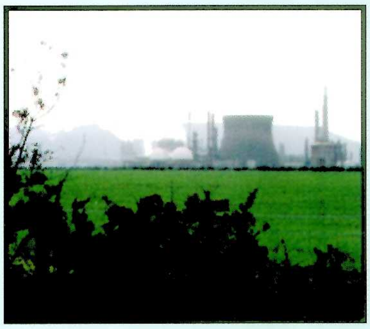
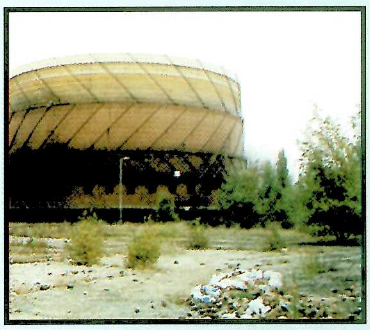
Contents

Chemical contaminants impinge on organisms in the environment at all scales, from the local to the international. Interdisciplinary research and a close relationship between scientists and policy makers is increasingly important in chemical regulation.

Pollution





Pollution research has been a major component of the Institute's work since its formation in 1973, and is the largest single contributor to the Centre for Ecology and Hydrology (CEH) Strategic Science Programme 7 on Pollution Assessment and Control. There are five themes in the Programme covering:

- radionuclides
- acidifying pollutants
- photochemical oxidants
- toxic metals
- organic pollutants.

Interest in pollution had been a strong feature of ITE's predecessor – The Nature Conservancy. Organochlorine pesticides were implicated in the deaths and reduced reproductive rates of birds in the 1950s and 1960s. Research at the ITE Monks Wood site first established DDE (a metabolite of DDT) to be the cause of egg-shell thinning in birds of prey. Other organochlorines were measured in samples from the wild and soon adverse effects were demonstrated for these also. Government reaction to proven effects in wildlife populations resulted in the first regulatory systems for chemicals in the UK.

Although input to the regulation of chemical use has been a feature of ITE research from the beginning, a more direct relationship between researchers and policy makers has developed over the last 25 years. The implementation of the Rothschild Principle, in which research is funded not from the science base but through departmental and agency budgets tied to the requirements of statute and policy, has had a major influence on pollution research in Britain. The Principle has had the advantage of making research scientists more aware of the day to day difficulties involved in changing patterns of chemicals use, and allowed them to exert considerable influence on the legislative framework. The funding pattern has made it more challenging to develop fully the theoretical framework, the dynamic models and sensitive environmental monitoring schemes that are really required.

The Pollution Assessment and Control Programme within CEH, is attempting to balance contract funded research directly linked to policy with science base-funded research to provide the theoretical background. This is one of the largest Programmes with very strong support from a broad user community.

Radionuclides

Public concern on radionuclides in the environment originated with weapons testing and, as this was reduced in scope, focussed on reprocessing plants within the UK The nuclear accident at Chernobyl extended both interest and scope of ITE's radionuclide research Initial work to measure and model the fate of radioisotopes locally to reprocessing sites has been extended to an international scale The work has succeeded in establishing exposure models for farm animals and humans which have contributed to regulatory decision making in different responsible departments of the British government Models have also been developed which have moved from prediction of deposition and fate locally to determine likely exposure for the whole of the northern hemisphere

Acidifying pollutants

Original concern over deposition of acid rain from sulphur emissions has extended over the last 25 years to other atmospheric pollutants contributing to the acidification and also to increased nutrient input to ecosystems with effects on biodiversity Public and government concern led to both national and international effort to monitor the extent and origin of acid pollutants, map the degree of environmental damage and determine control measures to reduce effects to acceptable levels The research has been cooperative across Institutes, Universities and national boundaries All aspects of the problem, from theoretical atmospheric chemistry to end effects on populations and communities of organisms, have been included in one of the most comprehensive studies of a pollution issue ever attempted ITE scientists have contributed in developing predictive models for all of these processes and in the development of the unique 'critical loads' approach to a pragmatic legislative solution

Photochemical oxidants

The newest theme within the Programme builds on the methods and models developed for other atmospheric pollutants to establish emission, formation and effects of photochemical oxidants Extensive monitoring of levels in the atmosphere has already established sources and transport data that have been used in modelling exposure of vegetation to oxidants Direct measurement of chemical reaction rates has validated initial model assumptions The work is moving towards experimental approaches to quantify effects on plant communities

Toxic metals

Early work established the wide geographical spread of metal contamination, some of which was from natural sources Effects seen in the laboratory were found to closely match those seen in field situations so that impacts on individuals and groups of birds could be predicted with a fair degree of accuracy Working with small mammals and invertebrates has shown the inter-relationships that can exist between 'essential' and 'toxic' effects of certain metals (like copper, calcium and zinc) and is now exploring the significance of toxic metals for population parameters Recent cellular and molecular approaches have identified novel biomarkers of metal exposure and effect

Organic pollutants

Although pesticides dominated early research on organic chemicals, there has been increased focus on industrial chemicals in recent years The Programme has conducted extensive monitoring of levels of organics in wildlife representing the longest running programme of its kind in the world This has been coupled with both laboratory and field studies of effects at the levels of individuals, populations and communities for vertebrates and, more recently, invertebrates and microorganisms The overall focus of the work has been to develop testing, fate modelling and hazard and risk assessment of organic chemicals in the regulatory process, both nationally and internationally One of the Programme's main achievements has been the demonstration that regulatory action, based on sound science, leads to environmental recovery

Although pesticides dominated early research on organic chemicals, there has been increased focus on industrial chemicals in recent years.

S Dobson

Plate 1. Marsh Harrier chicks (*Circus aeruginosus*) removed from areas affected by the massive spill of mire water in Spain that is currently being studied in association with RSPB

The complexity of the behaviour of chemicals in the environment and their effects on wildlife were demonstrated in a number of studies on metals such as cadmium, mercury and lead.

Environmental behaviour and ecotoxicology of xenobiotic chemicals in terrestrial wildlife

Introduction

The environmental consequences of the use of pesticides, toxic metals and industrial chemicals has been a main subject of research since the foundation of ITE. Particular groups of compounds have attracted attention because they are persistent in the environment, accumulate in living organisms and, once there, have the potential to do harm. These groups include:

- organochlorine compounds (OCs) – a very broad group including the older pesticides and a wide range of industrial chemicals (eg polychlorinated biphenyls (PCBs) and dioxins)
- inorganic and organic forms of metals
- current pesticides (eg rodenticides and wood preservatives)
- other industrial substances (such as the polyaromatic hydrocarbons (PAHs) and solvents found in contaminated land).

This work has improved understanding of the way chemicals behave in the environment and affect biological processes, such as reproduction, and has helped develop an international system of hazard and risk assessment. This article sets out some of the specific contributions the research groups have made to the debate on the wise use of chemicals.

Mechanisms of action and environmental behaviour of chemicals

At the time of the formation of ITE, Monks Wood staff had already shown wildlife in many places was seriously contaminated and affected by pollutants (Ratcliffe 1967, Sheail 1985). More basic research was then needed on the scientific principles underlying interactions between contaminating chemicals and wildlife. The practical goal was a predictive system of risk assessment that would:

- prevent harmful compounds being used or released into the environment
- minimise risks arising from [illegible] compounds that were in use

The scientific challenge this presented was very considerable. It was evident that very different information would be required to regulate chemical use in the environment than that used for assessing the safety of medicines, or chemicals used in the work place. Scientific understanding needed to be developed, not only about the sources of chemicals and their effects on a wide range of species, but also on:

- spatial and temporal dynamics of chemical movement through the environment
- biotransformations that could increase or decrease toxicity
- bioavailability
- exposure estimates for individual organisms
- dose-response relationships that allowed effects measured on individuals to be linked to population processes, community structure and ecosystem function.

The complexity of the behaviour of chemicals in the environment and their effects on wildlife were demonstrated in a number of studies on metals such as cadmium, mercury and lead. In essence, a series of studies on birds of land, estuary and sea were able to

- define spatial patterns of contamination of wildlife (Bull *et al.* 1977)
- develop an understanding of the biochemical mechanisms, physiological processes and seasonal factors that could influence metal accumulation and toxicity (Osborn 1979)
- establish the cellular mechanisms of toxicity (Nicholson *et al.* 1983).

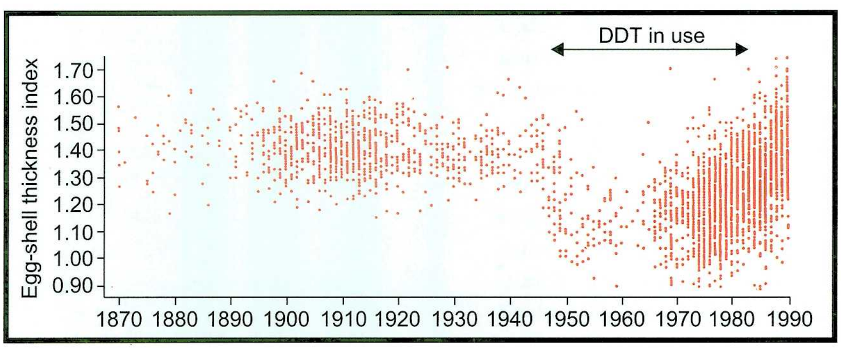


Figure 1. Egg-shell thickness in sparrowhawks showing egg-shell thinning following the introduction of DDT in agriculture and subsequent recovery following the DDT phase-out

Some of the results obtained were quite counter-intuitive. For example, seabirds from north Atlantic colonies were more contaminated than those from the North Sea, despite the latter's substantial industrial inputs.

This work, together with that of former colleagues and university collaborators on organic chemicals (eg Walker & Ronis 1989), established that:

- although fundamental cellular and biochemical mechanisms and processes of toxicity were common to many vertebrates, important environmental and ecological factors would have to be taken into account if predictive methods were to protect populations and communities of organisms and the ecosystem processes that supported them
- on the basis of a more theoretically sound framework a more coherent response could now be made to practical pollution problems, such as those arising in pollution 'hotspots' or as a result of changes in chemical use or environmental conditions.

For example, on the Mersey estuary in autumn 1979, over 5 000 birds were killed after industrial discharges of alkyl lead were flushed by a high tide from the Manchester Ship Canal into the open estuary. Establishing the cause of the bird deaths, and finding a resolution of the problem required a combination of field and experimental observations (Bull *et al.* 1983, Osborn *et al.* 1983). A follow-up monitoring programme showed the bird deaths stopped once levels of alkyl lead in birds dropped below a critical value determined from field and experimental data. In another example, deaths of mute swans (*Cygnus olor*) from lead poisoning (Simpson *et al.* 1979) were traced to consumption of lead fishing weights. Eventually, lead was replaced by some more environmentally acceptable alternatives. Such studies confirmed that particular pollution problems could be resolved if:

- close similarities could be demonstrated between laboratory findings and those from the field
- predictive models could be constructed from well defined exposure-effect relationships and knowledge of chemical behaviour in the environment.

The next challenge was to determine the full ecological significance of wildlife's exposure to chemicals.

The ecological significance of effects

From the 1970s on, although OCs were being found in a wide range of species all over the world, it was uncertain whether they were having ecologically significant effects on wildlife populations. For example, it was possible to demonstrate in the laboratory that high levels of dietary DDE led to susceptible species of birds laying thin-shelled eggs. It was, however, another matter to establish anything more than a correlative relationship in the field where there was wide variation in both egg-shell thickness and the levels of DDE in birds. A complicating factor was the mixture of toxic chemicals found in wild birds. This made it harder to extrapolate between laboratory and field, because of potential interactive effects.

In a bench mark study, Newton and colleagues (Newton 1986) compared the breeding biology of the sparrowhawk (*Accipiter nisus*) in different parts of the UK with the concentrations of OCs found in birds' eggs. They concluded distinct influences of OCs on sparrowhawk population biology could be discerned. First, HEOD killed individual adult birds, greatly affecting population numbers. Second DDE had a role in reducing hatching success (most probably through egg-shell thinning) (Figure 1). Third, it seemed PCB residues (although known to affect certain hormone systems; see Jefferies 1975) had no influence on breeding that could be separated from the effects of DDE. Studies on seabirds provided no evidence that survival and breeding success were affected by acute exposure to PCBs sufficient to raise levels in tissues well above background concentrations (Harris & Osborn 1981), although limited evidence for a sublethal response was later obtained.

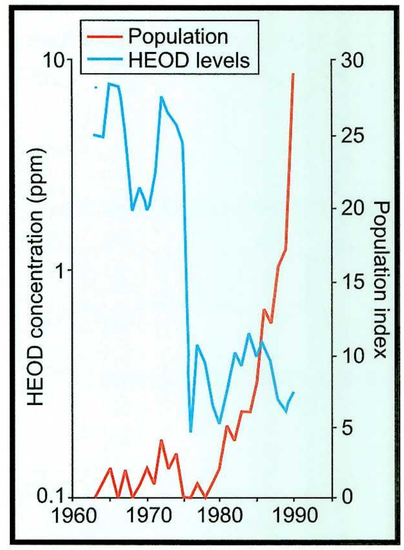


Figure 2. Recovery of sparrowhawk populations in eastern Britain and the decline in HEOD levels in sparrowhawk livers

Monitoring contamination and predatory bird populations after restrictions on OC manufacture

Since the mid-1970s, regulatory action has been taken to phase out the use of these chemicals. OCs had become very widespread in the environment and had a wide range of effects on wildlife. It has been possible to show the benefits of these actions through various studies.

It was a far sighted decision to set up the Predatory Birds Monitoring Scheme at ITE Monks Wood in the early 1960s to track the levels of OC residues in a wide range of predatory birds and selected seabirds, and a brave decision to keep the scheme running during periods where long-term, large-scale studies of environmental processes were not fashionable. As a result of the continuous programme of work (Newton *et al.* 1993), it is now clear that, following increasing restrictions on the use of OCs, levels of the OCs with the shorter environmental persistence have declined (Figure 2). Amongst this group are DDE and HEOD, the chemicals most likely to have caused population decline in predatory birds.

It is encouraging that birds of prey like the sparrowhawk have returned to breed in areas where they had been all but locally extinct, once pollutant levels in the population dropped below a

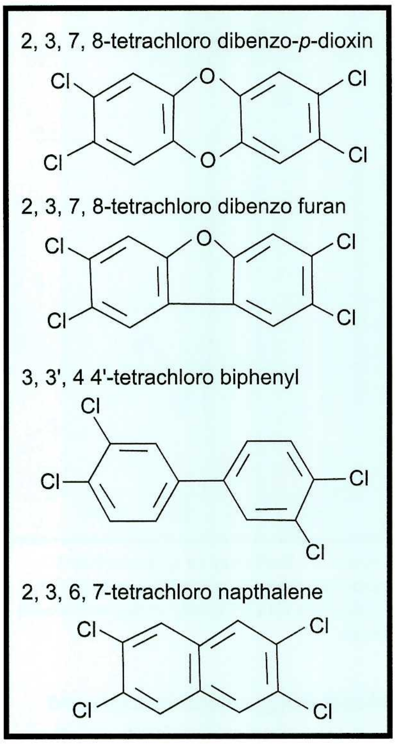


Figure 3. Structure of Dioxin-like compounds showing the structural similarity of some PCB and PCN congeners

It is encouraging that birds of prey have returned to breed in areas where they had been extinct, once pollutants dropped below a critical level.

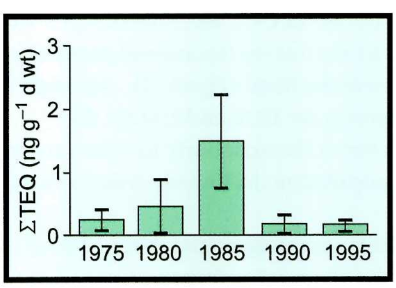


Figure 4. Trends in the (dioxins) Toxic Equivalents (TEQ's) in kestrel livers showing a maximum in the mid-1980s and a subsequent decline

threshold or 'critical level' (Newton 1988). In particular, there has been a strong recovery in eastern England where pesticides like DDT, and dieldrin were used extensively.

The most difficult findings to interpret are those for the PCBs. In some species the total amount of PCB does not appear to have decreased significantly over the entire monitoring period, despite the fact that voluntary restrictions on use and manufacture in the UK began as long ago as the 1970s. Detailed studies, in collaboration with colleagues at Lancaster University, suggests the decline in levels in seabird eggs is most marked for the more volatile PCBs. Preliminary work with terrestrial species suggests the pattern is more complex.

This long-term, geographically widespread monitoring programme continues to prove its value. In recent years samples from its tissue and egg store have been used to examine the occurrence of materials other than OCs in predatory birds, such as the second generation rodenticides. This work has in turn inspired parallel studies on rodenticides in predatory mammals (Newton *et al.* in press).

Much remains to be done to improve large-scale and long-term environmental monitoring. It will surprise some that there are still many unidentified substances present in predatory birds. The significance of these compounds for species of conservation interest, and the environment as a whole, remains unknown.

Identifying hazards and reducing risks

Since the late 1970s there has been an increasing focus on:

- preventing potentially harmful chemicals coming into use
- research into the environmental risks associated with the ways chemicals are used in everyday practice (see *Rio Declaration on Environment & Development, 1992 & Agenda 21, Chapter 19* for the importance attached to this type of study by governments worldwide).

Much of the Institute's work in this area has taken the form of providing expert advice to UK government committees or international bodies such as the International Programme on Chemical Safety (IPCS) of the World Health Organisation (WHO). ITE staff have written or taken a significant part in the preparation of over 100 of the IPCS/ WHO/International Labour Organisation (ILO) Environmental Health Criteria (Dobson 1992, Dobson & Cabridenc 1990, Dobson & van Esch 1993). They have also been instrumental in increasing the importance attached to effects on ecosystems in these documents (originally they were concerned largely with matters related to environmental aspects of human health). The work involves making expert judgements from a synthesis of findings in the open literature with data from industry. Originally much of the work with international bodies was concerned with establishing the hazards presented by chemicals. However, the emphasis is moving increasingly towards considering how risk assessments can best be produced. Two major challenges in this area are to improve:

- the use of real environmental data on chemical concentrations so as to estimate an organism's exposure more reliably
- the scientific interpretation of standard laboratory toxicity tests so that extrapolation of lab findings to the field takes more account of real world conditions.

The breadth of world-wide work on various aspects of risk assessment has recently been reviewed as part of a series of publications on ecological and environmental toxicology being edited by ITE staff and national and international colleagues (Douben 1998).

Other research of practical use has involved original scientific research of a more classical nature. Examples of these types of studies are given below. They have all deepened the knowledge of relevant scientific principles.

Spray Drift

One of the most widespread ways in which known toxic chemicals enter the environment is through the application of pesticides to agricultural land through the use of sprays. This procedure happens all over the world, but the significance for non-target animals and plants was virtually unquantified until the 1980s. Thus there was no basis on which to draw up guidelines representing best environmental practice. This in turn led staff at ITE Monks Wood to conduct trials, during the past ten years, with both plants and invertebrates. These trials established the considerable distances (>100 m) over which invertebrates might remain susceptible to drift from either aerial or ground based sprays, and the lesser – but operationally just as important – distances over which drift might affect plants or land of conservation importance (Davis & Williams 1990). This work helped pesticide regulators set 'buffer zone' distances to protect valuable habitats from damage resulting from spay drift. Also, some spraying practices were changed. The results helped to raise the profile of the possible indirect effect of pesticides, as some of the more dramatic results showed that about 80% of certain non-target invertebrates could be killed by drift, thus reducing food supplies for other species.

Mixtures of chemicals

Pesticides are often used in combination, and wildlife often contain mixtures of pesticides and other chemicals. The fact that the regulatory safety systems only consider one chemical at a time prompted a study of the possible interactions of two different classes of pesticides commonly used in agriculture, organophosphorous compounds (OPs) and fungicides. These studies, with Reading University, were developed from the first principles of pesticide metabolism. They showed that dramatic increases in the effects of OPs occurred following prior-exposure of birds to a certain class of fungicide (Johnston *et al.* 1994). Although evidence of direct toxic effects of environmental significance arising from the use of mixtures are limited at present, the work showed regulators and industry that such interactions were far from hypothetical.

Industrial accidents involving chemical release

More recently ITE staff have carried out a comprehensive study and review of the environmental significance of industrial accidents. Studies of dioxins have proved to be particularly interesting. Soon after the formation of ITE, it became clear that groups of chemicals attracting the OC "sobriquet", other than pesticides and PCBs, could be released into the environment during regulated incineration and recycling of a wide range of halogenated compounds (PCBs, DDT, PVC etc). These substances were the halogenated dioxins and dibenzofurans that attracted much attention because of relatively high toxicity at low environmental levels. Dioxins and furans that have 2,3,7,8-chlorine substitution patterns (Figure 3) bind to the Ah receptor of animals and can cause a wide range of toxicological symptoms such as hepatic damage and reproductive effects. These symptoms vary greatly between species. The emissions of dioxins and furans from industrial processes are tightly regulated and the Environment Agency has set targets for substantial emission reductions. However, known sources of dioxins and furans only represent a proportion of total residues found in the UK environment. ITE's work on accidents has identified large-scale accidental fires, involving plastics and PVC, as an important unregulated source of these chemicals (Meharg & Osborn 1995). Recent work has shown that dioxins and furans released from accidents can accumulate in small mammals from contaminated areas.

Other classes of environmental pollutants have the same toxicological modes of action as 2,3,7,8-substituted dioxins, namely the 'dioxin-like' PCBs and polychlorinated napthalenes (PCNs), the forerunners of PCBs (Figure 3). In fact, the principal environmental source of dioxin-like compounds are PCBs, not the dioxins and furans themselves. Recent work in ITE has enumerated 2,3,7,8-dioxin toxic equivalents (TEQs) for PCBs in historic samples of kestrel (*Falco tinnunculus*) tissues. These initial results indicate there was a sharp rise in TEQs measured in kestrel livers in the mid-1980s; but it had rapidly declined by 1990 (Figure 4). Interestingly there was a lag in the peak and decline in PCBs in bird tissues compared to abiotic media (Harner *et al.* 1995), perhaps reflecting the longevity of birds of prey (OCs are accumulated over the bird's lifetime), or the slower decline along the food-chain.

PCB movements through catchments

Much uncertainty remains over the way PCBs are behaving at various scales in the environment. In general, it appears that PCBs are in global decline. Yet studies in industrial regions in Britain conducted by ITE (as part of NERC's

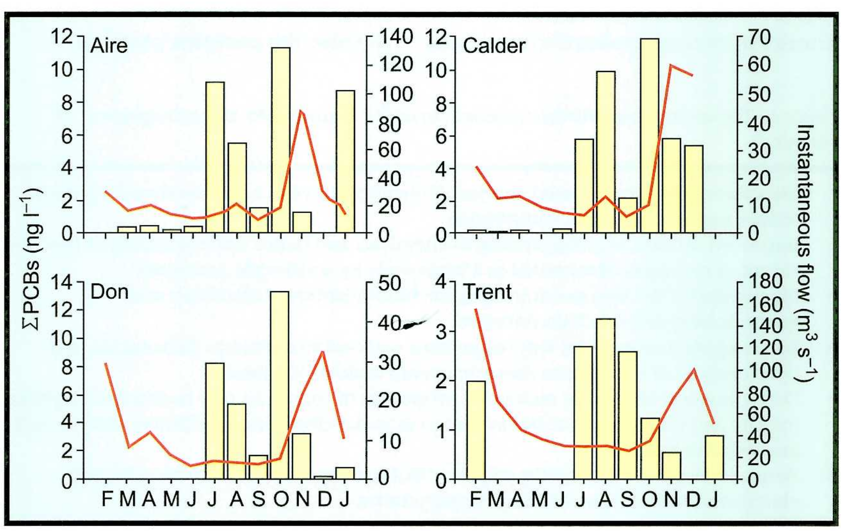


Figure 5. Spatial and Temporal Trends in the total PCB Concentrations in rivers of the Humber Catchment. The solid red line is the river flow rate

Land Ocean Interaction Study (LOIS) programme) have recently shown that PCB reserves in industrial catchments are considerable and that mobility is highly regulated by seasonal factors such as rainfall and water flow PCB data for four rivers in the Humber catchment showed that PCB concentrations increased in open waters during the summer and autumnal months when water levels were low (Figure 5) There was also significant variation between years, indicating that PCB regulation and release by urban catchments is not constant and may not be in general decline – findings of some significance for the UK's commitments to cleaning up discharges of these substances to the North Sea The uncertainty is not restricted to PCBs In the same study, marked differences were found between the ways in which different isomers of hexachlorocyclohexane behaved A better understanding of such differences could be of considerable significance since one of the isomers is a known carcinogen and the other a pesticide (lindane) that was in quite common use until recently

Research priorities

Since its inception, the work at ITE Monks Wood has been done in line with the theoretical framework emerging from the developing science of ecotoxicology (or environmental pharmacology) Thus, Jefferies (1975) in seeking theoretical justification for his ideas that the effects of some OCs might be mediated by impacts on hormonal systems, pointed to structural similarities between xenobiotic chemicals and certain hormones, and hormone agonists and antagonists Later Moriarty (1983) argued for the adoption of dynamic compartmental models by those interested in properly assessing the movement and effects of chemicals in ecosystems, and earlier, Moore (1967) had set out the basic principles of scientifically sound environmental monitoring and surveillance

ITE has made full use of the challenges and opportunities of the Rothschild Principle in pollution research by

- working closely with departments and agencies in areas where novel research can have a high impact on everyday practice whilst still making significant scientific progress
- making best use of the funding opportunities presented by the increased access Natural Environment Research council (NERC) has provided centrally to both non-thematic funds and by the advent of new Thematic programmes (such as LOIS, Environmental Diagnostics and the Urban Environment Programme (URGENT))

The goal now is to make the manufacture, use and disposal of chemicals more sustainable Increasingly, interdisciplinary research will be required to make good progress with our scientific aims and to solve the complex practical problems involved in the wise use of chemicals Thus, much research in ITE is done in collaboration with other Institutes and Universities (both in the UK and in the EU), resulting in significant advances in knowledge of the environmental fate and behaviour of several major classes of pollutants The wide range of relevant issues being addressed by ITE (Table 1), and the scientific quality of the work, attracts funding by

- government (eg DETR, MAFF, EA, JNCC)
- NERC Thematic programmes, NERC underpinning science projects (eg through the Centre for Ecology and Hydrology (CEH) Integrating fund)
- various environmental charities (such as the European Environmental Research Organisation and the Vincent Wildlife Trust)
- the European Union

In this way, new research initiatives have expanded work on the lower end of food chains, particularly to the invertebrates and microbial organisms found in soil and soil-plant systems This work is aiming to develop tools such as

- bacterial biosensors for assessing the bioavailabilty of chemicals in soils (as an aid to assessing contaminated land problems and the potential for remediation) (Boyd *et al* 1997)
- biomarkers of exposure and effect in animals that may enable more biologically relevant risks to be calculated and early warnings of ecologically important effects (Svendsen & Weeks 1997)

Other new initiatives are interacting with more traditional approaches in ITE, to provide a better understanding of the flux of potentially toxic chemicals through food chains At the molecular and sub-molecular level, ITE scientists are currently combining their expertise together with that of university groups, to research the predictive power of classical (Meharg *et al* 1998) and more modern molecular approaches to quantitative structure activity relationships (Warne *et al* in press)

Table 1 Topics requiring further research in order to underpin the management of chemicals

- Identification of unregulated sources of chemicals, as these will confound efforts to reduce exposure to these compounds
- Improved models of global cycling of chemicals and better understanding of how the extent of cycling is determined at a large scale by small scale processes
- Elucidation of the factors controlling the bioavailability of chemicals and quantification of food chain transfers
- Better appreciation of the ways organisms respond to mixtures of chemicals, and development of methods to estimate overall toxicity of mixtures
- Determination of the role molecular properties of chemicals play in determining both toxicity and environmental behaviour so as to develop better predictive models well grounded in theory
- Better estimates of the toxicity of planar PCBs, dioxins and dibenzofurans, and elucidation of their ecotoxicological importance
- Explanation of the wide variation that exists in the propensity to accumulate and respond to chemicals

The biological interactions and transformations of pollutants can be studied with much greater insight due to key technological developments, such as

- the accessibility of high powered computers (to facilitate molecular-modelling of complex polyaromatic compounds and flux-modelling of environmental processes containing large uncertainties)
- the increasingly routine use of molecular techniques (including antibody fragment technology)
- the ever increasing sophistication of analytical techniques (LC-MS, NMR, HR-MS, EC-MS)

Progressively these technologies will be combined with developments in experimental methodologies that are making research on the impacts of chemicals more ecologically relevant For example, the use of mesocosms is enabling populations to be studied in more controlled ways Behavioural studies are beginning to provide insights into the ways animals react on exposure to chemicals (DellOmo & Shore 1996), and modern statistical approaches hold much potential both for the study of changes in community structure and the analysis of temporal and spatial trends in environmental contamination

It is an ongoing challenge to use these techniques to ensure that the environmental problems caused by chemicals in the environment do not happen in the future with new generations of compounds

D Osborn and A A Meharg

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Plate 1. Upland sheep in the area of Cumbria where movement and slaughter are still restricted after the Chernobyl accident

Studies on the behaviour of Chernobyl fallout in GB

In the spring of 1986, fallout from the Chernobyl accident was deposited in varying amounts over western Europe, including the UK. The available models predicted the behaviour of the fallout in intensive agricultural areas reasonably well. However, it soon became evident that the models had a limited geographical application as they failed to reliably predict the behaviour of a major contaminant, radiocaesium, in unimproved upland ecosystems. In some of these areas radiocaesium activity concentrations in sheep meat and some game animals exceeded intervention limits and the causal factors were not allowed for in the models. Thus, we needed to improve understanding of the behaviour of radiocaesium in such ecosystems and to adapt predictive models accordingly. ITE has been one of the major European research groups addressing these issues since 1986. The major goal of these studies has been to provide practical guidance to control the different exposure rates to people living in contaminated areas and to the general population.

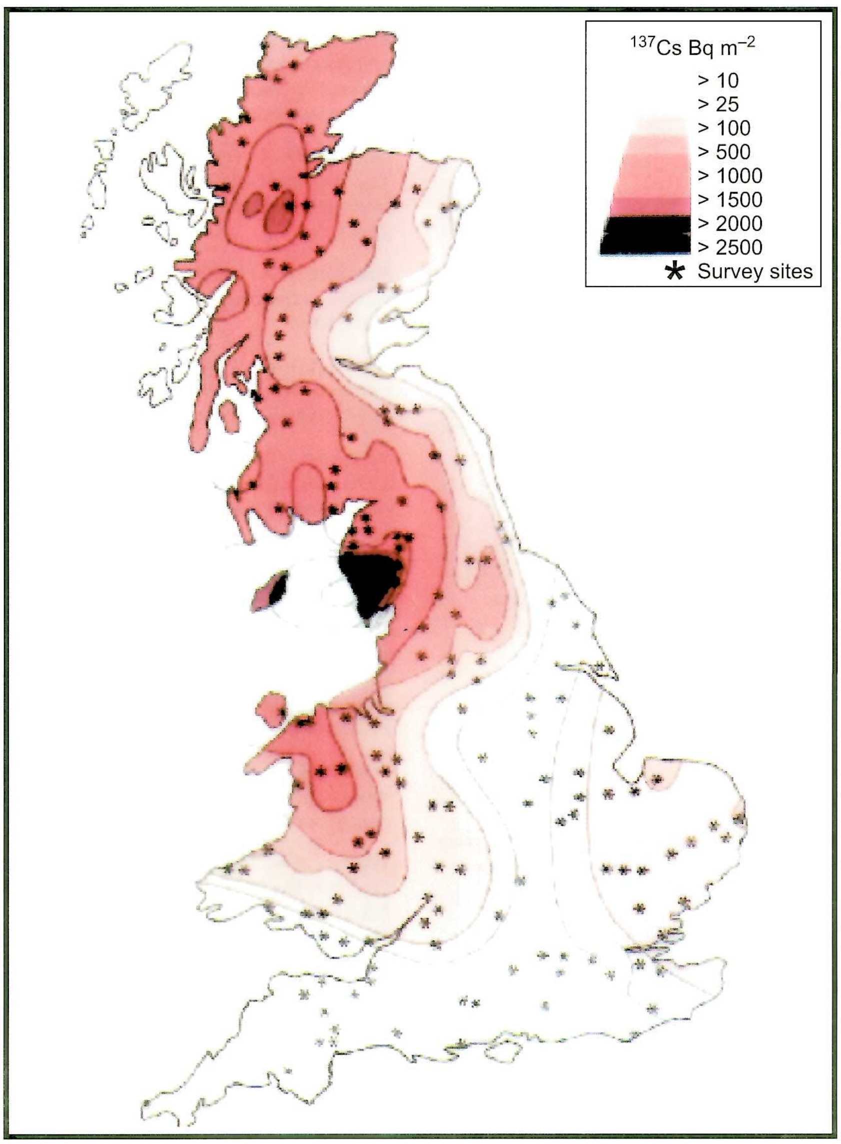

Figure 1. Caesium deposition on vegetation (Bq m^{-2}) May 1986

Fallout in the UK from the Chernobyl accident was greatest where the passage of the cloud coincided with heavy rainfall in north Wales, Cumbria, parts of Scotland and northern Ireland. CS-137 activity concentrations in vegetation at one site in upland west Cumbria increased from 40 to 10 000 Bq kg^{-1} dry weight. ITE was a major source of information on Chernobyl contamination and published the first map of Chernobyl fallout in GB (Figure 1, Allen 1986).

Transfer from soil to plants

In the first few weeks after fallout had been deposited, the degree of interception by plants and subsequent weathering were the most important factors determining the rate of transfer of radionuclides to biota. After this phase, when the fallout was largely present in the soil, the rate of fixation and uptake from the soil became more important in determining environmental mobility.

Behaviour of radiocaesium in soil

The soil type in contaminated areas is a fundamental factor in determining contamination levels in both plant and animal food products. The uptake of radiocaesium from soils in unimproved, semi-natural ecosystems had not been extensively studied before the Chernobyl accident – possibly because the fallout from atmospheric weapons testing was deposited continuously onto plant surfaces over a long period, thereby masking the importance of root uptake. Nevertheless, the high uptake of ^{137}Cs from soil with a high organic matter content had been noted (Barber 1964).

Research since the Chernobyl accident has shown that small numbers of highly selective frayed-edge sites of clay minerals dominate the sorption of radiocaesium onto soil particles. Soils containing a large proportion of layered clays retain most radiocaesium on the solid, leaving only a small amount in the soil solution, thus reducing the uptake by plants. Conversely, soils lacking these minerals allow high levels of radiocaesium in soil solution, readily available for plant uptake. As time progresses, caesium on the frayed-edge sites can migrate between clay lattice sheets and replace potassium, thereby becoming effectively immobilised in the soil. The high bioavailability of radiocaesium in upland soils, combined with its long residence time in the organic horizons, is associated with low amounts of clay minerals in organic soils and the high, but reversible, sorbing capacity of organic matter. The low capacity of many of the soil types characteristic of semi-natural ecosystems to immobilise radiocaesium, and retain the radiocaesium in the upper soil horizons, proved to be the main factor responsible for the continuing high activity concentrations in plants and animals. Radiocaesium levels in upland vegetation have decreased (Figure 2) since the deposition of Chernobyl fallout due to both physical decay (radioactive decay which varies which each isotope: ^{134}Cs – 2 years: ^{137}Cs – 30 years) and gradual fixation in soil. Although ^{137}Cs activity concentrations at one of the sites monitored in Cumbria is close to pre-Chernobyl levels (c. 40 Bq kg^{-1}), the power functions shown in Figure 2 predict that current ecological half-lives (the time taken for the activity concentration in vegetation to decline by a half) are in the order of 12–17 years.

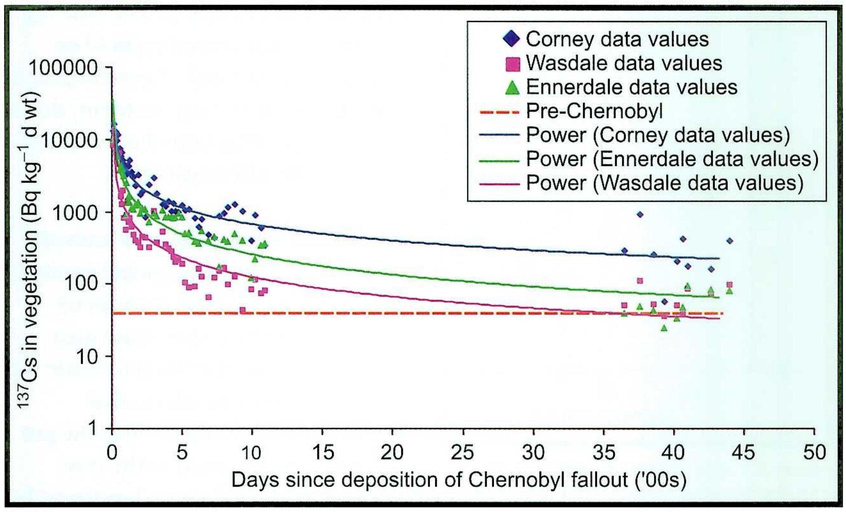

Figure 2. Changes with time in ^{137}Cs activity concentrations in vegetation at three upland Cumbrian sites with fitted power functions

Uptake by plants and macrofungi

The ability of different plants to absorb radiocaesium from the soil varies. An example of a plant with high uptake rates is the heather (*Calluna vulgaris*) which becomes much more highly contaminated with radiocaesium than other herbaceous plants. In upland Cumbrian pastures, ^{137}Cs activity concentrations in graminaceous vegetation varied by over two orders of magnitude, whereas ^{137}Cs deposition was 5 k Bq m^{-2} to 40 k Bq m^{-2}. The factors responsible for inter-species variation, such as rhizosphere interactions, effect of mycorrhizas and rooting depth, have yet to be fully described and require further research.

The rate of transfer of radiocaesium to mushrooms is also high, but varies considerably between and within species. A survey by ITE of radiocaesium contamination of different edible species within GB in the last few years has detected the highest values in forest species. Radiocaesium contamination of fruit bodies is dependent on ecological strategy, with mycorrhizal species being more contaminated than saprophytic or parasitic species (Figure 3, Beresford *et al.* in press). A survey of wild mushroom consumers showed that current radiation doses were not high, since the most commonly consumed species were of the least

The high bioavailability of radiocaesium in upland soils, combined with its long residence time in the organic horizons, is associated with low amounts of clay minerals in organic soils and the high, but reversible, sorbing capacity of organic matter.

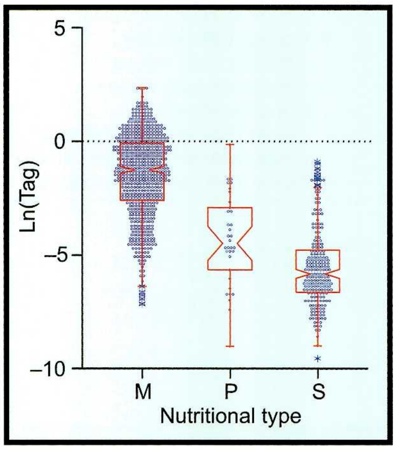

Figure 3. Comparison of variability in the transfer of radiocaesium (quantified as natural log of the aggregated transfer coefficient (Tag), defined as the activity concentration in mushrooms (Bq kg^{-1} dw) divided by deposition (Bq m^{-2})) to edible fungi of different nutritional types (M = mycorrizal; P = parasitic; S = saprotrophic) (Beresford *et al.* in press). In the box whisker plot the notch denotes the median value and the boxes encompass 50% of the observed values

A number of factors contributed to the variability in ^{137}Cs activity concentrations within sheep flocks, but the largest contributor is individual grazing behaviour.

contaminated saprophytic type (eg *Agaricus* spp. including field or horse mushrooms). Nevertheless, in the event of a future accident, doses to this special group of consumers will need to be considered.

Transfer from plants to animals

Studies after the Chernobyl accident have shown that the transfer of radionuclides to sheep and goat products is greater than to cattle. In addition, ITE has shown that radiocaesium absorption in the gut of sheep (measured as the true absorption coefficient developed by the MaCaulay Land Use Research Institute (MLURI) and ITE (Mayes *et al.* 1996) varies over 50 fold, depending on the chemical form. The absorption of radiocaesium within plant tissues is higher than that of radiocaesium in soils or absorbed to sediments. Rapid *in-vitro* prediction techniques have now been developed to quantify absorption after an accident. Using a simple extraction technique, the absorption of different forms of radiocaesium can be predicted using the relationship shown in Figure 4.

Transfer to game animals is also high compared with agricultural animals, partly due to high transfer from the diet but also due to diet selection of highly contaminated plants and fungi by the animal. In particular, the consumption of highly contaminated heather by red grouse (*Lagopus lagopus*) led to high levels of radiocaesium in grouse meat in parts of Scotland.

Sheep restrictions

There are continuing restrictions on the movement and slaughter of sheep in parts of Scotland, north Wales and Cumbria due to persistently high radiocaesium activity concentrations in a few sheep within restricted flocks (Beresford *et al.* 1996) (Plate 1). This is due to:

- high initial deposition
- the presence of organic soils
- high uptake rates by certain vegetation species
- high transfer rates of radiocaesium to sheep
- long ecological half lives.

Restrictions are imposed if any individual sheep in a flock exceeds the 1 000 Bq kg^{-1} (fresh weight) limit at which meat cannot enter the foodchain.

There is considerable variation in the ^{137}Cs activity concentrations of individual sheep within flocks and relatively few sheep in each flock are now above the intervention limit. ITE has investigated the reasons for individual variation in three Cumbrian flocks. Repeated *in-vitro* monitoring indicated that the same sheep tend to have the highest ^{137}Cs activity concentration. Furthermore, the most contaminated lambs within a flock in the subsequent year are likely to be born to the same ewes. Therefore, it is likely to be the same few sheep on a given farm, which necessitate the continuation of restrictions on many affected holdings in the short-term.

A number of factors contributed to the variability in ^{137}Cs activity concentrations within sheep flocks. The largest contributor appears to be grazing behaviour whereby sheep within a flock graze vegetation containing different levels of ^{137}Cs. Differences in daily radiocaesium intakes contributed 60% of the observed variability in radiocaesium levels in the muscle of ewes. Breed was shown to be a parameter resulting in variability within sheep flocks. This was, however, related to differences in grazing behaviour between sheep of different breeds. At the various farms, additional effects of both management and weather were also observed. Under controlled conditions, the transfer of radiocaesium to the muscle of ewes varied by a factor of three. This was explained by differences in feed intake and changes in live-weight during the experiment. The level of radiocaesium in muscle was also related to the degree of absorption in the gut. Using novel methods of estimating radiocaesium intake in grazing animals (slow release rumen dwelling Cr_2O_7 faecal marker) 97% of the variability in the radiocaesium levels in ewes was explained by differences in radiocaesium intake and the transfer of radiocaesium from diet to the muscle.

Overall, it was not possible to make generalised recommendations to limit the number of sheep with high radiocaesium levels on farms within the restricted area of west Cumbria, as there is considerable variability in the contributing factors between different flocks.

Ecosystem variation

It is now clear that the environmental behaviour of radionuclides varies in different types of ecosystems. Agricultural ecosystems are important, in terms of radiation dose, in the early stages of most accidents for the majority of radionuclides as they provide the main food for most of the exposed population. One of the important agricultural products, which is readily contaminated by radioiodine, radiostrontium and radiocaesium, is milk. However, for many radionuclides the contamination of agricultural foodstuffs declines rapidly, especially if countermeasures are effectively applied. In contrast, some foodstuffs from semi-natural ecosystems, such as uplands and forests, can be important contributors to ingested radiocaesium dose (especially for people who harvest from these ecosystems such as hunters and mushroom foragers), because of high transfer rates from unimproved soil with high organic matter contents and long ecological half-lives (Howard *et al.* 1991).

The long ecological half-lives in many semi-natural products compared with agricultural products means that the comparative importance of semi-natural products as sources of radiocaesium in the diet increases with time. For instance, no observed decrease has occurred in some species of mushroom, which means that for some species we expect the ecological half-life to be equivalent to the physical half-life. To acquire suitable data for estimation of long-term trends, measurements of biota will need to be continued for many more years.

Countermeasures

The use of many established countermeasure techniques for the areas where restrictions on the movement and slaughter of sheep are imposed is difficult due to the nature of animal management in the affected areas. ITE, in collaboration with MLURI and Norwegian colleagues, has developed and tested a bolus containing the radiocaesium binder ammonium hexacyanoferrate (AFCF) designed to be suitable for administration to small lambs of hill-sheep breeds used in the UK. A bolus 14 x 50 mm in size, containing 20% AFCF, could be safely administered to lambs of 10 kg. Administration of three boli per lamb reduced the ^{137}Cs activity concentration in muscle by 50% between 3 and 8 weeks after dosing. We concluded that the

It is now clear that the environmental behaviour of radionuclides varies in different types of ecosystems, and foodstuffs from semi-natural habitats can contribute to the long-term dosage.

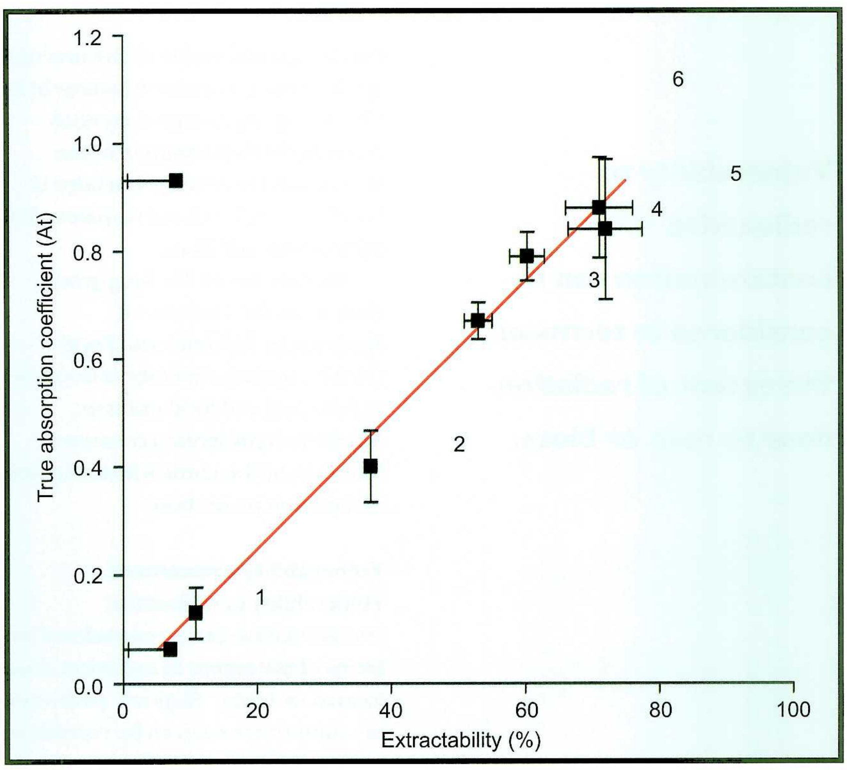

Figure 4. The relationship between *in-vitro* extractability and the true absorption (At) of radiocaesium from various dietary sources as presented in Singleton *et al.* (1992). (1) - Ravenglass silt (2) - CsCl absorbed to silica (3) - *Calluna vulgaris* (4) - CsCl absorbed on to bentonite (5) CsCl absorbed onto filter papers (5) - Upland grassy vegetation

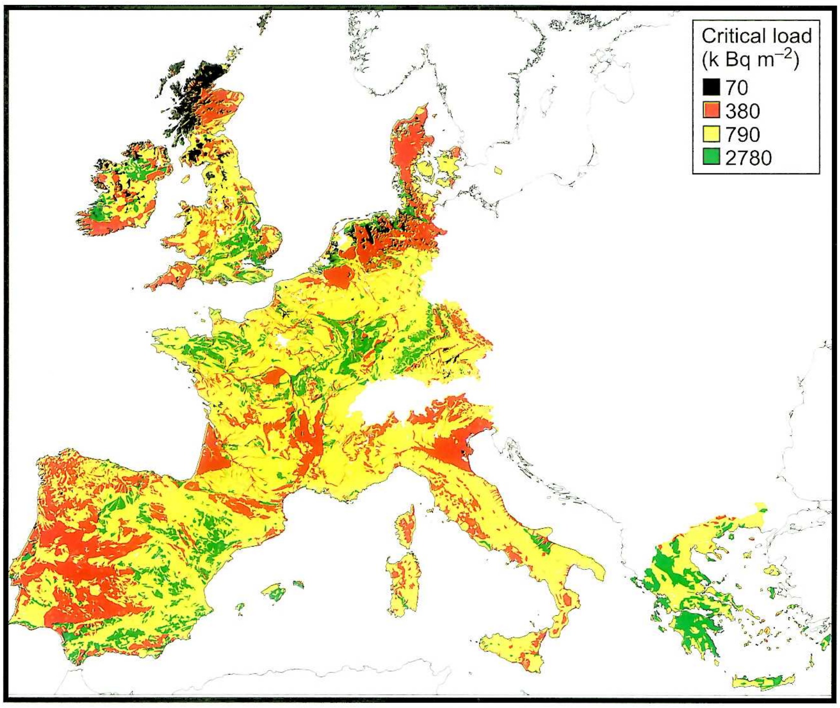

Figure 5. Estimated critical loads for cow milk in the mid-long term in western Europe. The critical load value is the estimated radiocaesium deposition level above which we would predict that radiocaesium activity concentrations in milk would exceed the intervention limit. The values were obtained by sub-dividing the soil CORINE categories into "clay", "sand", "loam" and "peat" on the basis of soil texture

Vulnerability to radioactive contamination can be considered in terms of the extent of radiation dose to man or biota.

AFCF bolus could be used effectively to reduce the radiocaesium activity concentration in lambs within hill and upland areas of the UK.

Further consideration of the practical application of countermeasures in the UK is ongoing within a recently convened sub-committee of the Working Party of Radionuclides in Food, in which ITE participates. This Agricultural and Food Countermeasures Working group, chaired by the Ministry of Agriculture, Fisheries and Food (MAFF), includes members from the agricultural and food industry, members representing consumer interests, and scientists from the field of radiation protection.

Vulnerability assessment

Vulnerability to radioactive contamination can be considered in terms of the extent of radiation dose to man or biota. Regions, pathways or communities can all be considered to be vulnerable to radioactive contamination if they give rise to, or receive, relatively high radiation doses. Thus, vulnerable areas or communities can be defined using different perspectives. Some examples include:

- geographical factors such as proximity to potential sources
- high annual precipitation rates
- presence of organic soil
- utilisation of semi-natural ecosystems such as upland pasture and forests.

In addition, anthropogenic factors such as the use of certain management practices (eg high milk production rate or dominance of 'small' animals such as sheep) and the presence of special groups with high consumption rates of contaminated products, (such as mushroom foragers or game consumers) are also important variables.

The focus of recent research on vulnerability has been on the production of dynamic models, which have spatially variable input parameters, with initial attention focused on cow milk as a major potential source of radiocaesium after a nuclear accident. For any given area, the model predicts the amount of radiocaesium that would need to be deposited (the critical load) to give rise to radiocaesium activity concentrations in cow milk which would exceed intervention limits for the period from 2–3 months after an accident. Recently, ITE has produced the first critical load map for radiocaesium contamination of cow milk (Figure 5, Wright *et al.* in press).

Studies on vulnerability can contribute to emergency response plans. Prior studies of vulnerability and its spatial and temporal variation can identify areas, and types of foods, which would be contaminated above intervention limits. Identification of vulnerable areas, combined with contamination maps, can guide monitoring and implementation of countermeasures.

Radioecological issues for the future

A prime objective of radioecology is to understand how the interaction between radionuclides and the environment affects radiation dose to both man and biota There has been a considerable advance in our understanding of radionuclide behaviour since the Chernobyl accident, which has clearly demonstrated that good science allows well informed decisions Much basic mechanistic information has been acquired on how radionuclides interact with the environment allowing a better appreciation of the environmental consequences of the accident and the resulting radiation dose to the population

The focus of attention before the Chernobyl accident was on the agricultural farm system and estimation of collective doses, and used traditional radioecological approaches such as transfer ratios More recently, the contribution of community-based private farming, semi-natural and aquatic ecosystems to radiation dose has been given more attention In addition, possible ecological side effects arising from soil amelioration are now being considered including possible detrimental effects on water quality and ecologically sensitive ecosystems such as peat bogs

One major goal for the future is to devise methods of applying the mechanistic information that ITE now has to develop process-based radioecological models, which complement generic radiation protection models These dynamic models must be able to integrate spatially varying information on factors which substantially alter either collective or individual doses Furthermore, they must be able to incorporate the contribution of semi-natural ecosystems Such factors are important components of current studies in the heavily contaminated areas of the former Soviet Union, where an integration of radioecological knowledge with social and psychological expertise is helping to develop approaches whereby communities can be encouraged to take the initiative in reducing their own individual doses

B J Howard

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Future work will focus on enhancing the understanding of processes and factors affecting radionuclide mobility. These are identified as important in dynamic models which integrate spatially varying information.

Plate 1. Trace gas flux measurements in Norfolk

A programme of research into the 'acid rain' problem began at ITE Edinburgh and Banchory research stations in 1975.

The pollution climate of the UK, 1975–1998

'Acid rain' and long-range transport of pollutants

In the early years of ITE (the mid-1970s) the air pollution climate of the UK was dominated by sulphur dioxide both in major cities and rural areas. The country was among the largest emitters in Europe with annual emissions of six million tonnes of SO_2. The rainfall chemistry of northern Europe, monitored by Scandinavian scientists showed a broad region in which rain had become more acidic during the 1960s. Monitoring of poorly buffered freshwaters in southern Scandinavia showed acidified lakes and streams, reduced or absent fish populations and evidence of links between the water chemistry and the changes in fish populations. There was also concern that the acid deposition was reducing the health or productivity of forests.

The concerns of ecologists and geochemists received popular support throughout Scandinavia because long-range transport of acidity and sulphur from the major industrial countries, notably the UK and Germany, was suspected as the primary cause of acid deposition in Sweden and Norway. The processes regulating the atmospheric transformations of sulphur, the rates of dry and wet deposition and the source-receptor relationships were largely unknown during these early years and the UK public had not taken any interest in the problem until the 1980s.

A programme of research into the 'acid rain' problem began at ITE Edinburgh and Banchory research stations in 1975. A network of precipitation collectors throughout northern Britain was established to quantify wet deposition inputs in some of the most acid sensitive ecosystems of the UK. The processes controlling dry deposition of SO_2 and other pollutants and the interaction between forest canopies and the chemistry of precipitation were studied at Devilla Forest in central Scotland.

The rainfall chemistry studies at ITE published initially in *Nature* (Fowler *et al.* 1982) attracted considerable scientific and public interest. They showed that the amounts of acidity deposited in many acid sensitive areas of northern Britain were similar to those in Norway. The research activity expanded rapidly and pioneering work on the relationship between freshwater chemistry and the phytoplankton species composition of freshwater lakes in the UK, allowed the trends in acidification of lakes to be reconstructed from diatom records in lake sediments, (Batterbee *et al.* 1984).

Rapid developments in understanding the atmospheric aspects of the science during the early 1980s were incorporated within long-range transport models of sulphur (and nitrogen) in Europe (Figure 1). The models constructed 'blame matrices' for the exchange of pollutants between countries and formed the basis for the international political interaction necessary to develop control measures. The early agreement (the 30% Club) identified a fixed and entirely arbitrary reduction in sulphur emissions. The UK did not sign this agreement, although it met the target, achieving the specified reductions for other reasons. There were at that time no quantitative methods to provide a measure of ecosystem or freshwater chemistry response to the agreed changes in emissions.

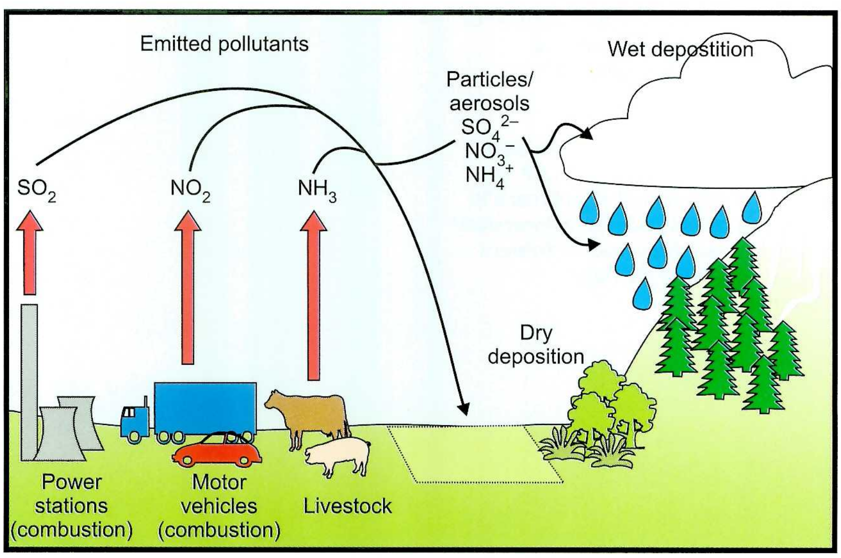

Figure 1. Emission, transportation and deposition of acidifying pollutants

Forest decline

Just as the underpinning research on acid deposition and freshwaters seemed secure, forest health in parts of Europe (and North America) appeared to be declining and links with air pollutants were suspected. The 'forest decline' issue became an important focus of research in Europe and North America and a cause of the rapid introduction of control measures on pollutant emissions in the European countries most affected, Germany in particular.

The forest decline issue led to much heated debate within the scientific community. It became clear that there was no single explanation for the observed changes in forests. Several types of decline have been recognised over the years. Thus, direct SO_2 toxicity combined with acute soil acidification were thought to be the cause in the areas with the most extreme damage and widespread tree death, the 'Black Triangle' of south-east Germany and the north-west of the Czech Republic. Some areas of forest in decline throughout central Europe were shown to be significantly deficient in magnesium, partly as a consequence of acid deposition and partly due to management practices (Roberts *et al.* 1989). Other areas were shown to be suffering chronic damage by a combination of very large inputs of acidity, sulphur and nitrogen especially in areas frequently immersed in cloud water dominated by very large concentrations of the major ions (SO_4^{2-}, NO_3^-, H^+ and NH_4^+). In many cases throughout Europe, an interaction seems to be important between pollutants, (eg acidity and ozone) or between pollution and environmental stresses, (eg acidity and drought). The identification of very acidic cloud water in Europe and North America (Fowler *et al.* 1989), led to the hypothesis that red spruce (*Picea rubens*) decline in the Appalachians of eastern North America was caused by the deposition of acidic cloud water.

Subsequent research in collaboration with the University of Lancaster provided the direct link between increased sensitivity to cold stress in red spruce and the deposition of acidic pollutants (Cape *et al.* 1988, Leith *et al.* 1989). Similar work on Norway spruce (*Picea abies*) in Europe has shown that contaminated cloud water is an important pollutant input to high elevation forests, and a potential interactive factor in forest decline (Sheppard *et al.* 1997). In the UK, the large atmospheric inputs of magnesium from seasalts mitigate against the development of forest decline through magnesium deficiency. Sitka spruce (*Picea sitchensis*), which is the main tree species in commercial UK forest plantations is extremely tolerant of acidic soil conditions, although effects of acidic deposition have been observed under experimental conditions and these are most likely to be caused by interactions with the supply of phosphorus (Crossley *et al.* 1998). The challenge now is to disentangle quantitatively the relative roles of these interactive factors and it is in this area that the Institute's current work is focussed.

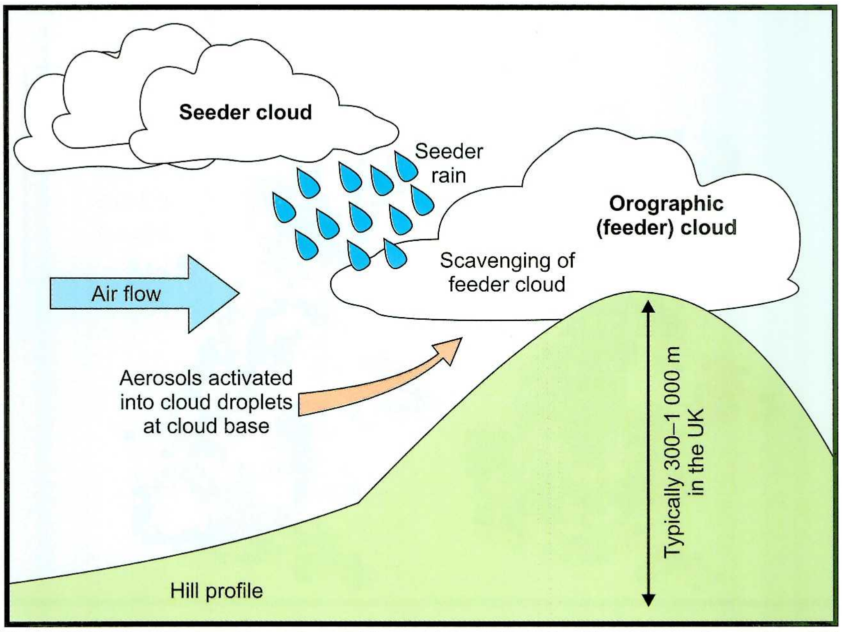

Figure 2. Seeder-feeder process by which wet deposition of pollutants is enhanced on hills

Effects on soils and freshwaters

ITE research has included work on forest soils and atmospheric processes. Forests were shown to be enhancing the capture of pollutants by terrestrial surfaces as a consequence of their aerodynamic roughness (Fowler *et al.* 1989). Also upland forests in acid sensitive catchments were shown to increase the acidification of freshwater, (Reynolds *et al.* 1986).

The high rainfall uplands of western and northern Britain are areas over which orographic processes greatly increase rainfall and the wet deposition of pollutants. The studies of orographic enhancement of wet deposition through the seeder-feeder process (Figure 2, see also Fowler *et al.* 1995) and the application of models to simulate the process throughout the UK have strongly influenced the deposition and exceedance maps. Field studies to test and validate the models have been a feature of recent research. In particular, methods have been developed to measure the long-term (annual), large area (catchment) hydrochemical budgets (Reynolds *et al.* 1997, Fowler *et al.* 1995) to test the predictions of the orographic enhancement models. Even longer-term estimates of the orographic and land use effects have been studied using the ^{210}Pb inventory methods. Both of these approaches have confirmed the wet deposition mapping methodologies, but they also show that spatial variability in wet deposition at the sub- 20 km x 20 km scale currently limits the spatial scale at which exceedance of critical loads can be quantified.

From basic research into the interactions between acid deposition and upland land use, ITE developed methods to quantify the sensitivity of freshwaters to acidification using

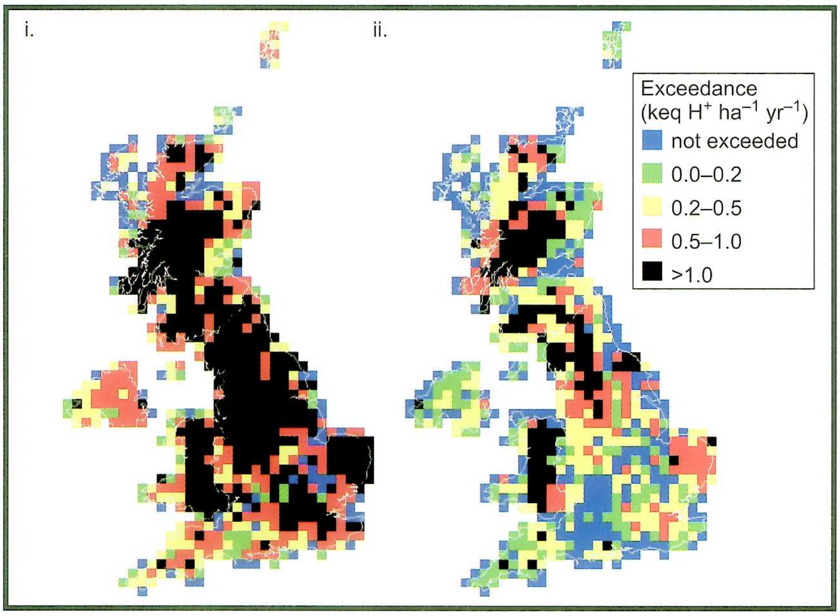

Figure 3. Excess acid deposition over critical loads of acidity set to protect 95% of sensitive ecosystems, as given by (i) the earliest available mapped sulphur and nitrogen deposition from measurements (annual averages for 1986–1988), (ii) 1986–1988 nitrogen and modelled predicted values for sulphur for approximately 2010 (which meet international emission control obligations). Data acknowledgement: UK Critical Loads Network (CLONE)

regional mapped data for geology, soils and land use (Hornung *et al.* 1990). This subsequently formed the basis for assessing the risk of stream acidification resulting from proposed new conifer forest plantations throughout Wales. ITE also played an important role in the development and testing of the underlying equations used in the critical loads/levels approach to quantifying ecosystem sensitivity to acidification (Cape 1993, Reynolds *et al.* 1998).

Critical loads concept

While the late 1980s were dominated by the causes of forest decline, the early 1990s saw the development of the critical loads approach to pollution control. The philosophy of this approach was to quantify the maximum pollutant concentrations or deposition to which ecosystems could be subjected, without damaging the component of the ecosystem selected (eg soil, freshwater, crops or semi-natural vegetation). These critical loads or levels could be entirely empirical, supported by experimental data or be based on a more theoretical approach. The UK abatement strategy for acid deposition is, in line with strategies developed at the European level, focused on maximizing environmental benefits from the investment on control measures (Bull 1992, Bull *et al.* 1995). By calculating the amount by which deposited acidity across the UK exceeds the critical load, and comparing a range of options for the control of sources of deposition, UK policies on abatement of emissions have been developed and implemented. The consequences of policies to reduce sulphur emissions in the UK and Europe are reflected in the exceedances observed in maps for 1986–1988 and modelled deposition projection for 2010.

The critical load exceedance maps for the UK (Figure 3) are closely linked to those areas which are both sensitive to acidification and in which atmospheric inputs are large. Sensitive areas are found where the weathering of soils and rocks is slow and there is little to buffer deposited acidity. This is a feature of many upland areas of Britain where, coincidentally, deposition of acidity is high.

Consequences of emission reductions (non-linearity)

The reduction in sulphur emissions and deposition in the UK caused large decreases in the concentrations of SO_2 close to the major sources. In the east Midlands for example, concentrations declined by almost an order of magnitude between 1983 and 1996. This very rapid decline has been observed at many sites in source regions. A consequence of the rapid decline in SO_2 concentration is that dry deposition has also declined very quickly. The trends in wet deposition have been much smaller and, overall for the UK, has been substantially smaller than the decline in emissions. The changes in emissions and wet and dry deposition for the UK are summarised in Figure 4, and show that for the entire country emissions declined by 25% while dry deposition declined by 40% and wet deposition by 19%.

The change in partitioning of the deposited acidity is very important because the areas of the UK receiving most of their deposition in rain are the acid sensitive uplands and the areas of greatest critical loads exceedance. The areas experiencing the largest decline in deposition, however, are the agricultural areas close to major sources and nearby urban areas.

The consequence of these changes has, therefore, been that the greatest benefit of the emission reduction was apparent in the areas least affected by acid deposition, and vice versa. The processes responsible for the non-linearity appear to those regulating

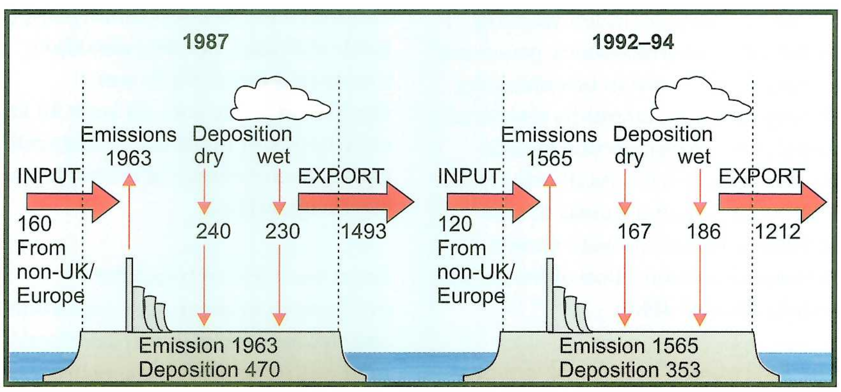

Figure 4. UK sulphur budgets for 1987 and the average of 1992–94

the oxidation of SO_2 to particulate SO_4 within a few hundred kilometres of the major sources and are the focus for current research. The policy implications of these findings are as yet uncertain, but it is likely that links between SO_2 oxidation and NH_3 emissions will be involved and, therefore, policies to control both gases will need to be developed in a multi-pollutant strategy.

Ecosystem recovery

Amounts of wet deposited sulphate at remote, rural sites dominated by wet deposition have declined since the mid-1980s in response to reduced SO_2 emissions, whereas, there have been no distinct trends in ammonium and nitrate deposition. The chemical response of acidified freshwaters to the changes in acid deposition loading is mixed. There has been little evidence of recovery at acidified UK Acid Waters Monitoring Network (AWMN) sites between 1988 and 1997. However, longer records at some sites such as Plynlimon indicate a slow increase in pH and dissolved organic carbon (DOC) concentrations over the last 16 years (Reynolds *et al.* 1997). This response is consistent with findings from manipulation experiments in Norway where acid deposition has been artificially removed from small catchments using a roof (Wright *et al.* 1993). In the Norwegian study, strong acid anion concentrations in runoff decreased in response to lower atmospheric inputs but acidity was buffered by increasing concentrations of organic anions so that the pH change was very small. This suggests that the pattern of recovery in acidified upland streams in the UK will be complex depending on the acidification history, the types of soil present and the land use. In many upland catchments, replenishment of soil exchangeable base cations by weathering will be very slow, and there are likely to be confounding effects from organic anion buffering in catchments with peaty soils, sulphate desorption from podzolic B horizons and acidification by atmospheric nitrogen deposition.

While recovery may be complex, the nine year report of the International Co-operative Programme on Waters (based on 220 sites across 21 countries in Europe and North America), concludes that sulphate is decreasing at almost all sites monitored, while at many, changes in alkalinity and pH are consistent with recovery from acidification (Skjelkvaale & Ulstein 1998). In view of the small changes in chemistry, it is not surprising that data from the AWMN sites and the recent Welsh Acid Waters Survey (Stevens 1997) have provided little evidence of biological recovery. However, at some sites in Scandinavia and Germany significant improvements have been reported (Skjelkvaale & Ulstein 1998).

Continuing concerns

The reduction in sulphur emissions by about 50% from the maximum values in the late 1970s has contributed to reduced ecosystem inputs throughout the country. However, emissions are still considerable (Figure 5) and exceedances of critical loads are still widespread (Figure 3). The decline in sulphur emissions took place during a period in which emissions of oxidized and reduced nitrogen remained fairly constant or increased. The relative importance of nitrogen as a component of the acidifying input has, therefore, increased steadily over the last two decades.

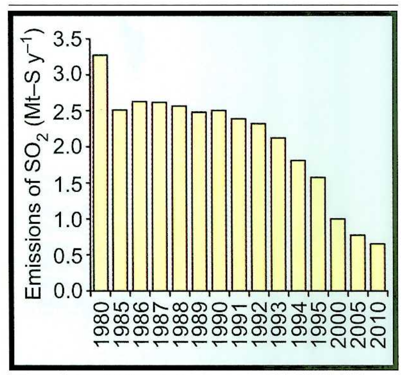

Figure 5. UK sulphur emissions from 1980 to 2010 (EMEP/MSC-W)

Throughout the early 1990s the deposition of nitrogen as gaseous NH_3, NO_2, HNO_3, and wet deposited NO_3^- and NH_3 has become an important issue in its own right (Emmet *et al.* 1998, Sutton *et al.* 1993, 1998). The ambient concentration of oxides of nitrogen now exceed concentrations of SO_2 everywhere and especially in cities where the NO_x/SO_2 ratio is generally greater than ten. While exceedances of critical loads of acidity for soils occur widely in the UK, the deposition of sulphur and acidity are declining along with exceedance of critical loads, and the acidifying effects of deposited nitrogen now exceed those of sulphur in many areas of the country.

The emitted NO_x (and Volatile Organic Carbon (VOC)) compounds provide the precursor for photochemical oxidant formation (O_3, Peroxyacyl nitrates (PAN), H_2O_2) (Figure 6). These oxidants now represent the

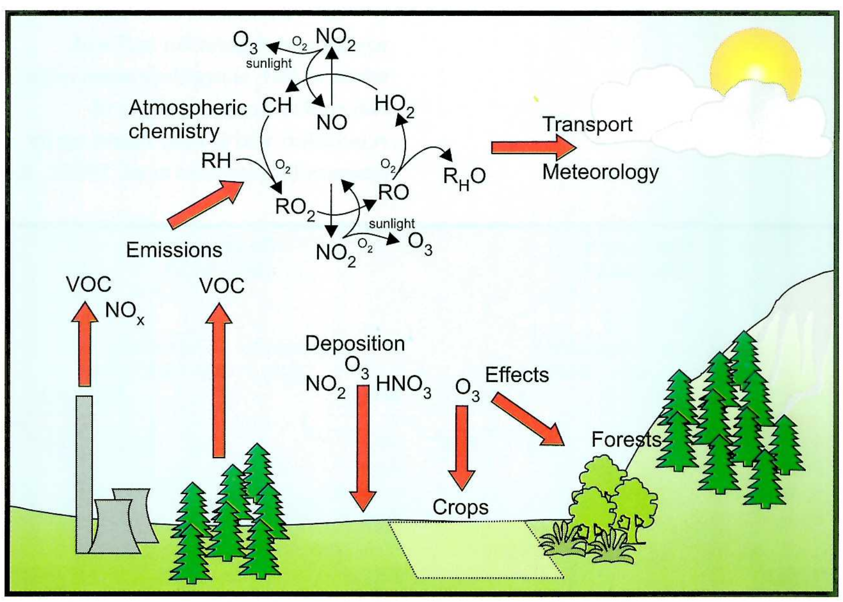

Figure 6. Processes in photochemical oxidant formation and deposition

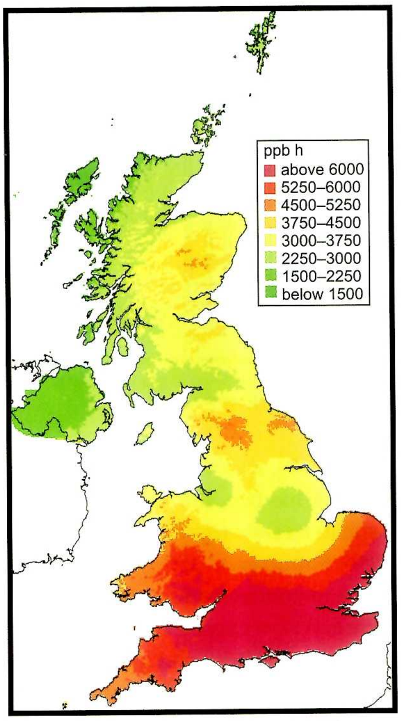

Figure 7. Exceedance of the critical levels of ozone for effects on UK cereal crops (the critical level (AOT40) is 3 000 ppbh above 40 ppb)

The relative importance of nitrogen as a component of the acidifying input has increased steadily over the last two decades.

major phytotoxic pollutants in the UK, and ITE research has made important contributions to the UK assessment of this problem (PORG 1993, 1997).

Photochemical oxidants

For ozone, critical levels for crops are exceeded widely in the UK (PORG 1997) as shown in Figure 7. Ozone concentrations also occasionally exceed the thresholds for effects on human health. The degree to which international agreements, currently being negotiated, will reduce exceedances seems to be limited over the next decade. Furthermore the magnitude of the current ambient NO_x concentrations is so large that as the controls on NO_x emissions begin to take effect, ozone concentrations will increase (Fowler *et al.* 1998). The models of ozone production and transport show that episodes of enhanced ozone will remain a major problem in the UK for many years to come and quantifying the exceedance and magnitude of yield loss and the effects on human health will remain a focus for research within ITE.

Ammonia

The deposition of ammonia from agriculture dominates terrestrial inputs of nitrogen from the atmosphere in the UK, even though ambient concentrations of NO_2 are substantially larger than those of NH_3 almost everywhere (Figure 8). This arises because NH_3 is very soluble and is readily deposited onto external surfaces of vegetation and soil, whereas NO_2 is not deposited onto external cuticular surfaces of vegetation and is only taken up by stomata (Hargreaves *et al.* 1992). A complication for ammonia is that, as the apoplast fluids of vegetation contain NH_4^+ there is an effective equilibrium NH_3 concentration within sub stomatal cavities determined by the pH and apoplast NH_4^+ concentration. Thus for fertilised crops, NH_3 fluxes may be of emission rather than deposition (Sutton *et al.* 1993). The underlying mechanisms of NH_3 exchange have been an important focus for ITE pollution research throughout the 1990s. (Sutton *et al.* 1993, 1998, Flechard & Fowler 1998). Uncertainty in the overall budget of reduced nitrogen over the UK, the direct eutrophication effects of deposited nitrogen (Pitcairn *et al*, 1995) and its importance for policy purposes will maintain the level of activity in this area.

The future

The atmospheric pollution research programme in ITE has been at the leading edge of the developments in understanding the acid deposition issues (Plate 1) and the growing interest in the fate and effects of atmospheric nitrogen compounds and photochemical oxidants. The 25 years cover a period of dramatic change in the pollution climate of the UK. While reductions in sulphur deposition are occurring and some recovery is to be expected, the current exceedances of acidifying inputs are large and will be with us well into the next century. The focus of attention within both the research and policy development has turned increasingly towards nitrogen compounds, photochemical oxidants and aerosols. The current development of control measures throughout Europe will continue to modify the composition and concentrations of pollutants and the research focus will turn to other regions of the planet where pollution emissions are increasing rapidly, especially in south-east Asia and the tropics. The other equally sobering fact is that so far, all of the regional pollution issues have been discovered by chance, through unrelated research activity and it is very improbable that we have seen the last of the major surprise consequences of the pollutants emitted as a result of human activity.

Future work within ITE will focus on the anthropogenic modification of the

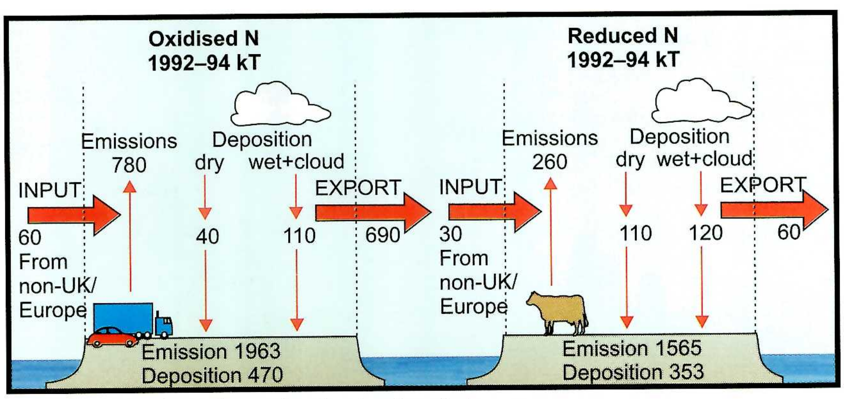

Figure 8. UK budgets for oxidised and reduced nitrogen

nitrogen cycle through emissions of oxidized and reduced nitrogen At a global scale, the anthropogenic emissions now substantially exceed those from natural sources The work necessarily includes studies of the processes which regulate the emission, atmospheric transformation and deposition of the gaseous compounds, but includes the effects of the deposited nitrogen on ecosystem function and primary productivity The other rapidly developing area is that of atmospheric aerosols, which play a central role in the current concerns about human health effects of air pollutants, and in the radiative forcing of climate as well as being the main form by which the long range transport of acidifying pollutants occurs The formation and removal processes for atmospheric aerosols, which contain many important unknowns provide the initial focus of activity

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Future work within ITE will focus on the anthropogenic modification of the nitrogen cycle through emissions of oxidized and reduced nitrogen.