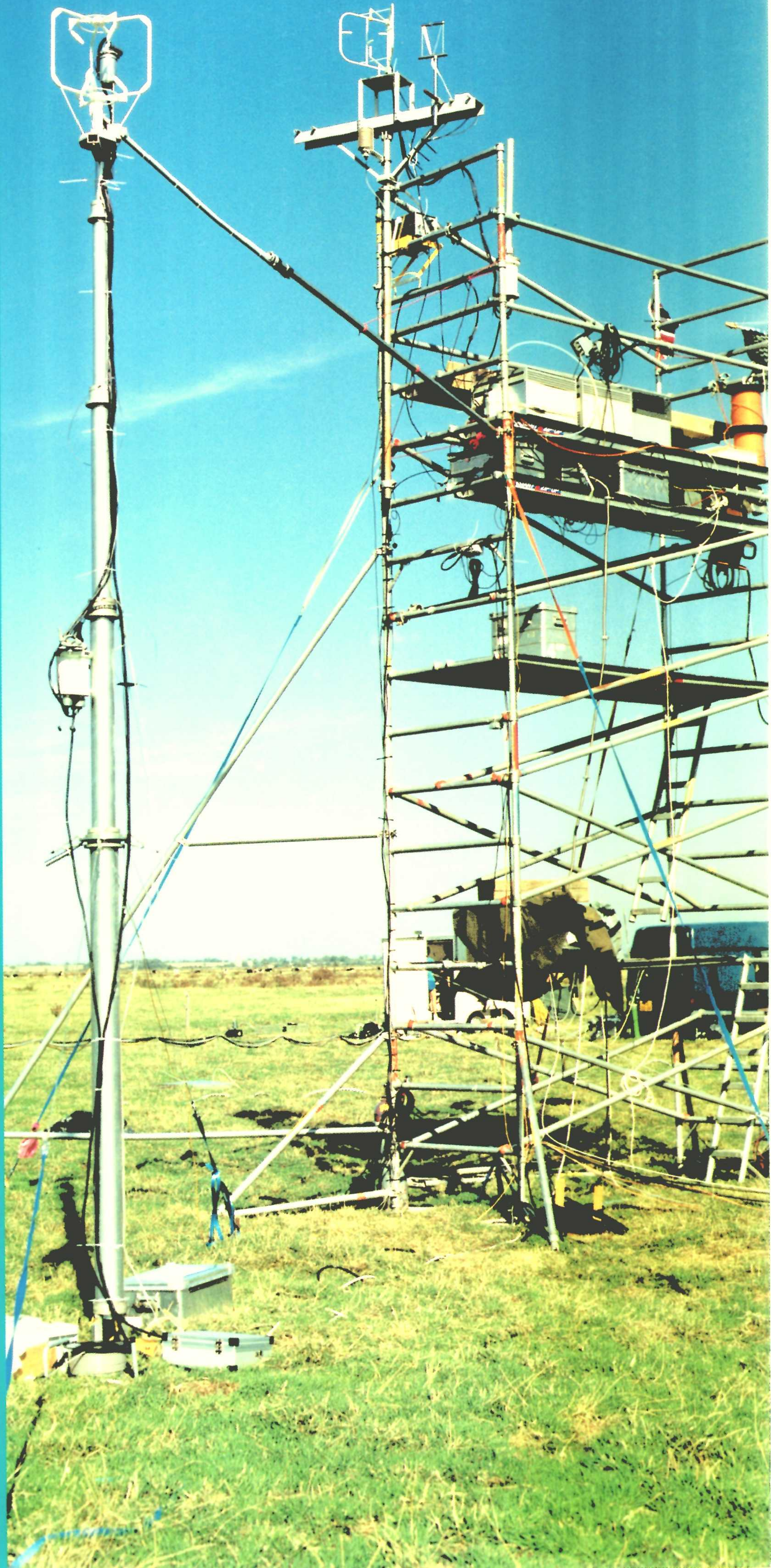

Institute of Terrestrial Ecology

Annual Report 1994–95

Centre for Ecology and Hydrology

Natural Environment Research Council

The ITE mission

The Institute of Terrestrial Ecology will develop long-term, multidisciplinary research and exploit new technology to advance the science of terrestrial ecology, leading to a better understanding and quantification of the physical, chemical and biological processes of the land.

Priority is placed on developing and applying knowledge in the following areas:

- the factors which determine the *composition*, *structure*, and *processes* of terrestrial ecosystems, and the *characteristics* of individual plant and animal species
- the dynamics of *interactions* between atmospheric processes, terrestrial ecosystems, soil properties and surface water quality
- the development of a sound scientific basis for *monitoring*, *modelling* and *predicting* environmental trends to assess past, present and future effects of natural and man-made change
- the securing, expansion and dissemination of ecological data to further scientific research and provide the basis for impartial advice on environmental protection, conservation, and the sustainable use of natural resources to governments and industry.

The Institute will provide training of the highest quality, attract commissioned projects, and contribute to international programmes.

ITE will promote the use of research facilities and data to enhance national prosperity and quality of life.

Report of the Institute of Terrestrial Ecology
1994–1995

Centre for Ecology and Hydrology

Natural Environment Research Council

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Science Reports

Environmental pollution **50 - 65**

Pollution of air, land, sea and freshwater in relation to environmental and human health

- Observational and modelling studies to provide improved and quantitative understanding of the interaction of chemistry and transport in the troposphere; further development of models to simulate the spread of airborne pollutants to incorporate the effects of diffusion and deposition to the surface and to address full 3-D dispersion of airborne materials from point sources.

- Studies of environmental impacts of pollution and its implications for water, air and land quality issues. Further development of the critical loads concept, using geographical information system approaches to integrate information on the location and sensitivity of environmental receptors to pollutants.

- Investigation of the molecular, cellular, physiological and genetic mechanisms underlying responses to pollution stress; identification of potential biomarkers and effects indicators; integrating findings on responses to stress at the various levels of biological organisation and development of models to predict the potential consequences for the health of organisms and their populations.

- Identification and development of new technologies to reduce pollution (eg specific biopesticides as an alternative to less specific chemical pesticides).

(NERC priorities 1995)

Environmental pollution

Introduction

The Institute continues to maintain a large programme of research on environmental pollution. The work covers:

- pollutant emission/release,
- transport and inputs,
- pollutant pathways and transfers in terrestrial ecosystems, and
- impacts at the level of the individual organism and the population.

It involves a wide range of pollutants, including toxic metals, organic compounds such as pesticides, solvents and dioxins, radionuclides, and acidic atmospheric pollutants at the site-specific, regional, national and transboundary scale. The studies involved include:

- long-term monitoring,
- laboratory studies,
- controlled environment and field experiments, and
- modelling.

The research is closely aligned with the requirements of our customer community. It supports and underpins the UK's input to international negotiations on pollution control, international hazard assessments, and the development of guidelines and evaluation methodologies by the regulatory agencies.

This year has seen further progress in international agreements on the control of transboundary air pollution with the signing of the Oslo protocol, under the auspices of the United Nations Economic Commission for Europe, for the control of emissions of sulphur dioxide. Critical load calculations and maps provided the scientific underpinning to the negotiations leading to the framing of the protocol. Negotiations of a NO_x protocol are due to begin in 1996 and, again, they will rely heavily on the critical load concept. Methodologies are now being developed for calculating and mapping critical loads of heavy metals and persistent organic pollutants (POPs) in preparation for possible future protocols on these substances. The Institute has a central role in the UK critical loads programme, directed and supported by the Department of the Environment (DoE). The UK National Critical Loads Mapping Centre is located at ITE Monks Wood, and the development and testing of methodologies, along with underpinning research, are carried out at ITE Bangor, Edinburgh, Merlewood and Monks Wood. One of the following articles presents a report on some recent developments in the critical loads mapping programme.

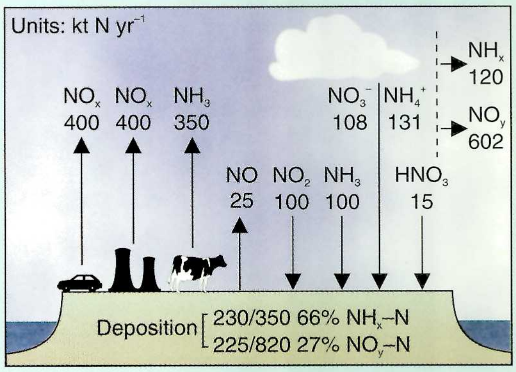
A key concept in the calculation of critical loads for nitrogen is that of nitrogen saturation. This can be defined as the point at which available inorganic N in the soil system exceeds the demand of the soil/plant system. At this point, the excess nitrogen is likely to be leached to ground- or surface waters, largely as nitrate. The critical load is set to avoid N saturation. The mass balance approach to the calculation of critical loads seeks to determine the atmospheric inputs which will not result in N saturation. It is important, however, to test the N saturation concept and its quantification empirically. The report by Emmett, Brittain and Reynolds summarises ITE's involvement in a European study to determine the critical load of N for forest systems and to test the N saturation concept.

Understanding and quantification of nitrogen emissions and deposition are clearly important in the setting of critical loads for N, but are also important in the consideration of global warming, as nitrous oxide is an important greenhouse gas. Considerable efforts are being made to improve our estimates of current emissions of this gas in the UK. The emphasis of ITE's work has been on emissions from land which is not under intensive agriculture, and has involved work at the laboratory, plot and landscape scale, deploying a range of equipment and expertise. Although total emissions of nitrogen gases from these types of sites are generally lower than from intensive agricultural soils, a larger proportion of the emitted gases are nitrous oxide rather than nitrogen. The report by Fowler, Skiba and Hargreaves gives an overview of recent research which is contributing to improved national estimates of nitrous oxide emissions.

The critical load and trace gas programme is mainly focused at the larger scale. Much of the work on metals and organic pollutants relates, however, to point source emissions. While many of the releases are associated with specific, planned industrial operations or activities, such as pesticide applications, recent work in the Institute has attempted to quantify the magnitude of accidental releases of some organic compounds. Thus, calculations have shown that accidental releases may make a major contribution to the total emissions of dioxins. A case study reported by Meharg *et al.* has also shown that releases following accidents can have a significant impact on the environment, with effects on vegetation and fungi, biochemical changes in soil biota, and the accumulation of the pollutants in the food chain.

Activities on hazard and risk assessment continue to expand. ITE is involved in evaluations of chemicals at the national, regional (European Union) and international level. We have developed systems to allow Her Majesty's Inspectorate of Pollution to produce site-specific risk assessments of the hazards and risks of chemical emissions to UK birds and mammals, using ecotoxicological research and the Countryside Information System. Work on testing methods for assessing risk to bats has been completed. Input has been made to European programmes on 'existing' industrial chemicals, and we continue to support the International Programme on Chemical Safety with sponsorship from DoE. Work on biomarkers and behavioural toxicology for both invertebrates and birds is increasing.

M Hornung



Atmospheric budget of reduced and oxidised nitrogen over the UK

Recent developments in the mapping of critical loads

(This work was partly funded by the Department of the Environment)

The Environmental Information Centre at ITE Monks Wood is the home of the UK National Critical Loads Mapping Centre, which forms part of a multi-national programme organised under the auspices of the United Nations Economic Commission for Europe (UNECE) Critical load data for the UK, developed by various subgroups of the Department of the Environment's Critical Loads Advisory Group (CLAG), are transmitted from Monks Wood to the European Coordination Centre for Effects (CCE), at Bilthoven in The Netherlands, where they are incorporated into European maps These maps and supporting data form the scientific underpinning to the UNECE negotiations on the control of emissions of transboundary air pollutants The initial emphasis of the critical loads mapping programme in the UK and elsewhere in Europe was on acidity and sulphur In 1994, a new sulphur protocol was negotiated within the UNECE which was largely based on the consideration of critical loads for European ecosystems Although work still continues on critical loads for sulphur, the emphasis has now moved towards nitrogen, to support the negotiations for a nitrogen protocol which are due to begin in 1996 To provide a platform for the work on critical loads of nitrogen in the UK, the DoE established a review of the 'Impacts of nitrogen deposition on terrestrial ecosystems (INDITE)', co-ordinated by ITE, and the report produced by this review was published in 1994 (UK Review Group on Impacts of Atmospheric Nitrogen 1994)

Three main approaches have been used for the calculation and mapping of critical loads

- empirically based methods, where the critical load is assigned to a receptor on the basis of existing data, experiments or field surveys,
- mass balance methods, where the critical load is calculated from a mass balance equation which balances the sources and sinks of the pollutant of interest,
- dynamic models, which incorporate the main processes and mechanisms controlling the fate of the pollutant in the receptor system

The UK national mapping programme is based on empirical and mass balance approaches, but dynamic models have been applied to specific sites in the UK for which the required input data are available

Critical loads for acidity

Critical load maps for the UK of acidity and sulphur have been produced for soils and for surface waters The soils maps are developed under the auspices of the CLAG soils subgroup, led from ITE Merlewood The first critical load maps for soils were based on an empirical approach in which a critical load was assigned to 1 km grid squares on the basis of the mineralogy and chemistry of the most widespread soil in the square The empirical map could be described as a general critical load map for soils More recently, the application of a mass balance model has been assessed The mass balance model is solved with respect to a specific ecosystem or soil/plant combination It incorporates a critical chemical limit for a given variable, above or below which ecosystem damage will occur to a selected biological indicator organism or species The critical chemical limit most commonly used is the ratio of base cations to aluminium in soil solution at which damage to fine roots occurs The form of the model equation recommended by the UNECE Task Force on Mapping and the CCE has evolved over the last three years, following test applications of the equation All the various versions of the equation have been tested in the UK by application at specific sites and in the generation of national maps The current version, listed below, incorporates modifications developed at a workshop held by the CLAG soils subgroup at Grange-over-Sands (Sverdrup *et al* 1995)

Equation 1

$$CL = ANC_w \times \left(1.5 \times \frac{(x_{bc} \times ANC_w + BC_D - BC_U)}{(BC/AL)_{crit} \times K_{Gibb}}\right)^{1/3} \times Q^{2/3} + 1.5 \times \left(\frac{x_{bc} \times ANC_w + BC_D - BC_U}{(BC/AL)_{crit}}\right)$$

where

CL = the critical load of acidity,

ANC_w = annual production of base cations from mineral weathering

x_{bc} = the proportion of the base cations released by weathering measured as Ca + Mg + K

BC_D = base cation deposition

BC_U = the net base cation uptake,

$(BC/Al)_{crit}$ = the critical base cation to aluminium ratio (with different values for different vegetation types)

K_{Gibb} = the Gibbsite equilibrium constant

Q = runoff

Several input variables vary with soil type and vegetation, eg the critical chemical limit, net uptake of base cations and base cation deposition The above form of the equation, and the previous versions, have been tested in Britain for three different habitats coniferous forest, acidic grassland, and heathland The critical chemical value (ie the base cation/aluminium ratio at which fine root damage occurs) has been set for Norway spruce (*Picea abies*), wavy hair-grass (*Deschampsia flexuosa*) and heather (*Calluna vulgaris*) respectively The initial maps are produced assuming the relevant habitat occurs throughout the UK, and then data can be extracted for those grid cells in which the habitat actually occurs

In parallel with the testing of the different forms of the mass balance equation, improved databases are being established for the input variables to the equation Thus, the Institute of Hydrology has recently produced a new dataset for mean annual runoff for each 1 km grid cell in the UK, and the dataset for base cation deposition has recently been revised Figure 36 shows a critical load map for coniferous forest produced using equation 1 with the recent updates of input databases The three maps produced for the different soil/vegetation ecosystems using the mass balance model show larger critical loads over most of the UK than the empirical map, however, the spatial pattern of variation of critical loads is similar, with the smallest values in the west and north For a given soil, the critical load calculated using the mass balance equation is smaller for the coniferous forest than for acidic grassland or heathland

The UK critical load maps for soils are derived using information on the most widespread soil in each 1 km square However, this approach can mask considerable variability in soils and vegetation, and hence in critical loads at the landscape scale Also, the most

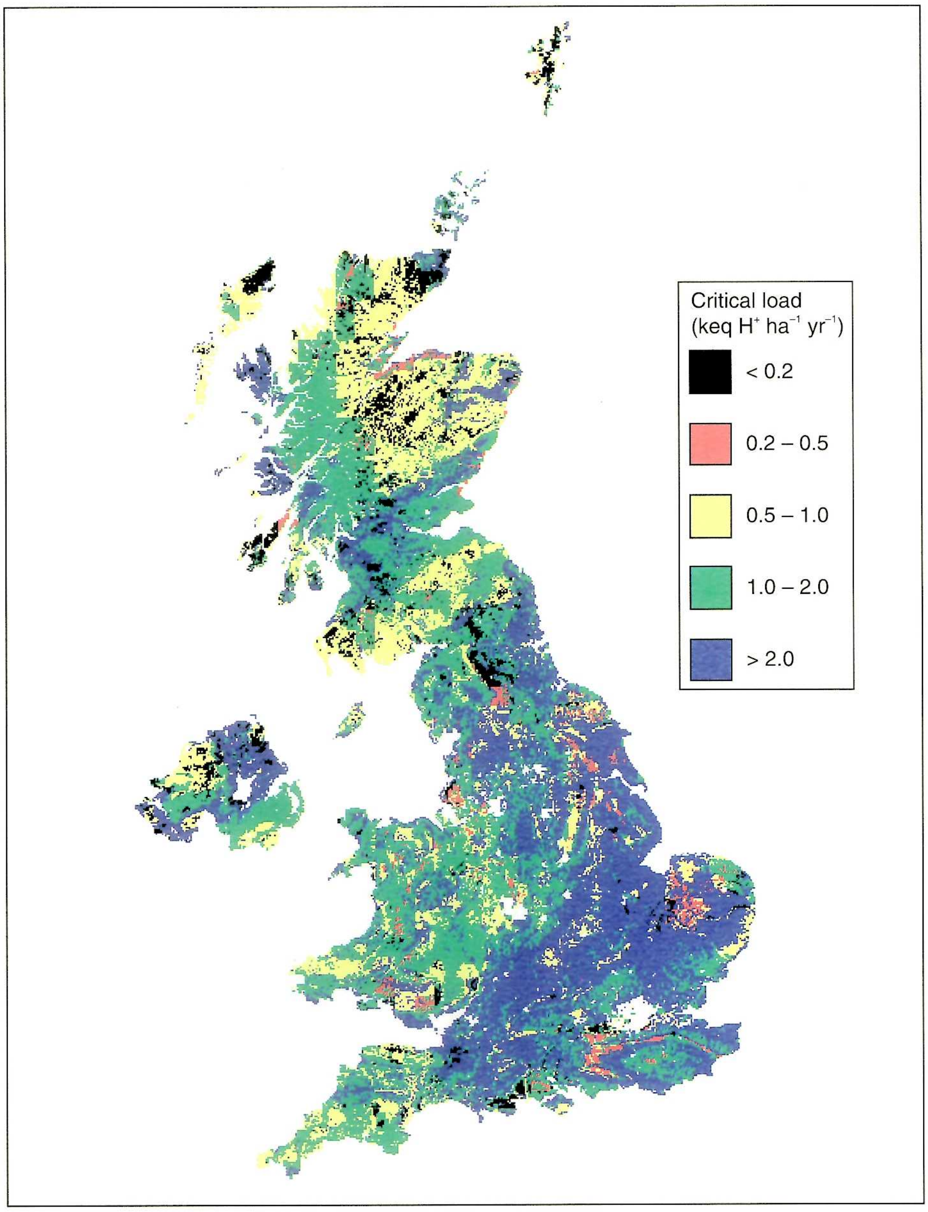


Figure 36. Critical loads of acidity for coniferous forest, derived using the simple mass balance equation

widespread soil may not be the most sensitive soil within a square. The consequences of using the most widespread soil approach is being assessed by applying the empirical critical load approach and the mass balance model to a series of 1 km grid squares surveyed as part of the Countryside Survey 1990 (Barr *et al.* 1994). Detailed maps of soils and vegetation for the squares are being overlaid in a geographical information system to produce a series of polygons representing the range of soil/plant combinations within the square. A critical load is assigned to each soil in the square by the approaches used in creating the GB empirical map, and the mass balance equation is also solved for each of the soil/vegetation polygons. The results to date show that the most widespead soil is also the most sensitive in 60–70% of squares, but the most widespread soil/plant combination is only the most sensitive combination in some 50% of squares.

Critical loads are also being calculated and mapped at the landscape scale in an exploratory assessment of the impact of emissions from individual power plants.

Critical loads of nitrogen

Nitrogen deposition can contribute to acidification of ecosystems. It can also disturb nutrient balances within systems, leading to changes in plant growth and species distributions, and to an excess of nitrogen over the requirements of the plant/soil system. The latter is sometimes referred to as nitrogen saturation; when a system is saturated, increased leaching of nitrogen takes place. Critical loads for nutrient nitrogen are set to avoid these disturbances to plant growth and nutrition, and the consequent changes in plant species distributions.

Empirical critical loads of nutrient nitrogen

Using available literature data, ranges of empirically estimated critical load values for nutrient nitrogen have been proposed for a number of different vegetation types at UNECE workshops held at Lokeberg, Sweden and Grange-over-Sands (Hornung, Sutton & Wilson 1995). These have been based upon observed effects upon individual species and plant communities. For some vegetation types, a single value was suggested. Where a single value was not provided, the mid-range value has been used for GB maps.

In the UK, the mapping of critical loads for nutrient nitrogen using the empirical approach has been co-ordinated by the CLAG vegetation subgroup and ITE Monks Wood. Two methods have been used.

The first method uses the National Vegetation Classification (NVC) to identify the species indicative of the vegetation types for which empirical critical loads have been defined. Data from the Biological Records Centre (BRC) at ITE Monks Wood are used to map the presence of the species on a 10 km grid across the whole country. The appropriate critical loads value is applied to 10 km squares where the most representative species are present (Eversham & Roy 1995). In this way, critical loads maps can be drawn for each vegetation type. To generate national maps representing all vegetation types, the lowest critical load of the vegetation types present in each 10 km square may be mapped. While this method offers great flexibility and is able to make use of the extensive database of species records, it is currently limited to the relatively coarse spatial resolution of the 10 km grid.

The second method uses the ITE Land Cover Map (Fuller, Groom & Jones 1994) to identify the dominant vegetation type for each 1 km square of the whole country. The land cover vegetation descriptions have been matched with the vegetation descriptions for which critical loads are defined, and the appropriate empirical critical loads value has been applied to each 1 km square. While this method benefits from the better spatial resolution of the Land Cover Map, the land cover categories do not clearly define the vegetation types present.

In the future, a combination of both of the above methods may provide the means of generating the best national map of empirically based critical loads for nutrient nitrogen. The CLAG vegetation subgroup is reviewing both methods for defining the distribution of the different vegetation types and exploring ways of combining the benefits of both.

Application of a mass balance approach for nutrient nitrogen

The mass balance approach aims to prevent nitrogen saturation and to ensure sustainable growth. It balances atmospheric inputs to the system with long-term sinks and fluxes out of the system. The current form of the equation (Equation 2) was formulated during a recent international UNECE workshop, held in Grange-over-Sands and organised by ITE on behalf of DoE.

Equation 2

$$CL_{(N)nut} = N_{l(crit)} + N_{i(crit)} + N_{U(crit)} + N_{de(crit)} - N_{fix(crit)} + N_{fire(crit)} + N_{erode(crit)} + N_{vol(crit)}$$

where:

$CL_{(N)nut}$ = critical load for nutrient nitrogen

$N_{l(crit)}$ = total annual N leaching (NO_3 + NH_4 – dissolved organic N) from the rooting zone under natural conditions in the absence of pollutant N inputs, plus any enhanced leaching following forest harvesting or following natural fires or fires used as part of traditional management regimes

$N_{i(crit)}$ = an acceptable annual level of N immobilisation in soil organic matter (including forest floor), at N inputs equal to the critical load, at which adverse ecosystem change will not take place

$N_{u(crit)}$ = net annual removal of N in vegetation and harvested animals at N inputs equal to the critical load

$N_{de(crit)}$ = annual flux of N to the atmosphere as a result of denitrification at N inputs equal to the critical load

$N_{fire(crit)}$ = N losses in smoke from natural wildfires or from fires used as part of traditional management regimes

$N_{erode(crit)}$ = annual N losses through erosion under natural conditions, plus enhanced erosion losses following forest harvest, natural fire or fires used as part of traditional management regimes

$N_{vol(crit)}$ = annual N losses to the atmosphere from NH_4 volatilisation

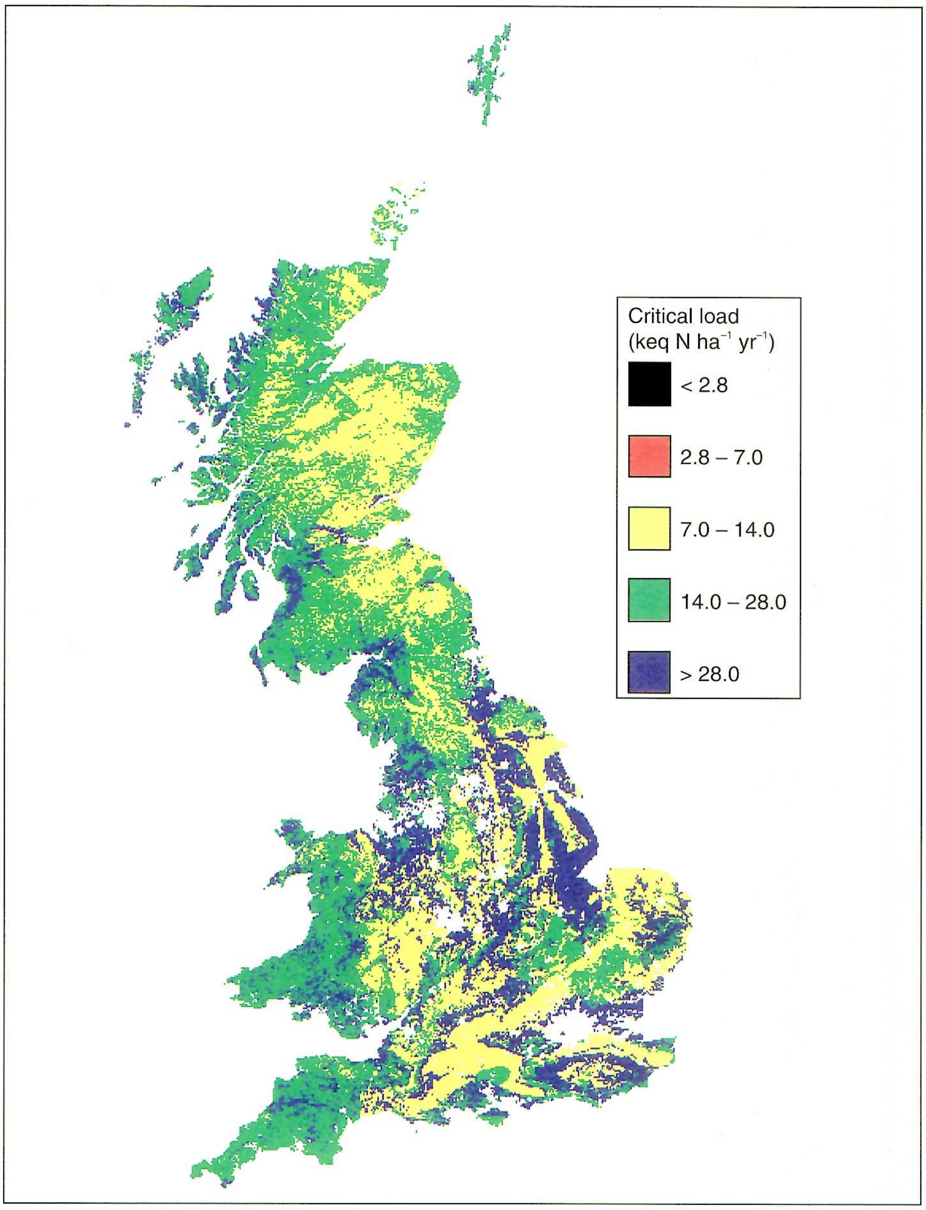


Figure 37. Critical loads of nutrient nitrogen for coniferous forest, derived using the simple mass balance equation

The calculated critical load will vary with soil type and vegetation/land management. Thus, for example, immobilisation of N will vary with soil pH and C/N ratio of soil organic matter, while harvesting practices will determine the net removal of N. Thus, the equation is solved for specific soil/ vegetation combinations. It has been used to produce exploratory critical load maps for GB and for application to specific sites. The GB maps are based on 1 km grid cells and the equation has been solved with respect to the most widespread soil in each cell. Maps have been generated for the same three habitats used in the tests of the acidity mass balance approach: coniferous forest, acidic grassland and heathland. Specific values for most of the input variables to the equation are not available, and thus a series of default values have been used Figure 37 shows the map of critical loads for coniferous forest A major overall control on the critical load is the assumed N removal at harvest The spatial pattern mainly reflects the underlying pattern of soils, in particular rates of N loss by denitrification and the N sink represented by immobilisation Critical loads calculated using the mass balance equation for a given soil type and geographical area are smallest for the acidic grassland as net removal was set at zero, the critical load for coniferous forest is larger than for heathland, reflecting the greater assumed net N removal The critical load for coniferous forest calculated in this way is exceeded by N deposition over most of GB, except northern Scotland

The future

The critical load maps for sulphur, nutrient nitrogen and total acidity will continue to be refined as input databases are improved Work at the landscape scale will be expanded to all 508 1 km survey squares from Countryside Survey 1990, which cover all the main types of land in Britain In the medium term, the UNECE is considering the development of methodologies for the calculation and mapping of critical loads for trace metals and persistent organic pollutants (POPs) The application of the various proposed approaches will be evaluated in the UK over the next two years

M Hornung, J Hall and K R Bull

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Consequences of atmospheric nitrogen deposition on ecosystem functioning in coniferous forests – NITREX (a European study)

(This work was partly funded by the European Union Third Framework Programme and the Joint Environment Programme of National Power and Powergen)

The atmospheric deposition of both oxidised and reduced forms of nitrogen has increased in the UK and across Europe due to the combustion of fossil fuels and the intensification of agriculture respectively In Europe, this increase has been associated with damage to vegetation and soils and a decline in water quality Of particular relevance to the uplands of the UK is the link between nitrogen deposition and the acidification of soils and waters

Areas at risk from excessive inputs of nitrogen are currently identified by the application of the nitrogen critical load concept If nitrogen inputs exceed the critical load, possible damage to sensitive components of the ecosystem may follow Preliminary empirical nitrogen critical load exceedance maps for the UK have identified large areas of Wales where deposition exceeds the nitrogen critical load, indicating that some ecosystems are at risk (Figure 38) Ten years of experimental and monitoring work in north and mid-Wales by ITE Bangor also provide evidence that certain upland ecosystems, in particular plantation forests, receive nitrogen deposition in excess of the critical load These ecosystems can be identified by large nitrate leaching losses which indicate that nitrogen inputs are in excess of ecosystem requirements and are thus 'nitrogen saturated'

To investigate the potential risk of damage to these plantation forests and the waters draining from them, we are experimentally determining the effects of enhanced nitrate and ammonium deposition on a mature Sitka spruce (*Picea sitchensis*) stand in Aber forest, N Wales The experiment is part of the European NITREX project, which focuses on the impacts of excessive nitrogen deposition on coniferous forest ecosystems to improve our understanding of the link between atmospheric nitrogen deposition and changes at the ecosystem level (Wright *et al* 1995)

The NITREX project

The NITREX project involves the experimental manipulation of nitrogen inputs in coniferous stands across a European nitrogen pollution gradient In sites currently receiving low to medium atmospheric nitrogen deposition (eg Scandinavia and the UK), nitrogen is applied in small frequent doses to the soil to simulate increased nitrogen deposition, thus testing the risk of damage at these sites In forest stands already receiving high nitrogen pollutant loadings, water is collected during each rain event using a subcanopy roof structure and pollutants are removed using deionisation resins (Plate 22) The 'cleaned' throughfall water is then applied to the forest floor by a spraying system The timing of recovery in areas which currently exceed the nitrogen critical load (eg The Netherlands and Germany) can thus be determined

The response in terms of soil and stream water quality, and in particular nitrate and aluminium leaching losses, is of particular interest to the NITREX consortium because of the link between nitrate and aluminium leaching in acid coniferous soils

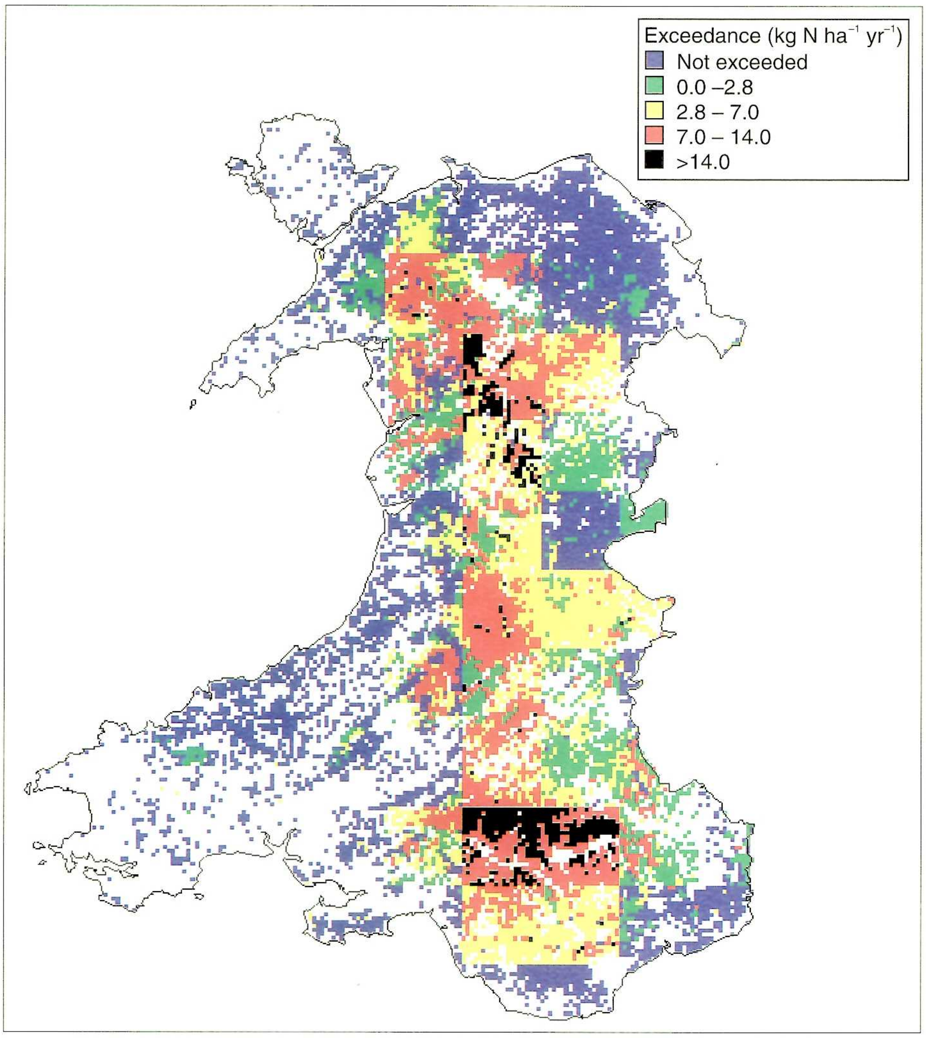

Figure 38. Exceedance of empirical critical loads of nutrient nitrogen for 14 vegetation types by total (oxidised and reduced) nitrogen deposition, 1989–92 (data supplied by CLAG vegetation subgroup, National Critical Loads Mapping Centre (ITE Monks Wood), Environmental Information Centre (ITE Monks Wood), ITE Bangor, AEA Technology, and ITE Edinburgh)

Effects on water quality

Results from the NITREX sites show rapid changes in soil water chemistry following a reduction in nitrogen inputs (Figure 40). For example, nitrogen leaching losses were reduced by 80–90% within a few months of a major reduction in nitrogen inputs to the sites in The Netherlands (Speuld and Ysselsteyn). For the Solling site in Germany, soil water concentrations were significantly reduced but no flux data are currently available. The response to nitrogen additions has been less consistent. Little response was recorded in the Scandinavian sites of Klosterhede and Gårdsjön. In contrast, nitrate leaching increased immediately at the UK Aber site in parallel with nitrate inputs (Emmett *et al.* 1995b). As predicted, this increase in nitrate leaching was associated with an increase in soil water aluminium concentrations as aluminium is the dominant exchangeable cation in these acid soils.

The different response at the Scandinavian and UK sites to nitrogen additions can be explained by the nitrogen status of the sites prior to treatments. Aber was already in a state of nitrogen saturation and any increase in nitrate inputs directly contributed to nitrate leaching. The Scandinavian sites were nitrogen limited and thus tree and soil microbes have acted as sinks for the applied nitrogen, thus limiting release of the nitrogen to surface waters.

The Aber experiment

The experimental site in north Wales is located in the middle of the NITREX nitrogen pollution gradient (Figure 39) and is already exhibiting some characteristics of nitrogen saturation as nitrate leaching losses (10 kg N ha^{-1} yr^{-1}) are already twice those expected in unpolluted areas. Leaching losses exceeding 5 kg N ha^{-1} yr^{-1} are characteristic of many Sitka spruce stands over 30 years of age planted on freely draining acid soils in upland Wales. Losses as great as 30 kg N ha^{-1} yr^{-1} have been observed at some sites (Emmett *et al.* 1993). At Aber, nitrogen has been applied weekly, in reduced or oxidised form and at two application rates (35 and 75 kg ha^{-1} yr^{-1}), to the forest floor of 15 large experimental plots since 1990 (Plate 23), and the response of waters, soil and trees has been routinely recorded (Plate 24).

Plate 22. A NITREX nitrogen reduction experiment

Plate 23. Nitrogen spraying at Aber (photo: Royston Photographic)

Effects on the soil nitrogen status

In addition to the direct effects on soil water chemistry, the possible effect of excessive nitrogen deposition on the soil nitrogen store is of concern. Large quantities of nitrogen have been retained within the soil since the last glaciation. If this nitrogen store is mobilised due to the effects of incoming nitrogen on soil nitrogen transformations, this may further increase nitrate leaching losses and the risk of acidification of soils and waters.

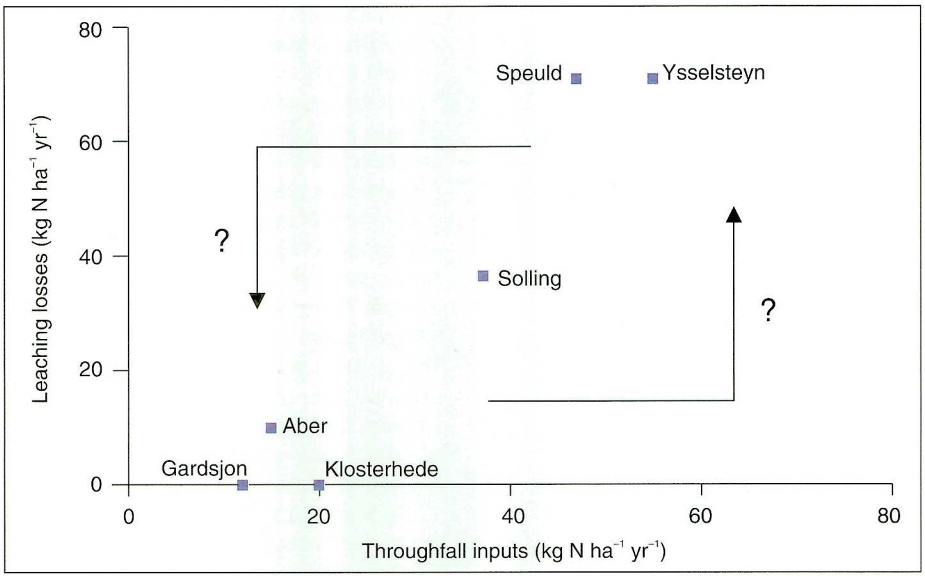

Figure 39. The relationship between nitrogen inputs in throughfall and nitrogen leaching losses at the NITREX sites (the arrows indicate the predicted responses to experimental changes in nitrogen deposition)

Experimental work on soils from the Aber manipulation experiment and from sites along a nitrogen-limited to nitrogen-saturated continuum in Wales has indicated that incoming nitrogen is directly stimulating mobilisation of the soil nitrogen store and increasing the rate of soil nitrate production in nitrogen-saturated stands where the nitrogen content of the forest exceeds approximately 1.7%. No immediate effect on soil nitrogen transformations is observed in soils from nitrogen-saturated sites with lower soil nitrogen concentrations. At these sites, long-term increases in nitrogen inputs are required before impacts on soil nitrogen transformations and the nitrogen store will be observed. This requirement has been demonstrated by the Aber experiment, which is a nitrogen-saturated site with a forest floor of relatively low nitrogen concentration. Three years of nitrogen additions were carried out before effects on the soil nitrogen store and nitrate production were observed (Figure 41), with the magnitude of response being dependent on the amount of nitrogen applied.

Effect on trees

The elevated nitrate leaching losses from the treated plots at Aber are linked to increased soil water aluminium concentrations which can have an adverse effect on tree growth and health, because of impacts on roots and mycorrhiza. Once the soil water drains into streams, fish and aquatic biota may be damaged. However, trees are known

Plate 24. Soil water measurements at Aber (photo: Royston Photographic)

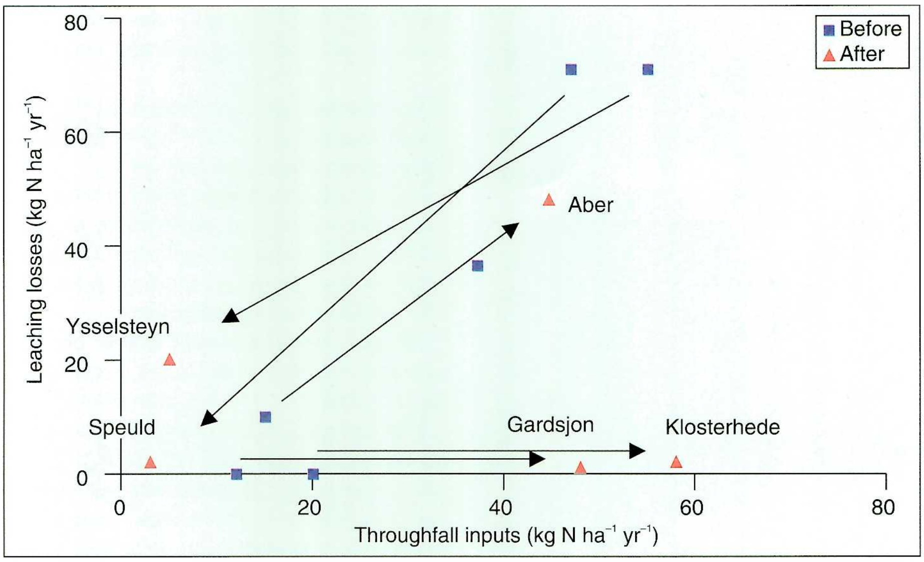

Figure 40. The effect of experimentally changing nitrogen inputs on nitrate leaching losses: before and after nitrogen reduction or addition treatments (redrawn from Wright *et al.* 1995)

to respond more slowly than water quality and aquatic biota. At some Dutch sites, the growth and nutritional status of Norway spruce (*Picea abies*) improved only after prolonged reduction of nitrogen inputs (eg Boxman *et al.* 1995). Little effect has been recorded at the other NITREX sites, including Aber, which have shorter treatment periods (Emmett *et al.* 1995b). Continued monitoring is vital if the long-term effects of elevated atmospheric nitrogen deposition and soil acidification on tree growth and health are to be determined. Effects are expected to vary with tree species and soil type. Sitka spruce, the main tree crop in the UK, is predicted to be the most resilient to soil acidification.

B A Emmett, S A Brittain and
B Reynolds

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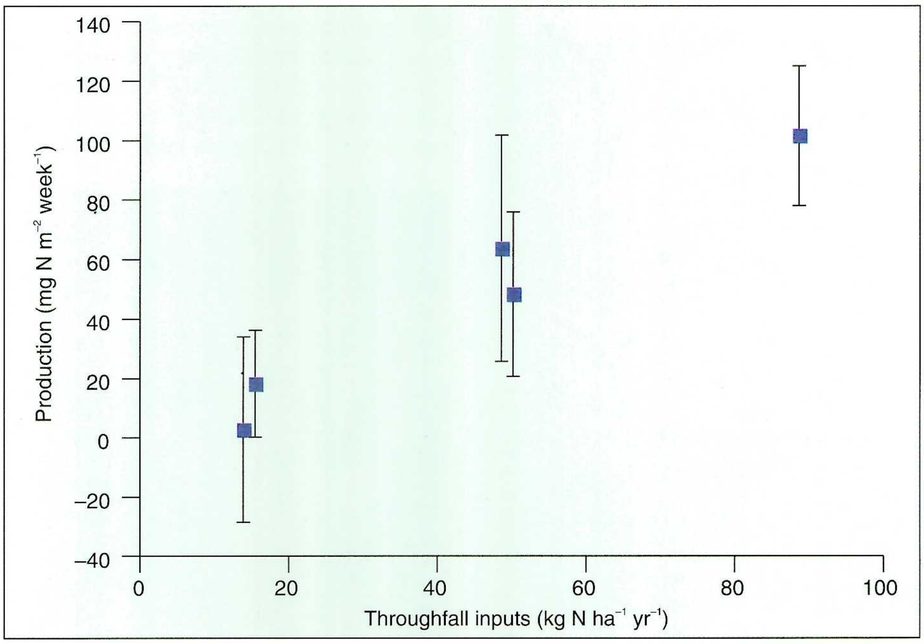

Figure 41. The rate of soil nitrate production (± standard error) after three years of nitrogen additions in the Aber experimental plots

Emissions of N_2O at the landscape and national scale

(This work was funded by the NERC Terrestrial Initiative in Global Environmental Research (TIGER) Programme and the EC Environment Research Programme)

Concentrations of nitrous oxide (N_2O) have been increasing in recent years by 0.2–0.3% per year and the global average concentration of 310 ppbV exceeds values in the pre-industrial atmosphere (285 ppb) by about 9%. In addition to contributing 7% to the radiative forcing of global climate, nitrous oxide also influences the chemistry of the stratosphere, where it represents a major source of nitrogen oxides and is important in regulating stratospheric ozone concentrations. Atmospheric N_2O is of considerable interest, therefore, but the magnitude of the individual sources is very uncertain. The global budget for N_2O, reproduced from the Inter-governmental Panel on Climate Change assessment (Houghton *et al.* 1995), estimates the total source strength of N_2O to range from about 10 to 17 Tg N yr^{-1}, a large range and including many very uncertain items (Table 1). However, from the known rate of accumulation of atmospheric N_2O (which has an atmosphere lifetime of 150 years) and the rate of chemical destruction in the

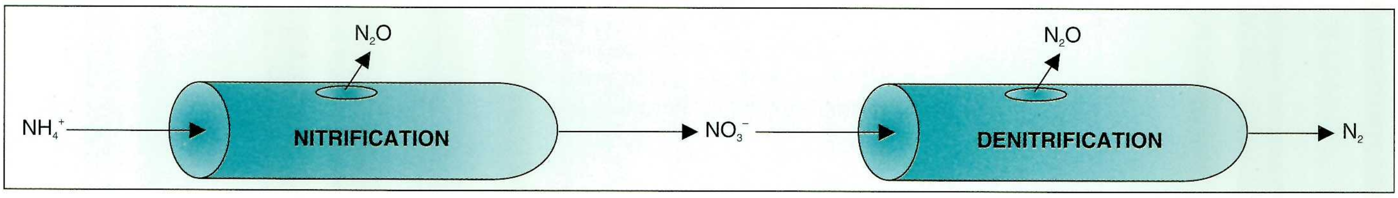

Figure 42. In soil nitrifying and denitrifying micro-organisms are the principal producers of N_2O

stratosphere (7–13 Tg N yr^{-1}), the annual increase is equivalent to 3–4.5 Tg N yr^{-1}. Quantifying components of the global budget of N_2O is the ultimate objective of many of the current studies of N_2O emission. There are also national commitments to quantify the emission inventories for radiatively active gases, and for CO_2, CH_4, N_2O in particular. Within most estimates of the global N_2O budgets, soils, both temperate and tropical, are identified as the major sources (Table 3). Thus, much of the focus in N_2O research is on soil emissions, the processes which regulate them, and methods of up-scaling from short-term flux measurement to annual emissions for countries and regions.

The national budget for N_2O for the UK, while representing a very small fraction of the global terrestrial surface, is an important goal for the current work, including that within the Terrestrial Initiative on Global Environmental Research (TIGER II) Programme on N_2O emissions. Many measurements have been made of N_2O emission from fertilized soils in mid-latitude agricultural countries. These measurements show great spatial and temporal variability as a consequence of the soil conditions which regulate nitrification and denitrification, the two microbial processes that lead to N_2O release. The loss of N_2O from soil may be considered as 'leakage' of volatile N during the reduction of NO_3^- to N_2 (denitrification) and the oxidation of NH_4^+ to NO_3^- (nitrification) shown schematically in Figure 42.

Table 3. Estimates of global emissions of N_2O for various source types (source: Houghton *et al.* 1995)

Sources	Emission range (Tg N yr^{-1})
Natural	
Oceans	1–5
Tropical soils	
Wet forests	2.2–3.7
Dry savannas	0.5–2.0
Temperate soils	
Forests	0.1–2.0
Grasslands	0.5–2.0
Anthropogenic	
Cultivated soils	1.8–5.3
Biomass burning	0.2–1.0
Industrial sources	0.7–1.8
Cattle and feed lots	0.2–0.5
Total	10–17

The work of the last five years on N_2O emission under the TIGER II Programme has been carried out by research groups at ITE Edinburgh and Merlewood, the Scottish Agricultural Colleges (SAC), Edinburgh, and the Universities of Nottingham and Dundee. The field measurement programme by the two ITE groups and SAC provided emission fluxes of N_2O from both fertilized arable and grassland and from woodland and forest soils.

To overcome spatial variability (fluxes may range over two orders of magnitude along a 10 m transect) commonly observed using conventional small chambers (typically 0.01–0.1 m^2 in area), micrometeorological methods were developed in which the average flux was measured over 10^2–10^4 m^2 over the field sites (Hargreaves *et al.* 1994).

The measurements, made using eddy covariance (ITE) and relaxed eddy accumulation methods (Institute of Ecology and Resource Management (IERM), University of Edinburgh), were compared during the three-week period following the application of NH_4NO_3 fertilizer to the wheat crop during April 1994 (Figure 43). The N_2O fluxes measured using relaxed eddy accumulation, averaged over 30–270 minutes, were in agreement with those of the eddy covariance system within 60%. During the period of significant emission fluxes, a clear diurnal cycle in N_2O emission was observed by the eddy covariance measurements, with the daytime maximum coinciding with the soil temperature maximum at 12 cm depth (Figure 44). The temperature dependence of the N_2O emission was equivalent to an activation energy for N_2O production of 108 kJ mol^{-1}. The total emission of N_2O over the period of continuous measurement (ten days) by eddy covariance was equivalent to about 10 kg N_2O–N, or 0.77% of the N fertilizer applied (Skiba *et al.* 1996a).

A similar field experiment took place in Denmark, again over arable land, as part of a European Union collaborative study of N_2O emissions illustrated in the photograph (Plate 25). The study included micrometeorological and chamber methods and provided an opportunity to compare the different techniques. Fluxes determined by all methods were generally in good

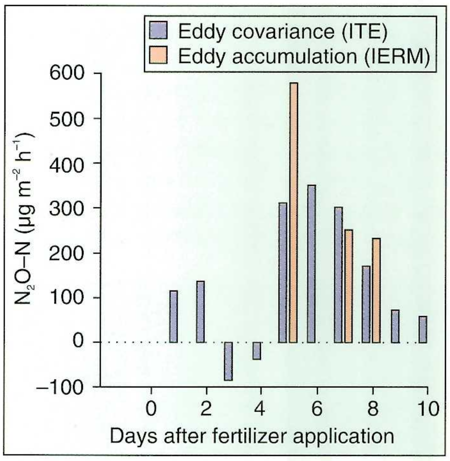

Figure 43. Nitrous oxide emissions from winter wheat, April 1994, south-east Scotland

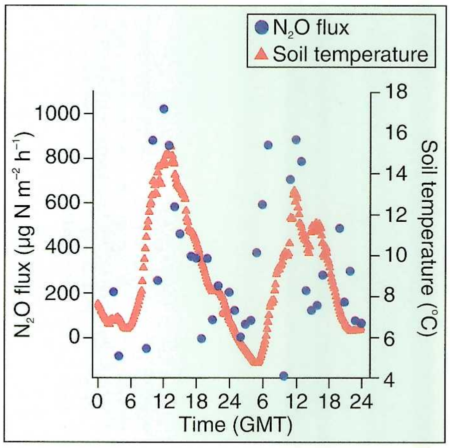

Figure 44. Diurnal variations of N_2O fluxes five and six days after fertilizer application. Soil temperature was measured at 5 cm depth

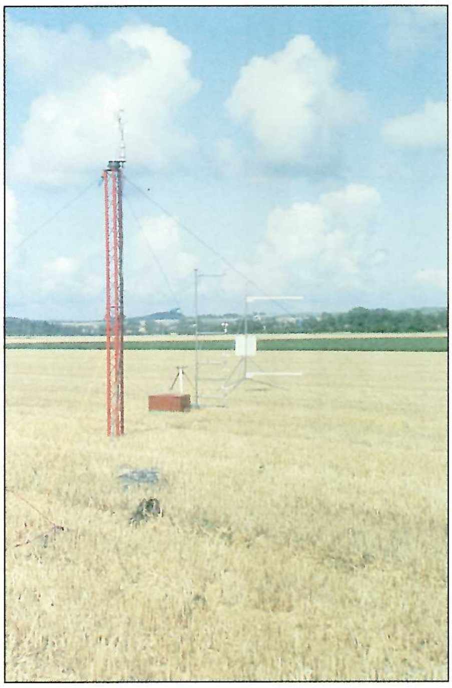

Plate 25. Micrometeorological equipment to measure large-scale trace gas fluxes at Lammefjord, Denmark, 1993

agreement; fluxes by chamber and micrometeorological methods were in the range of 162–467 µg N_2O–N m^{-2} h^{-1} and 149–495 µg N_2O–N m^{-2} h^{-1}, respectively. However, some consistent differences were observed; for example, eddy covariance flux measurements by two tunable diode laser spectrometer-based systems (TDLs) (ITE and Max-Planck Institute (MPI), Mainz) differed significantly, as shown in the polar diagram (Figure 45) (Hargreaves *et al.* 1995).

The differences in mean emission rates of the two TDL eddy covariance systems have been attributed to different areas of the site being measured by the two systems. A section of the field in which substantially larger N_2O fluxes were present was in the 'footprint' of the ITE instrument and not in that of the MPI system. The measurements for the two TDL instruments show a broadly similar range and sector dependence for the fluxes. The absolute values at this site are large relative to many other sites, which has been attributed to a substantial quantity of organic matter at depth within the soil profile (Christensen *et al.* 1995). The interpretation of micrometeorological flux measurements using footprint analysis is further outlined by Fowler *et al.* (1995).

In addition to the extensive measurements over arable and intensive grassland, measurements have been made over forest soils, moorland and shelterbelts close to large sources of ammonia. A thorough review of the measurements lies outside this brief report; however, for some of these studies, a clear relationship between the N_2O emission flux and soil NH_4^+ and temperature has been obtained (Figure 46). Such data may be used as the basis for simple empirical models to estimate emissions of N_2O over regional or country scales to provide emission estimates for the UK. Using ITE land use data to classify the countryside, Skiba *et al.* (1996b) have estimated the annual N_2O emission from UK soils to be 27 kt N. The bulk (69%) is emitted from managed grasslands, 17% from tilled land and 14% from semi-natural and natural ecosystems (Table 4). For the latter, emissions largely increased in areas of high N deposition (Skiba, Fowler & Smith 1994).

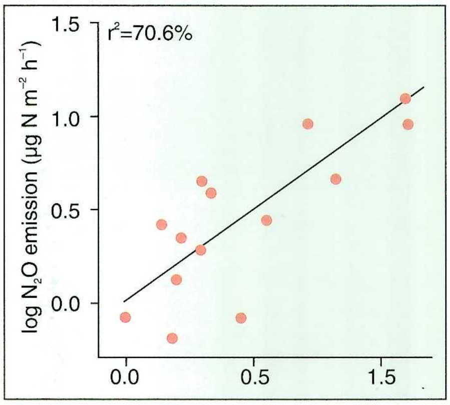

Figure 46. The dependence of N_2O emissions on soil temperature changes and soil available NH_4^+ concentrations in a coniferous forest at Dunslair Heights, south Scotland (units on the y axis are provided as the output of the equation: $-0.633+(0.0192\times NH_4^+)+(0.112\times$soil temperature$)$)

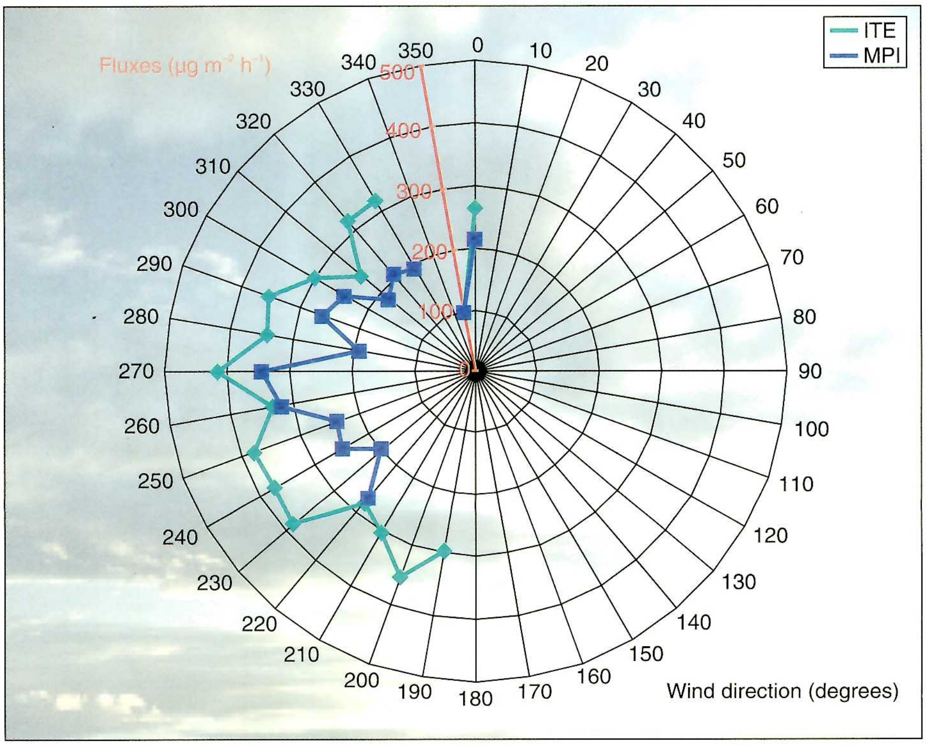

Figure 45. Eddy covariance N_2O fluxes at Lammefjord, Denmark, August 1993, measured with the wind in different directions by ITE and the Max-Planck Institute

The synthesis of the programme of TIGER II N_2O measurements over the next year will provide the basis for a much more rigorous estimate of soil N_2O emissions. These developments will be used to improve the soil N_2O emissions for the UK, northern Europe and, in collaboration with international groups, the global inventories. At present, soils contribute only 27% of the total N_2O emissions in the UK (Table 5). Industry, principally nylon manufacture, is the largest single source

Table 4. N_2O emissions from soil in the UK

	Emissions (kt N_2O–N yr^{-1})
Managed grassland	18.6
Tilled land	4.7
Deciduous woodland	1.2
Coniferous woodland	0.5
Rough grass, moor grass	0.8
Heath/bog/bracken	1.3
Total	27.1

Table 5. Total annual emissions of N_2O in the UK

	Emissions kt N_2O–N yr^{-1}	%
Industry	51	54
Road	3	3
Other fuel combustion	2	2
Agricultural soils	23	24
Other soils	4	4
Livestock waste	12	13
Total	95	100

of N_2O. However, as these sources can and will be easily eliminated – in the case of nylon manufacture this will occur very soon, agricultural N-fertilized soils will become the major source of UK N_2O emissions.

The non-soil N_2O emissions, accounting for 72% of the total annual emissions, remain a target for research in this field. Valuable information on their contribution to the UK budget will be provided by the programme of measurements in collaboration with the Meteorological Office Research Flight, in which direct measurements of the UK source strength may be obtained by measuring budgets of N_2O (and other gases) in the atmospheric boundary layer downwind of the UK downwind coastline.

Recent measurements in winter conditions confirm the very small winter N_2O fluxes from soils, but have identified major anthropogenic sources. Further work of this nature will be used to check national emission inventories for radiatively active gases.

D Fowler, U Skiba and K J Hargreaves

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Environmental consequences of industrial accidents

(This study was partly funded by the Department of the Environment)

Rationale and aims

The release of chemicals from industrial processes is carefully regulated with the aim of preventing harm to people and the environment. One of the more difficult areas to control is accidental releases from industrial or commercial premises. These releases occur when there are explosions, leaks of gas or vapour, fires, or spills (Plate 26).

To support work on the Control of Industrial Major Accidents and Hazards (CIMAH) Regulations (which implement the European Union's Seveso Directive in the UK), the Toxic Substances Division of the Department of the Environment commissioned ITE to investigate the environmental consequences of accidents, both at industrial sites covered by the CIMAH Regulations and also at similar non-CIMAH sites. The work was necessary because there was only a limited appreciation of the role of accidents in contaminating and damaging the environment.

The work over the past three years has aimed to:

- improve understanding of the environmental importance of accidents;
- determine the types of installations at which accidents occur;
- discover the sorts of chemicals released;
- determine the qualitative and quantitative nature of the impacts of accidents;
- ascertain the components of the environment most at risk from chemicals released from accidents.

Focus of the work

The work has concentrated on impacts on land, as the National Rivers Authority already collects information in relation to major impacts on certain waterways. The work has involved co-operation with a large number of organisations, including:

- site owners,
- the Health and Safety Executive,
- several National Rivers Authority regional offices,
- local authorities at both county and district level (including emergency services),
- the Department of the Environment, and
- the Ministry of Agriculture, Fisheries and Food.

Plate 26. Contamination resulting from a fire at a plastics recycling plant

Over 25 incidents have been investigated in the last three years. CIMAH sites are required to take special precautions to prevent accidents and contain their impact, but there were incidents at CIMAH sites during this period that had biological impacts outside the site. There were many incidents at non-CIMAH sites which released a wide range of materials into the environment. Much is being learnt from these accidents that will help develop management strategies for accidents both at these sites and at CIMAH sites. A number of the non-CIMAH site incidents (mostly in eastern England) have been investigated, and one incident – which led to the contamination of a coniferous woodland plantation with molten plastic – has been investigated in considerable detail.

The most common type of accident investigated is fire, and a surprising number of these fires have been at sites where plastic material is stored, either for secondary manufacturing process or for recycling (Meharg 1994a). Other cases cover buildings used to store chemicals intended for recycling, general chemical warehouses, chemical storage facilities, main industrial production installations, and even a dairy products processing plant.

When the opportunity arose, accidents with chemicals in transit were investigated. Both road and rail accidents have been examined in which oil and industrial feedstocks have been spilt from split or corroded containers.

Nature of accidents

Every incident differs in detail, but some general principles are emerging. Thus, fires release chemicals that can contaminate the environment by a number of different routes. A mixture of materials is released into the air. Some of it is distributed widely in a smoky plume that rises buoyantly from the fire and deposits material over an area, perhaps up to 20 km from the source. Other material is deposited relatively close to the source, presumably because of eddying air currents at the base of the fire. From transects measuring metal deposition, significant contamination can return to background at distances varying between 10 m to about 200 m from the fire's location. Depending on local topography, geology and hydrology, runoff from fire-fighting can cause pollution of ground- and/or surface water, and, subsequently, affect fish stocks or threaten water supplies for people or livestock. Some of these effects may extend 20 km, or more, from the source. Once in the ground, or even when running across the surface of an industrial area, fire water is often applied to fires in such volume that it causes bulk flow of material through or over the ground.

Types of chemical released

A wide range of materials are released from accidents (Meharg 1994b). Metals deposited relatively close to the fire can be used to act as markers for contamination (eg at plastics fires where antimony can be used to ascertain the extent of contamination of both land and water). Pesticides and polyaromatic hydrocarbons have been amongst the organic substances released. Some of the chemicals released are 'priority' pollutants, whose presence above certain limits is regarded as a cause for concern. On occasion, chemicals have been detected in the vicinity of accidents that do not appear to be related to current industrial activity on the sites involved; they could possibly have been flushed into the open environment by fire-fighting water. For example, at one site, preliminary evidence for the presence of styrene compounds was observed, which may be important because some styrene compounds may cause cancer.

Some local authorities have expressed concern about the possible release of dioxins from fires involving chlorinated substances, because some dioxins and dioxin-like compounds are suspect carcinogens, and affect the immune and reproductive system in some animals. Partly because of this concern, a scoping study of the scientific literature was done and published in *Nature* (Meharg & Osborn 1995). The study showed that many chemical accidents (fires, explosions and spills) had released either dioxins or dioxin-like compounds. Further, a range of different source materials produced dioxins when pyrolysed, and thus had the potential to release dioxins in fires at industrial and commercial premises. The study underlined the uncertainty that exists about sources of dioxins and dioxin-like compounds in the environment. ITE scientists are now discussing the implications of their findings with the Department of the Environment.

Accidents can release other chemicals of concern to human health. For example, where building roofs are asbestos, a fire can cause fragments and dust from the damaged roof to be widely distributed in the local area.

The most notable transport accident involved leakage of vinyl chloride (a carcinogen) – despite its volatility, the chemical released from a single drum damaged crops up to a distance of about 200 m from the lorry involved.

Impacts on the terrestrial environment

In addition to discovering the types of chemicals released, several studies of the impacts of accidents have been conducted and reviews published (Meharg 1994c). Some of the incidents investigated have also been studied to obtain information on the types of natural resources that accidents put at risk. In addition to the risk to water resources, a number of accidents have occurred near or even immediately adjacent to Sites of Special Scientific Interest, and some damage to them has resulted from the accident or its aftermath. The impacts of one accident, a large plastics fire, have been studied in detail to obtain information on the possible effects on the terrestrial environment. To date, the main findings of this study, in addition to ones described above, include the following.

- Metals (eg cadmium) released from a fire can accumulate in a wildlife food chain (soil, leaf litter, invertebrate, mammal). Some evidence of contamination with organic chemicals has also been found.

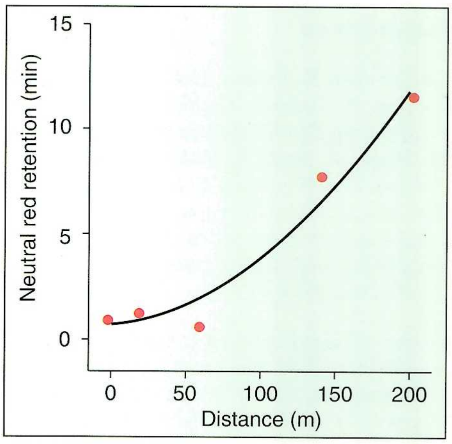

Figure 47. Cells from control (unstressed) earthworms have neutral red retention times of about 30 min. At 200 m from the study site, neutral red retention times are still half the expected control value

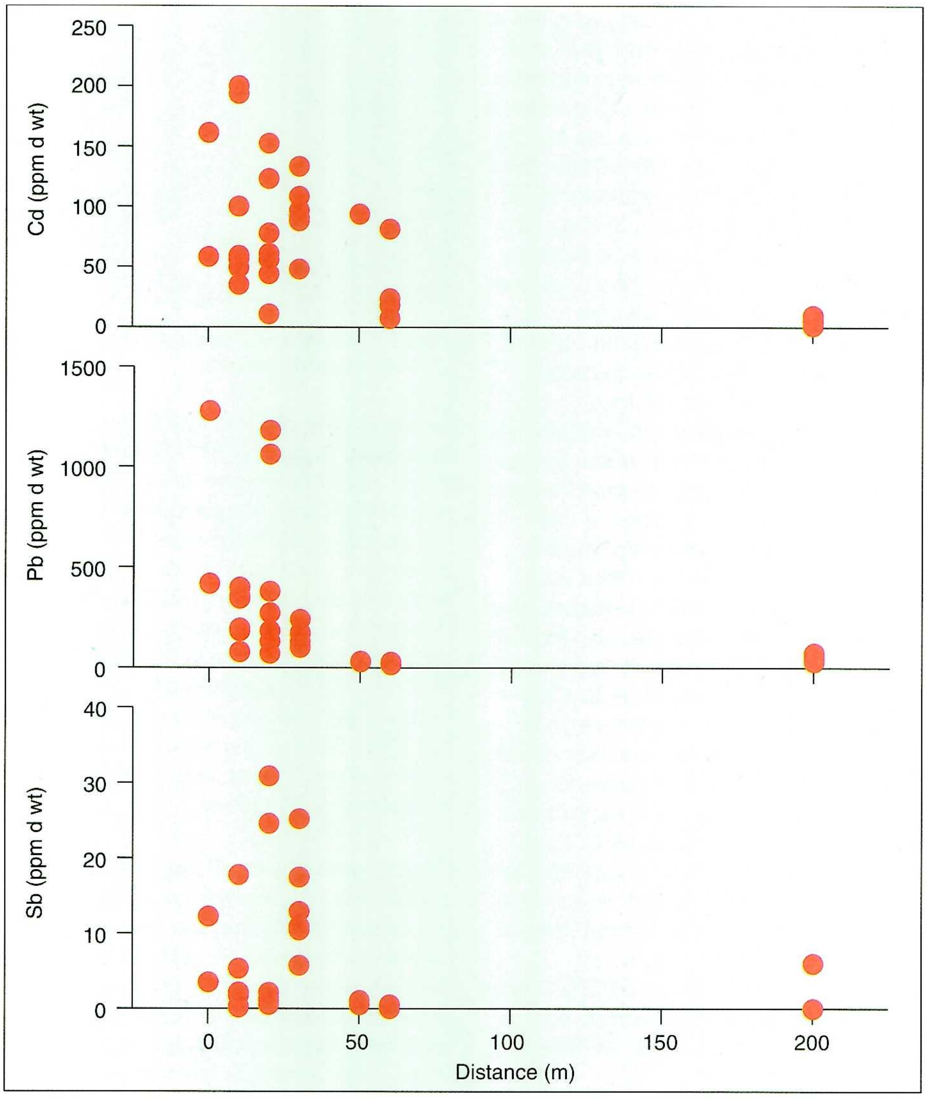

Figure 48. Metal contamination in earthworms is confined to the region nearest the boundary of the fire site (0 m), contamination being much closer to background levels at greater distances. The data were obtained from a transect across a contaminted area. Cd – cadmium; Pb – lead; Sb – antimony

- Studies with biomarkers (cellular indicators of chemical impacts on biochemical systems) have shown that earthworms living near the fire site were biochemically stressed in contrast to control animals. The stress was assessed by determining the time taken for a dye to be released from the lysosomes of earthworm body fluid cells (Figure 47). Evidence for this type of impact has been found further from the site than measurable levels of contamination (Figure 48). This finding implies than there is more extensive, as yet undetected, chemical contamination of the area; if the contamination were due to contaminated animals migrating away from the area, they might be expected to retain metals such as cadmium. Done in association with a student from Odense University in Denmark working at Monks Wood, these studies are illustrating how a combined biomarker and chemical analysis approach can be used to quantify the impacts of accidents.

- Studies in progress with UK university colleagues and NERC CASE students have shown that the soil fungal community near a fire site has changed, which could have implications for soil nutrient cycling and general soil ecosystem functioning. Studies of tree seedlings on soils contaminated with plastic from the fire have shown that seedlings on contaminated soils grew less well than controls. It is not yet entirely clear which aspects of the fire's effects are involved, possibly both metals and organic materials.

These results show that accidents can have notable impacts in the terrestrial environment, leading to:

- increased chemical contamination,
- food chain accumulation of chemicals,
- changes in the structure of fungal communities,
- biochemical impacts,
- impacts on plant growth.

Moreover, the effects may persist for several years after the accident.

A A Meharg, D Osborn, P K Hankard, C Svendsen, J M Weeks, J Hartley and M C French

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Hazard and risk assessment of chemicals

(This work was partly funded by the Department of the Environment)

There are some 70 000 chemicals in use in industry worldwide. Many of these have been in use for decades and some for more than a century. Whilst new chemicals coming on to the market for the first time are tested extensively for toxicity to humans and the environment, older chemicals have frequently never undergone testing either for effects or fate in the environment.

The last 20 years have seen international harmonisation in requirements for testing new chemicals. Test protocols have been developed for all the major endpoints of fate and toxicity, first nationally and then internationally. The Organisation for Economic Cooperation and Development (OECD) has taken responsibility for co-ordinating the development of these protocols, and OECD guidelines have been accepted internationally as definitive. The reason for OECD involvement is the freeing of trade in chemicals; testing in one country should be acceptable worldwide to prevent duplication of effort. Similar international co-operation occurs regionally, for example in the countries of the European Union (EU), so that a chemical tested and assessed in one Member country is accepted in others. Peer review of assessments across national boundaries ensures that a common standard is applied. Increasingly, the assessment of chemicals is being internationalised to prevent the overloading of limited resources in individual countries.

Only recently has this internationalisation been applied to the large number of chemicals which have not, so far, undergone testing through national regulatory procedures. These 'existing chemicals' present a much greater challenge than new chemicals because of the large numbers involved and the general lack of information in many cases. The EU and OECD have developed existing chemical programmes to be compatible, a major development in chemical control. Most developed countries are contributing to generating assessments of chemicals which feed into these international efforts.

The United Nations Conference on Environment and Development (UNCED) in Rio de Janeiro in 1992 resolved to increase activity in chemical hazard and risk assessment; it set targets for 200 more chemicals to be assessed by 1997 and a further 300 before the end of the century. Responsibility for co-ordination of such activity was given to the International Programme on Chemical Safety (IPCS), a joint programme operated by the World Health Organisation (WHO), the United Nations Environment Programme (UNEP) and the International Labour Office (ILO). IPCS was expanded both in scope and responsibility and acted as the Secretariat for an international forum which included all organisations involved in chemical assessment. Through this forum, OECD and other international efforts are co-ordinated with IPCS activities which are largely aimed at developing countries and those in economic transition.

A stepwise approach is being adopted in assessing existing chemicals. The large number of chemicals involved requires a prioritisation step, which is being done in a general fashion based on acute toxicity studies and simple fate information. Lists of chemicals ranked according to initial perceived hazard to human health and the environment have been generated within the EU. Two priority lists have now been agreed and a third is under discussion. These lists form the basis of national decisions to assess particular chemicals. The first step in the assessment is to gather data available in the published literature and from industry, which is legally required to provide data held. Data gaps are identified at this stage and decisions taken on whether such gaps need to be filled. The data packages are collected and disseminated by OECD; EU chemicals are also fed into this process. Detailed reviews on priority chemicals are required when data are adequate to make an assessment in at least some of the areas of interest: direct human health implications, indirect human exposure through environmental routes such as drinking water or food, and effects on organisms or communities in the environment. These reviews have, so far, been done at the national level for regulatory purposes or at the international level through IPCS. IPCS has produced a series of documents at several levels since the first UNCED Meeting in Stockholm in 1972. Comprehensive assessment documents are published as IPCS Environmental Health Criteria (EHC) Documents; almost 200 of these are now complete. Whilst primarily aimed at developing countries, these Documents are also used as reference works in the developed world. Health and Safety Guides (HSGs) provide practical information on protection of human health and the environment in a simplified form for direct use at the industrial plant or farm where chemicals are used. International Safety Cards are aimed at workers handling the chemicals and are presented as simple risk phrases and guidance which can be reduced to pictorial indicators of safe handling in the workplace, even to the illiterate. Environmental Hazard Assessments (EHAs) have been produced for UK domestic use through contracts with the Department of the Environment.

Plate 27. A selection of risk assessment documents produced by ITE

ITE has been involved in producing assessment documents at all levels of the EU, OECD and IPCS programmes for several years. We have been involved in producing 57 EHCs, 24 EHAs and seven assessments for OECD/EU (eg WHO 1992; Crookes & Howe 1993) (Plate 27). A substantial body of information is held on all aspects of environmental fate and behaviour and the toxic effects of more than 250 chemicals. In addition, ITE is represented on the Advisory Committees (the Advisory Committee on Pesticides, the Advisory Committee on Hazardous Substances, and the Advisory Committee on Toxic Substances) which advise UK Government departments on the regulation of chemicals.

Hazard assessment of chemicals involves identifying *potential* effects on organisms or human health. This has universal application worldwide, though frequently test organisms are of particular relevance to developed countries which lie mainly in temperate zones. Extrapolation from species to species is often done but the basis for such extrapolation is far from scientifically validated. ITE is conducting research to improve such extrapolation for a variety of species, including bats, other small mammals and birds.

Risk assessment is a quantitative process whereby the likelihood of effects actually being manifested in the real world is judged. Risk is a local problem related to local exposure scenarios. At a national level, it is possible to estimate exposure with reasonable accuracy given the knowledge of production and use patterns. As assessments widen to the regional or international level, risk assessment becomes more difficult and may become impossible. Lack of monitoring of environmental concentrations or loads of chemicals in developing countries means that exposure can only be assessed by extrapolation from the situation in developed countries. Differences in use patterns, local regulation, local attitudes to safety, and climatic differences all make such extrapolation unreliable.

Conclusions for the tropics, where many developing countries lie, are frequently tentative or lacking Models, which are increasingly used to fill data gaps, are often not appropriate for tropical climates

Hazard and risk assessment of chemicals remains very much in its infancy, and many fundamental questions are as yet unanswered However, the process has been started on a large scale internationally, and the commitments needed from developed countries have been entered into Whilst the majority of chemicals coming through such assessments demonstrate little real risk either to humans or the environment, despite media claims to the contrary, we can expect new problem chemicals to emerge as the process develops

S Dobson, P D Howe and H M Malcolm

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