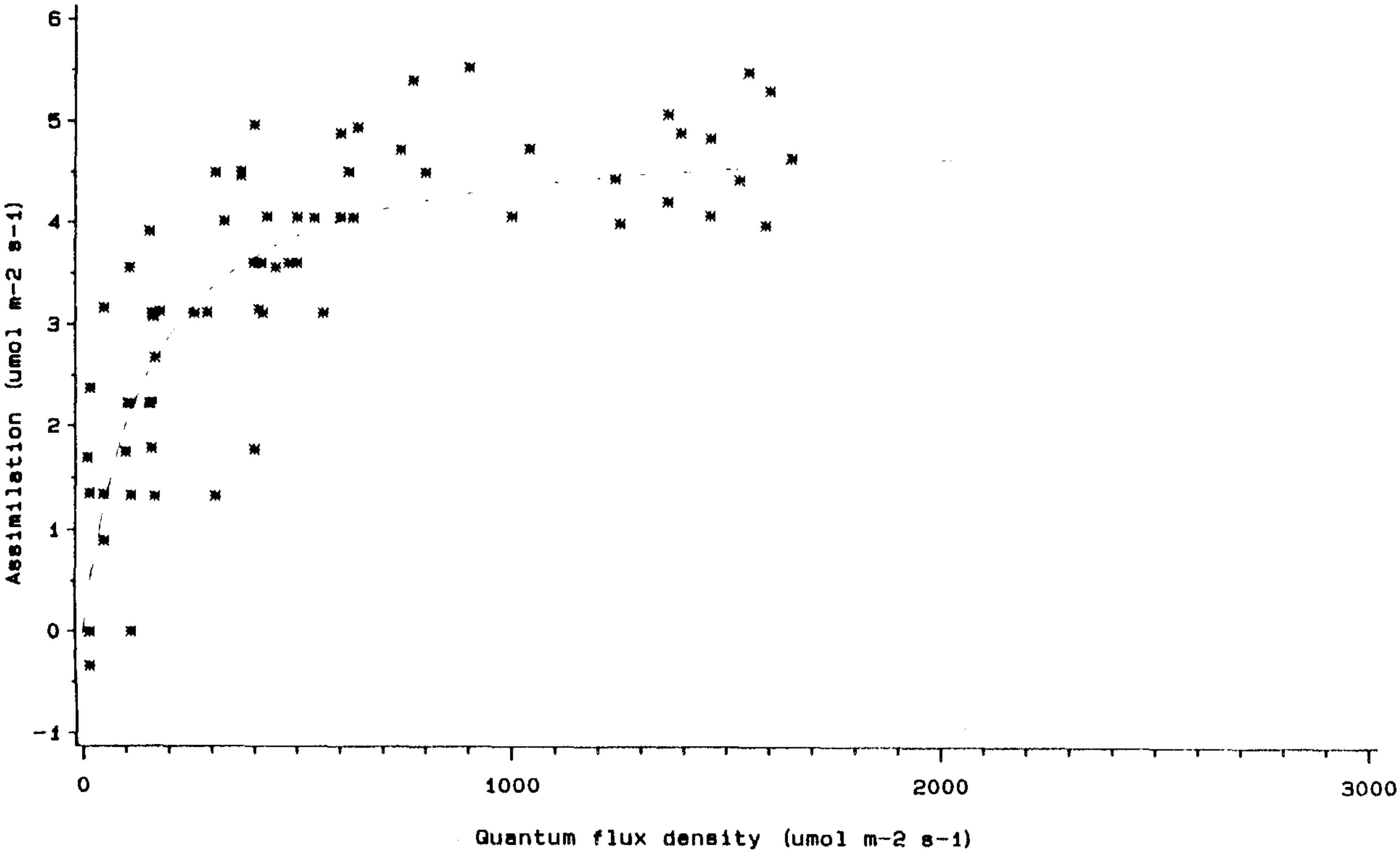
Acid mist - as Table 1.

O_3 EFFECTS ON PHYSIOLOGICAL PROCESSES

Beech

Figure 16 shows changes in assimilation rate of beech trees as quantum flux density increases. Fig. 16a shows that a rectangular hyperbola curve fitted the data well, with 69.4% of the variance accounted for. When the quantum flux density was greater than 700 umol m^{-2} s^{-1}, assimilation was predominantly independent of photon flux density (PFD). A similar relationship was observed for ozone fumigated beech trees, and 71.3% of the variation was accounted for by the rectangular hyperbolic curve. The data points for both curves were coincidental, and when the fitted curves were plotted together, no significant difference was observed, although the ozone treated trees showed a slight stimulation of the light saturated rate of assimilation (A_{max}).

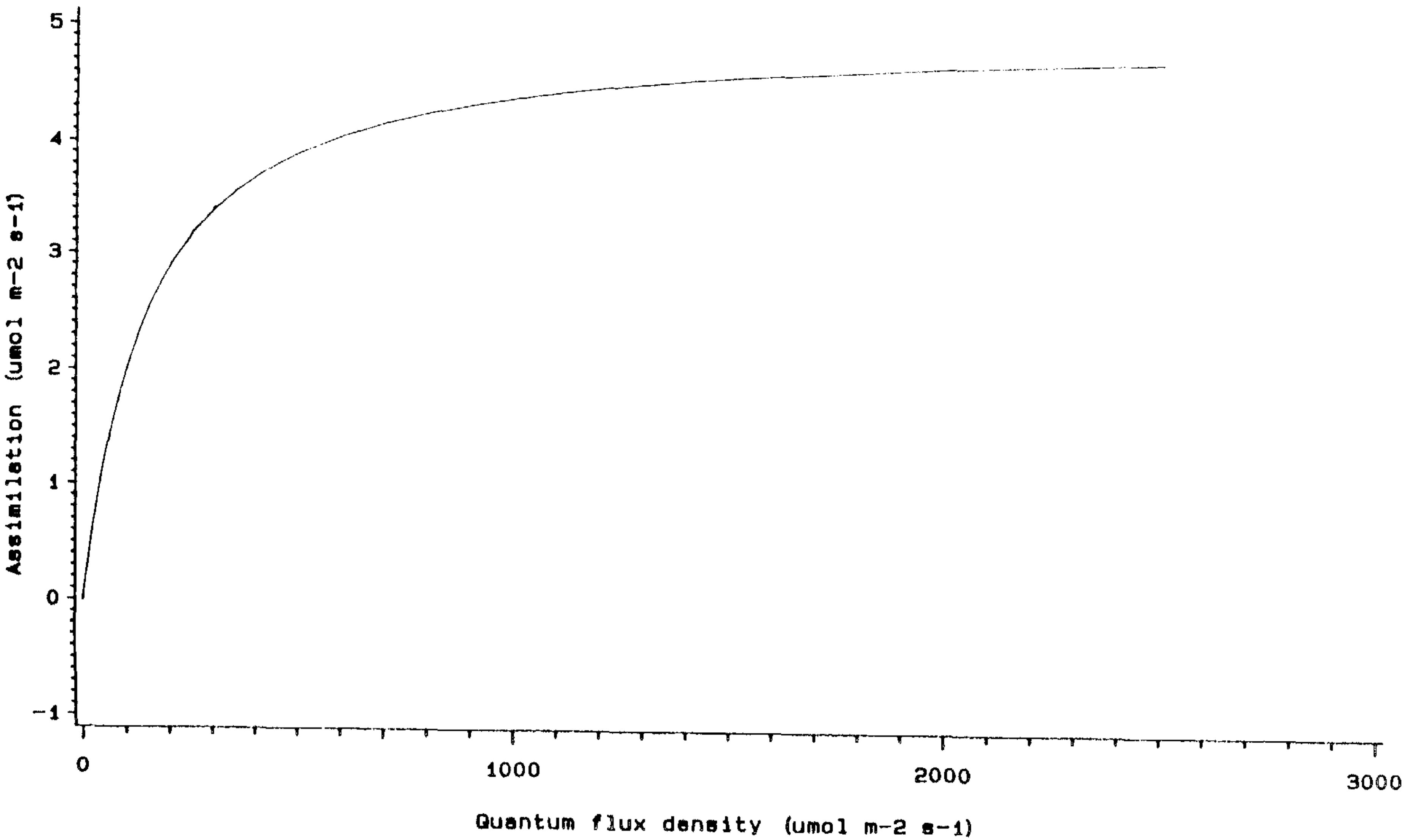
AN A/Q CURVE FOR BEECH TREES RECEIVING FILTERED AIR



Fitted line predicted from Jarvis et al 1985 model with gs = 0.135

AN A/Q CURVE FOR OZONE FUMIGATED and FILTERED BEECH TREES

Green line=ozone fumigated, red line=filtered trees



Fitted line predicted from Jarvis et al 1985 model with gs = 0.12

The photosynthetic and gas exchange parameters derived from the curve fitting process are summarised in Table 13. For both treatments, apparent quantum efficiency was 0.0477 ∓ 0.0002, a value in close agreement with published values of 0 for C_3 species. A_{max} of charcoal filtered treated trees was 4.4 ∓ 0.23 umol m^{-2} s^{-1}, and for the ozone fumigated trees, A_{max} = 3.8 ∓ 0.2 umol m^{-2} s^{-1}. The average value of A for the entire day was 3.45 ∓ 0.19 and 3.51 + 0.17 for charcoal filtered and ozone fumigated trees respectively. Stomatal conductance (g_s) was significantly reduced in ozone treated trees, from a value of 93.2 ∓ 2.9 mmol m^{-2} s^{-1} (control) to 66.8 ∓ 3.3 mmol m^{-2} s^{-1}. This decrease in g_s with the observed (non-significant) increase in A_{max}, indicates that water use efficiency (WUE) was increased in ozone treated beech.

Figure 17 shows changes in assimilation rate of beech leaves as a function of PFD for both charcoal filter treated trees and ozone fumigated trees. Table 14 summarises the gas exchange and photosynthetic parameters of these trees. The apparent quantum efficiency (ϕ) of charcoal filtered trees (0.012 ∓ 0.00023) was significantly lower than for ozone treated trees (0.016 ∓ 0.00056). Stomatal conductance was also significantly greater for ozone fumigated trees (57.8 ∓ 6.2 mmol m^{-2} s^{-1}) than control trees (39.5 ∓ 2.4 mmol m^{-2} s^{-1}). The increase in average daily assimilation (A) and A_{max} for ozone fumigated trees was on the border of significance ($P < 0.1$; $P < 0.1$; respectively). Carboxylation efficiency (g_m) was not significantly influenced by treatment.

ASSIMILATION RATE OF BEECH LEAVES AS A FUNCTION OF PFD

Star = ozoned, square = filtered

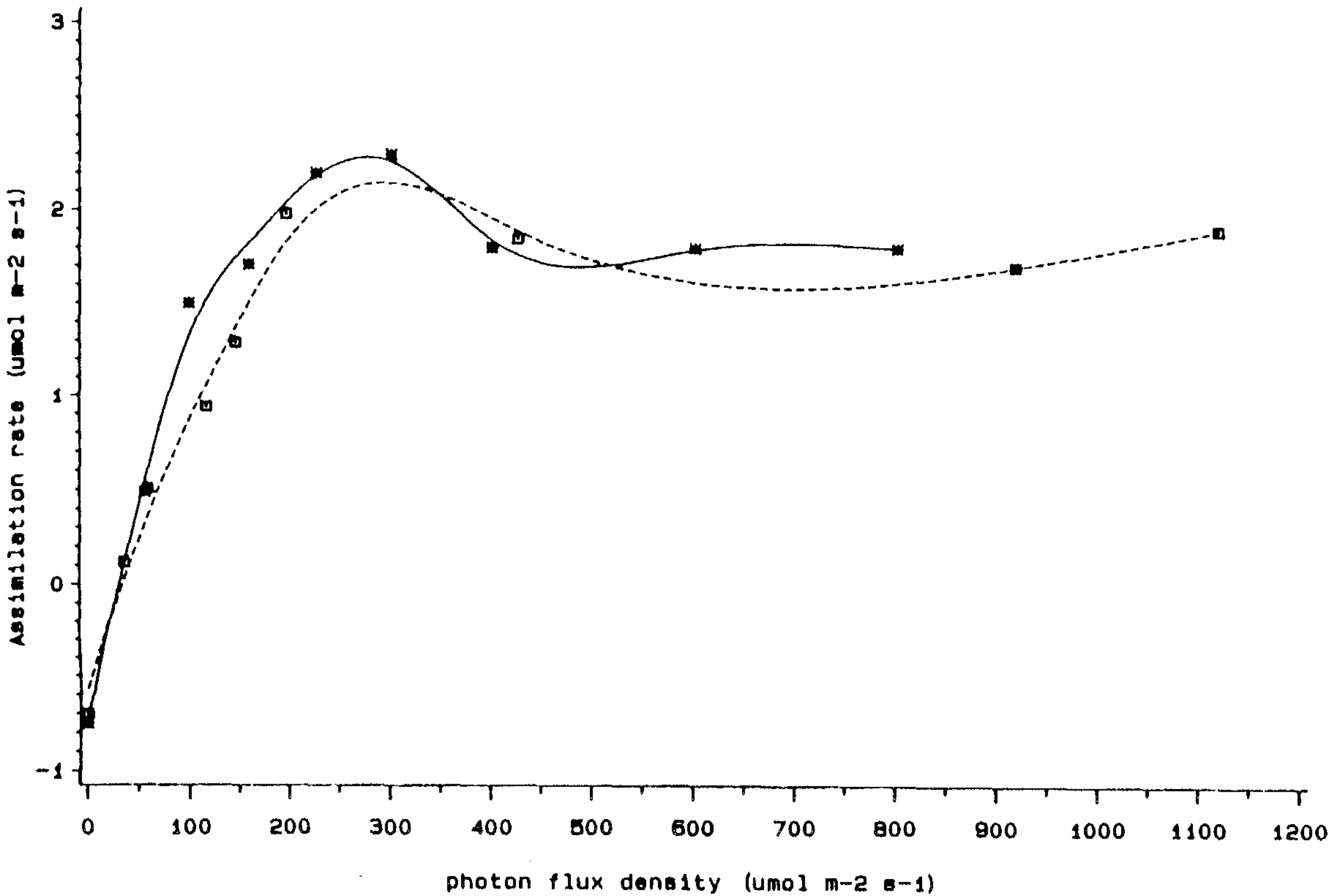


Table 13 A summary of the photosynthetic and gas exchange properties of beech trees that had received either charcoal filtered or ozone enriched air. Measurements were made in early August in the field.

	Charcoal filtered					Ozone fumigated				
Parameter	N	Mean	se	Max	Min	N	Mean	se	Max	Min
Assimilation daily mean	68	3.45	0.19	7.1	0.0	61	3.51	0.17	6.32	0.7
g_s**	68	93.2	2.9	133.2	8.1	61	66.8	3.3	122	17.4
Q	68	483	71	1650	11	61	513	61	1780	13
Temp	68	18.6	0.26	23.6	14.8	61	18.8	0.3	22.9	14.6
0	-	0.0477	0.0002	-	-	-	0.0477	0.0002	-	-
Convexity	-	$0.1x 10^{-17}$	-	-	-	-	$0.1x 10^{-17}$	-	-	-
Amax*	23	4.4	0.2	-	-	27	3.8	0.2	-	-

** indicates significantly different at $P < 0.05$

* indicates significantly different at $P < 0.10$

Table 14 A summary of the gas exchange and photosynthetic parametes of beech trees that had received either charcoal filtered or ozone enriched air. Measurements were made in early September in the lab.

	Charcoal filtered					Ozone fumigated				
Parameter	N	Mean	se	Max	Min	N	Mean	se	Max	Min
Assimilation, daily mean*	23	1.26	0.2	2.17	0.25	24	1.7	0.23	3.95	0.9
g_s**	27	39.5	2.4	76.5	19.9	19	57.8	6.2	177	25.6
Q	27	331.5	74.6	1150	0.0	27	293.7	49.1	800	0.0
Tem	27	17.3	0.14	18.7	16.0	27	16.7	0.1	17.5	16.0
0 **	18	0.120	2.3×10^{-4}	-	-	15	0.16	5.6×10^{-4}	-	-
Amax	8	1.75	0.07	-	-	12	2.03	0.31	-	-

* indicates significantly different at $P < 0.10$

** indicates significantly different at $P < 0.05$

Table 15 A summary of the photosynthetic and gas exchange parameters of Norway spruce shoots that had received either charcoal filtered or ozone enriched air. Measurements were made in August 1988 in the field.

	Charcoal filtered					Ozone fumigated				
Parameter	N	Mean	se	Max	Min	N	Mean	se	Max	Mean
Assimilation daily mean	47	1.9	0.1	3.7	0.79	48	1.98	0.1	3.1	0.73
g_s	47	53.7	3.5	119.6	23.6	48	49.9	3.3	115.7	20.4
Q	47	569	25.8	1960	80	48	603	78	2200	90
Temp	47	19.8	0.2	23.5	16.6	48	19.8	0.2	23.9	16.8
0 **	27	0.033	0.0057	-	-	48	0.018	-	-	-
Amax*	17	2.15	0.12	-	-	19	2.7	0.07	-	-
Convexity	47	$1x10^{-17}$	-	-	-	48	$8.5x10^{-17}$	-	-	-
g_m	-	0.0085	0.00049	-	-	-	0.0095	0.00034	-	-

* indicates significantly different at $P < 0.1$

** indicates significantly different at $P < 0.05$

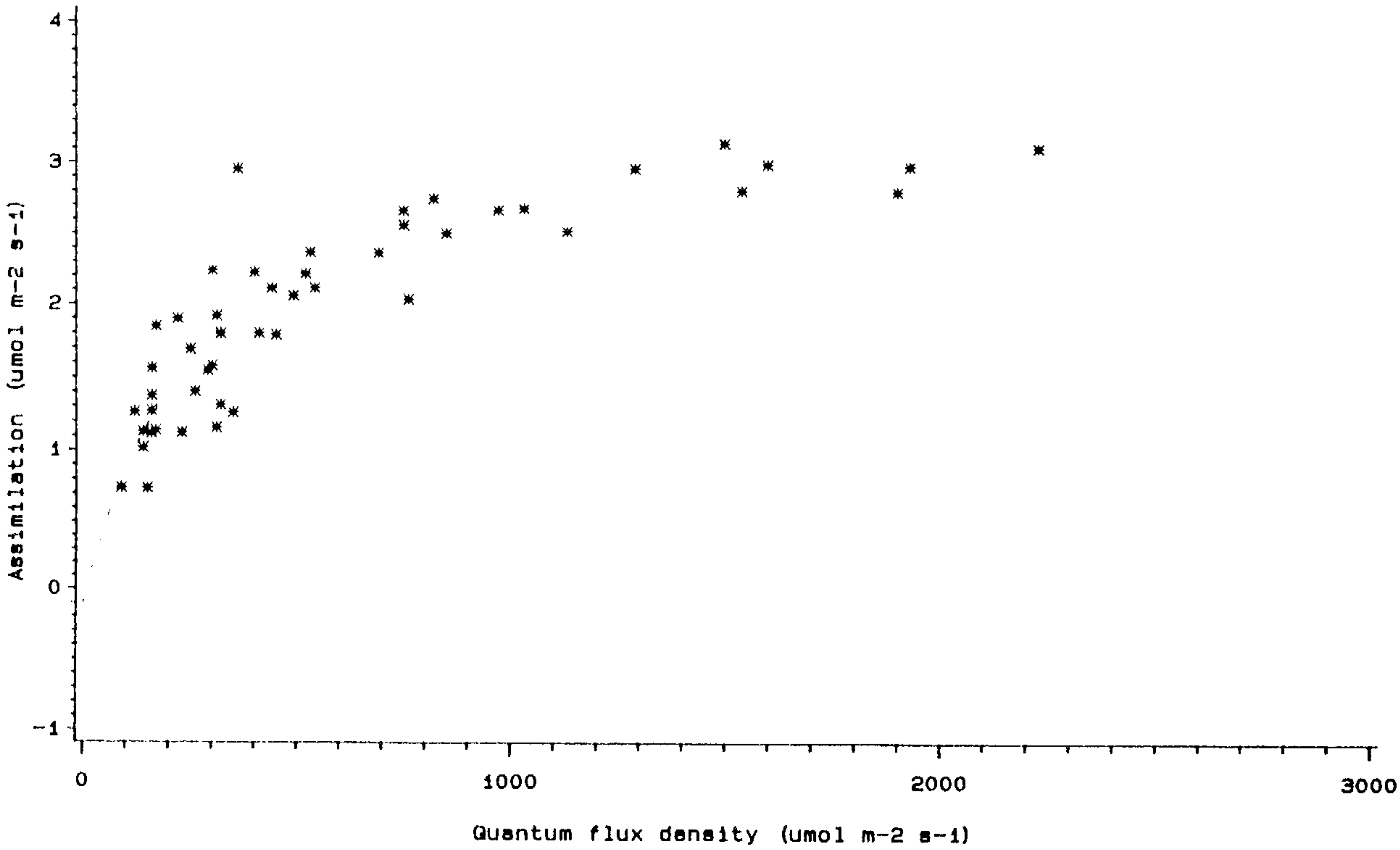
Norway spruce

Figure 18 shows changes in assimilation rate as a function of photon flux density (PFD) for charcoal filtered (Fig. 18) and ozone fumigated (Fig. 18) Norway spruce. In both treatments, a rectangular hyperbolic curve fitted the data well, with 73% and 83% of the variance accounted for respectively.

For charcoal filtered treated trees, assimilation was essentially independent of PFD when PFD > 500 umol m^{-2} s^{-1} (whilst for ozone treated trees, this was not observed until PFD > 800 umol m^{-2} s^{-1}). The rate of light saturated assimilation (A_{max}) was significantly greater ($P < 0.01$) for ozone treated trees than control. Table 15 summarises the gas exchange and photosynthetic parameters. The average daily rate of assimilation (A) was unaffected by treatment (1.9 ∓ 0.1 umol m^{-2} s^{-1} and 1.98 ∓ 0.1 umol m^{-2} s^{-1} for charcoal filtered and ozone fumigated trees respectively), although the A_{max} value was significantly ($P < 0.05$) greater for ozone treated trees (2.7 ∓ 0.07 umol m^{-2} s^{-1} for ozone fumigated trees, 2.15 ∓ 0.125 umol m^{-2} s^{-1} for charcoal filtered trees). Stomatal conductance (g_s) was not influenced by treatments, and averaged approximately 52 mmol m^{-2} s^{-1}. Carboxylation efficiency (g_m) was not influenced by treatment and averaged 0.00905.

Table 16 is a distilled summary of the results of an investigation into the influence of rewarming and subsequent frost sensitivity (as determined by the decline in 0 and A_{max} following a night-time freeze) of ozone and ozone + acid mist treated Norway spruce. Measurements were made during February of 1989. We observed no significant differences in A_{max}, prior to rewarming and freezing, between the charcoal filter treated and ozone treated trees. However, A_{max} for the ozone fumigated plus acid mist treated trees was

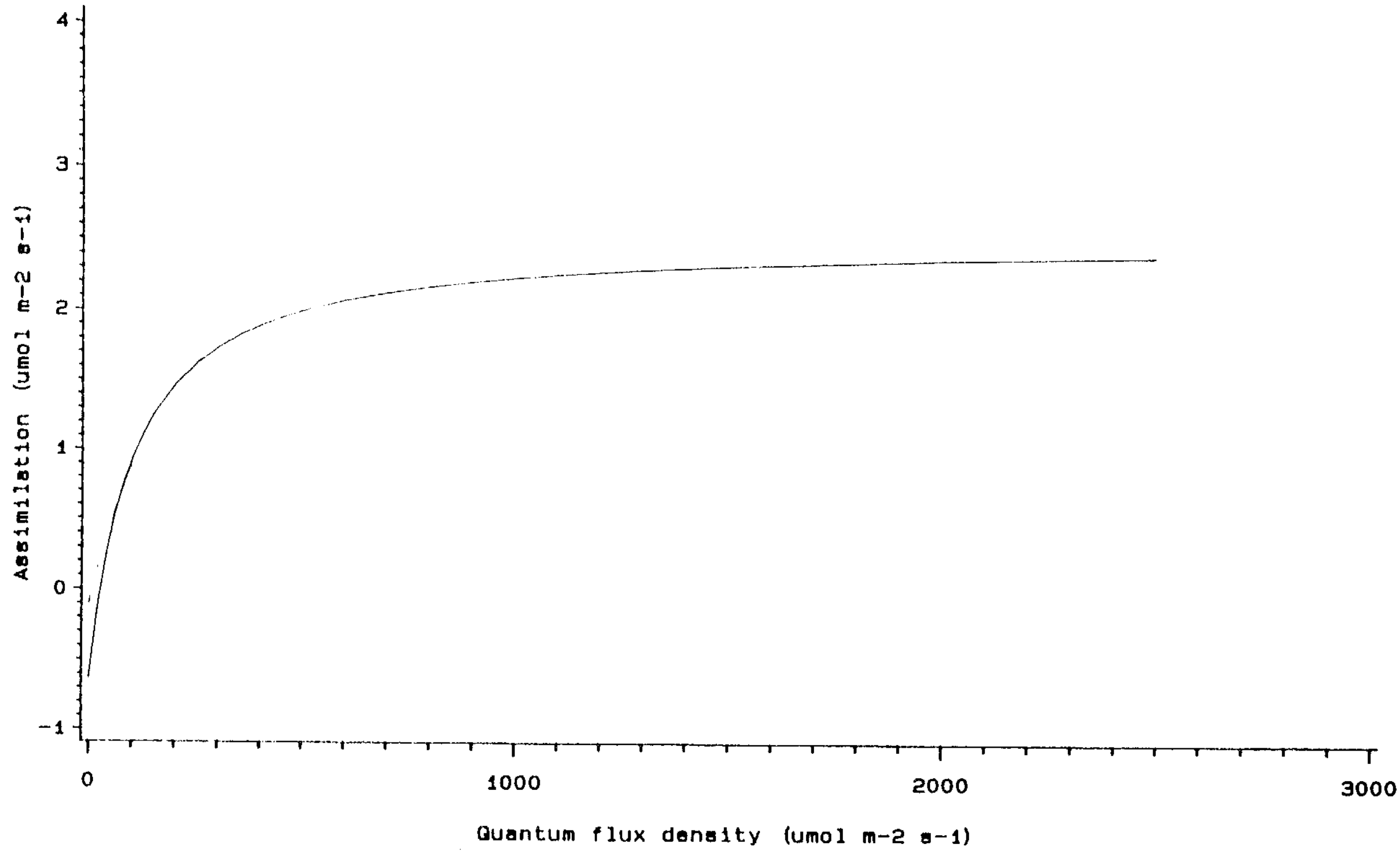
AN A/Q CURVE FOR OZONE FUMIGATED NORWAY SPRUCE TREES



Fitted line predicted from Jarvis et al 1985 model with gs = 0.12

AN A/Q CURVE FOR OZONE FUMIGATED and FILTERED NORWAY SPRUCE TREES

Green line=ozone fumigated, red line=filtered trees



Fitted line predicted from Jarvis et al 1985 model with gs = 0.12

significantly ($P < 0.05$) greater than the other 2 treatments both prior to rewarming and following rewarming. Similarly, the apparent quantum efficiency (ϕ) of the charcoal filtered and ozone treated trees did not differ (ϕ = 0.0046; 0.0042, respectively). However, ϕ for ozone plus acid mist treated trees, was significantly greater (0.014) than the other 2 treatments.

Upon freezing for 3 hrs to ca -10°C, charcoal filtered trees

showed a non-significant decrease in A_{max}. In contrast, the ozone and ozone + acid mist treated trees showed a significant decrease in A_{max} following a 3 hr freeze to -10°C. Upon freezing on the subsequent night, to -18°C for 3 hrs, charcoal filtered and ozone plus acid mist treated trees showed a significant decline in A_{max}, such that A_{max}, following the -18°C freeze was approximately half that prior to freezing (but following rewarming). However, for trees receiving ozone and acid mist, the -10°C freeze significantly reduced A_{max} to 50% of the value prior to freezing. This reduction was further enhanced following freezing to -18°C, such that A_{max} was reduced to approximately 29% of the pre-freeze and post rewarm period.

Table 16 A summary of the gas exchange and photosynthetic properties of Norway spruce trees that had received either charcoal filtered or ozone enriched air. Measurements were made prior to a warming period, of 12°C for 5 days, following the warming period, following a 3 hr freeze to -10°C or following a freeze to -18°C

	Charcoal filtered	Ozone fumigated	Ozone + acid mist
Amax before rewarming	1.3+0.3 (n = 9)	1.05 + 0.25 (n=15)	2.4 + 0.3 (n = 9)
Amax, after rwarming	1.6 + 0.4 (n = 9)	1.45 + 0.5 (n=15)	4.0 + 0.6 (n = 9)
0 after rewarming	0.0046 (p = 0.006)	0.0042 (p = 0.005)	0.014 (p = 0.001)
Amax after -10°C	1.32 ÷ 0.4 (n = 18)	0.77 + 0.2 (n=18)	2.0 + 0.68 (n = 19)
Amax after -18°C	0.62 + 0.2 (n = 18)	0.7 - 0.35 (n=18)	1.2 - 0.5 (n = 18)

MODIFICATION OF THE PLANT MICROCLIMATE BY OPEN-TOP CHAMBERS

The application of open-top chambes to air pollution effects research arose through the need to modify chemical properties of the air with a minimal effect on the physical environment of plants. In practice a compromise is reached between the filtration efficiency of the chamber and the changes in the physical environment ... a totally closed system would permit 100% filter efficiency to be achieved. During the last year as a part of the CEC open-top chamber effects research programme we have collated information of OTC systems in use throughout Europe, and have made detailed measurements in our own chambers to quantify the major effects.

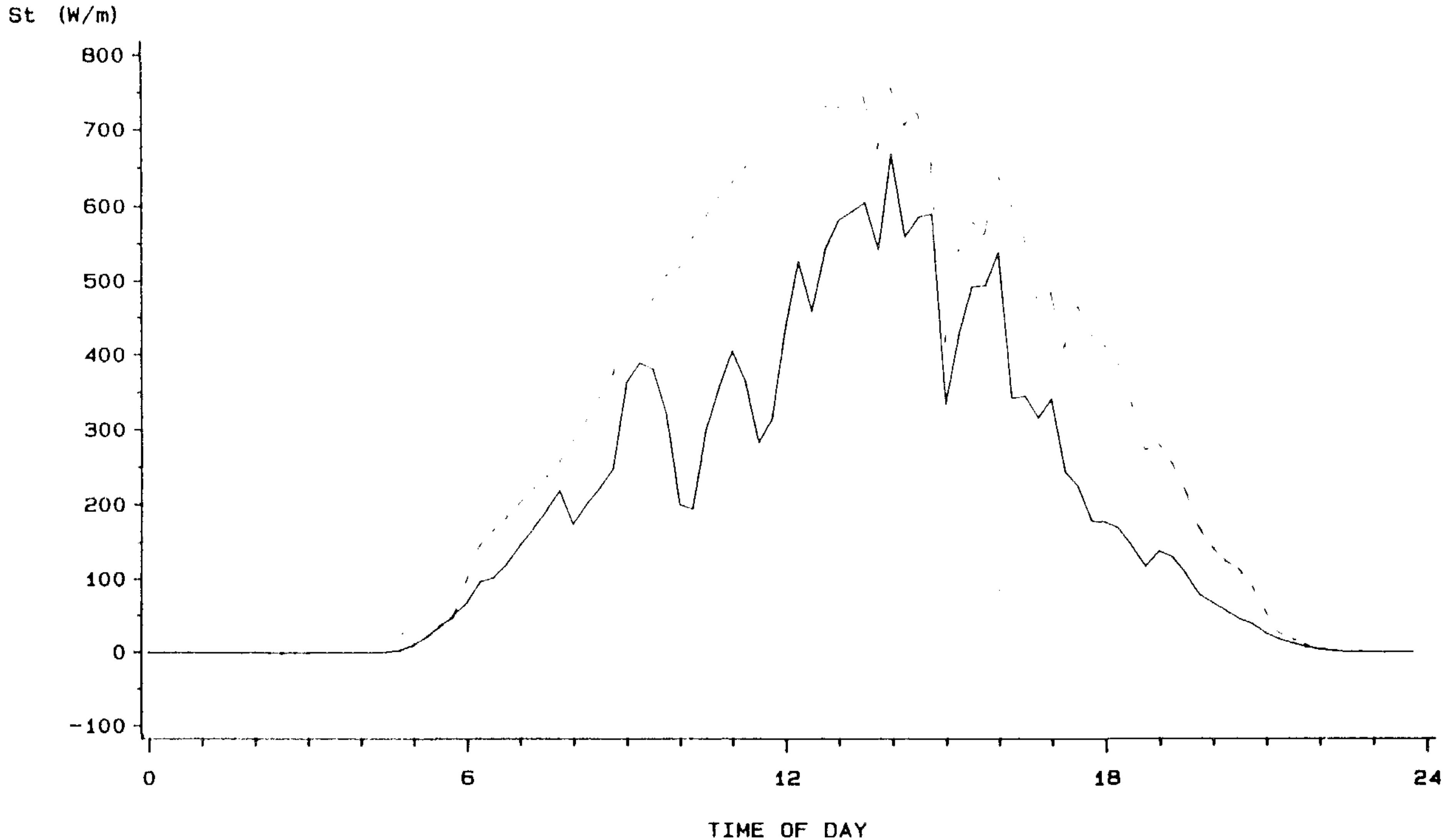
In this report we have summarized the properties of our OTC and show examples of major components of radiation budget within the chambers during hot sunny days.

The dimensions of the chamber and the major properties are listed in Table 17 While valuable as a guide to the general properties they do not show the detail of the modifications to the energy budget of the chamber.

The reduction in short wavelength radiation averages 15% over the chamber floor but there are areas which are shaded by parts of the chamber structure and areas which receive enhanced incoming short wave radiation. Figure shows an area which for a significant fraction of the day is shaded by the air inlet manifold which though polythene and transparent, casts a significant shadow. Similarly, the net radiation within the chamber shows marked spatial variability (Figure).

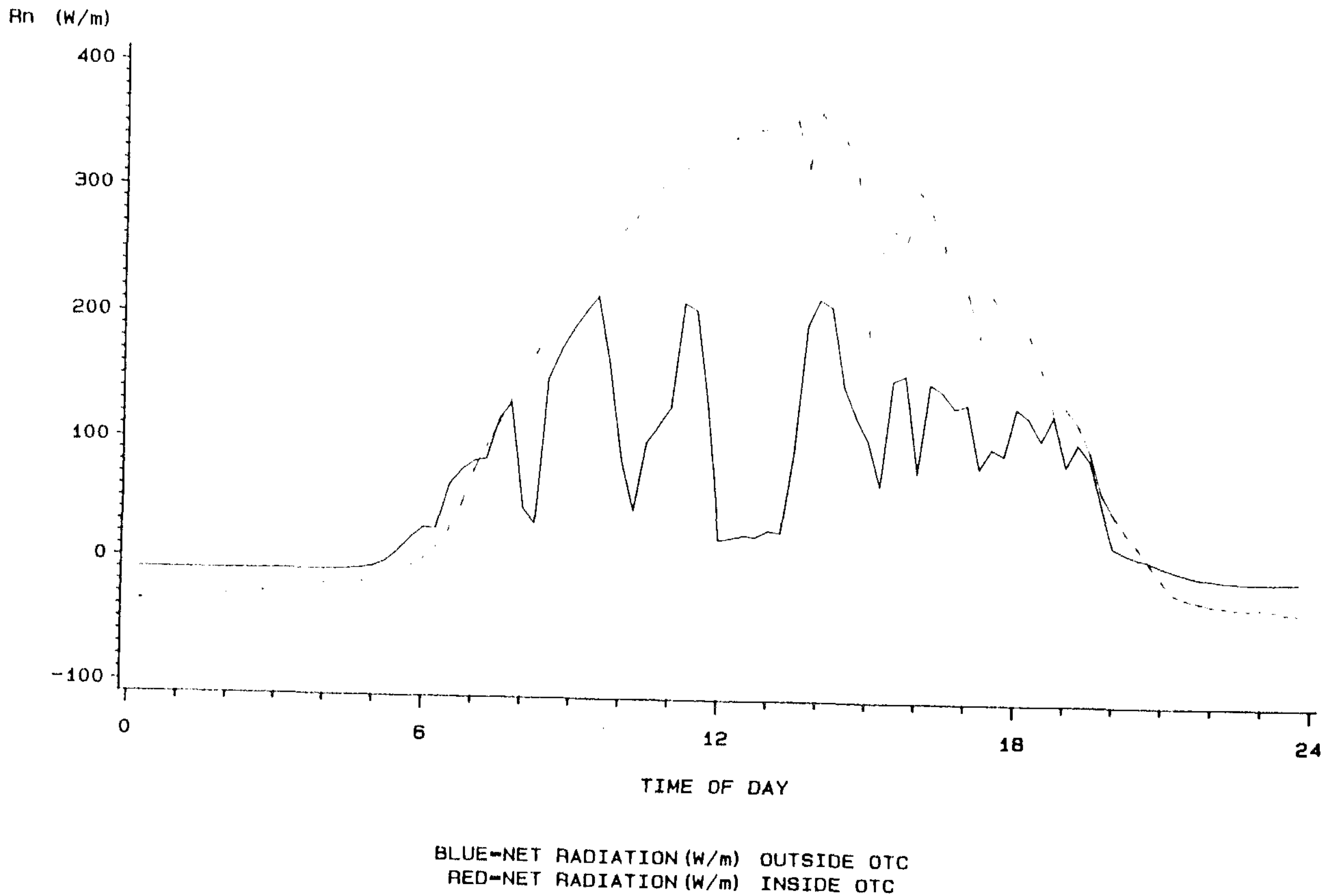
The incoming air is warmer than ambient temperature due to the pump. The manifold temperature is smaller than air temperature within the chamber at night due to net radiation loss from the chamber to cool the air. By contrast the reduction in longwave heat loss by radiation to a cool stay support due to the presence of walls leads to air temperatures within the chamber exceeding the manifold temperature.

SOLAR RADIATION INSIDE & OUTSIDE OTC (DAY185 1989)



BLUE-SOLAR RADIATION (W/m) OUTSIDE OTC
RED-SOLAR RADIATION (W/m) INSIDE OTC

NET RADIATION INSIDE & OUTSIDE OTC (DAY185 1989)



SUMMARY

O_3 AND ACID MIST - NORWAY SPRUCE AND BEECH

1. Year 1 - no growth effects.

2. Reductions in autumn frost hardiness by about 5°C in 140 ppb O_3 and 140 ppb O_3 + acid mist. NO effects at 100 ppb O_3. (No additive effects observed).

3. Reduction in autumn frost hardiness of about 8°C by acid mist. SO_4^{2-} appears to be the ion primarily responsible for frost hardiness effects (in Norway spruce - this was also the case for Red spruce, but Red spruce much more sensitive to treatment).

4. Visible injury to Norway spruce in acid mist + O_3 (140 ppb), no visible injury with acid mist or O_3 140 ppb alone.

5. Beech stomatal conductance reduction of 30% in 140 ppb O_3 (cf. CF) mid summer. Beech light saturated photosynthesis 10% greater in 140 ppb O_3, cf. CF mid summer.

6. Beech during senescence (September). Beech stomatal conductance increased by 40% in 140 ppb O_3 and apparent quantum yield increased by 30%.

7. Norway spruce apparent quantum yield decreased by 40% at 140 ppb O_3. No stomatal effects and no chlorophyll effect observed.

8. Mid-winter study of O_3 fumigated plants in previous summer. Norway spruce light saturated photosynthesis rates larger in O_3 treatments following warming (+ 12°C) and <u>much</u> more sensitive to 'non-killing' frosts (-10°C) than clean air plants. Consistent with other winter hardiness studies.

Freezing temperatures causing 20% shoot death in Norway spruce in response to acid mist or ozone exposure.