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Edited by A. Jensen, G. Gissel Nielsen, V. Gundersen, O.J. Nielsen, H. Østergård and A. Aarkrog
Abstract

The Environmental Science and Technology Department aspires to develop new ideas and methods for industrial and agricultural production through basic and applied research thus exerting less stress and strain on the environment.

The department endeavours to develop a competent scientific basis for future production technology and management methods in industrial and agricultural production. The research approach in the department is mainly experimental.

Selected departmental research activities during 1993 are introduced and reviewed in seven chapters: 1. Introduction, 2. The Atmospheric Environment, 3. Plant Genetics and Resistance Biology, 4. Plant Nutrition and Nutrient Cycling, 5. Applied Geochemistry, 6. Ecology and Mineral Cycling, 7. Other Activities. The department's contribution to national and international collaborative research programmes are presented together with information about large experimental facilities used in the department. Information about the department's contribution to education and training are included in the report along with lists of publications, publications in press, lectures and poster presentations at international meetings. The names of the scientific and technical staff members, visiting scientists, Postdoctoral fellows, Ph.D students and M.Sc. students are also listed.
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1 Introduction

1.1 The Department of Environmental Science and Technology

Research objectives

The department strives to improve the scientific basis for the development of new ideas for production and management methods in industrial and agricultural production.

Through basic and applied experimental research, the department aspires to develop new methods for future industrial and agricultural production.

Approach

The department's expertise spans a wide range of subjects including atmospheric chemistry, chemical kinetics in the liquid and gas phase, geochemistry, biogeochemistry, geochemical modelling, hydrochemistry, analytical chemistry, process chemistry, plant molecular biology, plant pathogens, plant genetics, population biology, techniques for plant breeding, plant nutrition, biological interaction, nutrient cycling, marine and terrestrial ecology, radioecology, trace metal ecology and ecotoxicology.

The results of research and development are disseminated to companies, institutions, organizations and public authorities through scientific publications, research reports, lectures and posters at scientific and other professional meetings, personal communication with collaborators and through teaching courses at Universities.

The research and development activities in the department are planned for three years and reassessed every year. The research activities are mainly funded directly from the government or from National Science Research Councils, but national and European research programmes, private foundations and commercial contracts make a substantial contribution to the total budget of the department.

1.2 The Atmospheric Environment and Air Pollution

Atmospheric research aims to establish a firm scientific basis for sensible and effective legislative measures to reduce the industrial and agricultural impact on the atmospheric environment.

The effect of human activity on the global atmosphere has become very evident during the last decades. Changes in the atmospheric composition and chemistry influences both the regional and global climate. Deposition of airborne pollutants can give rise, either to direct injuries to plants and animals, or to indirect damage through bio-accumulation in ecosystems. In order to model and predict changes in the atmospheric composition, it is essential to develop a better understanding of the chemical processes in the atmosphere.

Research activities in the department include basic atmospheric chemistry, gas kinetics, determination of primary and secondary pollutants, transport and dispersion of air pollutants and the effect of air pollution on trees, crop plants and terrestrial ecosystems.

1.3 Plant Genetics and Resistance Biology

The department aims to develop the scientific basis for breeding crop plants with new and stronger resistance to diseases and with improved nutrient efficiency. Crop plants, highly resistant to diseases and efficient in nutrient uptake, are a prerequisite for the low input plant production of the future, and will reduce a number of environmental problems related to modern high yield plant production.

The use of genetic variability, related to attributes of economical and environmental importance in crop improvement, can be greatly facilitated by the use of genetic markers in the selection process. A large proportion of the
research effort, within plant biology and genetics, is devoted to the identification of genetic markers. The research in this field relies on the command of a number of techniques such as RFLP, RAPD, QTL, genetical analysis and cytophenetic methodology.

Identification of changes in genetic variability, under different environmental conditions, can be enhanced by a better understanding of the interaction between plant species, as well as the interaction between plants and pathogens.

In population biology experiments and theoretical studies of interactions between populations are important in the understanding of ecosystems. The research involves inter-relationships between crop plants and weeds, and between crop plants and their pathogens.

The possible exchange of genes between related species and the competitive abilities of crop plants are being investigated. The risk of gene flow, from genetically modified cultivated plants into wild natural relatives, and the effect of new genes transferred to natural plants, are being assessed. This type of research is needed to evaluate the risk of transgenic varieties escaping into the environment.

1.4 Plant Nutrition and Mineral Cycling

Research in plant nutrition and mineral cycling aims to provide basic scientific information for better understanding of the mechanisms and processes involved in the root-microbe symbiosis in relation to carbon, nitrogen and phosphorus. It also aims to provide basic scientific information about the processes involved in the turnover of carbon, nitrogen and phosphorus in agro-ecosystems.

The research emphasizes biological, physiological, biochemical, chemical and physical processes involved in the transfer of plant nutrients, especially nitrogen and phosphorus, through the Soil-Plant-Air-Continuum.

The plant nutrition research involves five aspects. Firstly, research on symbiotic nitrogen fixation, which highlights the exchange of compounds between the host plant and the microsymbiont across the membrane interface. Secondly, studies of the interaction between VA-mychorhiza, plant roots and the rhizosphere. Thirdly, studies on turn-over of nitrogen from crop residues and farmyard manure. Fourthly, biological transfer of nitrogen from legumes to non-legumes. Fifthly, the effect of air pollution with ammonia.

These research activities are essential for the future development of new plant production methods, based on biologically fixed nitrogen and phosphorus uptake mediated by VA-mychorrhiza. To reduce the loss of plant nutrients due to surface run off, losses of nutrients to the atmosphere or leakage to the ground water, highly effective assimilation and recycling of nutrients are required.

1.5 Chemistry of the Geosphere

The department contributes to the scientific basis for developing the wet oxidation technique in the treatment of soil and waste water polluted with organic compounds and heavy metals. New methods are being developed for the conditioning and treatment of soil, sludge, sewage and other waste products from industrial productions contaminated with heavy metals. Wet oxidation readily solubilizes lignin in straw and the product is susceptible to enzymatic treatment.

In geochemical modelling, the JENSEN programme has been developed further to predict geochemical transformations which may occur when foreign minerals are added as reactants to polluted waters. Attempts are being made to model humic behaviour. A genuine thermodynamic modelling tool, describing humic acid reactions, seems within reach.

The research in applied geochemistry includes studies on polycyclic organic matter (especially azaarenes in polluted soils), rare and precious metals and ferromanganese complexes in marine sediments. New techniques to estimate sedimentation rates based on direct gamma-ray spectrometry are being developed.

In analytical chemistry, the instrumentation has been expanded with a new GC/MS and a proposed HPLC/MS for 1994. New analytical methods for trace metal analysis and stable isotope analysis are being developed.
1.6 Ecology and Mineral Cycling

Research within ecology and mineral cycling aims to improve the scientific basis and understanding of the impacts of environmental pollution on marine and terrestrial ecosystems with emphasis on natural and semi-natural ecosystems. Further, the research aims to establish better knowledge about transport and the fate of pollutants by the use of stable and radio isotopes, and trace metal techniques.

Radioactive tracer techniques are used in studies on metal toxicity to fish and Baltic mussels, as bioindicators for marine monitoring programmes for radionuclides and heavy metals.

Radionuclides, discharged from La Hague, are used to trace the advection and dispersion of water in the European Coastal Current from the English Channel to the entrance to the Baltic.

Indoor aerosol deposition is studied by using neutron-activatable tracers as substitutes for airborne contaminants, such as bacteria, fungi and radon progeny which are attached to ambient aerosols. The process of aerosol deposition is an important factor for aerosol concentration and thereby for potential health hazards in buildings.

1.7 Organisation

The Environmental Science and Technology Department includes approximately 130 scientific and technical staff members, and the department is organized in 6 sections with Dr. Arne Jensen as Department Head.

Ecology Section,
   Head: Dr. Asker Aarkrog.
Chemical Reactivity Section,
   Head: Dr. Ole John Nielsen.
Dr. Arne Miller is in charge of the Risø High Dose Reference Laboratory.
Chemistry Section,
   Head: Dr. Vagn Gundersen.
Plant Genetics Section,
   Head: Dr. Hanne Østergård.
Plant Nutrition Section
   Head: Dr. Gunnar Gissel Nielsen.
Growth chambers, green houses and the experimental farm, Dyskærgaard.
   Head: Dr. Vagner Haahr.
2 The Atmospheric Environment

2.1 Introduction

Because the biosphere consumes atmospheric oxygen, factors affecting the atmosphere have important biological implications. The two long term goals for atmospheric chemistry research should be:

1) To understand the chemical cycles in the atmosphere through field investigations, laboratory studies and theory with numerical modelling. Progress in each area is dependent upon contribution from the others.

2) To predict responses to both natural and human perturbations of the atmosphere.

It is interesting to review two decades of activity in atmospheric chemistry. In that period, 4 potentially serious environmental problems were identified: acid deposition, photochemical smog, stratospheric ozone depletion and global warming. These potential problems strongly motivated and directed the efforts of the scientific community. The atmospheric research of our department has several aspects: a) Determination of air pollutants to determine the source contribution; b) Determination of primary and secondary pollutants in rural areas to determine the influence of atmospheric processes; c) Laboratory investigations of chemical mechanisms in all three phases.

2.2 The Gas Phase

The work in the gas phase took place within several different projects: Fundamental chemical kinetics, CFC (chlorofluorocarbons) substitutes and related compounds, nitrogen and sulfur species, including aromatics and NO, reduction chemistry.
reactions. Gas phase UV absorption spectra were measured for C$_2$ to C$_5$ alkyl radicals, and are well characterized and understood theoretically. As part of a continued study of alkyl radicals in our laboratory, using the pulse radiolysis kinetic spectroscopy technique, we report here the first data on the UV spectrum and the kinetics for the self reactions of a C$_4$ alkyl radical, (CH$_3$)$_2$CCH$_2$. (Nielsen et al., 91).

Peroxy radicals, RO$_2$, are important intermediates in the atmospheric degradation of organic compounds emitted to the atmosphere. The alkyl radical, R, can be produced from emitted organic compounds in several ways, e.g., by reactions with OH, or NO$_2$ radicals, or by photolysis. Alkyl radicals will react rapidly with atmospheric O$_2$ to form peroxo radicals, RO$_2$:

$$\text{R} + \text{O}_2 + \text{M} \rightarrow \text{RO}_2 + \text{M} \quad (1)$$

where M is a third body, N$_2$ and O$_2$ in the atmosphere. The fate of RO$_2$ radicals in the atmosphere is determined by reaction with NO, NO$_2$, HO$_2$, or other RO$_2$ radicals:

$$\text{RO}_2 + \text{NO} \rightarrow \text{products} \quad (2)$$

$$\text{RO}_2 + \text{NO}_2 + \text{M} \rightarrow \text{RO}_2\text{NO}_2 + \text{M} \quad (3)$$

$$\text{RO}_2 + \text{HO}_2 \rightarrow \text{products} \quad (4)$$

$$\text{RO}_2 + \text{R'O}_2 \rightarrow \text{products} \quad (5)$$

The relative importance of reactions (2-5) depends on the NO, NO$_2$, HO$_2$, and RO$_2$ concentrations and the values of the respective rate constants. In remote areas, NO$_2$ concentrations are as low as 1 ppt, decreasing the importance of reactions (2) and (3). However, in urban areas with higher NO$_2$ concentrations, reaction (2) and (3) should be the major sink for RO$_2$ radicals.

The reaction of RO$_2$ radicals with NO proceeds through two channels:

$$\text{RO}_2 + \text{NO} \rightarrow \text{RO} + \text{NO}_2 \quad (2a)$$

$$\text{RO}_2 + \text{NO} + \text{M} \rightarrow \text{RONO}_2 + \text{M} \quad (2b)$$

We have used the pulse radiolysis technique to investigate reaction 2 for a number of alkyl peroxy and halogenated alkyl peroxy radicals:

CH$_3$O$_2$, C$_2$H$_4$O$_2$, (CH$_3$)$_2$CCH$_2$O$_2$, (CH$_3$)$_2$CC(CH$_3$)$_2$O$_2$, CH$_3$O$_2$, CHF$_2$O$_2$, CHF-CH$_2$O$_2$, CHF$_2$F$_2$O$_2$, CHF$_2$O$_2$, CF$_2$O$_2$, CFCl$_2$O$_2$, CH$_2$ClO$_2$, and CF$_2$CFClO$_2$.

As shown in Fig. 2.2.1, the rate constants now available for RO$_2$ + NO cover a range of one order of magnitude, from the lowest value of $(1.8 \pm 0.2) \times 10^{-12}$ cm$^3$/molecule$^{-1}$s$^{-1}$ for RO$_2$ = (CH$_3$)$_2$CC(CH$_3$)$_2$O$_2$, to the highest value of $(18.7 \pm 2.0) \times 10^{-12}$ cm$^3$/molecule$^{-1}$s$^{-1}$ for RO$_2$ = CH$_2$ClO$_2$. Comparison of all the available data demonstrates two different trends. Firstly, the rate constants decrease with increasing alkyl chain length and branching going from C$_2$ to C$_5$. Secondly, halogen substituents, especially chlorine, increase the RO$_2$ + NO rate constant. We consider the implication of the results from the present work to our understanding of atmospheric chemistry of halogenated organic compounds. In all cases the peroxy radicals derived from halocarbons were observed to react rapidly with NO, with rate constants in the range of $(9.7$-$18.7) \times 10^{-12}$ cm$^3$/molecule$^{-1}$s$^{-1}$. A reasonable estimate for the global average tropospheric NO concentration is $2.5 \times 10^9$ cm$^{-1}$. Hence, the lifetimes of halogenated peroxy radicals with respect to reaction with NO will be 4-7 min. In the atmosphere, reaction (2) competes with reactions (3), (4) and (5) for available RO$_2$ radicals. Clearly reactions (2), (3), (4) and (5) could all play significant roles in the atmospheric degradation of organic compounds. Kinetic data for reactions (3), (4) and (5) are needed for a more complete understanding of the atmospheric chemistry for organic compounds (Sehested et al., 91b).

In recent years, significant progress has been made in defining structure-reactivity relationships for kinetics and mechanisms of reactions of RO$_2$ radicals, and the influence of a variety of substituent functional groups on their reactivity can be addressed. In collaboration with a group at AEA Harwell and a group at Ford Motor Company, we have investigated the simplest alkyl peroxy radical, (CH$_3$)$_2$CCH$_2$O$_2$, formed in the atmosphere from the oxidation of dimethyl ether. The results, among which was the discovery of a most surprising H atom ejection mechanism, have now been published (Jenkin et al., 91).
Nitromethane, CH₃NO₂, has been the subject of a large number of theoretical and experimental studies and is frequently used as a model molecule for nitrocompounds. Thus, the reaction of nitromethane with a number of atoms and radicals was previously investigated. We have studied the reaction between H atoms and CH₃NO₂ using a discharge flow system with electron paramagnetic resonance and modulated molecular beam mass spectrometry for detection of reactants and products. Two reaction channels were observed. This is described in a recent publication (Lund Thomsen et al., 91).

Halogenated Organic Compound in the Troposphere

The STEP project, HALOCSIDE, involving 9 European laboratories is concerned with the kinetics and mechanisms of oxidation of chlorine-, bromine- and iodine-containing compounds under atmospheric conditions. This project was extended for one more year in 1993. It is the aim of this study to determine the tropospheric sinks for these halogenated compounds in order to provide the basis for calculation of the ozone depletion potential for released halogenated species.

Fig. 2.2.1. Lifetimes of the CF₃O radical with respect to trace species in the atmosphere, calculated from rate constants determined in our work. It can be seen that at 25 km CF₃O has a lifetime with respect to O₃ reaction that is 10 times shorter than that with respect to NO reaction. This gives a maximum chain-length of 10 for the O₃ reaction cycle.

Understanding of the kinetics and spectroscopy of alkyl peroxy radicals has long been recognized as important due to the central role peroxy radicals play in the degradation of volatile organic compounds in the troposphere. Comprehensive knowledge has been achieved about several series of alkyl-, haloalkyl-, acyl-, oxygen-substituted, and also unsaturated peroxy radicals. The halogenated alkyl peroxy radicals have received special interest due to the importance
ance of chlorine and bromine atoms in the degradation of stratospheric ozone, and a number of these have previously been studied in our laboratory. Of the monohalogenerated methylperoxy radicals, the fluorne, chlorine, and bromine species have so far been investigated. The objective was to examine iodine methylperoxy radicals, which have not yet been studied, probably because they are of limited importance from an atmospheric viewpoint. This is in spite of the large natural production of CH\textsubscript{3}I in the marine boundary layer. Methyl iodide has a broad UV absorption spectrum with a maximum at 260 nm which extends into the UVA and UVB spectral regions. The photolysis lifetime for CH\textsubscript{3}I is about 8 hours making photolytic cleavage the primary degradation channel for CH\textsubscript{3}I in the atmosphere:

\begin{equation}
\text{CH}_3\text{I} \rightarrow \text{CH}_3 + \text{I}
\end{equation}

The UV spectrum of CH\textsubscript{3}O\textsubscript{2} radicals is broad and distinctly different from that of other peroxy radicals. The absorption cross section at 370 nm was $(2.1 \pm 0.5) \times 10^{-18}$ cm\textsuperscript{2} molecule\textsuperscript{-1}. The rate constant for the self reaction of CH\textsubscript{3}I radicals, k = $4 \times 10^{-11}$ cm\textsuperscript{3} molecule\textsuperscript{-1} s\textsuperscript{-1} at 1000 mbar total pressure of SF\textsubscript{6}, was derived by kinetic modelling of experimental absorbance transients. The observed self reaction rate constant for CH\textsubscript{3}O radicals was estimated also by modelling to k = $9 \times 10^{-11}$ cm\textsuperscript{3} molecule\textsuperscript{-1} s\textsuperscript{-1}. As part of this work, a rate constant of $(2.0 \pm 0.3) \times 10^{-10}$ cm\textsuperscript{3} molecule\textsuperscript{-1} s\textsuperscript{-1} was measured for the reaction of F atoms with CH\textsubscript{3}I. The branching ratios of this reaction for abstraction of an F atom and an H atom were determined to be $(64 \pm 6)%$ and $(36 \pm 6)%$, respectively.

Furthermore, we have investigated the atmospheric degradation of HFC-125 and CF\textsubscript{3}CF\textsubscript{2}I, and have identified several products of which CO\textsubscript{2} and CF\textsubscript{3}CO\textsubscript{2} was dominant (Sehested et al., 91a).

CFC Substitutes

By international agreement, industrial production of chlorofluorocarbons (CFCs) will be phased out. Hydrofluorocarbons (HFCs) are one class of potential CFC substitutes. Prior to large scale industrial use, it is important to establish the environmental impact of the release of HFCs into the atmosphere. Following release, HFCs will react with OH radicals in the lower atmosphere to produce fluorinated alkyl radicals which will, in turn, react with O\textsubscript{3} to give peroxy radicals. In the case of CF\textsubscript{3}H (HFC-23):

\begin{align*}
\text{CF}_3\text{H} + \text{OH} &\rightarrow \text{CF}_3\text{H}_2 + \text{O}_2 \quad (7) \\
\text{CF}_3\text{H} + \text{O}_2 + \text{M} &\rightarrow \text{CF}_3\text{H}_2 + \text{M} \quad (8) \\
\text{CF}_3\text{O} &\rightarrow \text{CF}_3\text{O}_2 + \text{M} \quad (9)
\end{align*}

In addition, the atmospheric oxidation of other HFCs, such as HFC-134a (CF\textsubscript{3}CF\textsubscript{2}H) and HFC-125 (CF\textsubscript{3}CF\textsubscript{2}H) containing a CF\textsubscript{3} group, is known to produce CF\textsubscript{3}O\textsubscript{2} radicals. Because HFC-134a is a potential substitute for CFCs in cooling systems, a substantial production of this compound is likely to occur before the year 2000. Consequently, investigation of the fate of HFC-134a, CF\textsubscript{3}O\textsubscript{2} and CF\textsubscript{3}O in the atmosphere has been the subject of a substantial international research effort.

Recently, attention has been drawn to the behaviour of CF\textsubscript{3}O\textsubscript{2} and CF\textsubscript{3}O in the stratosphere. It is well known that 5-10% of the HFC-134a released into the atmosphere reacts with OH in the stratosphere and initiates a series of reactions leading to CF\textsubscript{3}O\textsubscript{2} and CF\textsubscript{3}O.

In the stratosphere, CF\textsubscript{3}O\textsubscript{2} and CF\textsubscript{3}O may be involved in a catalytic destruction of ozone as is the case for Cl, Br, OH, etc.:

\begin{align*}
\text{CF}_3\text{O} + \text{O}_3 &\rightarrow \text{CF}_3\text{O}_2 + \text{O}_2 \quad (10) \\
\text{CF}_3\text{O} + \text{O}_3 &\rightarrow \text{CF}_3\text{O}_2 + \text{O}_2 \quad (11)
\end{align*}

A value for the rate constant for reaction 4, $k_{11} = 1 \times 10^{-16}$ cm\textsuperscript{3} molecule\textsuperscript{-1} s\textsuperscript{-1} was reported recently by a group at Oxford. This would give an ODP (ozone depletion potential) for HFC-134a that would make it unacceptable for widespread use. In their study, $k_{11}$ was determined in an indirect way and further investigations of these reactions are needed.

The main objective of our work was to determine $k_{10}$ and $k_{11}$. This was done by measuring ozone concentration in a stainless steel cell as a function of time, by UV absorption spectroscopy.
in the presence of CF₂O₂ and CF₂O radicals. The observed absorption transients at 254 nm and 276 nm could be fitted by a model, which did not include reactions (10) and (11). By including these reactions and varying their rate constants, upper limits for \( k_{10} \) and \( k_{11} \) could be established. The upper limits were derived as \( k_{10} < 0.5 \times 10^{14} \text{ cm}^{-3} \text{ molecule}^{-1} \text{s}^{-1} \), and \( k_{11} < 1 \times 10^{13} \text{ cm}^{-3} \text{ molecule}^{-1} \text{s}^{-1} \). In Fig. 2.2.2 the estimated lifetimes of CF₂O with respect to the trace species in the stratosphere are displayed as a function of altitude. For the reactions of CF₂O with ozone, upper limits of \( k_{10} < 0.5 \times 10^{14} \text{ cm}^{-3} \text{ molecule}^{-1} \text{s}^{-1} \) and \( k_{11} < 5 \times 10^{14} \text{ cm}^{-3} \text{ molecule}^{-1} \text{s}^{-1} \) were used in the calculations. It can be seen from Fig. 2.2.2, that the reaction of CF₂O radicals with ozone is still the main reaction channel for these radicals in the stratosphere.

It should be emphasized that these calculations are only an approximation and that several assumptions had to be made e.g., using the room temperature rate constants, and assuming reaction products between reaction of CF₂O radicals and NO at stratospheric temperatures to be the same as at ambient temperature. However, this work suggests that the ODP of HFCs due to a CF₂O₂ cycle is negligible (Nielsen and Sehested, 9.1).

We have been involved in several investigations of reactions of CF₂O radicals with different atmospheric species, many of which have already been published during 1993 (Nielsen and Sehested, 9.1).

For the CF₂O+NO \( \rightarrow \) CF₂O+FNO reaction, one of the most important permanent sinks for CF₂O radicals in the atmosphere, we found a value for the rate constant of \((5.2 \pm 2.7) \times 10^{-11} \text{ cm}^{-3} \text{ molecule}^{-1} \text{s}^{-1}\), with which all scientists now seem to agree (Sehested and Nielsen, 9.1e).

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![Graphical representation of the RO₂+NO rate constants determined in our work (closed symbols) together with those available from the literature (open symbols). The three groups are: alkyl peroxy, halogenated ethyl peroxy, and halogenated methyl peroxy radicals.](image-url)
For the rate constant of \( \text{CF}_3\text{O} + \text{H}_2 \rightarrow \text{CF}_3\text{OH} + \text{OH} \) reaction, we found a range (0.2-40)x10^{-17} \text{ cm}^3\text{molecule}^{-1}\text{s}^{-1} (Wallington et al., 9.1c).

In collaboration with Dr. Howard Sidebottom's group, we have investigated the reactions of \( \text{CF}_3\text{O} \) radicals with a series of hydrocarbons (Kelly et al., 9.1).

**Organonitrogen and Sulphur Atmospheric Transformations**

Under a four-year Danish Environmental Research programme, we are involved in a project concerning heterogeneous processes in the atmosphere. During the first year, we observed particle formation for the oxidation of dimethyl sulfide (DMS). DMS is the major source of organo-sulfur compounds in marine environments and has been detected in the upper levels of the oceans. Each year 75-85 Mega-tonnes of DMS escapes into the atmosphere from the oceans. DMS represents approximately 25% of the total flux of sulphur into the atmosphere and so plays an important role in the global sulphur cycle. Atmospheric oxidation of DMS leads to methanesulfonic and sulfuric acids which serve as cloud condensation nuclei and contribute to the natural acidity of precipitation. It has been proposed that emission of DMS may provide a means of biological climate regulation, see Fig. 2.2.3. Recognition of the importance of DMS has led to a significant research effort to understand the atmospheric chemistry of this compound.

The principal atmospheric fate of DMS is the reaction with \( \text{OH} \) radicals. This reaction (12) proceeds via two processes. Under ambient conditions (295°K, 760 Torr of air) approximately 70% of reaction (12) proceeds via process (12a) to give \( \text{CH}_3\text{SCH}_2 \) radicals with the remaining 30% giving the adduct via process (12b):

\[
\text{OH} + \text{CH}_3\text{SCH}_2 \rightarrow \text{CH}_3\text{SCH}_2 + \text{H}_2\text{O} \quad (12a)
\]

\[
\text{OH} + \text{CH}_3\text{SCH}_2 + \text{M} \rightarrow \text{CH}_3\text{S(OH)}\text{CH}_3 + \text{M} \quad (12b)
\]

The \( \text{CH}_3\text{SCH}_2 \) radical formed in reaction (12a) is thought to rapidly add molecular oxygen to give \( \text{CH}_3\text{SCH}_2\text{O}_2 \).

\[
\text{CH}_3\text{SCH}_2 + \text{O}_2 + \text{M} \rightarrow \text{CH}_3\text{SCH}_2\text{O}_2 + \text{M} \quad (13)
\]

The peroxy radical, \( \text{CH}_3\text{SCH}_2\text{O}_2 \), will react with trace species in the atmosphere such as \( \text{NO}, \ \text{NO}_2, \ \text{HO}_2 \), or other peroxy radicals (\( \text{RO}_2 \)), to give a variety of products. By analogy with other peroxy radicals, reaction with \( \text{NO} \) is likely to be an important fate of \( \text{CH}_3\text{SCH}_2\text{O}_2 \) radicals.

\[
\text{CH}_3\text{SCH}_2\text{O}_2 + \text{NO} \rightarrow \text{CH}_3\text{SCH}_2\text{O} + \text{NO}_2 \quad (14)
\]

There has been an extensive experimental research effort to investigate the kinetics and products of the \( \text{OH} \) initiated atmospheric photo-oxidation of DMS. However, to the best of our knowledge, the key gas-phase radical intermediates \( \text{CH}_3\text{SCH}_2 \) and \( \text{CH}_3\text{SCH}_2\text{O}_2 \) have not yet been observed directly.

As part of a collaboration with Ford Motor Company to study the atmospheric chemistry of peroxy radicals and the environmental fate of volatile organic compounds, we have performed an experimental study of \( \text{CH}_3\text{SCH}_2 \) and \( \text{CH}_3\text{SCH}_2\text{O}_2 \) radicals. The results of this first investigation of the \( \text{CH}_3\text{SCH}_2\text{O}_2 \) radical have been published (Wallington et al., 9.1a).

The atmospheric lifetimes of \( \text{CH}_3\text{SCH}_2\text{O}_2 \) radicals with respect to reaction with \( \text{NO}_2, \ \text{HO}_2 \)
and RO$_2$ are estimated to be 7, 3, and 8 minutes respectively.

\[
\begin{align*}
\text{CH}_3\text{SCH}_2\text{O}_2\text{+NO}_2\text{+M} & \rightarrow \\
\text{CH}_3\text{SCH}_2\text{O}_2\text{NO}_2\text{+M} & \quad (15)
\end{align*}
\]

\[
\begin{align*}
\text{CH}_3\text{SCH}_2\text{O}_2\text{+HO}_2 & \rightarrow \text{CH}_3\text{SCH}_2\text{OOH}+\text{O}_2 & \quad (16)
\end{align*}
\]

\[
\begin{align*}
\text{CH}_3\text{SCH}_2\text{O}_2\text{+RO}_2 & \rightarrow \text{products} & \quad (17)
\end{align*}
\]

Clearly, reactions (14-17) could all play significant roles in the atmospheric degradation of DMS. Kinetic data for reactions (15-17) are needed for a more complete understanding of the atmospheric photooxidation mechanism of DMS.

**Oxidation of Aromatics**

This project was carried out in collaboration with atmospheric chemistry laboratories at the University of Lille, the University of Patras and The Fraunhofer-Institute in Hannover. A final report on the experimental work was submitted to the CEC in March 1993. The contribution from our laboratory has concentrated on spectrokinetic studies of free radicals produced in the reactions of hydroxyl radicals with benzene and toluene, i.e.

\[
\begin{align*}
\text{OH}+\text{C}_6\text{H}_6 & \rightleftharpoons \text{HO-C}_6\text{H}_6 & \quad (1)
\end{align*}
\]

\[
\begin{align*}
\text{OH}+\text{C}_6\text{H}_5\text{CH}_3 & \rightleftharpoons \text{HO-C}_6\text{H}_5\text{CH}_3 & \quad (2a)
\end{align*}
\]

\[
\begin{align*}
\text{OH}+\text{C}_6\text{H}_5\text{CH}_3 & \rightarrow \text{H}_2\text{O}+\text{C}_6\text{H}_5\text{CH}_2 & \quad (2b)
\end{align*}
\]

We have recorded the ultraviolet absorption spectra of the OH-adducts of benzene and toluene produced in the reactions (1) and (2a). In the case of toluene, the adduct formation (2a) takes place in competition with the abstraction reaction (2b), giving rise to the formation of benzylic radicals which were also detected by ultraviolet spectroscopy. The reactions (1),(2a) and (2b) represent the most important reactions which initiate the tropospheric oxidation of aromatic molecules. Absolute bimolecular rate constants for the reactions (2a) and (2b) were derived from the observed formation kinetics of \(
\text{HO-C}_6\text{H}_5\text{CH}_3
\)
and \(
\text{C}_6\text{H}_5\text{CH}_2
\)
which are formed simultaneously with an overall rate constant of \(k'=k_{2a}+k_{2b}\), while the ratio of the rate constants \(k_{2a}/k_{2b}\) was calculated from the observed relative yields of the two channels (Markert and Pagsberg, 9.1).

The benzylic radical reacts with molecular oxygen, \(\text{C}_6\text{H}_6\text{CH}_3+\text{O}_2 \rightarrow \text{C}_6\text{H}_5\text{CH}_2\text{O}_2\), and we have recorded the ultraviolet absorption spectrum of peroxyradical, which has an absorption maximum at 240 nm. The OH-adducts produced in the reactions (1) and (2a) react much more slowly with molecular oxygen. Work is in progress to identify the products and reaction mechanisms of these two reactions. Our experimental studies of reaction mechanisms, involved in the tropospheric oxidation of aromatic molecules continue within a new CEC joint project, "CYTROXA" which will be carried out during 1994-96, in collaboration with the laboratories mentioned above.

**Infrared Spectroscopy of Reaction Intermediates**

We have developed a powerful new experimental technique based on pulse radiolysis, combined with infrared diode laser spectroscopy. Free radicals are produced by irradiation of a gas mixture with a short pulse of high energy electrons. Detection of free radicals and other reaction intermediates is accomplished by monitoring the transient infrared absorption signals corresponding to selected vibrational-rotational transitions. Using tunable infrared diode lasers, we obtain a very high spectral resolution combined with a time resolution of about \(10^{-6}\) sec. This new experimental technique was employed in spectrokinetic studies of methyl radicals, produced and consumed in those elementary reactions of interest in atmospheric chemistry and combustion processes (Sillsten et al., 9.1), (Jodkowski et al., 9.1). Infrared spectroscopy of free radicals offers a number of advantages when compared with ultraviolet spectroscopy. Employing high resolution infrared spectroscopy, it is possible to avoid an overlap between the spectra of different species, a major problem with UV-spectroscopy, as many radicals have absorption bands in the same spectral region.

Another advantage of infrared spectroscopy is that the observed decay kinetics of various free radical species can be compared directly with the formation kinetics of stable products. This technique will be employed in studies of carbonyl
compounds, which are the expected products of "ring-opening reactions" occurring during the oxidation of aromatic hydrocarbons.

**Chemistry of Nitrogen Oxides**

Emission of nitrogen oxides from power plants and automobiles is recognized as one of the most serious sources of air pollution, giving rise to "acid rain" and severe air pollution problems, such as smog-formation. The formation of nitrogen oxide during combustion processes has been the subject of intensive studies for more than fifty years. This research has resulted in the development of efficient processes for the removal of nitrogen oxides in stack gases from power plants. A fairly high efficiency of NO, removal was obtained with the "Thermal De-NO, process" invented by R.K. Lyon in 1975. This process has been studied extensively because of its practical importance. Later a number of other methods were developed, including selective catalytic reduction (SCR) and RAPRENO. NO, chemistry is a very complex and interesting field of fundamental research, and previously we have investigated one of the key reactions in the Thermal De-NO, process, i.e. NH, + NO → N, + H,0. More recently, we have studied some interesting elementary reactions which may eventually lead to the development of a new De-NO, process based on the following reaction sequence, "NO → HONO → NH,NO, → N," showing the important intermediates in the conversion of NO to N,. Using infrared diode laser spectroscopy, we studied the reversible gas phase reaction HONO + NH, ⇌ NH,NO, for which we determined the equilibrium constant and the rates of the forward and reverse reactions.

While the subsequent reaction, NH,NO, → N, + 2 H,0 is strongly exothermic, we observed that the reaction is very slow at low temperatures, indicating a fairly high activation energy. Work is in progress to determine the rate of this reaction at elevated temperatures where we expect to observe a strong increase in the rate coefficient.

The preliminary work has been supported by a grant from the Ministry of Energy.

### 2.3 The Liquid Phase

The equilibrium between sulphate (SO,;) and nitrate (NO,) radicals in an aqueous phase is of importance to the atmospheric chemistry especially during volcanic activities when sulphuric acid aerosols are discharged. These aerosols may remove atmospheric NO, compounds, converting them into nitric acid.

Rate constants for the following equilibria were determined by pulse radiolysis:

\[
\begin{align*}
\text{SO}_4^{2-} + \text{HNO}_3 & \rightarrow \text{HSO}_4^- + \text{NO}_3^- (1) \\
& k_{1f} = (2.7 \pm 0.5) \times 10^8 \text{ M}^{-1}\text{s}^{-1} \\
& k_{1r} = (5.6 \pm 1.0) \times 10^6 \text{ M}^{-1}\text{s}^{-1} \\
\text{SO}_4^{2-} + \text{NO}_3^- & \rightarrow \text{SO}_2^- + \text{NO}_3^- (2) \\
& k_{2f} = (5.0 \pm 2.0) \times 10^4 \text{ M}^{-1}\text{s}^{-1} \\
& k_{2r} = (1.0 \pm 0.2) \times 10^5 \text{ M}^{-1}\text{s}^{-1}
\end{align*}
\]

The extrapolation of the latter rates to zero ionic strength condition yields an approximation of the reduction potential of the NO, /NO, couple \(E_{0} = 2.45 \pm 0.05\, \text{V} \) (Logan et al., 9.1).

Nitrogen monoxide is a very important molecule in atmospheric chemistry. Only in recent years, has its biological importance, in fields like neuroscience, physiology and immunology, been recognized. While gas phase chemistry of NO is well studied and understood, only rudiments of its aqueous chemistry are established. NO is the smallest stable free radical and therefore shows an interesting and diversified reactivity. Its reactions with other free radicals, as well as products of its free radical oxidation in aqueous phase i.e. peroxonitric and peroxonitrous, were studied. Using our high pressure pulse radiolysis technique, the formation and properties of peroxonitrous and peroxonitric acids were also examined.

Peroxonitrous acid/peroxynitrite ONOOH/ ONOO" were formed by reaction of OH and NO, radicals in two different chemical systems (A) N,0-saturated nitrite and (B) Ar-saturated nitrate. The rate constant was determined to be \(k(\text{OH} + \text{NO}_2) = (4.5 \pm 1.0) \times 10^6 \text{ M}^{-1}\text{s}^{-1}\). The absorption spectrum of peroxonitrous acid was measured and the extinction coefficient at the maximum 240 nm was found to be \(\epsilon_{240}(\text{ONOOH}) = 770 \pm 50 \, \text{M}^{-1}\text{cm}^{-1}\) on the basis of known ONOO" spectrum. The \(p_{K_a}(\text{ONOOH}) = 6.5 \pm 0.1\)
was found from the absorption measurement. Peroxynitrous acid decays by first-order isomerisation into nitric acid HNO₃ with the observed rate constant expressed by

\[ k_{obs} = k_{iso} (1 + K_1 [H^+] ) \] with \( k_{iso} = 1.0 \pm 0.2 \text{ s}^{-1} \) and \( K_1 = (1.0 \pm 0.2) \times 10^{-7} \text{ M} \).

The experimental results, accessible in the studied system, represent complex kinetics. Computer modelling of the experimental data was applied using CHEVISIMCL, a programme developed at Riso for numerical simulation of chemical reactions. The following rate constants essential for the modelling were determined:

- \( k_{OH + NO_2} = (4.5 \pm 1.0) \times 10^9 \text{ M}^{-1} \text{s}^{-1} \)
- \( k_{HO_3 + NO_2} = (3.0 \pm 1.0) \times 10^9 \text{ M}^{-1} \text{s}^{-1} \)
- \( k_{H + NO_2} = (1.0 \pm 0.3) \times 10^7 \text{ M}^{-1} \text{s}^{-1} \)
- \( k_{H + NO_2} = (1.0 \pm 0.2) \times 10^7 \text{ M}^{-1} \text{s}^{-1} \)
- \( k_{NO_2^- \rightarrow NO_2} = (5.6 \pm 0.5) \times 10^8 \text{ s}^{-1} \)
- \( k_{HNO_2 \rightarrow NO_2} = (2.0 \pm 0.5) \times 10^5 \text{ s}^{-1} \)
- \( k_{H_2NO_2 \rightarrow NO_2} = (7.0 \pm 0.2) \times 10^5 \text{ s}^{-1} \)

(Engager and Sehested, 9.1a).

The same technique as above was applied to study the formation and decay of atmospherically important peroxy nitric acid. The mixture of peroxy nitric acid and peroxy nitrate O₃NOOH/O₃NOO was formed by the reaction of peroxide radical HO₂/O₂ with nitrogen dioxide NO₂ and the formation-rate constant was determined to:

\[ k_{OH + NO_3} = (1.8 \pm 0.2) \times 10^7 \text{ M}^{-1} \text{s}^{-1} \]
\[ k_{O_2 + NO_2} = (4.5 \pm 1.0) \times 10^9 \text{ M}^{-1} \text{s}^{-1} \]

An absorption spectrum of both formed species was measured, giving maximum extinction coefficients of \( \epsilon_{280}^{OH} = 400 \pm 30 \text{ M}^{-1} \text{cm}^{-1} \)
\( \epsilon_{280}^{O_3NOOH} = 1650 \pm 100 \text{ M}^{-1} \text{cm}^{-1} \)

A \( pK_a(O_3NOOH) = 5.85 \pm 0.10 \) was determined from the pH-dependent absorbance of the anionic form at 290 nm in accordance with the less accurate \( pK_a(O_3NOOH) = 5.65 \pm 0.20 \) obtained from the decay kinetics. The peroxy nitric acid/peroxy nitrate decay by unimolecular elimination of \( O_2 \) forming nitrous acid/nitrite HNO₂/NO₂. This process is pH-dependent and its rate is expressed by \( k_{obs} = k_3 + k_6 (K_2 [H^+] ) \) where \( k_3(O_3NOOH) = (7.0 \pm 2.0) \times 10^{-13} \text{ s}^{-1} \) and \( k_6(O_3NOO^-) = 1.0 \pm 0.2 \text{ s}^{-1} \) are the rate constants for the decay of the respective forms. Peroxynitric acid was found to oxidize nitrous acid forming nitric acid with the rate constant \( k_{O_3NOOH + HNO_2} = 12 \pm 2 \text{ M}^{-1} \text{s}^{-1} \) (Engager and Sehested, 9.1b).

A study on the exchange between water and the OH radical was performed by mass-spectrometric measurements. \( O_3NO \) and \( BrO_2 \) solutions enriched in \( H_2^{18}O \) were irradiated with 2-4 µs pulses of 10 Mev electrons at different temperatures. Based on isotopic distribution of the oxygen developed from \( H_2O_2 \) formed in the irradiated sample, the degree of oxygen atom exchange in the reaction \( O^- + H_2O \rightarrow OH^- + OH \)
\( 0 \leq \alpha < 0.25 \) was found and the rate constant of \( k_{OH + H_2^16O \rightarrow OH^- + H_2O} = (62 \pm 5) \text{ s}^{-1} \). The work was carried out in collaboration with Aarhus University (Klanning and Sehested, unpublished).

By using high pressure pulse radiolysis technique, the rate of reaction \( OH^- + OH^- \rightarrow O^- + H_2O \) was measured directly for the first time. The back reaction \( O^- + H_2O \) was measured in competition with \( O^- + O_2 \rightarrow O_3^- \) observing the kinetic formation of \( O_3^- \). The same reactions were studied in heavy water in cooperation with Saclay, France (Hickel and Sehested, 9.5).

The work on high-temperature (up to 300°C), high-pressure (up to 15 MPa) aqueous radical chemistry was carried out in collaboration with Studsvik Material AB, Sweden. The following rate constants (at 20°C) and activation energies were determined for reactions of hydrated electrons:

\( k(e^- + H) = 2.4 \times 10^{10} \text{ M}^{-1} \text{s}^{-1} \), \( E_a = 14.0 \text{ kJ mol}^{-1} \)
\( k(e^- + OH) = 3.1 \times 10^{10} \text{ M}^{-1} \text{s}^{-1} \), \( E_a = 14.7 \text{ kJ mol}^{-1} \)
\( k(e^- + H_2O_2) = 1.2 \times 10^{10} \text{ M}^{-1} \text{s}^{-1} \), \( E_a = 15.6 \text{ kJ mol}^{-1} \)
\( k(e^- + H_2PO_4^-) = 1.5 \times 10^9 \text{ M}^{-1} \text{s}^{-1} \), \( E_a = 7.4 \text{ kJ mol}^{-1} \)

(Christensen et al., 10). The study of reaction of Fe(II) ions with hydrogen peroxide resulted in

\( k(20°C) = (52 \pm 2) \text{ M}^{-1} \text{s}^{-1} \), and
\( k(300°C) = (2.5 \pm 0.4) \times 10^8 \text{ M}^{-1} \text{s}^{-1} \) with
\( E_a = (42 \pm 1) \text{ kJ mol}^{-1} \)

(Christensen et al., 9.1).
The radicals formed from pyridine, 3-methylpyridine, 3,5-dimethylpyridine, 2,6-dimethylpyridine and 2,4,6-trimethylpyridine by attack of H, e., OH and O' in aqueous solutions were investigated by pulse radiolysis in the pH-range 1-13. The UV-vis absorption spectra, as well as the formation and decay kinetics for the protonated and unprotonated forms of the methylypyridine radicals studied, are presented. The pK\textsubscript{a} values for the OH adducts were also determined in collaboration with the University of Vienna, Austria (Solar et al., 9.1).

The oxidation of chromium(III) by hydroxyl radical in alkaline solution was studied by a stopped-flow method and pre-mix pulse radiolysis. The pK\textsubscript{a} for the equilibrium Cr\textsuperscript{3+}(H\textsubscript{2}O\textsubscript{4})(OH)\textsubscript{2}+HM\textsuperscript{+} was determined to be 12.8 at 25 °C. The dimerization of the two monomeric forms was studied in alkaline solutions using the stopped-flow method:

\[
k_1(Cr\textsuperscript{3+}(H\textsubscript{2}O\textsubscript{4})(OH)\textsubscript{2}+Cr\textsuperscript{3+}(H\textsubscript{2}O\textsubscript{4})(OH)\textsubscript{2}) = 2.5 \times 10^4 \text{ M}^{-1}\text{s}^{-1};
\]

\[
k_2(Cr\textsuperscript{3+}(H\textsubscript{2}O\textsubscript{4})(OH)\textsubscript{2}+Cr\textsuperscript{3+}(H\textsubscript{2}O\textsubscript{4})(OH)\textsubscript{2}) = 3.8 \times 10^3 \text{ M}^{-1}\text{s}^{-1};
\]

\[
k_3(Cr\textsuperscript{3+}(H\textsubscript{2}O\textsubscript{4})(OH)\textsubscript{2}+Cr\textsuperscript{3+}(H\textsubscript{2}O\textsubscript{4})(OH)\textsubscript{2}) = 124.0 \text{ M}^{-1}\text{s}^{-1}.
\]

The absorption spectra of the monomeric species are also reported. The oxidation of chromium monomer Cr\textsuperscript{3+} and dimer (Cr\textsubscript{2})\textsuperscript{3+} by hydroxyl radicals was studied by the pre-mix pulse radiolysis technique. The kinetic parameters were established for: a) Cr\textsuperscript{3+} monomer formation; b) formation of mixed (Cr\textsubscript{2})\textsuperscript{3+} dimer; c) dissociation of (Cr\textsubscript{2})\textsuperscript{3+} dimer and d) formation of polymers e.g. [Cr(VI)(OCr(VI))\textsubscript{n}]. Furthermore, a second-order reaction between two Cr\textsuperscript{3+} monomers, to yield a species which may be either a (Cr\textsubscript{2})\textsuperscript{3+} or (Cr\textsubscript{2})\textsuperscript{3+} mixed valence dimer, was observed. The corresponding spectra, in both the UV and visible range were determined carried out in collaboration with Professor B.H.J. Bielski, Brookhaven National Laboratory (Zhongwei Zhao et al., 10).

### 2.4 Field Atmospheric Chemistry

#### Particulate Organic Nitrates

Concurrent measurements of NO\textsubscript{2} and the individual nitrogen species (NO, NO\textsubscript{2}, HNO\textsubscript{3}, PAN, PPN and inorganic nitrate) in background areas have implied observation of an unidentified fraction being at least 25% of the total NO\textsubscript{2}. Formation of significant amounts of particulate organic nitrates was observed in smog chamber experiments, e.g. by photooxidation of isoprene, \beta-pinene and 1-octene.

A simple FTIR method has been developed to determine the total amount of particulate organic nitrates in extracts of filter samples. Fig. 2.4.1 shows a FTIR spectrum of a sample. Eleven 24 h samples, from the period 23/3 - 22/6, 1993 were analysed. This appears to be the first European measurements.

The average amount of particulate organic nitrates was 15±7 ngN/m\textsuperscript{3}, and it made up 0.2% of the total NO\textsubscript{2}. The air pollution of odd nitrogen species was dominated by NO\textsubscript{2}, NO (0.97±0.45 μgN/m\textsuperscript{3}) and particulate inorganic nitrate (0.92±0.55 μgN/m\textsuperscript{3}). The dominance of NO\textsubscript{2} and NO demonstrates the influence of local sources, indicating a moderate conversion to NO\textsubscript{2} species. Photochemical air pollution was moderate, and the average level of ozone was 37±3 ppb.

The levels of particulate organic nitrates showed significant positive correlations with the levels of other atmospheric products, nitric acid (r = 0.76), formic acid (r = 0.73) and acetic acid (r = 0.73). The local ozone levels are influenced by the local NO levels. This might be the cause of the weak correlation (r = 0.45) between particulate organic nitrates and ozone. The significant positive correlation (r = 0.65) with SO\textsubscript{2} suggests that continental long-range transport, in association with atmospheric reactions, is the major source of particulate organic nitrates. Conversely, the particulate organic nitrates levels appear to be very low in clean marine air, as demonstrated by a negative significant correlation with methane sulphonic acid (r = -0.91).
Fig. 2.4.1. The FTIR spectra of the extract of a filter sample. The peaks at 1640.4 and 1633.7 cm⁻¹ are both assigned as organic nitrates. The identity of the shoulder is unknown. The area between the curve and the drawn baseline has been used for the determination of the amount of organic nitrates in the sample.

In addition to this, the correlation with gas NOₓ (r = 0.62) indicates that the measured particulate organic nitrates are nitrogen compounds formed in the atmosphere by secondary chemical reactions. This is also confirmed by a comparison of two episodes:

The first was observed at 08:00 a.m. on 26-27 April, 1993. It was characterized by sunny weather and warm continental air from the south-east with an average wind-speed on 4.7±0.6 m/s and a max. temperature of 22°C. The elevated SO₂ (3.9 ppb) and ozone levels (44 ppb) confirmed the transport of photochemical polluted air from the south-east. It seems that local sources also influenced the air pollution situation, as suggested by the NO (10%) and the gas NOₓ proportion (92%) of NOₓ. The content of particulate organic nitrate was 43 ngN/m³ (0.5%), and the levels of the other atmospheric products, formic (4.3 μg/m³) and acetic acid (5.6 μg/m³), were also elevated, while the marine air tracer, methane sulphonic acid, could not be detected.

The second episode was observed at 08:00 a.m. on 21-22 June, 1993. It was characterized by cloudy weather, cold marine air coming from the northwest with inversion seen for half of the period, an average wind-speed of 6.0±0.5 m/s and a max. temperature of 15°C. The level of the marine air tracer, methane sulphonic acid (0.18 μg/m³), was elevated, while the concentrations of other air pollutants were low, e.g. formic (0.7 μg/m³) and acetic acid (0.7 μg/m³). The concentration of particulate organic nitrates was 0.5 ngN/m³ and made up only 0.03% of total NOₓ.

The results show that the formation rate ratio, between particulate organic nitrates and NOₓ, is low in conditions with relatively high NOₓ levels. They also reveal a dominance of anthropogenic over biogenic hydrocarbons and subsequently, a dominance of alkanes over alkenes. An investigation to see if the formation rate ratio might be different in conditions with low NOₓ levels and a dominance of biogenic hydrocarbons towards anthropogenic hydrocarbons should be carried out.
Peroxyacetyl Nitrates

The first identification in European air of peroxyacetyl nitrate, peroxymethacryloyl nitrate (MPAN, CH$_2$$\cdot$C(CH$_3$)C(O)OONO$_2$), has been made. MPAN is probably an oxidation product of the biogenic hydrocarbon, isoprene. However, it is present in levels below 0.1 ppb, close to the detection limit, in eight out of several thousand samples. It has been checked that the MPAN standard does not self oxidize to the peroxyacetyl nitrate of pyruvic acid. The dominant peroxyacetyl nitrates in ambient air are peroxyacetyl nitrate (PAN) and peroxypropionyl nitrate (PPN). The levels of PPN were approximately 12% of those of PAN:

$$PPN = (0.117 \pm 0.002) \times PAN + (0.023 \pm 0.016).$$

This, and the previous work was performed within DCAR under the leadership of the Section of Chemical Reactivity in collaboration with the National Environmental Research Institute as the Danish contribution to EUROTRAC-TOR. The investigation was supported by the Danish Environmental Research Programme (SMP) within the Centre of Air Pollution Processes and Models. The results have been presented at the EUROTRAC-TOR-workshop and at the National SMP meeting (Nielsen et al., 9.5).

Diurnal Variation of Street Air Pollution with PAH

Air pollution by polycyclic organic matter (POM), including polycyclic aromatic hydrocarbons (PAH), has been investigated for many years, one reason being that several of the compounds are carcinogenic.

Within DCAR, the Section of Chemical Reactivity is conducting a traffic PAH project. The project is supported by the National Environmental Protection Agency. The project provides PAH data from different locations in the initial phase of the introduction of catalyst-equipped cars. Another aim of the project is to determine the total, as well as the individual, contributions from gasoline- and diesel-driven engines.

Fig. 2.4.2 shows the diurnal variation of some of the PAH in ambient air in a busy street in central Copenhagen. Cyclopentenolc)pyrene (CedP), benzo(ghi)perylene (BghiP) and coronene (Cor) are known to be good indicators of traffic pollution. The major source of the PAH pollution is the traffic. This is demonstrated by the diurnal variation. The PAH levels are highest in the morning and in the late afternoon, and lowest during the night and at midday. This same pattern is shown by the traffic intensity.

Fig. 2.4.2. The diurnal variation of PAH (ng/m$^3$) in a busy street in Central Copenhagen. Identity of the PAH: BbKF Benzo(b) + benzo(j) + benzo(k)fluoranthene, CedP cyclopenteno(c)pyrene, BghiP benzo(ghi)perylene, Cor coronene, BeP benzo(e)pyrene, and BaP benzo(a)pyrene.

Riso-R-744(EN)
2.5 Effects of Air Pollution of Plants

Forest Decline and Ammonia

The forest decline of "rude rodgraner" (red Norway spruce) is still a very serious problem on nutrient-poor sandy soils in plantations, particularly in Jutland. In some areas it has been necessary to cut more than 10% of the trees prematurely, at a time when prices are very low. Among the many hypotheses, such as ozone injury, salt damage, low K, low Mg, low P, and combined stresses, the following two are considered most likely as possible explanations: mild winter damage and ammonium overfertilization from the air. Norway spruce grow where the mean January temperature is below -2°C, in areas with little wind: it does not do well under oceanic conditions, for example in England. The ammonium hypothesis postulates that the trees are overfertilized with atmospheric ammonium derived from agricultural animal wastes. Ammonium deposition from the air may be 40 kg per hectare in certain areas of Jutland.

In pot experiments we are overfertilizing small Norway spruce over several seasons with ammonium nitrate and urea, and are investigating injury symptoms, growth and free amino acid composition. We have found that heavily N-fertilized trees accumulate very large amounts of the free amino acids arginine, ornithine and lysine (up to 2% of the needle dry weight). This amino acid accumulation however, is not specific for N-overfertilization; similar accumulation occurs with P deficiency, and perhaps, to a much smaller extent, with K deficiency.

Lightly N-fertilized trees grow very well, but heavily fertilized trees grow less well, and on the latter, by the second year, the needles turn brown and drop off. These symptoms are probably not exactly those of "red Norway spruce" where the needles redden from the shoot tip, before they turn brown and fall off. We hope to use amino acid measurements in simple field or kitchen-type modifications to find out if Danish spruce plantations suffer from N-overfertilization or any other nutrient imbalance.

2.6 Transport of Pollutants from the Atmosphere to Ecosystems

Riso's Integrated Environmental Project (RIMI) provided, in 1990, the base for a vigorous involvement in the study of airborne pollutants and their interaction with ecosystems. These studies were strongly supported by the establishment of a field station and the acquisition of equipment funded by Riso and the National Science Research Foundation. This enabled Riso scientists to join large national and international research programmes.

An important milestone in the research is the ability to measure fluxes by the eddy correlation technique. This method is built upon fast simultaneous measurements (~10 Hz) of the vertical wind speed and the concentration of the pollutant in question. We are now able to measure fluxes of nitrogen oxides (NO and NO₂), ozone (O₃) and carbon dioxide (CO₂).

Measurements using this technique are made jointly by the Environmental Science and Technology Department and the Meteorology and Wind Energy Department in Riso. During 1993, three field trials were carried out. Two of these were in a Norway spruce plantation in Ulborg (western Jutland) as part of the Danish Strategic Environmental Programme, and the third was a field campaign in The Netherlands as part of an EEC project with TNO in Delft and UMIST in Manchester.

To illustrate the kind of results obtained from these studies, data from two days of measurements in Ulborg were selected for presentation. During this trial only O₃ was measured. The concentration of O₃ varied between 20 and 40 ppb during the two days, showing only a weak diurnal pattern (Fig. 2.6.1), which is probably due to very low concentrations of NO and other chemical constituents that may react with O₃. A maximum flux of 0.4 μg m⁻² s⁻¹ was found and only on the second day showed a diurnal pattern in the flux. The results from two different analyses were very similar. The deposition velocities (Fig. 2.6.1 and Table 2.6.1) ranged from 0 to 7 mm s⁻¹ with the highest values found just after sunrise.
Fig. 2.6.1. Concentrations, fluxes and deposition velocities of $O_3$ at Ulborg, 22 - 23 July, 1992.

Fig. 2.6.2. Concentrations, fluxes and deposition velocities of $O_3$ and $NO_2$ at Ulborg, 10 - 11 February, 1993.
The concentrations of \( O_3 \), during the February 1993 experiment, showed very little variation except on the 10-2 and 11-2 when it dropped from 25 ppb to 10 or less. A corresponding rise in \( NO_2 \) concentrations from 1-2 ppb to 10-30 ppb was observed. This can probably be regarded as a pollution episode, due to long-range transport, and the results from these dates were therefore selected for presentation. The fluxes and deposition velocities (Fig. 2.6.2 and Table 2.6.1) show no diurnal pattern. The temperature was very low during this period and strongly reduced stomatal activity could be expected. This might explain the absence of a diurnal pattern. On the other hand, the deposition velocities were high compared to the summer experiments, so it has been suggested that chemical transformations, especially reactions on the needle surfaces, might be responsible for the deposition.

Table 2.6.1. Average day and night values of deposition velocity\( (V_d \text{ mm s}^{-1}) \) from Ulbjerg (Norway spruce). Day (summer) = 07:00 - 19:00, day (winter) = 06:00 - 18:00.

<table>
<thead>
<tr>
<th>July 92</th>
<th>February 93</th>
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<tr>
<td>Day</td>
<td>Night</td>
</tr>
<tr>
<td>3.0</td>
<td>2.9</td>
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3 Plant Genetics and Resistance Biology

Methods for identification, characterization and quantification of genetic variability are essential to many basic and applied research programmes in the agricultural and environmental sciences. Exploitation of genetic variability, related to traits of economic and environmental importance in crop improvement, can be greatly facilitated by the use of marker-assisted selection. In particular, the new methods for identifying molecular markers may help in understanding the genetic basis of many agronomical traits which are of a quantitative nature and governed by the interaction of many Quantitative Trait Loci (QTLs) impossible to assay independently. An understanding of the regulation and expression of genes and the characterization of the gene products, the proteins, is important for developing plants with improved characteristics, e.g., a better quality of grain proteins or a higher level of resistance to pathogens.

An understanding of the genetic variability under various environmental conditions and the establishment of genetic markers, construction of genetic-physical chromosome maps, and analysis of genetic diversity in populations. With these tools, the mechanisms of plant-pathogen interactions are studied with the aim of describing those gene products which are important for resistance or virulence. Further, the evolutionary processes imposed by interactions between crop plants and wild plant species or pathogens are being studied.

3.1 Gene and Chromosome Mapping

Linkage Map of the Barley Genome for Qualitative and Quantitative Traits

We are trying to identify and map genes that control agriculturally important traits in barley. This helps to obtain a better understanding of the genetics controlling the different characters and also supports the plant breeders in the selection of new promising genotypes.

Traits which are easily scored, have already been utilized and fixed in released varieties. The present problem is to deal with traits that are difficult to score and quantify due to lack of knowledge about these loci involved.

In order to map QTLs, it is important that polymorphism for many neutral qualitative genetic markers distributed evenly over the genome. With regard to molecular markers, it has been possible to increase the density of neutral markers on linkage maps by orders of magnitude morphological markers. For most practical applications, map saturation is not necessary, but a substantial effort is required to obtain an even distribution of markers across the genome, when carrying out genetic analysis of QTLs.

We are mapping QTLs for various agronomical traits in the barley genome by using progenies from chromosome doubled haploid lines (DH-lines) by means of RFLP (Restriction Fragment Length Polymorphism) and RAPD (Random Amplified Polymorphic DNA) markers. We have constructed maps on the basis of two crosses 'Vogelsanger Gold' × 'Alf' and 'Vogelsanger Gold' × 'Tystofte Prentke' with 80 and 85 markers respectively. Special attention has recently been given to RAPD markers. The RAPD technique has several advantages over RFLP: it is rapid, it requires only nanogram of DNA, and
it exploits the use of universal DNA primers. As
RAPD markers have had a reputation for being
unstable, we carried out a detailed analysis of
them in comparison with conventional and RFLP
markers. We found that RAPD technique gave
reproducible results and displayed a relatively
high level of polymorphism in the varieties
analyzed. Some of the RAPD markers mapped
to the same chromosomal position indicate that
certain regions of the genome favor the RAPD
reaction. Otherwise, the RAPD markers appear
to be randomly distributed throughout the
genome and cover regions that were poorly
covered with RFLP markers. Only three RAPD
were mapped in the 'Vogelsanger Gold' ×
'Tysiiske Prentice' cross, but the amplified
products had the same sizes and mapped to the
same loci as that of the 'Vogelsanger Gold' ×
'Alt' cross. This suggests that the RAPD
markers can be used in different plant material,
which is important if they are to be used in plant
breeding.

By studying deviations from expected segre­
gation ratios, we were able to verify the reported
location of one spring-habit locus (Sh2) on chro­
nosome 7 and to suggest the chromosomal position of another spring-habit locus (Sh3) previously
associated with chromosome 5. Furthermore,
the map positions of deviations from expected segregation ratios on chromosome 2
and 3 coincided with the positions of loci re­
ported to affect regeneration ability, possibly
explaining the deviating segregation ratios.

The final estimation and evaluation for the
QTL in the two crosses awaits the final field
data to complete the analysis.

In cooperation with Danish barley breeders,
DH-lines from crosses between modern spring
and winter barley varieties were carried out with
the aim of identifying RAPD markers mapping
QTLs for important agronomical traits. RFLP
markers, which facilitate correlation between
new and 'old' barley maps, will also be
included. Chromosome 7 already has good
coverage with RAPD markers and mapping is
rapidly progressing.

**Cytogenetics of Barley and related Species**

Thorough information about the cytological
location of gene loci on the single chromosomes
of organisms is indispensable for preparing
physical linkage maps. These maps are needed
as a basis for the exploitation of some new
advanced breeding methods, e.g., transformation
(see 3.2). The information is presently best
obtained using *in situ* hybridization of DNA
probes to chromosomes. After having optimized
the technique, we used a 2-step *in situ*
hybridization technique including the rDNA probe pTA71
and a microsatellite sequence (GAA-), to localize
6 rDNA loci on the chromosomes of barley. One
minor rDNA locus, Nar-10, on the short arm of
chromosome 4 was previously unrecognized
(Pedersen and Linde-Laursen, 10). All 6 loci
conform suitable cytological markers. Congruence between patterns, produced from
probing with the microsatellite sequence and
Giemsa N-banding patterns, identified each
barley chromosome unequivocally.

The microsatellite GAA-sequence was further
probed in DNA from 7 wild Hordeum species,
where it was found to be present in high copy
numbers. In 6 of the 7 species, *in situ*
hybridization produced distinct banding patterns in the
chromosomes. The rDNA probe was hybridized to the somatic chromosomes of 6 Hordeum
species and 2 Elymus species. In these species, it
identified previously unrecognized ribosomal
sites.

Two genomic probes, one for a barley pro­
ein-Z locus (see 3.2), the other for the *Hordeum*
locus, provided additional cytological
markers. The first probe hybridized distally to
the short arm of chromosome 4 (4I), the second
distally to the short arm of chromosome 5 (11).
In a cooperative project with Professor Vershini
Novosibirsk, and Sergei Svitassev, Agricultural
University, Svalo, 5 repetitive DNA
probes of barley were shown to hybridize along
the full lengths of all 7 chromosomes.

Chromosome banding patterns produced
through Giemsa C- or N-banding, can be used to
identify species, chromosomes and chromosome
arms, and to study relationships between species.
Both techniques were applied to 2 alloetraploid
Elymus species. C-banding produced bands in
both parental genomes, the H genome from the
genus *Hordeum* (barley) and the S genome from
the genus *Pseudoroegneria*. In contrast, N­
banding produced bands in the H genome only,
thus elucidating the generic origin of the single
chromosomes. In spite of widely separated areas
of distribution, the karyotypes differed only by the substitution of a metacentric chromosome pair in one species, for a satellite pair in the other. In collaboration with Professor Roland von Bodman, M.S., Svalova, the tetraploid Hordeum eurynemum was subjected to C-banding in an attempt to elucidate its parentage. It may combine genomes of the genera Tausenatherum and Poatherum.

**In situ Hybridization to Tissue Preparations of Barley Embryos**

In barley, we have a well-established microspore culture system where the microspores undergo direct embryogenesis. The embryogenic route of microspore development was investigated by use of *in situ* hybridization to tissue preparations. Embryo-specific cDNA clones, provided by Dr. D. Bowles at The University of Leeds, were used as probes for the *in situ* studies. Dr. Bowles' group has isolated and characterized a number of genes from zygotic embryos and has studied the temporal and spatial regulation of these genes during embryogenesis in the plant. The cDNA probes, already in use on zygotic embryos, will also be used as markers for embryogenesis in microspore culture and to describe the developmental transformation process from microspore to embryo. This process has not yet been described for any plant species.

Application of the sensitive *in situ* hybridization technique to embryo-specific tissue preparations has been more difficult than expected. One hundred slides were investigated and five different embryo-specific probes were used without giving any specific hybridizations. Further investigations will concentrate on RNA isolation and Northern hybridization.

**Search of DNA-markers well suited for Genome-mapping in Norway Spruce**

The main aim of this project is the identification of QTL (Quantitative Trait Loci) during 1997. Several investigations were carried out to demonstrate the reliability of RAPD (Random Amplified Polymorphic DNA) as reproducible Mendelian markers expressed in different tissues, age classes and generations - both haploid and diploid. The seed endosperm in crosses represent the haploid megagametophyte.

To use this information for identification of QTLs, it is necessary to grow seedlings which correspond to the analyzed endosperms. Methods have been developed which allow DNA-extraction, subsequent PCR amplification and satisfactory recovery of the seedlings from the same seed.

As RAPD-markers show full dominance, a special procedure called pseudo-in-cross was demonstrated to work on a set of 20 parent clones. Among the large number of available RAPD-markers, our aim is to identify those, which in a particular cross between two parents, shun the test-cross situation. This option makes it possible to map diploid individuals if controlled crosses - full sibs - are available.

As a synopsis of these investigations, actual mapping of a set of 90 RAPD-hits expressed in 80 megagametophytes (1200 observations) is well under way. The PCR-reactions, and the subsequent electrophoresis and interpretation are nearly completed. The observations await data processing with current software for linkage analysis.

**Gene and Chromosome Mapping in Oilseed Rape**

Three different C-chromosomes from oilseed rape were mapped by the use of addition lines (2n = 21, AA + one C-chromosome). RAPD analysis revealed 10 markers on the C-chromosome in the W-line. 20 C-chromosome markers in the B-line and 12 C markers in the U-line. Recombination took place between the single C-chromosome present and chromosomes of the A-genome. Based on recombinants, a closer linkage has been established between agronomic characters for seed quality (genes for eruc acid and oil contents) and specific RAPD markers. Localization of RAPD markers to the chromosomes of oilseed rape is relevant also to project 3.3.
3.2 Proteins of Importance for Stress Resistance and Quality

Barley Peroxidases

Peroxidases are involved in many biological processes in plants. They are, 1) tissue-specific, developmentally regulated, or modulated by environmental stress factors, and 2) involved in the biosynthesis of the cell walls, in the regulation of the auxin level, and in response to microbial attack. Barley peroxidases are studied at the biochemical, physiological, genetic and molecular levels to delineate the biological function of the individual enzymes.

The sequence analyses of barley peroxidase genes show that some contain a C-terminal extension, which might be a targeting signal. Barley seed peroxidase (BP 2) was localized subcellularly by electron microscopy in collaboration with Professor A.B. Maunsbach, University of Aarhus. Gold-labelled BP 2 antibodies showed labelling over the proteinbodies in the vacuoles of scutellum cells (Theilade et al., 9.2). During germination it has been reported that lignin is synthesised in the embryo - a process requiring peroxidase activity (fig. 3.2.1).

The genes for the two barley peroxidases induced differentially by the powdery mildew fungus have been cloned from the cv 'Pallas'. Further analysis showed that in addition, one of these is induced by ethylene. Two genes encoding barley seed peroxidases have been cloned (Theilade, 11.1). A survey on peroxidases in plant genome mapping indicates that 9 peroxidases gene(-families) encode functional distinct enzymes (Rasmussen and Kerby, 9.2).

An international symposium was held from 10-14 July, 1993, in Elsinore for 180 scientist from 38 countries on "Plant Peroxidases: Biochemistry and Physiology". (Welinder et al., 9.2). The most recent results from this fast-growing research field was covered by 50 lectures on Protein Structure, Enzymology, Genes and Expression, Ascorbate Peroxidase, Cell Wall, Localization, Growth, Pathogens and Defence, Stress, Cell Culture and Heterologous Expression.

Quality of Barley Grain Protein

The storage protein (hordein) from barley grain is poor in the essential amino acids lysine and threonine. The nutritional quality of barley may be improved by an increased synthesis of proteins rich in lysine. Five high-lysine barley mutants and a control were yield-tested in a three-year field experiment (1992-94). The mutants are being analyzed for the contents of lysine, threonine and other amino acids. Protein Z is a barley seed storage protein with a favourable lysine content. We are aiming to modulate the barley seed protein composition, thus balancing the nutritional quality of the grains. This is done by increasing the amount of protein Z by two approaches. In one, we try to duplicate locus \( Paz4 \) by classical genetic methods. In the other, we isolate protein Z genes and attempt to increase the number of gene copies by genetic transformation. Both procedures imply that the
increased number of gene copies will lead to an increase in protein Z production and lysine content in the barley grain. The work is carried out in collaboration with Dr. B. Eggum, Foulum, and Dr. J. Hegård, Technical University of Denmark.

The new protein Zx gene (Rasmussen, 9.1) was RFLP mapped to barley chromosome 4. The Zx locus shows no linkage to the Z4 locus. The single copy protein Zx gene was also localized to chromosome 4 by means of in situ hybridization, using a 18,000 basepair Eco I restriction fragment carrying the gene (see 3.1). Thus the genetic and the physical chromosomal assignments are in agreement.

As a first step in a Ph.D. programme on the structure and function of barley serpins, a cDNA encoding Z4 was used to produce recombinant protein Z4 in Escherichia coli as a soluble and uncleaved protein (S.W. Dahl et al., 9.5). (Fig. 3.2.2).

Hybridization analysis shows that not only barley, but also wheat expresses members of the serpin superfamily. Northern and Southern blots of wheat RNA and DNA, respectively, show that wheat expresses genes related to the barley Zx and Z7 genes. This suggests that plant serpin families exist as a counterpart to mammalian superfamilies.

3.3 Gene Dispersal in Relation to Risk Assessment

Risk Assessment in Relation to Release of Genetically Modified Plants

Genetically modified plants in the agro-ecosystem pose possible environmental risks. The transgenic crop plants may hybridize with wild relatives and introduce the transgene into species in natural or agro-ecosystems. The transgenic crop plants may themselves invade the natural ecosystem and possibly outcompete established wild species. These risks are assessed in an interinstitutional research programme headed by Risø “Risk assessment in relation to release of genetically modified plants” under the Danish Biotechnology Research Programme. The other participants are The University of Aarhus (Docent Freddy B. Christiansen) and RVAU (Dr. Jesper Fredshavn). The industrial collaborators are Danisco (Denmark), Plant Genetic System (Belgium) and Montanto Europe (Belgium). The purpose of the programme is to gain knowledge about transgenes, plants and their recipient ecosystem and this is obtained by understanding fundamental mechanisms in plant population biology and molecular genetics. Oilseed rape and its related wild species Brassica campestris and B. juncea are used as model systems. The programme participates in the evaluation of applications for EU marketing and the national releases of transgenic plants. Risø's contribution to the programme focuses on gene dispersal.
Gene Dispersal from Oilseed Rape to Brassica campestris

In order to characterize the transfer of genetic material from oilseed rape to B. campestris, we have crossed a number of transgenic and non-transgenic oilseed rape varieties with cultivated and weedy B. campestris. The resulting hybrids were backcrossed to B. campestris. In the interspecific cross, we have obtained an average of 10.5 seed/pollination (382 pollinations). The backcross produced a much lower number of seed, the average being 0.4 seed/pollination (493 pollinations). The backcross plants are being characterized by suitable molecular markers (RAPDs).

Since oilseed rape is self-compatible and B. campestris is self-incompatible, we have performed experiments to determine whether interspecific hybrids can self-fertilize. This is of importance when estimating the potential spread of a transgene.

Preliminary results indicate that most hybrids can self, though they have a seed set after selfing, which is much lower than the seed set in the parental species, oilseed rape.

Previous data obtained in field experiments indicate that spontaneous hybrids between oilseed rape and weedy Danish B. campestris are easily obtained. The hybrids also backcrossed to the wild species in the field. Offspring from 16 backcross families were analyzed morphologically and by way of enzyme electrophoresis of phosphoglucomutase (PGM). The PGM locus (Pgmn-2C) localised on the C-genome of oilseed rape was transferred to half of the offspring plants. Some of the plants with the Pgmn-2C locus were morphologically similar to B. campestris and they produced seeds. Assessment of chromosome numbers of these plants are in progress.

A self maintained population with a mixture of B. napus and B. campestris has been under observation for two years. In the first year, spontaneous interspecific hybrids were produced in a frequency of 13% (B. campestris ♀) and 9% (B. napus ♂). This year, 7% spontaneous hybrids were detected by enzyme electrophoresis and chromosome counting. In the field, the hybrids produced an average of 3.3 seeds/pod, 122 seeds per plant. Analysis of morphology, chromosome number and isozyme profile from the first 50 backcross plants indicate that the hybrids predominantly backcrossed to B. napus.

A field trial with mixtures of transgenic oilseed rape (male sterile line and restorer line; both resistant to the herbicide Basta) and B. campestris was carried out. Seeds were harvested from both species and the interspecific hybridisation is being estimated by way of enzyme electrophoresis and PCR for specific transgenes. Expression of the Basta tolerance in the hybrids is also being analyzed.

In this field trial, we also investigated the possible backcrossing of interspecific hybrids to B. campestris. Transgenic male-sterile hybrids and B. campestris plants were mixed with oilseed rape. We have harvested seed on the hybrids and are now analyzing this material in order to detect backcrossing to B. campestris.

Transgenes, present in the hybrid B. napus x B. campestris, are subject to a different genetic environment from those present in oilseed rape. To test whether this could have an effect on the expression of a transgene, we have analyzed plants harbouring transgenes which encode male-sterility and Basta-resistance. We found no differences between transgenic oilseed rape and transgenic hybrids with regard to these phenotypes.

We have undertaken an investigation of wild Danish B. campestris populations, to detect any introgression of genes from oilseed rape. Using RAPD technique, we have identified promising markers by screening 18 accessions of oilseed rape. Currently, we are investigating the distribution of these markers in wild B. campestris populations.

Another line of work concerns the germination pattern of wild B. campestris, oilseed rape and their hybrids. This is studied in the field, as well as in the laboratory. Preliminary data indicate a large fraction of dormant seeds in wild B. campestris, in contrast to hybrids and oilseed rape where no dormancy is detected. This lack of dormancy could make the hybrids germinate at the wrong time of the year, resulting in a reduction of seed production and consequently in the interspecific gene flow between oilseed rape and wild B. campestris.
Gene Dispersal from Oilseed Rape to Brassica juncea

Results from a mixed population of oilseed rape and B. juncea showed that spontaneous interspecific hybrids were produced with the wild species as female.

Sixty-three plants from the backcross combination B. juncea x (B. juncea x B. napus) were analyzed to obtain knowledge about the gene transfer from oilseed rape to the B. juncea. A transgene, providing tolerance to the herbicide Roundup, and 25 RAPD markers were used as oilseed rape specific markers. All the markers were transferred to the backcross generation; 10 markers were transferred in a significantly higher frequency than expected (> > 50%).

3.4 The Barley/Powdery Mildew System

Cloning of the Entire Powdery Mildew Genome in Yeast Artificial Chromosomes

The powdery mildew fungus Erysiphe graminis f. sp. hordei is an obligate parasite on barley. Until now, it has not been possible to develop methods that allow cultivation of the fungus on artificial media. The production of fungal material for analytical purposes is thus dependant on cultivation on barley leaves, which is a time-consuming and laborious task. The representation of the fungal genome in yeast artificial chromosomes (YACs) is very desirable for the study of genome organization in this obligate fungal parasite and will also facilitate isolation of specific genes by chromosome walking.

We have succeeded in isolating high molecular weight fungal DNA from conidia by a combination of enzyme treatment and pulse field gel electrophoresis (PFGE). This DNA was cloned into YACs and a library consisting of about 1500 clones has been established. The clones were characterized using a highly repetitive element, which is distributed throughout the mildew genome. This sequence makes it possible to characterize individual YACs by fingerprint analysis. It should be possible to assemble YACs by matching overlapping banding patterns from individual YACs.

YAC clones were analyzed for the presence of RFLP markers and we have developed a way to analyze for the presence of particular RFLP polymorphic bands in individual YACs. Most of our RFLP markers represent multicopy sequences at different positions in the genome. This hampers identification of these specific YAC clones containing only a particular segregating RFLP band. Restriction digests of DNA from the parents, used to construct our map of the fungal genome, and pools of YACs were subjected to southern blot analysis. Hybridization with RFLP markers has clearly demonstrated that the method is working and we hope to identify YACs containing RFLP bands which are linked to avirulence genes.

Our linkage map of the fungal genome now contains 102 RFLP and RAPD markers and we can identify 5-6 linkage groups. However, no very close linkage to an avirulence gene has been found.

Isolation and Characterization of Stage Specific Genes of Erysiphe graminis hordei

The specificity of the interaction between E. g. hordei and barley is controlled by avirulence genes in the fungus and corresponding resistance genes in the plant. Cloning of genes controlling conidium germination, host cell penetration, nutrition uptake etc. will provide an insight into the general factors controlling the establishment and growth of E. g. hordei in the barley epidermal cell layer. The aim of this study is to clone genes expressed during germination of E. g. hordei conidia.

A subtractive hybridization strategy was used in an attempt to identify genes expressed within the first 6 hours of infection, where a germ tube is developed from the fungal conidium. mRNA was isolated and cDNA was prepared from ungerminated conidia and from conidia collected 6 hours after inoculation onto a glass surface. Subtractive hybridization between PCR-amplified cDNA from ungerminated and germinating conidia was performed in order to achieve enrichment for germination specific sequences. A cDNA-library, prepared from germinating conidia, was differentially screened with cDNA synthesized from ungerminated conidia and with the enriched cDNA from the subtractive hybridization experiment.
Two cDNAs, which are turned on during germination of the conidium, were identified. The corresponding genes are currently being isolated from a genomic cosmid library. Preliminary sequence analysis of the cDNAs has not shown extensive homologies to protein sequences in the database. The genomic clones will also be sequenced in order to get information about the gene structure of *E. g. hordei*.

**Genetics of Virulence in the Barley Powdery Mildew Fungus**

The incidence of powdery mildew on barley is determined genetically by the resistance genes in the host, as well as the virulence genes in the pathogen.

A compilation of data in the literature on virulence genes comprised 20 apparently different virulence loci, each with two alleles. The 81 recombination percentages that could be calculated showed that 9 loci were in 3 linkage groups with 4, 3 and 2 loci, respectively.

In a recent study (Jørgensen *et al.* 9.4), two isolates of the barley powdery mildew fungus were crossed and 165 progeny isolates were tested for virulence on 12 differential barley lines representing 8 sources of resistance important in European barley production. The progeny displayed segregation in 17 different virulence loci. Ten loci belong to one linkage group, and 3 were independently inherited.

There was evidence that the previously reported virulence loci *V(Ru3)*, *V(Mu2)*, *V(No3)* and *V(LG2)* are different. We cannot, however, be certain that locus *V(Mu2)* is not identical with locus *V(Ru3)* or with the previously established locus *Val3*. We found segregation for 4 new virulence loci tentatively designated *V(MC3)*, *V(MC4)*, *V(No4)* and *V(LG3)*. This suggests, according to the gene-for-gene system, the existence of 4 new resistance genes corresponding to the new virulence loci. The powdery mildew resistance genes and the *Mla* gene are different although they are found together in 'Lyallpur', 'Multan' and 'Long Glumes'.

In our experiment on the genetics of virulence, the offspring from crosses of different parent isolates are often tested on two sets of near-isogenic barley lines, 'Manchuria' and 'Pallas' lines, respectively. The two sets are experimental lines, which have been made near-isogenic by several generations of back-crossing to 'Manchuria' or 'Pallas' and selection for different powdery mildew resistance genes. From one cross with segregation for a very frequent virulence gene *Va8*, we have shown that the corresponding resistance gene *Mla8* is present in most of the 'Pallas' near-isogenic lines with resistance genes outside locus *Mla*.

**Mlo Aggressiveness of the Barley Powdery Mildew Fungus**

Until now, only one powdery mildew isolate aggressive on *Mlo*-resistant barley has been described. This isolate was selected for its high aggressiveness in the laboratory (E. Schwarzbach, Barley Genet. Newslett. 1979) and is characterized by giving an infection frequency 50 times higher than non-aggressive isolates (measured as colony number). A Japanese field isolate (Race I), was tested on different barley varieties and mutants carrying the resistance genes in locus *mlo* against barley powdery mildew. Instead of giving occasional colonies characteristic for *Mlo*-resistant barley, it seemed that Race I was aggressive on *Mlo*-lines without *Mla8* to which the isolate is avirulent. Our Race I isolate originates from the Japanese physiological Race I, which was the dominant physiological race in the early fifties in Japan. Race I and the laboratory-selected isolate were tested on two commercial varieties and four mutants (Totem, Atem, M66, MC20, SR1 and SR7), along with a non-aggressive isolate, in order to compare the quantitative level of aggressiveness between them. Race I had a level of aggressiveness larger or similar to the laboratory-selected isolate on *Mlo*-resistant barley not carrying *Mla8* (Lyngkjaer *et al.* 9.2). This result shows that the presence of powdery mildew aggressiveness on *Mlo*-resistant barley is not restricted to a laboratory-selected isolate, but can occur spontaneously in field-collected isolates.
Population Studies of the Barley Powdery Mildew Fungus

Barley varieties with Mlo-resistance have, during the last fifteen years, become more and more common and now cover more than one-third of the spring barley area in Europe. The selection pressure for developing aggressiveness in barley powdery mildew to Mlo-resistance has thereby increased. The level of Mlo-aggressiveness was obtained for 42 mildew isolates which were isolated from leaves of the Mlo-resistant barley variety 'Apex' in Foulum, summer 1992, as part of the National Virulence Survey (Dr. Mogens Hovmøller, National Institute of Plant Science). All isolates were non-aggressive. This is not surprising, because Mlo-resistance occasionally allows non-aggressive isolates to develop. The amount of non-aggressive mildew on barley Mlo-varieties depends on environmental factors, especially heat and water stress. A simple model, describing the development of Mlo-aggressiveness in populations of barley powdery mildew, shows that it will take many growing seasons before measurable amounts of Mlo-aggressive isolates in the population are seen.

Identification of Powdery Mildew Resistance Genes in Barley

During the year, we have attempted to identify powdery mildew resistance genes in a number of barley varieties and lines. This was done by inoculation experiments with selected powdery mildew isolates from the Riso stock collection. There were about 40 varieties and lines of barley from the research and breeding programme at the Agricultural University of Norway, Dr. A. Bjønstad, Norway, participated in this work. Thirty-five varieties and lines from the Cereal Research Institute, Kromeriz, the Czech Republic, were examined. Dr. A. Dreiseitl (Czech Republic) participated in the research. Also included, were a few barley lines from Drs. J. Frankoviack and B.J. Steffenson, USA, and some chromosome-doubled haploid lines supplied by Dr. D. Falk, Canada, from the North American Barley Genome Mapping Project. Part of Riso's material comprised ~ 20 relatively primitive barley lines from a co-operative project with Danish cereal breeders. Another part comprised a large number of barley lines with known powdery mildew resistance genes and some with tentatively designated genes. This enabled us to assign gene symbols Mla30 and Mla31 to genes in the barley lines 'Nigrata' and 'Turkey 290' and other symbols to genes tentatively designated in Japan. This was done in conjunction with the publication of a comprehensive review, 'Genetics of Powdery Mildew Resistance in Barley' (Jørgensen, 9.1), and the current update of 'Coordinators Report: Disease and Pest Resistance Genes'. (Jørgensen, 10).

Phenolic Compounds and Disease Resistance

The possible relationship between the content of putative phenolic compounds and the degree of partial resistance against powdery mildew was studied in collaboration with Dr. Bodil Sogaard, RVAU. (Doll et al., 10). Loss in grain yield, without fungicide treatment of the varieties studied, varied from 3% in the most resistant, to nearly 20% in those with little resistance.

The content of potential phenolic compounds was measured by high performance liquid chromatography (HPLC) using leaf extracts of plants at different stages. The chromatogram revealed about 15 compounds of which 9 were present in significant amounts in all 5 varieties at all 3 harvest times. A large quantitative variation in the amount of these components was found. One variety contained 4 elements that were absent or very low in the others (Fig. 3.4.1).

Some of the phenolic compounds were affected significantly by treatment with fungicide or by application of nitrogen fertiliser. These effects, however, were relatively small compared with the influence of plant age or the differences between varieties. No obvious similarities were seen between the degree of partial resistance or mildew attack and the content of some of the components studied.
3.5 Interaction between Crop Plants and Weeds

The influence of crop plant density on the competition with weeds was studied in winter wheat and winter barley in collaboration with Dr. Bodil Sogaard, RVAU. Cereals at normal-, half-, and quarter-plant density were grown with and without herbicide treatment, and in mixtures with 100 plants per m² of corn cockle. This weed is a large plant, and it produced almost as much biomass in pure stand per unit area as the cereals.

The amount of naturally occurring weeds was negligible, and herbicide treatment had no significant effect on cereal grain yield. Losses in grain yield in mixtures with corn cockle were strongly dependent on crop plant density. In barley, grain production was reduced 4, 6, and 9%, respectively, at normal, half, and quarter seeding rate; the corresponding values for wheat were 15, 20 and 27%. Hence, barley was more competitive than wheat against corn cockle. However, the barley variety used had about the same plant height as corn cockle, while the wheat variety was somewhat shorter than this weed.

3.6 Seeds for Educational Purposes

The Plant Biology Section offers seed samples of barley and other plant species for teachers in biology. The samples illustrate Mendelian gene-segregations and the effect of ionizing radiation on various plant species. In 1993, a total of 1401 individual "experiments" were distributed.
4 Plant Nutrition and Nutrient Cycling

The objective of the projects in this research area is to provide a better understanding of those biological and chemical processes in the soil-plant-atmosphere environment, which are important for plant nutrition. The processes must be utilized and managed in such a way that nutrient uptake by plants is optimized. This will lead to a reduced requirement for energy-consuming fertilizers and to a smaller loss of nutrients to the aquatic and atmospheric environments.

Mutualistic symbiosis between plant roots and microorganisms is directly involved in the nutrient uptake by plants. Nitrogen is provided by *Rhizobium* bacteria, fixing atmospheric nitrogen in symbiosis with legumes. The soil-plant transport of mineral nutrients, especially phosphorus, is mediated by arbuscular mycorrhizal fungi in symbiosis with most plant species.

The general soil microflora is of fundamental importance to the mineralization of nutrients contained in plant residues and in farmyard manure. Special attention is directed towards processes involved in the cycling of nitrogen, which is a major nutrient source for plants. There is, however, also a risk to the environment by nitrate leaching and losses as volatile nitrogen compounds. The study of these research topics will provide the basic information needed for increasing the economic and ecological sustainability of plant production.

4.1 Nitrogen Cycling in Agroecosystems

The aim of the present research is to improve the understanding of N-cycle processes in agroecosystems, to find the optimal amount of N to crop requirement and to minimize the environmentally unacceptable leaching of N from cultivated soils. Major emphasis is on the following: the mineralization-immobilization, plant uptake and losses of N after applying fertilizers, crop residues and animal manure to soils and on symbiotic N₂ fixation by legumes. Much of the work is based on ¹⁵N-methods for studying the N-transformation processes.

Nitrate Leaching from Soil amended with Pea Crop Residues

The management of crop residues after harvest may significantly influence the mineralization-immobilization turnover and losses of N by leaching and denitrification. The leaching of nitrate, derived from ¹⁵N-labelled pea residues and soil to below 45 cm in small lysimeters, was studied over a 2 to 3 year period after incorporation of residues in September (Jensen, 10). The peak flux of labelled nitrate-N from uncropped soil occurred in December. In two experiments during the first leaching period (September - April), 15% and 7% of the residue N was recovered as nitrate in the percolate; corresponding to 18% and 13% of total nitrate-N in the percolates, respectively. The difference observed in the leaching of labelled N in the two experiments was mainly due to a much higher drainage volume in the first experiment. Pea residue-N constituted 10-15% and 5% of total nitrate-N leached from unplanted soil in the second and third leaching periods, respectively.

Incorporating ground pea residues, reduced the total amount of nitrate leached by 15% during the first leaching period, indicating that the pea residue may be an important factor in controlling leaching losses. Ryegrass, established on lysimeters at the time of residue incorporation, reduced the total leaching of N in the first leaching period by 15%, but in the second and third leaching period, grass eliminated nitrate leaching completely.

Factors Affecting the Decomposition and N-mineralization of Crop Residues

Amending soil with pea crop residues (straw with 2.3% N) of particle size 10 mm (cut residue) caused a higher soil respiration than amending with residues of particle size < 3 mm (ground residue) during the first month of decomposition. Similarly, the net mineralization of residue N was higher with the cut than with the ground residues. Simultaneously, the net immobilization of non-labelled soil N during initial decomposition was higher in the treatment with
the ground residues. It is suggested, that the more intimate mixing of the ground residue with the soil, the higher the stabilization of organic residue $^15$N, so that a higher proportion of the residue carbon is available for microbial immobilization of N and C in the ground residue treatment (Jensen, 10c).

The rate of N-cycle processes in agroecosystems may be influenced by previous cropping and manuring strategy. The decomposition of organic matter and N-mineralization in soils, with and without $^{15}$N-labelled ryegrass material, was studied in soils from a long-term (100 years) field experiment (Askov B2-field). The previous manuring strategy (no manure, low FYM, high FYM and N-fertilizer) did not significantly influence the soil respiration or overall net mineralization of N after 90 days of incubation. However, the net mineralization of residue-N was significantly higher in the high FYM-treated soil than in that of the other treatments. It is suggested that the higher net mineralization of residue-N in the high FYM treatment is due to the physical protection capacity of this soil being occupied to a greater extent (Jensen et al., 10).

When crop residues of high C:N ratios decompose in soil, availability of N may limit the rate of decomposition. Similarly, availability of phosphorous (P) may limit the decomposition rate of plant materials. P supply (40 ppm) to a low P soil (Rorrendegård, 16 ppm NaHCO$_3$ extractable-P) did not influence the decomposition of wheat straw materials containing 0.3% and 0.7% N. The high-N straw decomposed more quickly than the low-N straw, but after 6 months of incubation the mineral-N content was found to be 2, 6, and 76 $\mu$g N g$^{-1}$ soil in the low-N straw, high-N straw and the unamended control soil, respectively.

**Cycling of N in Animal Manure**

The amount of animal manure-N, consisting of both organic and inorganic N pools, which becomes available to plants, is influenced by the net mineralization of N in the soil and the losses of N after application.

A dairy cattle slurry was applied to three soils with different textures, either by mixing into the top soil or by simulated injection. The slurry NH$_4$-N was labelled with $^{15}$N, and no significant gaseous losses of labelled-N occurred from the soils mixed with slurry. When mixing slurry into the topsoil, the net-immobilization of N was correlated with the clay content of the soil. Incorporation of slurry by simulated injection increased the plant accumulation of both total- and labelled-N compared to mixing the slurry with the soil, especially in the soil with the highest clay content. It was concluded, that the slurry application method and soil type influenced net mineralization of N to the same degree.

**4.2 Root-Microbe Symbioses**

The deliberate exploitation of symbiotic associations between plant roots and microorganisms can reduce the demand for fertilizers in a future sustainable agriculture. Research is carried out in order to understand the physiology and ecology of the legume-*Rhizobium* symbiosis and of arbuscular mycorrhizal fungi in symbiosis with their host plants.

**Symbiotic Nitrogen Fixation**

The ability of legumes to establish symbiosis with bacteria of the genus *Rhizobium* provides enhanced fitness for this group of plants. The symbiotic relation enables the plant to benefit from the ability of the bacteria to fix atmospheric nitrogen into ammonia, which may be utilized by the plant. In efficient symbioses, the bacteria can provide all of the plant's nitrogen requirements.

The symbiotic bacteria inhabit nodules, which are formed on the plant as a response to specific signals exchanged between the symbionts. The maintenance of an effective symbiosis is based on a continuous exchange of molecular signals and metabolites between the two. This continuous communication is controlled in the interface separating the organisms. The interface consists of the plant-derived tissue specific peribacteroid membrane (PBM) and a space of variable size between this membrane and the bacteroid, the so-called peribacteroid space (PBS). The presence of PBM is essential for the symbiosis and a lack of this barrier leads to a pathogen-related response by the plant towards the bacteroid. The crucial role of the interface in
controlling the function of the symbiosis, makes it an obvious target for research into extending our understanding of close associations between organisms in general. The legume-
*Rhizobium*
symbiosis performs a perfect model for these studies, as the microorganism is enclosed in the cytoplasm of the plant cell like an organelle and the microorganism can, therefore, be isolated from the nodule tissue enclosed by an intact PBM.

We are involved in characterization of the interface between the symbionts (Rosendahl and Jochimsen, 9.2; Jochimsen and Rosendahl, 9.5; Mellor and Rosendahl, 10). We have acquired antibodies towards enzymes, which are likely to have key functions in the carbon- and nitrogen-metabolism, essential to the efficiency of the symbiosis (aspartate aminotransferase, glutamate synthase, phosphoenolpyruvate carboxylase). These proteins are localized within the nodule tissue by immunogold labelling techniques (Fig. 4.2.1). The location of the enzymes is likely to reflect their function in the symbiosis and by these studies, we are investigating a possible role of the interface in the exchange of carbon and nitrogen between the symbionts.

![Fig. 4.2.1. *Rhizobium* bacteroid in a pea root nodule as visualized by electron microscopy. The black dots are gold particles, located on an antibody. The antibody recognizes and binds to specific proteins (immunogold localization). In this way a specific protein can be localized within the tissue. Bar represents 1μm.](image)

We have established techniques to isolate PBM-enclosed bacteroids from pea and soybean nodules. Isolated PBM-enclosed bacteroids have previously been used to study transport of potential carbon substrates to the bacteroids by trace of $^{14}$C labelled compounds. We have initiated studies to investigate whether or not the transport properties of the PBM are affected by environ-
mental stress. Drought stress is known to result in an accumulation of the amino acid proline in plant tissue. Conflicting results exist about the ability of proline to cross the PBM and thus become a substrate for the bacteroids enabling them to survive the period of stress. We have established the growth conditions for controlled drought stress treatment, so transport studies using $^{14}$C-proline are about to be initiated.

We have developed an aqueous two phase partitioning system (dextran-PEG) to isolate PBM from other membranes in pea root nodules. A major advantage of the dextran-PEG two-phase partitioning method, compared to other cell fractionation methods, is the possibility to isolate membrane vesicles of a fixed orientation. The membranes are identified by marker enzymes: We have established the presence of 1,3-β-glucan synthase and a membrane bound alkaline pyrophosphatase on PBM from pea root nodules. Cytochrome C oxidase is used as a contamination marker for mitochondrial- and bacteroid membranes. The orientation of the membrane is estimated by the latency of 1,3-β-glucane synthase, as latent activity indicates a protection of the substrate-binding site by the membrane. Wrong site-out PBM vesicles will be an important tool in future studies of transport properties of PBM, with special emphasis on transport of signal molecules from the bacteroid to the plant.

**Phosphorus Transport by Mycorrhizal Fungi in Relation to Soil-P Status**

The phosphorus content in mycorrhizal plants results from the combined uptake of roots and their associated mycorrhizal fungi. Information is required on the relative contribution of each component and on factors regulating mycorrhizal functioning.

Dual labelling with the tracer isotopes $^{32}$P and $^{31}$P is used for the simultaneous measurement of P transport from a separate hyphal compartment and from a compartment with both roots and hyphae. The Ris 42 isolate of *Glomus caledonium* may transport just as much phosphorus to cucumber plants as that of fungus and roots in combination. Phosphorus uptake by roots is regulated by feed-back control, and mycorrhizal fungi, supplying large amounts of P directly to the inner cortex cells, seem to take over the role of roots in plant P uptake.

The effect of soil-P level on the relative contribution of fungus and roots to total P uptake by cucumber plants was investigated. Although plant growth responded markedly to the addition of 10 and 30 mg P kg$^{-1}$ soil, the P taken up by hyphae alone was similar to the combined uptake by hyphae and roots at each of these P levels. Consequently, the fungus seems to have a dominating role in plant-P nutrition over that range of soil-P levels, which is conductive to mycorrhiza formation.

Without additional P supply, the P uptake by hyphae alone was higher than the combined uptake of roots and hyphae. This difference could have been caused by competition for P between mycorrhizas and saprophytic soil microorganisms in soil with roots. Research carried out in collaboration with the Department of Microbial Ecology, Lund University, thus showed that growth and biomass of bacteria was considerably lower in soil with hyphae only, than in soil with roots and hyphae. Less bacterial P immobilization would, therefore, be expected in the root-free soil.

**Functional Compatibility of Arbuscular Mycorrhizas**

The overall symbiotic effectiveness of arbuscular mycorrhizas is influenced by the fungal efficiency, the mycorrhizal dependency of the host plant and the functional or physiological compatibility between the two partners. The functional compatibility of combinations of three host plants and two mycorrhizal fungi was measured as the fungal P transport to the plant.

All plant-fungus combinations were highly compatible with respect to mycorrhiza formation. Growth and P content of cucumber and wheat were only slightly influenced by mycorrhizas, whereas flax responded markedly to both fungi. The Ris 42 fungus transported large and similar amounts of P to all three plant species. In contrast, WUM 10, an Australian *Glomus* isolate, transported significant amounts of P to flax only. A well-developed soil mycelium was observed in all combinations with WUM 10. The mechanisms behind this host genotype effect on fungal P transport are unknown.
Use of Phosphorus in Organic Matter by Mycorrhizal Fungi

Phosphorus in organic matter constitutes a large proportion of total soil P and is potentially available to plants after mineralization by soil microorganisms. The influence of arbuscular mycorrhizas on the availability of soil organic P was investigated, using 32P-labelled clover leaves as a P source.

The release of 32P from the organic matter was 33-48% higher in soil with hyphae alone, than in soil with neither hyphae nor roots. The mechanism behind this increased utilization of P in organic matter could have resulted from hyphal exudation of phosphatases, which may hydrolyse simple organic P compounds to release inorganic P. However, no production of extracellular phosphatases by hyphae of two arbuscular mycorrhizal fungi could be measured in an experiment conducted in collaboration with the Department of Agricultural Sciences, RVAU, Copenhagen. Cucumber plants were grown in a two-compartment system and soil in the hyphal compartment was sectioned by a microtome. Large amounts of root-derived phosphatases were measured up to 1.5 mm away from the root surface but neither roots nor hyphae could deplete soil organic P extracted with 0.5 M NaHCO3.

The increased hyphal utilization of P in organic matter was probably caused by a temporal shift in P availability, as mycorrhizal hyphae could intercept some chemical and biological P fixation during mineralization due to their ubiquitous existence in soil.

Mycorrhizal Enhancement of Interplant Nutrient Transfer

The possible direct transfer of nutrients, from a legume to a neighbour plant via connecting mycorrhizal hyphae, could not be confirmed in a previous experiment with *Pueraria phaseoloides* and *Hevea brasiliensis*. However, the presence of mycorrhizas might enhance the indirect transfer of nutrients released as exudates or by mineralization of legume plant residues.

Pairs of pea and barley had their root systems separated by a 2 cm root-free buffer zone. A fine nylon mesh, confining the buffer zone, allowed the free passage of hyphae between the two plant species. Plant pairs were either inoculated with *Glomus intraradices* or left unincubated and pea plants (donors) were labelled with 15N and 32P by a split-root labelling technique. Shoots of donor plants in half of the containers were harvested 40 days after labelling and their roots left in the soil to decompose.

Barley plants (receivers), harvested 60 days after labelling, contained only insignificant amounts of the tracers when donor plants were left intact. In contrast, mycorrhizal receiver plants contained considerably higher amounts of the tracers than non-mycorrhizal receiver plants, when the donor plants were killed. The results confirm that arbuscular mycorrhizal fungi may significantly influence the flow of N and P between two plants when one of them is decomposing.

Interactions between Collembolans and Mycorrhizal Fungi

Growth responses to arbuscular mycorrhizas, obtained in experiments with semi-sterile soil under controlled conditions, are often less obvious in field experiments. This inconsistency is probably caused by uncontrolled biotic and abiotic factors in field soils, including fungivorous soil microarthropods. Hyphae of mycorrhizal fungi possibly serve as a food source for many of these organisms, e.g. the collembolans. It is therefore conceivable that grazing by microarthropods could modify the functioning of mycelia of arbuscular mycorrhizal fungi.

A model system has been established to directly measure the effect of collembolans on the transport of 32P by hyphae of intact mycorrhizas. Plants are grown in pots with a root-free hyphal compartment, where the presence and numbers of collembolans can easily be varied. The collembolan *Folsomia candida* reduced the transport of 32P by external hyphae of *Glomus* species in association with subterranean clover. This effect was not observed when soil in the hyphal compartment was amended with dry yeast, which constitutes an alternative food source. These results demonstrate that food preferences of collembolans must be considered in our studies of their interaction with mycorrhizal fungi.
5 Chemistry of the Geosphere

5.1 Geochemical Modelling

Humic Acid Behaviour

By a thorough analysis of the previously obtained equilibrium data for sodium calcium-humic acid interactions, systematic variations were observed, indicating that rather simple reaction schemes governed by a "solubility product" of a flocculate, combined with ion-exchange reactions might describe the overall behaviour of the system. However, too few data were available in the critical concentration ranges of interest to prove that the assumption was viable.

In some recent experiments, in which the experimental points were chosen close to the onset of flocculation, the equilibrium data indicates that the flocculation reaction is governed by a solubility product. A true thermodynamic modelling tool describing humic acid behaviour is, therefore a not too remote possibility. The flocculate formed by the addition of calcium ions has been shown to be an efficient scavenger for heavy radionuclides, therefore a quantitative modelling of humic acid behaviour is important for predicting the fate of accidentally released radionuclides.

The Uncertainties of Ignorance

Previous work by computer modelling, demonstrated that simulations of diffusion and convective migration in one and two dimensions are poor substitutes for a three-dimensional model. In the case of three-dimensional diffusion, it was found that this could be described by a simple volume-averaged diffusion coefficient plus an uncertainty factor.

In the case of convective transport, only the two-dimensional case could be handled mathematically, describing only the longitudinal dispersion. It was found that the magnitude of the dispersion was pronounced, when the flow had to bypass sharp corners (rough surfaces) and almost absent when passing smooth surfaces. It was argued that in the case of three dimensional systems, transverse dispersion should also be expected to occur and to be somewhat smaller than the longitudinal dispersion.

We hope to include these results in equations to model the migration of pollutants through a network of pathways. Each of these is characterised by permeabilities and dispersion coefficients. The model describes the mean migration lengths and mean dispersion coefficients with associated uncertainties. If successful, these calculations will give an estimate of the uncertainty associated with the modelling of a migration, when the detailed structure of the medium in which migration occurs is not well characterised.

5.2 Organic Geochemistry

Under the leadership of the Section of Chemical Reactivity, a project entitled "Polycyclic organic matter, especially azaarenes, in polluted soil" was planned and organized. The project integrates and coordinates several of the activities in the department. The project will be supported by the Danish Environmental Research Programme under the Danish Center of Ecotoxicological Research.

The aim of the project is to investigate the occurrence and distribution of mobile and genotoxic polycyclic organic matter (POM), especially the nitrogen-containing azaarenes, in soils. Furthermore, the toxicities, adsorption and solubility characteristics will be determined and chemical and hydrothermal methods for their removal from heavily contaminated soils will be investigated.

The toxic effect of a given harmful pollutant may be described by the following expression:

\[ \text{ToxEff} = k \times \text{Solubility(aq)} \times \text{Total Concentration} \times \text{Toxicity} \]

where \( k \) is a constant depending e.g. on the soil type.

The aqueous solubility is in the expression, because both mobility and bioavailability are dependent on this factor. A small minor amount of a polar POM may have a higher toxic effect than that of a large amount of a nonpolar PAH because of its higher aqueous solubility. The soil from a coke oven contaminated area strongly
indicates that the azarenes are such a group. It has been estimated that the active concentrations of azarenes are more than 30–100 larger than those of PAH.

The project comprises:

1) Experimental studies on adsorption and solubilities of POM in the presence of soil and soil components and the determination of their bioavailability.
2) Theoretical estimates, by means of topological indexes, of the effects of structure and substituents on the physico-chemical properties of the POMs.
3) The determination of acute effect levels of mobile- and bioavailable-POM on higher plants and VAM.
4) Experimental determination of the degradation of POM by chemical-hydrothermal methods, including product identification and determination of the fate of the products.
5) Chemical and genotoxic characterization of POM in soils before and after treatment.
6) The preparation of POM species not commercially available.
7) Relative risk assessment of the pollution of terrestrial systems with polar POM versus non-polar PAH compounds.

The project has been presented at a Symposium of the Danish Center of Ecotoxicological Research (Nielsen 9.5).

5.3 Applied Geochemistry

Methods

Chemical analysis of environmental samples is often carried out on relatively small samples of material (less than 1 g). To produce convincing analytical results due to inhomogeneities in, e.g., soils and sediments, larger samples of these materials are required. Although instrumental neutron activation analysis is usually applied as small powdered geological sample material (< 200 mg), larger samples may also be assayed by irradiation, e.g., several 7 g-samples with subsequent counting of an array of sub-samples (radial counting geometry). The most appropriate technology for this purpose was investigated at an irradiation site of the research reactor BR3 involving the study of several samples with varying weights in cooperation with the Tracechem Company in Copenhagen. The results of this study were expressed by one formula based on sample weight and counting geometry (Graubolt et al., 9.1).

Terrestrial Geochemistry

Within the framework of a completed energy research project (in cooperation with Copenhagen University), the method of fission track analysis (age dating technique) was described in detail in a recent book (Jessen et al., 9.1). Forward modelling of fission track annealing of apatites was used with results from hydrocarbon basin modelling, to estimate past heat flow and erosion dynamics in the N-Sea basin.

A geophysical study (Barton et al., 9.4) was initiated by the University of Galway to systematically investigate the Galway Granite, western Ireland. Field work along a geotraverse was carried out during 1993 and radiometric data were collected. The work is part of an ongoing Ph.D. study by the principal author of the presentation.

Marine Geochemistry

Marine ferromanganese phases are regarded as major indicators of chemical processes on the seafloor. These phases may accommodate heavy and rare metals such as lanthanides. Systematic investigations in the Southwestern Pacific Basin at 42° S revealed that three chemical processes are involved in the accumulation of these elements in the ferromanganese phases of both near-, micro and normal sediments. These were: 1) adsorption from seawater onto highly reactive Fe-rich particles from hydrothermal plumes at the crest of the East Pacific Rise, 2) adsorption from seawater onto the Fe-rich ferromanganese mineral vernadite, and 3) supply of terrigenous material. It was found that only the second process led to significant lanthanide enrichment. Furthermore, oxygen-rich northwards flowing Antarctic Bottom Water was found to enhance this process significantly (Kunzendorf et al., 9.1).
Sedimentation rate estimations on sediment cores from the Danish Skagerrak and Kattegat areas, by the combined $^{210}$Pb and $^{137}$Cs methods, are possible by using high-resolution dating of 10-mm slices of sediment cores. The technique, based on direct gamma-ray spectrometry, relies on the decay of continually produced (from U-series decay) $^{210}$Pb (22 years half-life) and on the Cs record in the sediments from nuclear weapons testing. Cs addition was maximum to terrestrial and marine environments in the sixties. In the case of relatively disturbed sedimentary records, such as the Skagerrak cores, however, estimations are difficult to achieve. All the cores, including those from the Kattegat area, could be assigned appropriate linear sedimentation rates. These data usually agree with known rates from nearby areas (Kunzendorf et al., 9.2).

Systematic investigations of long sediment cores taken during the Danish GEOKAT project (coordinated by Aarhus University), revealed that many of the CaCO$_3$ depth distributions yielded characteristic profiles, showing that the carbonate content of sediments generally increases significantly at depths corresponding to an age of 6000 BP. Because relatively high carbonate contents were observed in recent Skagerrak sediments decreasing towards the central Kattegat, it is argued that the abrupt increase in CaCO$_3$ is connected with the opening of the Baltic Sea at that time. Hence, saline waters generate high-carbonate content sediments (Christiansen and Kunzendorf, 9.2).

The recent net sedimentation in the southern Kattegat area, generating a sediment layer of up to 5 mm each year (dating by lead and cesium isotopes), is believed to be the result of resuspension processes. While the shallow areas are characterised by deposition of well-sorted coarse sediments (mainly sands), the finer sediments are predominately deposited in the deeper parts of the Kattegat, mainly by resuspension transport superimposed on the normal terrestrial supply. Taking into account the relatively low carbonate contents of southern Kattegat surface sediments, it is concluded that recent sedimentation in the deeper parts is less influenced by supply from the North Sea compared to early Holocene times (Christiansen et al., 9.1).

### 5.4 Geochemical and Applied Technology

#### Marine Environmental Technology

Several project proposals were channelled through the Baltic Marine Cooperation (BMC), a joint effort of Roskilde University Center, Riso and CAT. Riso's input has mainly been in the form of participating in international meetings.

#### 5.5 Chemical Analysis

The analytical procedure contains several parts, from optimizing sampling to presenting the final results. All parts are of almost equal importance in reducing faults arising from inhomogeneity, contamination, loss of material etc. In inorganic trace analysis, pre-treatment of the chosen sample, providing the most convenient form for the final determination, very often incorporates a destruction followed by desolvation. To this end, the Chemical Section has now been equipped with the most advanced microwave sample preparation system, where pressure and temperature conditions inside the closed sample vessels are monitored and controlled, to rapidly convert samples into solutions suitable for introduction to AAS and ICPMS.

AAS, IC and HPLC are important tools, but ICPMS is still the most important analytical procedure in:
- the establishment of chemical and isotopic purity of metals for the industry,
- the continued efforts of finding the final solution of inorganic analytical method in the FØTEK-project on raw nutrition products from agro-industry,
- the further use of enriched non-radioactive isotopes as trace elements in environmental and nutritional projects,
- the investigation of essential or toxic element effects to health,
- discovering the conditions of soil and sediment in relation to pollution and extraction,
- or participating in European efforts to create high quality reference material through BCR.
Since 1987, when the first commercial instrument available for ICPMS was installed in the Chemistry Section, the method has been further developed. The drawbacks in the form of interferences, especially from combination-ions formed in the interface between plasma torch and mass quadrupole, have grown in importance. Different methods are used in the effort to reduce or eliminate the interferences, e.g. by mathematical correction, separation of major elements in sample-solutions, and/or concentrating the trace elements by use of FIA, ETV, or sample introduction by direct injection. Mathematical correction is the major part of a Ph.D study started this year. Taking into consideration the limitations of all these methods for reducing interferences, the best way is to use an instrument with the quadrupole replaced by a high resolution mass spectrometer. Realizing this, about ten European laboratories have installed such instruments with great success and the Chemistry Section naturally wishes to follow in the steps of these advanced laboratories.

The Chemistry Section takes part in servicing Risø’s large facilities and act as consultants in technical analytical problems wherever needed.

6.1 Preexposure to Copper affects the Uptake and Distribution of $^{64}$Cu in the Eel.

Eels were treated with Cu$^{2+}$ at 0.02 and 0.10 ppm in the laboratory under flow-through conditions for 0, 6 and 28 days in fresh water, prior to exposure to radioactive $^{64}$Cu$^{2+}$ in trace amounts for up to 67 hours. The uptake of radioactivity in gill, liver and muscle tissue was measured. (Fig. 6.1.1).

The gills showed a saturation pattern dependent on exposure levels (0.02 or 0.10 ppm), but independent of preexposure time (0, 6 or 28 days). The uptake of $^{64}$Cu per gram tissue levelled off after about 70 hours.

In the liver, the uptake pattern was different. Here the levels of $^{64}$Cu per gram tissue continued to rise at 0.02 ppm, independent of preexposure time; at 0.10 ppm, however, the uptake was clearly dependent on preexposure time. Eels not preexposed at all, showed the largest uptake of $^{64}$Cu in liver tissue at 0.10 ppm Cu$^{2+}$. After 6 days of preexposure the corresponding liver uptake went down and after 28 days of preexposure, it had come down close to the uptake at 0.02 ppm.

In muscle, the uptake of $^{64}$Cu per gram tissue was much lower than in the liver or in the gills. The uptake pattern of $^{64}$Cu in muscle tissue resembled the saturation pattern in the gills. However, as in the liver, it was only independent of preexposure time at 0.02 ppm. At 0.10 ppm the final uptake of $^{64}$Cu, after 67 hours of incubation, was largest when the eels had not been preexposed to Cu$^{2+}$. The decreased accumulation rate in eel liver after preexposure is thus not followed by an increased rate in muscle tissue. On the contrary, we find that preexposure reduces the accumulation rate in muscle tissue as seen in liver tissue.

Fig. 6.1.1. Accumulation rates in different eel tissues of Cu, measured by the uptake of $^{64}$Cu, at two Cu concentrations, 0.02 ppm and 0.10 ppm. (-) Applies to all pretreatment periods; (■) no pretreatment; (□) pretreatment for 6 days; (△) pretreatment for 28 days.
In conclusion, eels seem to be able to excrete copper during prolonged exposure and the mechanism responsible for copper excretion is apparently stimulated by preexposure to 0.10 ppm. This finding suggests a marked difference between copper metabolism in eels and salmonids (Roch and McCarter, 1984; Comp. Biochem. Physiol. 77 No. 1).

6.2 Doses from the Chernobyl Accident to the Nordic Populations via dietary Intake

The main purpose of the NKS radioecology programme (RAD) 1990-1993 has been to make a dose assessment for the Nordic countries of the Chernobyl accident in 1986. This assessment comprised mean doses received via food production in these Nordic countries, as well as the calculation of individual mean effective doses to an "average" inhabitant in each of the five Nordic countries.

The dose estimates were obtained by two methods. The first used consumption data, i.e., information on the amounts of food eaten by an average individual in each of the five countries. The other method applied the production of food in the Nordic countries and neglected the export and import of food, but took the amounts actually eaten into account. The consumption method gave an individual mean dose commitment of 1.3 mSv and the production method gave 1.0 mSv. In comparison, the external mean dose for the Nordic countries was 0.8 mSv.

Fig. 6.2.1 shows how the collective doses to the Nordic populations from Chernobyl radioactive caesium in diet were distributed between Denmark, Finland, Norway and Sweden. The Danish population received only 1% of the total dose to the Nordic populations, whereas Sweden's portion was more than 40%.

Fig. 6.2.1. The collective dose to the Nordic populations from Chernobyl derived Cs-134 + Ca-137 in diet was 30000 manSv.
In Fig. 6.2.2 the relative intakes of $^{137}$Cs from different diet groups in the four countries are shown. It appears that wild produce (reindeer, moose, freshwater fish, mushrooms and wild berries) is a major source especially in Finland and Sweden. In Denmark, marine fish delivered nearly one third of the dose. In Norway meat (lamb) was the main source of $^{137}$Cs in the diet.

If we assume the same deposition rate of radiocaesium per unit area in the four Nordic countries, the radioecological sensitivity (Bq kg$^{-1}$ diet per Bq m$^{-2}$ year$^{-1}$) is 7 times higher in Norway than in Denmark and the diets in Finland and Sweden are 3 and 5 times respectively, more sensitive to Chernobyl radiocaesium than the Danish diet. Alternatively, if we assume that each of the four countries had been contaminated by the same total amount of Chernobyl radiocaesium, the collective dose from food produced in Denmark would have been nearly 5 times higher than that produced in each of the other Nordic countries. This is because food production per unit area is much higher in Denmark.

6.3 Radioactive Tracers and Oceanography: The MAST-52 Project

The MAST-52 project (EU, Marine Science and Technology Programme), utilizing man-made radionuclides as an oceanographic tool, has been finalized after 3 years of collaboration between 3 French, a British, a Dutch and a German Institute coordinated by the Ecology Section. Riso. Radionuclides - (mainly technetium-99 ($^{99m}$Tc) and antimony-125 ($^{125}$Sb)) - discharged from La Hague to the English Channel, were used to trace transport and dispersal of coastal water masses. A time-series of radionuclide measurements in water samples were taken in the English Channel, at the Dutch coast, in the German North Sea sector and in Danish waters. Rates of water transport, dilution of the coastal currents with other water masses and transit times were elucidated. The data were utilized to improve models capable of describing the transport quantitatively. The measured data from the sampling programme will provide a unique data set for
validating other models. The database will be made available through the British Oceanographic Data Centre. A series of 13 papers giving the results of the project will be published in refereed international journals, most of them in a special issue of the Journal of Marine Systems.

It is concluded, that the rare radionuclide $^{99m}$Tc is a valuable tracer for inflow of European coastal water to the Kattegat.

Generally, there is a northerly-bound coastal current from the Channel along the French, Belgian, Dutch, German and Danish coasts. This current receives a significant part of the aquatic discharges from continental Europe via major river outputs such as the Seine, the Rhein, the Weser, the Elbe etc. Knowledge of the hydrography, including various aspects of mixing and transport of the coastal current is, therefore, a fundamental tool for European coastal and marine environmental management.

Hydrographic models evaluated against radionuclide data have given transport times from La Hague in the English Channel to the outer German Bight as 10-12 months extending up to 15 months in the inner German Bight. A comparison of measured radionuclide concentrations in the English Channel and the North Sea with independently modelled values, computed on the basis of reported discharges from La Hague, gives <20% discrepancy. This is considered excellent, as the measured and modelled concentrations are the combined result of several years of discharges and long term transport. Furthermore, intercomparison exercises gave a similar level of error for low concentrations of $^{99m}$Tc analyzed randomly at the 5 participating radiochemistry laboratories. Fig. 6.3.1 gives a modelled response at an open North Sea location off NW Denmark after a single one month discharge from La Hague. The long "tail" effect, indicated by the model, appears to be even more pronounced in the Kattegat due to further mixing, i.e. an effect of an individual discharge is not restricted to the period around the transport time from the point of discharge.

It can be concluded that $\sim 10\%$ of the La Hague discharge and $\sim 2\%$ of the Sellafield discharge are transferred to the Kattegat. The high proportion of La Hague discharges into the Kattegat indicates the effect of the coastal current as an important water source for the Kattegat bottom water and thus as a potential source for the pollutant load. It is probable that contaminant discharges to the coastal current, occurring closer to Denmark than La Hague, are transported to the Kattegat in proportions greater than $10\%$.

![Fig. 6.3.1. Assumed response at the Danish north-west coast at 56°48'N, 7°36'E to a single discharge from La Hague according to the IFREMER/Salomon model.](image)
6.4 The Oceanic Background Level of $^{99}$Tc, $^{89}$Sr and $^{137}$Cs in the North Atlantic

The purpose of the present work was to establish background values for the studied tracers in the North Atlantic Current. This will form an essential component of a later study of shelf sea/open ocean exchange, based on an anticipated increase in the discharge of $^{99}$Tc and other radionuclides from the Sellafield site. Furthermore, we have attempted to identify the origin of the measured radionuclides. The term "background" refers, in the present work, to an observed concentration in oceanic Atlantic water without influence from European land-based sources, even if the source may still be anthropogenic.

In 1992, concentrations of the anthropogenic oceanographic tracers $^{99}$Tc, $^{89}$Sr and $^{137}$Cs were measured as 0.005, 1.6 and 2.5 Bq m$^{-3}$ in North East Atlantic surface water, east and north east of the Azores. Sampling locations are indicated in Fig. 6.4.1. The values are believed to represent global fallout only. This is apparently the first published value for "background" $^{99}$Tc in oceanic Atlantic water. In contrast, data from the Faroe Islands indicate that long range transport of old Sellafield discharges have slightly increased the fallout levels for $^{99}$Tc and probably also $^{137}$Cs.

Comparisons with older data, indicate an observed half-life $^1$ for $^{89}$Sr and $^{137}$Cs in the North East Atlantic surface water of ~20 years, corresponding to a mean residence time of 80-100 years for the stable elements. This is clearly longer than that observed in Faroese waters, where mean residence times of 33 and 23 years were observed for Sr and Cs, respectively. The difference may be explained by a larger mixing rate with other water masses around the Iceland-Faroe-Shetland ridge than by that in the deep North Atlantic at the Azores.

![Fig. 6.4.1. Map of study area with locations for present samples.](image)

$^1$ The observed half-life, $T_{\text{observed}} = \ln 2 / \lambda_{\text{obs}}$, where $\lambda_{\text{obs}}$ is the linear regression coefficient for the regression in observed concentrations versus time, includes physical decay ($T_{\text{phys}} = \ln 2 / \lambda$) as well as environmental factors such as dilution with other water masses and biogeochemical redistribution. The environmental half-life of an element refers to the half-life of a stable element without decrease due to physical decay, $T_{\text{env}} = \ln 2 / \lambda$, where $\lambda = \lambda_{\text{obs}} - \lambda_{\text{phys}}$ for the case of a radioactive element. The mean residence time is $1 / \lambda$. 

Risø-R-744(EN)
The observed \( ^{99} \text{Tc} / ^{90} \text{Sr} \) ratio \((3 \times 10^{-3})\) in the Azores samples is 10 times higher than the theoretical fission yield decay corrected up to 1992. This is in agreement with published data on rain water samples and may be characteristic for 1960's global fallout. Furthermore, the measured \( ^{137} \text{Cs} / ^{90} \text{Sr} \) ratio is not significantly different from that observed for global fallout. There are no obvious additional sources of artificial radionuclides in this region.

6.5 A Box Model for North-East Atlantic Coastal Waters compared with Radioactive Tracers

The Model

The box-model analysis uses first order differential equations to describe the transfer of pollutants between the boxes. The equations are of the form:

\[
\frac{dA_i}{dt} = \sum_{j=1}^{n} k_{ij} A_j - \sum_{j=1}^{n} k_{ji} A_i - k_i A_i + Q_i
\]

where \( k_{ij} = 0 \) for all \( i, \) \( A_i \) and \( A_j \) are activities (Bq) at time \( t \) in boxes \( i \) and \( j, \) \( k_{ij} \) and \( k_{ji} \) are rates of transfer (y\(^{-1}\)) between boxes \( i \) and \( j, \) \( k_i \) is an effective rate of transfer of activity (y\(^{-1}\)) from box \( i, \) taking into account loss of material from the compartment without transfer to another, e.g., radioactive decay. \( Q \) is a source of input into box \( i \) (Bq) and \( n \) is the number of boxes in the system.

The rates of transfer between the aquatic boxes, \( k_{ij} \) (y\(^{-1}\)) are related to the volume exchanges, \( R_{ij} \) (km\(^3\) y\(^{-1}\)) according to:

\[
R_{ij} = k_{ij} V_i
\]

where \( V_i \) is the volume of water represented by box \( i.\)

Fig. 6.5.1. Regions covered by the marine box model.
Fig. 6.5.1 shows the regions used in the marine box model and Fig. 6.5.2 shows the structure of the water boxes and their interconnections. Each of the water compartments has associated suspended sediment and the water compartments in contact with the seabed have underlying seabed sediment compartments. The water compartments have odd numbers and the surface sediment compartments have even numbers. The latter are not shown in Fig. 6.5.2.

At any given time, the activity in the water column is partitioned between the water phase and the suspended sediment material. The fraction of the activity \( F_w \) in the water column which is in solution is given by:

\[
F_w = \frac{1}{1 + K_d \text{SSL}}
\]

where \( K_d \) is the sediment concentration factor \((m^3 \text{ t}^{-1})\) and \( \text{SSL} \) the suspended sediment load \((\text{t m}^{-3})\). Activity on suspended sediments is lost to the underlying boxes when particulates settle out. The fractional transfer from a water column (box \( i \)) to the sediments (box \( j \)) due to sedimentation is given by:

\[
k_{ij} = \frac{K_d \text{SR}_i}{d_i (1 + K_d \text{SSL})},
\]

where \( d_i \) (m) is the mean water depth of the water column and \( \text{SR} \) \((\text{t m}^{-2} \text{ y}^{-1})\) the sedimentation rate.

The model also includes the transfer of radioactivity between the surface sediment layer and the bottom boundary layer. This diffusion through the pore water and mixing due to bioturbation is modelled as a diffusive process. Furthermore, removal of activity from the sediment...
surface to lower sediment layers is taken into account by assuming that the burial rate is equal to the flux of particles which settle from the overlying waters. Radioactive decay is included in all the boxes.

**Input Data**

For $^{137}$Cs the fallout from the atmospheric nuclear tests has been included based on measurements made in Denmark. The data cover the period from 1955 to 1993. Each model surface compartment thus receives an input of $^{137}$Cs according to the corresponding surface area and year. The input of $^{137}$Cs from the Chernobyl accident into the Baltic Sea was set at 4 PBq. Furthermore, reported discharges on $^{137}$Cs from Sellafield (box 29) and La Hague (box 53) have been taken into account.

**Observed Data**

Measurements were made of radionuclides in environmental samples. These are seawater samples which had been subject to radiochemical analyses and radiometric counting. The results are given in concentrations of the radionuclides in seawater (Bq m$^{-3}$). Since the aim of the box model is to predict annual mean concentrations of radionuclides in the environment, and to use these data to calculate radiation doses to man, the observed data were assigned to the appropriate water regions of the model, after which annual arithmetic mean values were calculated.

**Results**

Firstly, the model was run based on the input described and the predicted concentrations of radionuclides were compared with the annual means of the observed concentrations. Secondly, the exchange rates of the model were modified in order to improve the overall agreement between the model predictions and the observations. The exchange rates were modified in such a way that the mean advective water fluxes were not altered; the modifications concerned adjustments of the bi-directional exchange rates between adjacent water boxes, so that the differences between the two flows (the net advective flows) were unchanged.

Comparisons between the observed and the calculated data for $^{137}$Cs demonstrate that the initial version of the model does not adequately describe the water transport from the North Sea into the Baltic through the Skagerrak, the Kattegat and the Belt Sea. The results for $^{137}$Cs are presented in graphical form in Fig. 6.5.3 which shows the observed and the calculated values of the seawater concentrations in the boxes. The results of both versions of the model are shown to illustrate the degree to which the model has been improved.

The variability between the calculated and the observed results is analysed in terms of the ratios of the predicted to the observed values, for which geometric means and geometric standard deviations were calculated. The geometric mean for the annual data of the predicted-to-observed (P/O) values is 1.03 with a geometric standard deviation of 1.4. The model thus tends to overestimate the annual mean values at about 3% (predictive accuracy), and 68% of the values fall within a factor of 1.4 of the mean (or 95% of the values fall within a factor of 2.0).

Since the purpose of the present model is to predict consequences in terms of committed radiation doses to man, i.e. integrated dose rates from radioactivity in the marine environment, an additional comparison between observations and calculations was made. For each of the model compartments where observations were available, the annual means of the observed values were summed to give integrated values in terms of Bq y m$^{-3}$, and the corresponding calculations were done for the values predicted by the model. The geometric mean for the $^{137}$Cs values is 1.01 with a geometric standard deviation of 1.27.

The radioactive-tracer data demonstrate the usefulness of long time series (decades) of environmental observations, both for the purpose of testing and improving environmental models; they are also useful in the case of retrospective analyses for the purpose of evaluating the quality of historic records of discharge data.
Fig. 6.5.3. Calculated and observed concentrations of $^{137}$Cs in seawater (Bq m$^{-3}$) in different water regions. The dotted lines show the predicted levels prior to modification of the model and the full lines show the levels after modification. The circles show the annual arithmetic mean values of the observed levels.
6.6 Weathering of Radiocaesium on Urban Surfaces after the Chernobyl Accident

The wash-off and weathering of radiocaesium on pervious and impervious urban surfaces were investigated by in situ gamma ray spectrometry in Gävle, Sweden in July, 1993, using lead shielded high purity germanium detectors. This was the fifth measurement campaign conducted by Riso in the area, which, due to the Chernobyl accident, is probably the most heavily contaminated outside the former USSR.

As can be seen in Table 6.6.1, very little, if any, decrease in the levels of radiocaesium on walls of buildings in the Gävle area was identifiable 7 years after the contamination. In one case, the level has actually increased since it was last measured. The change is not highly significant, but may be due to a wash-down of radioactive substances from the upper parts of the wall. The levels of radiocaesium on asphalt surfaces have now decreased so much, that less than 10% of what was measured in 1988 remains. This means that probably less than 2% of the initially deposited radiocaesium is still present on the road. The levels are now below the detection limit.

Table 6.6.1. $^{137}$Cs levels measured in Gävle in 1987, 1988, 1990, 1991 and 1993 (kBq·m$^{-2}$).

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Plain red brick wall in 5-storey building (South-facing)</td>
<td>1.87±9%</td>
<td>1.65±9%</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Plain red brick wall in 5-storey building (North-facing)</td>
<td>-</td>
<td>3.82±7%</td>
<td>-</td>
<td>1.85±7%</td>
<td>2.13±15%</td>
</tr>
<tr>
<td>Yellow brick wall with roughened finish in single-storey building (South-facing)</td>
<td>-</td>
<td>1.03±11%</td>
<td>-</td>
<td>0.79±10%</td>
<td>0.76±10%</td>
</tr>
<tr>
<td>Asphalt surface 5.8 m wide road</td>
<td>-</td>
<td>1.48±9%</td>
<td>0.44±17%</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Asphalt surface on crossroads</td>
<td>-</td>
<td>1.19±9%</td>
<td>0.50±15%</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Concrete paved area 1</td>
<td>-</td>
<td>6.75±6%</td>
<td>3.15±7%</td>
<td>2.17±8%</td>
<td>2.12±9%</td>
</tr>
<tr>
<td>Concrete paved area 2</td>
<td>-</td>
<td>9.71±6%</td>
<td>4.26±7%</td>
<td>3.13±8%</td>
<td>3.10±9%</td>
</tr>
<tr>
<td>Grassed area 1</td>
<td>-</td>
<td>113.0±5%</td>
<td>117.0±5%</td>
<td>-</td>
<td>66.4±5%</td>
</tr>
<tr>
<td>Grassed area 2</td>
<td>-</td>
<td>85.2±5%</td>
<td>66.9±5%</td>
<td>58.7±5%</td>
<td>51.3±5%</td>
</tr>
</tbody>
</table>

As for the concrete paved surfaces, the remaining 10% of the initially deposited radiocaesium seems to be firmly fixed. No significant decrease has been found over the last 2 years. On the grassed surfaces, the unscattered photon flux decreases which might be expected (more or less according to the formula derived by Gale et al. in 1963).

The results are used to validate Riso's dynamic dose model, URGENT.

Clean-up of Urban Areas in the CIS Countries Contaminated by Chernobyl Fallout

In continuation of the measurements carried out on last year's field trip to the Ukraine, a further campaign was made. Here, different methods to bring down the dose-rate in various radioactively contaminated urban areas in the Ukraine and Russia were investigated, with the ultimate goal of providing a nuclear contingency plan for reclamation and decontamination.
The work was carried out under the framework of the Experimental Collaboration Programme (ECP 4), supported by the Commission of the European Communities. The tests were carried out in collaboration with the Russian All Union Institute of Inorganic Materials, the Ukrainian Institute of Geochemistry of Physics and Minerals and the international IAEA-EC CHECIR laboratory, which is based in the Ukraine, very close to the 30 km zone around the damaged Chernobyl reactor.

Two different types of radiation measurements were used for the tests:

1) Beta measurements, using a "CONTAMAT" instrument (measuring a surface area of 166 cm²), which had been calibrated for 137Cs and automatically allowed for background. This instrument can separate the beta activity from the total activity by repeated measurements with and without a stainless steel shield.

2) Gamma measurements, using a Ge detector system, where both collimation and shielding for measurements on horizontal and vertical surfaces were effected with lead shielding blocks assembled on an adjustable steel table.

Riso's specially adapted field campaign bus, which was equipped with supporting electronics, 220 volts electrical power, data handling facilities and decontamination equipment was used for the expedition.

In the town of Pripyat, less than 4 km away from the Chernobyl power plant, high levels of radioactive material were found compared with other investigated areas, although this area received a dry deposited contamination. In other, more remote Ukrainian towns and villages where tests were carried out, such as Poleskoe, Vladimirivka and Varovice as well as the Russian towns Yarlovka and Novozubkov, more than 30 km away from the power plant, deposition of Chernobyl debris occurred with rain.

Measurements made before decontamination testing, showed that the contamination levels in the town of Pripyat were comparatively high. With the shielded gamma equipment, it was found that the contamination level on sandstone walls was in the range of 110-350 kBq m⁻², compared to 0.9-28 kBq m⁻² in the more remote towns. In Pripyat, it was found that the contamination level on a grass cover was 2.90 MBq m⁻², or approximately ten times that on the walls, while this relationship was ten times as high in the other investigated towns. This confirms the assumptions which have generally been adopted concerning the deposition patterns from wet versus dry deposition, as the contamination levels on grass and vertical surfaces are known to decrease very slowly without intervention. This is not the case on the more impervious horizontal surfaces, such as roads and pavements, where 'natural' decontamination due to traffic and surface water flow has decreased the contamination level from presumably about 1.5 kHz/m² to 0-200 kHz/m² in the years following the Chernobyl accident, with the highest levels on concrete pavements and the lowest on asphalt.

Also, the orientation of the walls in Pripyat was found to be of importance concerning the dry deposition. Fig. 6.6.1 shows the difference between contamination levels measured on an east-facing and a west-facing wall on the same multi-storey building in Pripyat. As can be seen, the levels on the east-facing wall are clearly higher. This phenomenon was also detected on other walls in Pripyat.

The tests performed in 1992 showed that decontamination using ammonium nitrate was among those methods which had the least effect on a sandstone wall. DF (relation between contamination density before and after decontamination) of 1.1-1.2. This year, it was decided to apply the method on two similar sandstone walls, one in Pripyat and one in Vladimirivka, to determine the influence of the deposition mode on the decontamination effectiveness more than 7 years after the event. A 0.1 M ammonium nitrate solution was sprayed onto the wall, which became saturated with the solution and was washed with water half an hour later.

When the experiment was performed in Pripyat, the result was a decrease in the contamination level by 67%. This corresponds to a decontamination factor of DF = 3.03, with a 95% confidence interval from 2.96 to 3.10. The same experiment was performed in Vladimirivka. Here, the decontamination factor was found to be DF = 1.27, with a 95% confidence interval from 1.12 to 1.42.
The reason for this big difference could be that the radioactive matter, which was dry deposited over Pripyat (very close to the Chernobyl plant) was associated with rather large, insoluble core fragment particles, whereas the deposited caesium in, for instance Vladimirivka, was associated with condensation particles formed with evaporated caesium.

However, the decontamination efficiencies may have been over-estimated by these beta measurements. Gamma measurements of the ammonium nitrate experiment at Vladimirivka showed a DF of only 1.08. The result of any such decontamination treatment may be a substantial decrease in the radionuclide content of a thin surface shell of the brick. As the range of beta particles is much less than that of gamma photons, a comparatively larger part of the total beta signal (compared to the gamma signal) will have come from the now removed radionuclides in the surface shell. Differences in radioactivity profiles, prior to decontamination, may also be an explanation for the differences in DF at different locations.

On the other hand, it is possible that radioactive material from other parts of the treated wall were brought closer to the sensitive area of the gamma detector system after treatment.

High pressure water hosing, using a turbo nozzle, was applied on different surfaces, where the results were recorded using the gamma measurement system. The results obtained with this readily available cleaning equipment can be seen in Table 6.6.2.
Table 6.6.2. Results of decontamination tests with high pressure water jets.

<table>
<thead>
<tr>
<th>Site</th>
<th>Remarks</th>
<th>Reduction of $^{137}$Cs level (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Novozhibov</td>
<td>sandstone wall facing South (wet deposition)</td>
<td>32</td>
</tr>
<tr>
<td>Novozhibov</td>
<td>sandstone wall facing South (dry deposition - just below roof)</td>
<td>11</td>
</tr>
<tr>
<td>Yarlovka</td>
<td>sandstone wall facing S-W hot water (65°C) (wet deposition)</td>
<td>19</td>
</tr>
<tr>
<td>Yarlovka</td>
<td>clay brick wall facing S-W hot water (65°C) (wet deposition)</td>
<td>19</td>
</tr>
<tr>
<td>Poleskoie</td>
<td>limed wall hot water (65°C) (wet deposition)</td>
<td>38</td>
</tr>
<tr>
<td>Pripyat</td>
<td>sandstone wall facing S-E (dry deposition)</td>
<td>28</td>
</tr>
<tr>
<td>Pripyat</td>
<td>roughened concrete wall hot water (65°C) (dry deposition)</td>
<td>34</td>
</tr>
<tr>
<td>Pripyat</td>
<td>sandstone wall facing N-E (dry deposition)</td>
<td>28</td>
</tr>
<tr>
<td>Pripyat</td>
<td>clay brick wall facing S-E (dry deposition)</td>
<td>29</td>
</tr>
<tr>
<td>Varovice</td>
<td>asphalt road (wet deposition)</td>
<td>11</td>
</tr>
<tr>
<td>Pripyat</td>
<td>concrete pavement</td>
<td>40</td>
</tr>
</tbody>
</table>

On the asphalt road in Varovice, an attempt was first made to decontaminate with an industrial vacuum cleaner. However, this was found to have removed a mere 3% of the contamination.

Measured with the beta counter, the result of three successive sandblastings on a clay brick wall in Vladimirovka was a reduction in contamination level by 38% by the first sandblasting, 74% by the second, and 83% by the third sandblasting. A further sandblasting on a sandstone wall in Pripyat, showed a reduction in the beta signal by 83% due to the first treatment, and with a decrease by 95% after an additional treatment. The caesium removed was found to be entirely associated with the solid phase of the waste. This means that the filtered water used in the experiment could be disposed of through the drain.

As in 1992, clay treatments were also investigated for decontamination of houses. An improved clay emulgation, which was thought to be more suited for the purpose, was used to cover a sandstone wall in Pripyat. After drying,
the clay was removed with a vacuum cleaner. The reduction in beta activity was found to be 38\% by this treatment.

In a grassed garden area in Pripyat, an experiment was carried out to investigate the effect of digging the garden in the same manner as that performed by a trench plough. The procedure can be accomplished very easily in the urban area, using only a shovel. The experiment was carried out on a 3m\(^2\) area, and the collimated gamma detector was used to assess the decrease in gamma activity. The decrease was found to be 74.4\%.

For comparison, a removal of the upper 5 cm layer of soil was found to decrease the gamma level by 78.3\%, and when an upper 10 cm layer was removed, the decrease was found to be 84.9\%. Naturally, the decontamination procedure here is complicated by the generation of rather large amounts of radioactive waste, which must be disposed of.

Finally, an additional test was carried out, where the contaminated soil was covered with a shielding 2.5 cm thick layer of sand. The hereby obtained reduction was found to be 18.5\%.

The total dose-reducing effect obtained by digging the garden is generally very large. The computer model URGENT, developed at Risø, has shown that in certain cases, the dose contribution from grassed garden areas can be as much as 89\%. That means that this digging procedure alone can reduce the total dose by some 66\%.

### Measurements of Indoor Aerosol Deposition

During and after any air pollution episode, where pollutants are released to the atmosphere, people inside buildings will be exposed from different sources, depending on the nature of the pollutants. The buildings will normally provide some protection against airborne pollution in the outdoor air, due to deposition on floors, walls, ceilings and furniture, and to filtration during ingress, in cracks, crevices and pores in the building structure.

Experiments were carried out in test houses in order to identify important parameters concerning the differences between outdoor and indoor air pollutant concentrations. In these experiments, tracer labelled silica particles were dispersed and collected using an impactor technique. In the spring of 1993, a new test house became available in the village of Ferslev in Denmark. A two-week experimental campaign was arranged in collaboration with Imperial College, London. The visiting research assistant from Imperial College brought their new sub-micron equipment, consisting of an Indium powder, a nebulizer and an alpha source, used to neutralize the particles. Table 6.6.3 shows the results of the 13 tests which were performed. The introduction of sub-micron particles was a success, with reasonably straight decay lines and deposition velocities close to those predicted from earlier tests with larger particles. In general, deposition velocities increased with particle size and degree of furnishing, just as could be expected. Fig. 6.6.2 shows a decay curve for the sub-micron particles. The results agreed with earlier data (Fig. 6.6.3).

Particularly interesting was the comparison between the results obtained with the sub-micron particles and the earlier experiment by Roed and Cannell in 1987. Roed and Cannell used stratospheric \(^7\)Be as a tracer. Their conclusion was that there was no filtration by the building envelope and that the lower indoor concentration could be explained by an average deposition velocity of \(^7\)Be labelled particles to all surfaces of 0.000071 m/s. This tracer particle has since been found to have a size of 0.7 - 1.0 microns.

The sub-micron particles used in Ferslev had an AMAD of 0.7 microns and their average deposition velocity was found to be 0.000065 m/s. This close match is another indicator that the conclusion by Roed and Cannell was correct, i.e., that indoor deposition, rather than filtration over the building envelope, is the factor of importance concerning the concentration of indoor air particulates of outdoor origin.
Table 6.6.3. Review of results from the experiment in Ferslev.

<table>
<thead>
<tr>
<th>No.</th>
<th>Partic. size microns</th>
<th>Decay const. h(^{-1})</th>
<th>Air exch. h(^{-1})</th>
<th>Depos. veloc. 10(^{-4})m/s</th>
<th>Corr.</th>
<th>Furn. yes/no</th>
</tr>
</thead>
<tbody>
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Fig. 6.6.2. Decay curve for 0.7 micron Indium particles test 12. The correlation factor for this curve is 0.92.

Test 12 0.7μm
Fig. 6.6.3. Average deposition velocities in three different unfurnished houses. The three different test series are: RH27, tests performed in Riso Huse 27, Denmark, Autumn 1991; BRE, Building Research Establishment in Watford, Autumn 1991; and Ferslev in Denmark, Spring 1993.
7 Other Activities

7.1 Photochemistry and Photophysics

Electronic States of Polyenes

Collaboration has continued initiated with groups in Italy (Dr. G. Orlando) and The Netherlands (Dr. A.M. Brouwer).

In view of the importance of the twisted form for the dynamics of the T1 state of 1,3,5-hexatriene, it was of great interest to synthesize a hexatriene which was conformationally "locked" into a Z configuration. To achieve this, a "locked" Z-hexatriene (1,2-divinylcyclopentene) was synthesized by the group of Professor H. Jacobs at Leiden, The Netherlands. Its photophysical properties and resonance Raman spectrum of the T1 state were investigated in our laboratory. Theoretically, an increase in triplet lifetime by a factor 20 was expected and demonstrated for this molecule. The deactivation of the T1 state of 1,3,5-hexatriene, via a twisted intermediate was confirmed. This work is presently being written up and will be submitted by the beginning of 1994.

The potential energy surface of the ground electronic state of trans- and cis-hexatriene has been further explored. Ab-initio quantum chemical calculations, combined with overtone spectroscopy and previously obtained vibrational spectra, were used to determine the potential surface and vibrational states, including the anharmonic CH states, using our localized mode theory. This work is in the process of being written up. Our and other results were summarized in reviews.

Considerable effort has been spent on the investigation of the lowest triplet state of stilbene and three of its specially synthesized isotopomers, both experimentally and theoretically. The main issue in these studies was again the question of whether the T1 PES has a minimum at planar or twisted (or both) geometries. We were able to definitely demonstrate, from resonance Raman spectroscopy, that the spectroscopically observed molecules are planar in T1, but could not rule out the additional presence of "dark" twisted forms. A manuscript describing this work is completed and has been submitted to the J. Phys. Chem.

Ions and free Radicals

The activity in this area was concentrated mainly on three projects: 1) The vibronic structure and interactions of the benzyl radical, and some of its derivatives, were studied both experimentally and theoretically. 2) The technique of studying radical cations and anions, under stable conditions by resonance Raman spectroscopy in low temperature glasses, was established and as a first example the hexatriene radical cation was studied, and 3) the structure of radical cations of amine-based non-aromatic ring compounds, i.e., of electron donors important in supramolecular donor-acceptor complexes was investigated. This last project was found to overlap with the studies of macrocyclic compounds.

Much of our work concerned the benzyl radical. The benzyl radical, being one of the simplest aromatic free radicals, is of importance in both atmospheric and combustion chemistry. A characterization of its structural and electronic properties is, therefore, of general interest. A first short report on this work has appeared. A more extensive analysis is accepted for publication and will appear in the J. Chem. Phys. In these two articles, the resonance Raman spectrum of benzyl and fully deuterated benzyl excited in the near UV (in resonance with the D_n \rightarrow D_3 transition), is reported and analyzed by quantum chemical \textit{ab initio} calculations. It is demonstrated that vibronic coupling between two excited electronic states (D_n and D_3) is active in the benzyl radical. The geometric and electronic structure of the three different states (D_n, D_3, and D_2) is compared.

In collaboration with Dr. A.M. Brouwer from Professor Verhoeven's group in Amsterdam, we have started a time-resolved resonance Raman and theoretical \textit{ab initio} study of a large number of radical cations of piperidine and piperazine based chemical systems. These radical cations can easily be generated as tran-

\text{Piperidine (1) and piperazine (2)}
sent species in polar solution by laser photolysis. The resonance Raman spectra of these compounds are of excellent quality, yield a great amount of detail and will allow us to gain a much deeper understanding of intramolecular electronic charge distribution and interactions in these species which, from a structural point of view, are largely unknown. As these molecules form part of many supramolecular systems in the context of electron transfer, we expect that our results will be of general interest to the large community interested in electron transfer, molecular switching, molecular computers, supramolecular photochemical devices, etc. A first paper on the results of the dimethylpyperazine radical cation is in preparation and will be submitted by the end of 1993.

One of our other important projects was to study short-lived species of importance in the photoconductivity of polyacetylene. Such species include the hexatriene radical cation, but also other radical anions, cations and free radicals of conjugated polyenes. This project, being carried out as Ph.D. project by T. Keszthelyi from Hungary, turned out to be more difficult than anticipated. Low temperature techniques in pulsed resonance Raman spectroscopy were established. We succeeded in getting the first resonance Raman spectra of the radical cation of trans and cis-1,3,5-hexatriene. From a comparison of the experimental and a theoretical ab initio spectrum, we attribute the spectra to a mixture of the ttt and act rotamers. A first report on this work is completed and will be submitted by the end of 1993.

Photochemistry and Photophysics of Macrocyclic Compounds

The work in this field is related to the general area of material science and in particular optical switching on a molecular level, photochromism, and new optical materials (ferromagnetism, nonlinear properties, organic superconductors). It has concentrated on three topics:

1. In collaboration with Professor K. Bechgaard's group at CISMI, time-resolved optical studies (absorption and fluorescence) of a donor-acceptor complex, designed to act as an optical switch on the molecular level (MOLSWITCH project under ESPRIT-program) were carried out. The results were published, partly as an EC-report, partly as article. A final concluding article is in preparation.

2. In a Ph.D. project by John Frederiksen and in collaboration with lektor Niels Harrit, University of Copenhagen, we initiated a study of the photophysical, photochemical and spectroscopic properties of the polynuclear aromatic molecule truxen. This large molecule was suggested to be ferromagnetic and its organic superconductivity was studied by lektor Thomas Bjørnholm, CISMI, in collaboration with Professor K. Bechgaard. In particular, fluorescence and phosphorescence properties, but also time-resolved absorption and Raman investigations were carried out. Among other results, very interesting new, not yet fully understood experimental data with respect to the phosphorescence properties of this compound were found. These results prompted us to carry out a deeper theoretical analysis in order to understand the experimental data. In this respect we have initiated a theoretical collaboration with lektor P. Sommer Larsen, DIA.

3. In a collaboration with the Polish group of Professor Grabowska and Dr. A. Mordzinski, we have initiated investigations of photochromism by intramolecular proton transfer. Intramolecular proton transfer can, if it is coupled Bipyridinediol with subsequent conformational changes in large molecules, lead to photochromism and hence to the presence of very long-lived intermediates of potential importance in optical switching. A structural characterization of these species is of general interest in order to increase the stability of photo-switched species and to design new materials better suited as optical switches. We have studied a number of compounds undergoing intramolecular proton transfer in excited electronic states. A first report on heypidine-diol has been published. The theoretical analysis is carried out partly by us, and partly in collaboration with Professor
Theoretical \textit{ab initio} Calculations

With the general availability of both semiempirical and \textit{ab initio} programmes and the increasing computing power, both in the form of workstations and supercomputers, the general strength of the methods of vibrational spectroscopy of short-lived species has increased tremendously. Until a few years ago, it was very difficult indeed to reach a theoretical understanding of the time-resolved resonance Raman spectra observed in our experiments on short-lived intermediates. Today, with a reasonable effort, it is, in many cases, feasible to optimize the geometrical structures of open-shell intermediates and to calculate vibrational frequencies by either semiempirical or \textit{ab initio} methods at a level which at least yields a qualitatively meaningful picture. The main problems are still computations on large molecules on the one hand and the calculation of resonance Raman intensities, requiring higher excited states, on the other. We have, since the end of 1992, been allocated some limited CPU-time on the CONVEX 3840 supercomputer in Arhus, and have initiated various theoretical \textit{ab initio} calculations in order to reach a better understanding of our observed vibrational spectra of short-lived intermediates. In particular, calculations on the benzyl radical served to establish a basis platform, from which para-substituted species could be computed. Furthermore, calculations on proton-transferring systems and first calculations on truxen and stilbene were carried out.

7.2 Risø High Dose Reference Laboratory (HDRL)

During 1993, the following reports and certificates were issued by the Risø HDRL:

1. Irradiation at cobalt-60 gamma-cell of samples or dosimeters
2. Irradiation at 10 MeV accelerator of samples or dosimeters
3. Issue of calorimeters
4. Issue of dichromate reference dosimeters
5. Issue of FWT-60 reference dosimeters
6. Measurements of facility parameters
7. Measurements of dose distribution in irradiated products

Two types of calorimeters were used for measurements at electron accelerators, using graphite or a water-filled Petri-dish as an absorber. A new calorimeter was developed which uses a polystyrene disc as an absorber. This type of calorimeter offers better mechanical stability - important in an industrial environment - and better thermal characteristics. This new polystyrene calorimeter will also be covered by the accreditation, as soon as approval by DANAK (the Danish Accreditation Scheme) has been obtained.

We organized two training courses in Process Control and Validation for Electron Beam Sterilization. Seventeen participants from 8 countries had an opportunity to carry out the measurements necessary according to the newly approved standards from the European Standard Organization CEN and from the International Standard Organization, ISO.

The new standards require more documentation in order to verify that the radiation treatment of medical devices is actually rendering the products sterile. In collaboration with the Danish Medical Device Association, a meeting was organized to inform the Scandinavian producers of these demands.

7.3 Computer Aided Farming

In 1992, in collaboration with The Danish Institute for Plant and Soil Science and The Danish Agricultural Advisory Centre a project to elucidate the importance of a varied application of N-fertilizers inside a field on yield and environment was initiated. The amount of fertilizer of each subfield is determined on basis of N-min. analysis. Subdivision of the field is based on yield variation of the post crop measured by "Foldimeter" and DGPS-system.

Two experiments were performed at Risø in two fields, each 10 ha, belonging to the farm
"Dyskærgård". Autumn sown crops of barley and wheat, respectively, were grown.

Contrary to results obtained at a similar trial in Jutland, the results from Riso seem to demonstrate that it is possible to obtain a "normal" yield by a reduction in the application of N-fertilizers. Results showed a statistically significant yield improvement of a graduated application of N-fertilizer compared to the uniform.

In collaboration with the Department for Electronics at Riso, a device for DGPS-position and collection of data from continuous tele-measurements of reflected light was developed. In this way the biomass is indirectly determined several times during the crop development and mapping of these data could be used as an index of the final yield.

7.4 MODECS

In 1993 MODECS arranged a one-day meeting on "Plastics of the Future, the Environmental and Energy Aspects" and a two-day meeting on "Molecular Recognition and Self-organizing Systems". Both meetings, with internationally renowned specialists as main-speakers, were very successful. Topics for two meetings in 1994 have been selected and are being planned. The topic for the one-day meeting is "Light and Molecules" and for the two-day meeting is "Polymer Structures and Conformations".

The Ph.D. study sponsored by MODECS is proceeding well. However, due to difficulties in preparing micelleforming functional molecules, some of the experiments were somewhat delayed. It was decided to perform a physico-chemical study of some functionalized calixarenes to investigate the closeness effect on well-defined molecules.
8 Large Facilities

8.1 10 MeV Linear Electron Accelerator

In July 1993, the original American ITT klystron-type was replaced with a French TTE-type.

The decision for the replacement was taken in 1991. The reason was mainly due to difficulties with an unacceptably long delivery time of the ITT klystron and an expected life time of 12000 hours for the TTE type compared with 6000 for the ITT type. Normal operation hours for the Linac are 2000 per year.

After installation of the new klystron, the beam power of the Linac has increased by ~ 20%. The expenses for the modification of the installation 500 DKK was paid by the Risø Management. The Section of Chemical Reactivity has paid 830 DKK for two klystrons, one being a spare.

Irradiation of products has continued on the normal level of 2-3 days per week. The main activities are the sterilization of medical equipment and the modification of plastics.

8.2 Pilot Plant for Wet Oxidation

At the heart of the plant there is a 2000 meter-long pipe reactor which makes continuous treatment of suspensions possible under alkaline, neutral or acid conditions with oxygen at 280°C and 100 bar. The plant has been used to implement the Risø-NKT-wet oxidation process on a semi-industrial scale.

8.3 The RIMI Field Station

Risø's Integrated Environmental Project (RIMI) is an interdisciplinary project studying pathways, processes and effects on terrestrial ecosystems of nitrogen compounds derived from human activities.

RIMI is managed by the Ecology section and involves scientists from the Environmental Science and Technology Department, as well as scientists from the Meteorology and Wind Energy Department, and the Optics and Fluid Department at Risø.

The RIMI station is used in the Danish contributions to the EUROTRAC projects BIATEX (managed by the Ecology section), TOR (managed by the Chemistry section) and TRACT (managed by the Department of Meteorology and Wind Energy). A number of projects within the SMP Center for Air Pollution Processes and Models make use of the field station. One of these projects, concerning the atmospheric composition of nitrogen compounds, is managed by the Chemistry section and performed in collaboration with the National Environmental Research Institute.

The RIMI station also serves as a reference station for air pollution monitoring in Copenhagen by the National Environmental Research Institute.

8.4 Dyskærgård, the Experimental Farm

In 1993, the economic result of the farm was significantly lower than that of previous years. This was mainly caused by the new EU rules with 15% fallow, and also a severe spring drought resulting in a reduction of crop yields.

The acreage of arable land has been reduced by 1.5 ha to a total of 124.5 ha due to the erection of two buildings, CAT and the test station for windmills.

The barn at Dyskærgård has been reconstructed after storm damage in January.

8.5 Open Top Chamber Facility

In collaboration with the National Environmental Research Institute and the University of Copenhagen, the Department operates a large Open Top Chamber Facility situated at Risø. The facility consists of 19 large chambers (3.5 m in diameter) and 20 small chambers (1.5 m in diameter). The small chambers are equipped
with lysimeters for water and nutrient balance studies, and for measuring nutrient leaching from the soil profiles.

The Open Top Chambers are used for short- and long-term studies of the effects of air pollution on trees and crop plants.

8.6 Risø Ecological Risk Assessment Facility, RERAF

During 1993, a planning group was established with the purpose of formulating the exact requirements for the building of the RERAF-facility.

The RERAF-facility will become one of the most advanced systems for conducting genetic, physiological, ecophysiological, biogeochemical and ecological experiments. Natural physical, chemical and biological conditions can be simulated with good approximation. It will be possible to study the biological interactions between different plant species, symbiotic relations between plants, rhizobia and VA-mychorrhiza, and the effect of plant pathogens. The facility will also be well suited for experiments with model ecosystems to validate models.

In its final version, RERA will consist of three units: RERAF1: for studies in the field of geneticotechnology; RERAF2: a Phytotron; RERAF3: for modelling integrated eco-systems. RERAF1 and 2 are identical units and will embody 12 growth chambers (4 x 6 meters) planned as north-facing greenhouse cubicles, each equipped with an advanced climate control system which will not only control the amount of light, temperature, and humidity inside the growth chambers, but will also be capable of simulating the diurnal cycle for all three parameters in a near natural manner. The chambers will have mobile light roofs with high pressure Hg lamps, giving a maximum photonflux of approximately 1000 μmol m⁻² s⁻¹. All C₃-plants will, therefore, be light saturated. The chambers will be certified for experiments with radioisotopes and transgenic organisms.

The growth chambers can be supplied with either atmospheric air or special mixtures of gases such as nitrogen, oxygen, carbon dioxide or air pollutants such as ozone, NOₓ and SOₓ.

Each of the eleven growth chambers will have a 3 meter-deep root compartment with separate temperature controls. The growth medium can be homogenized soil in lysimeters, or monoliths of soils, or nutrient solutions in a continuous flow or recycling system. The system can be used for sand culture or for culture where the plants are grown in artificial rooting media, such as rockwool perlite or polyethylene beets.

The RERAF-facility has planned to combine the latest developments within analytical chemistry and computer technology, with advanced plant growth facilities, where separate root and shoot compartments are being used. In this way, it is possible to operate, and independently control, experimental conditions of both above- and below-ground parts of model ecosystems.

With the use of the RERAF-facility, it is possible to perform fully integrated ecophysiological experiments with higher plants, where climatic conditions, water consumption, assimilation and exchange of nutrients, as well as metabolic gasses, can be controlled and monitored continuously or within short time intervals.

Besides being suited for experiments with higher plants, the facility is also suitable for integrated experiments with submerged plants, macro algae, benthic algae, planktonic algae, and bacterial cultures. Further, the RERAF-facility can be used for experiments with transgenic plants and their relationships with herbivore insects.

The RERAF-facility will be the ultimate tool in a wide range of basic and applied research tasks related to plant species or plant strains. Their germination, ontogenetic development, growth, nutrient demands, and tolerance towards physical, chemical, biological and/or climatic stress can also be studied.

Using the RERAF-facility, it will be possible to conduct fully integrated multi-parameter experiments, where whole plants or plant materials are cultured under climatic and nutritional control over long periods of time. The biological material can be tested under steady state or transient conditions, or under conditions simulating the fluctuating natural environment. The climatic and nutritional control will be either by feedback, from analytical equipment, or from computer models.
Fig. 8.6.1. Cross section of RERAF. For further explanation see text.
9 Publications

9.1 Refereed Journals and Books


9.2 Proceedings and Abstracts


Skriver, Jensen, B., Halken, T. (1993). The role of colloids in the transport of radionuclides by groundwater. In: Migration of radionuclides in the geosphere. Progress meeting on migration of...


9.3 Research Reports


9.5 Presentations (Oral and Posters)


Christensen, S. Transformation of Erysipe graminis f.sp. hordei. Danisco, Copenhagen, Denmark. 24 Apr 1993.

Christensen, S. Molecular studies of mating type loci in Cochliobolus ssp. Plantepathologisk Selskabs generalforsamling. RVAU. Copenhagen, Denmark. 16 Apr 1993.


Dahlgaard, H. Grænseoverskridende havforurening. Dansk Selskab for Marinbiologi, Copenhagen, Denmark. 26 Jan 1993.


Granly, K., Egelov, A.H., Nielsen, T., Lohse, C. Vapor phase acidic components in ambient air, formic, acetic and nitric acid, in ambient air. Poster presented at the National Strategic Environmental Research Program (SMP) in Copenhagen, Denmark. 26 Nov 1993.


Jukola, L. The functioning of VA mycorrhizas.- Department of Microbiology. Swedish University of Agricultural Sciences, Uppsala, Sweden. 18 Nov 1993.

Jensen, E.S. Cycling of grain legume residue nitrogen. Workshop on Nitrogen Leaching in Ecological Agriculture, RVAU, Copenhagen, Denmark, Oct 1993.


Miller, A. Dosimetry for radiation sterilization. DMDA, Copenhagen, Denmark, 2 Feb 1993.

Miller, A. Requirements to the IAEA as a High-Dose Reference Laboratory. Advisory Group Meeting on High-Dose Dosimetry. IAEA, Vienna (AT), 8-10 Mar 1993.


Miller, A. Requirements to the IAEA as a high-dose reference laboratory. Advisory group meeting on high-dose dosimetry. IAEA, Vienna, Austria, 8-10 Mar 1993. Abstract available.

Miller, A. Electron accelerators for irradiation of industrial products. TEMPUS workshop on general accelerator application, Julich, Germany, 6-10 Sep 1993.


Miller, A. Electron Accelerators for Irradiation of Industrial Products. TEMPUS Workshop General Accelerator Application, Institut für Kernphysik, Julich (D), 6-10 Sep 1993.

Miller, A. Anwendung des strahlungs, Riso, Denmark, 30 Sep 1993.

Miller, A. A new polystyrene calorimeter, IAEA coordinated research meeting, Vienna, Austria, 4-7 Oct 1993.


Nielsen, O.J., Ellermann, T., Skov, H. Reactions of NO, with dienes in the gas phase at 295 K. Annual Meeting of the Danish Chemical Society, Odense, Denmark, 8 Jun 1993.


Pilegaard, K., Hummelshøj, P., Jensen, N.O. Deposition of ozone and nitrogen dioxide to open land and forest. BIATEX workshop, Aivero, PT, 4-7 May 1993.


Rasmussen, S.K. DNA-teknologi i planterproduktion. Rigshospitalets uddannelsesafdeling, Copenhagen, Denmark, 28 May 1993.


Sehested, J., Nielsen, O.J. Absolute rate constants for the reaction of CF₂O and CF₂O radicals with NO. Annual Meeting of the Danish Chemical Society, Odense, Denmark. 8 Jun 1993.


Sehested, J., Ellermann, T., Nielsen, O.J., Wallington, T.J. Laboratory studies of the atmospheric chemistry of HFCs. 6th European Symp. on Physico-Chemical Behaviour of Atmospheric Pollutants, Varese, Italy. 18-22 Oct 1993.


9.6 Patents

10 Papers accepted for publication


Chen Qingxiang, Dahlgaard, H., Nielsen, S.P. Determination of "Cs in sea water at ultra low levels. Analytica Chimica Acta.


Hansen, H.J.M., Olsen, A.G., Wilhjelsen, N. The influence of ambient salinity and temperature on lipid metabolism in toad (Bufo bufo) skin. Isophthaldicthanolamine an endogenous regulator of ion channels? Comparative Biochemistry and Physiology, rect. no. CBP 166A.


Jensen, B.K., Jensen, E.S., Magid, J. Decomposition of 15N-labelled ryegrass in soils from a long-term field experiment with different manuring strategies. - Biological Agriculture and Horticulture 3.

Jensen, E.S.a. Dynamics of mature pea residue nitrogen turnover in unplanted soil under field conditions. - Soil Biology and Biochemistry.

Jensen, E.S.b. Availability of nitrogen in 15N-labelled mature pea residues to subsequent crops in the field. - Soil Biology and Biochemistry.

Jensen, E.S.c. Mineralization-immobilization of nitrogen in soil amended with low C:N ratio plant residues with different particle size. - Soil Biology and Biochemistry.

Jensen, E.S.d. Leaching in small lysimeters of nitrates derived from 15N-labelled field pea residues. - Journal of Environmental Quality.

Jensen, E.S.e. Cycling of grain legume residue nitrogen. Biological Agriculture and Horticulture.

Johnsen, A., Jakobsen, J., Jensen, E.S. Hypthal N transport by a vesicular-arbuscular mycorrhizal fungus associated with cucumber grown at three nitrogen levels. Plant and Soil.


Kelly, C., Sidebottom, H.W., Trench, J., Nielsen, O.J. Reactions of CF,0 radicals with selected alkenes and aromatics under atmospheric conditions. Chem. Phys. Lett.

Keszei, T., Willibrordi, R., Cave, R.J., Johnson, J.I. Resonance Raman spectra of the radical cation of 1,3,5-hexatriene. J. Phys. Chem.


Pedersen, C., Linde-Laursen, I. Chromosomal locations of four minor rDNA loci and a marker microsatellite sequence in barley. - Chromosome Research 2.


Sørensen, P.S., Jensen, E.S., Nielsen, N.E.a. Labelling of the organic nitrogen fraction of animal manure with 15N. - Plant and Soil.

Sørensen, P.S., Jensen, E.S., Nielsen, N.E.b. The fate of 15N-labelled organic nitrogen in sheep manure applied to soils with different texture under field conditions. - Plant and Soil.

Thomsen, J.K., Jensen, E.S. Recovery in spring barley of nitrogen mineralized from 15N-labelled straw and catch crop material. - Agriculture, Ecosystems & Environment.


11 Education

11.1 Ph.D. Thesis


11.2 The Industrial Research

Education


11.3 M.Sc. Thesis


11.4 B.Sc. Thesis


11.5 External examiners

Engvild, K.C. censor in plant physiology at the University of Aarhus and at the Royal Veterinary and Agricultural University, Copenhagen.

Giese, H. censor in molecular biology at the University of Aarhus and molecular plant pathology at The Royal Veterinary and Agricultural University.

Gundersen, V. censor in analytical chemistry at the Technical University of Denmark.

Hauhe, V. censor in plant breeding at The Royal Veterinary and Agricultural University.

Jensen, E.S. censor in Plant Nutrition and Crop Physiology. The Royal Veterinary- and Agricultural University, Copenhagen.

Jorgensen, J. Helms censor in plant breeding and plant pathology at The Royal Veterinary and Agricultural University.

Jorgensen, R.B. censor in plant tissue culture and molecular biology at the University of Aarhus.

Linde-Larsen, I. censor in genetics at The Royal Veterinary and Agricultural University.

Pilegaard, K. Censor in environmental science at the Technical University of Denmark.

Rasmussen, S.K. censor in plant molecular biology at The Royal Veterinary and Agricultural University, and University of Copenhagen.
12 Exchange of Scientists

Anustusi, Dr. C., University of York, England (1 week).

Bajdor, Dr. K., Industrial Chemistry Research Institute, Poland (2 months).

Bjornstad, Å., Agricultural University of Norway (3 months).

Brouwer, Dr. A.M., University of Amsterdam, Holland (2 weeks).

Brown, A.H.D., CSIRO, Australia (2 weeks).

Burns, Dr. D., National Physical Laboratory, Teddington, UK.

Cubriules, J.J.P., Guanajuato, Mexico (1 week).

Christensen, Professor H., Studsvik AB, Nyköping, Sweden (1 week).

Domraichev, Dr. S., IOFFE Physico-Technical Institute, St. Petersburg, Russia (1 week).

Donka, Dr. K., Institute of Biology, NRCPS Demokritos, Athens, Greece (4 months).

Dreiseitl, Dr. A., Cereal Research Institute, Kromeriz, Czech Republic (2 weeks).

Getoff, Professor N., University of Vienna, Austria (3 weeks).

Glasby, Dr. G.P., University of Sheffield, England (4 weeks).

Güven, Professor O., Gammaster B.V. Ede, The Netherlands (1 week).

Hickel, Dr. B., CNRS, Saclay, France (2 weeks).

Jestin, Engineer J.M., University of Bordeaux, France (12 months).

Jmerik, Dr. V., IOFFE Physico-Technical Institute, St. Petersburg, Russia (1 week).

Joner, Stud.dr.scient., E., Agricultural University of Norway (12 months).

Kataoka, T., Okayama Prefectural Inst. for Environmental Science and Public Health in Japan (4 weeks).

Kovacs, Dr. A., Institute of Isotopes Co., Budapest, Hungary (3 weeks).

Laszczynska, P., Student from Poland (through Environmental Course, Aarhus, DK (1 week).

Locke, Dr. G., University College Dublin, Ireland (2 weeks).

Maciszewski, Dr. W., Institute of Nuclear Chemistry and Technology, Warsaw, Poland (1 week).

Malec-Czechowska, Ms. K., Institute of Nuclear Chemistry and Technology, Warsaw, Poland (1 week).

McDermott, J., ETH Zürich, Switzerland (2 weeks).

McLaughlin, W.L., National Institute of Standards and Technology, USA (1 week).

Mellor, Dr. R.B., Botanical Institute, University of Basel, Switzerland (10 months).

Mordzinski, Dr. A., Polish Academy of Sciences, Poland (4 weeks).

Mouznetsoy, Dr. D.M., IOFFE Physico-Technical Institute, St. Petersburg, Russia (1 week).

Mowitchan, N., Inst. of Geochemistry and Physics, Kiev, Ukraine (1 week).

Nakonieczny, M., University of Silesia, Dept. of Human and Animal Physiology, Poland (1 week).

Orlandi, Professor G., University of Bologna, Italy (1 week).

Peller, S., University of Lund, Sweden (5 months).

Quiros, C.F., Dept. of Vegetable Crops, University of California, Davis, USA (1 week).

Rutijczuk, Dr. E., University of Wroclaw, Poland (4 months).

Riberro, M.M.A., Escola Superior Agraria, Portugal (2 weeks).

Salazar, I., Agribiotecnologia de Costa Rica, Alajuela, Costa Rica (2 months).

Sharpe, Dr. P., National Physical Laboratory, England (1 week).

Sidetbottom, Dr. H., University College Dublin, Ireland (1 week).

Solar, Professor, S., University of Vienna, Austria (3 weeks).
Sučević, Z., Ruder Boskovic Institute, Zagreb, Croatia (3 months).

Svitashhev, S., Swedish University of Agricultural Sciences, Svalöv, Sweden (1 week).

Sørensen, P., Visiting Research Fellow at CSIRO, Division of Soils, Australia (4 months).

Wallington, Dr. T., Ford Motor Co., Dearborn, USA (2 weeks).

Wöhrman, K., Department of Population Biology, University of Tübingen, Germany (1 week).

Yamamoto, H., Japan Atomic Energy Research Institute (3 months).

Zlobenko, B., Institute of Geochemistry and Physics of Minerals, Ukrainian Academy of Science (1 month).
13 Main cooperative Projects

Riso project coordinators are marked with *
Principal investigators are marked with **

Radioactive tracers in the Greenland Sea. Part of the international Greenland Sea Project. H. Dahlgaard

Studies of the Transport of Coastal Water from the English Channel to the Baltic Sea using Radioactive Tracers. Marine Science and Technology Programme (MAST), CEC. Cooperative project including Risø National Laboratory; Federal Maritime and Hydrographic Agency, Germany; Netherlands Energy Research Foundation; Commissariat à l’Energie Atomique, France; Ministry of Agriculture, Fisheries and Food, Lowestoft, UK; and Centre de Spectrométrie Nucléaire et de Spectrométrie de Masse, CNRS, Orsay, France. H. Dahlgaard*, S.P. Nielsen

Nordic Radioecology Cooperation (NKS/RAD). RAD1 - Education; Quality Assurance; Methodology; RAD2 - Aquatic Radioecology; RAD3 - Agricultural Ecosystems; RAD4 - Natural Ecosystems. A. Aarkrog, H. Dahlgaard*, S.P. Nielsen

Arctic Monitoring Assessment Programme. A. Aarkrog

The radiological exposure of the EC population from radioactivity on the Mediterranean Sea (CEC). A. Aarkrog, S.P. Nielsen.

Pathways of radionuclides emitted by non-nuclear industries (²¹⁰Po, ²¹⁰Pb). EU project in collaboration with partners in Netherlands, Ireland, France, Spain, Portugal and UK. H. Dahlgaard.

Transuranics in the Marine Environment. EU project in collaboration with partners in Ireland, UK, France, Spain, Italy, Sweden and Norway. H. Dahlgaard, A. Aarkrog.

Radioecology of seminatural ecosystems (CEC). Cooperative project including Risø National Laboratory, (DK), Nuclear Energy Board (IR) (Coordination), Institute of Terrestrial Ecology, Merlewood (UK), Swedish University of Agricultural Science, Uppsala (S), University of Thessaloniki (G). A. Aarkrog, S.P. Nielsen.


Pilot project on radioactive environmental problems in the River Plouence. Cooperative project with Danish Hydraulic Institute and Water Quality Institute. S.P. Nielsen.


Biological monitoring of heavy metals. Collaborator: Laboratory of Environmental Research Institute, Science and Education, The Technical University, Lyngby, Denmark. K. Pilegaard*.

EUROTRAC-TRACT. Transport of pollutants over complex terrain. K. Pilegaard.

EUROTRAC-BIATEX. Biosphere/Atmosphere Exchange of Pollutants. K. Pilegaard**.

SMP-project NECO. Nitrogen deposition, exchange and effect in terrestrial ecosystems. K. Pilegaard*.
EU-project on Deposition in Urban Areas. Collaborators: UKAEA, Harwell, GSF, Munich. J. Roed.

EU-CIS Project on Countermeasures. CHECIR. Main collaborators: Cadarache, France; IGPM, Kiev. J. Roed*, K. Andersson.

EU-project on Indoor Deposition. Collaborator: Imperial College, London. J. Roed**.

EU-project on Weathering and Resuspension. Collaborators: UKAEA, Colchester, GSF, Munich. J. Roed.

EU-Project on Deposition of artificial radionuclides, their subsequent re-location in the environment and implication for radiation exposure. Collaborators: GSF, Munich; NRPB, England and Imperial College, London. J. Roed*, Chr. Lange, K. Andersson.


IAEA Project on Validation of Model Parameters VAMP. J. Roed.


European North Atlantic Margins (ENAM). EU-MAST-2 project with 7 European countries participating. H. Kunzendorf*.

Hydrothermal circulation and ore deposition (EU Human Capital and Mobility Network), 6 European countries involved. H. Kunzendorf*.

Cretaceous-Tertiary boundary studies (SNF project with University of Copenhagen, DGU and Riso). H. Kunzendorf*.

Marine geological mapping of the Skagerrak (University of Bergen and Geological Survey of Norway). H. Kunzendorf*.

Baltic Marine Cooperation. Marine environmental studies in the Baltic Sea. Collaborators: Roskilde University and Danish Road Laboratory. H. Kunzendorf*.

FOTEK. Collaborators: Levnedsmiddelstyrelsens Centrallaboratorier and others. P. Solgaard*.

CRM 482: Trace elements in Lichen. BCR, EU, Bruxelles. P. Solgaard*.

EF-akv system. Determination of Al. P. Solgaard.

Colloid Behaviour. A Joint CEC project within the MIRAGE group. B. Skytte Jensen*.

Uncertainties in the Modelling of Migration Processes. A joint CEC project within the MIRAGE group. B. Skytte Jensen*.

MODECS. Molecular Design of Chemical System. An R&D-forum for industries and institutions interested in the mentioned topic. B. Skytte Jensen**.

EU-project on Atmospheric chemistry of halogenated compounds. 9 European laboratories. O.J. Nielsen.

EUROTRAC-LACTOZ. Laboratory Studies of Chemistry Related to Tropospheric Ozone. O.J. Nielsen.

Ford Motor Company collaborative project on CFC substitutes. O.J. Nielsen.


Investigation of MOLSWITCH compounds. CISMI (University of Copenhagen), K. Berghgaard and Riso R. Wilbrandt*.

Danish Natural Science Research Council, common project on the characterization of potential energy surfaces of molecules and radicals. Riso R. Wilbrant, Odense University O.S. Mortensen.

Danish Natural Science Research Council, project on atmospheric chemistry. University of Copenhagen and National Environmental Research Institute. O.J. Nielsen.


IAEA. Research agreement no 6919: Reference dosimetry for industrial Electron Accelerators. A. Miller.

IAEA. Research agreement no 6612: Methods for measurement of absorbed dose and dose distribution at 200-1000 keV electron beams. A. Miller.


SJVF project "Plant-microbe interactions". Collaborators: University of Aarhus, University of Lund, University of Stockholm, University of Minnesota, University of Western Australia. L. Rosendahl.


EU-project "Characterization of the peribacteroid space from 3 types of legume nodules". Collaborator: University of Geneva. R.B. Mellor, L. Rosendahl*

Interaction between crop plants and weeds. Collaborator: B. Sogaard, The Royal Veterinary and Agricultural University. H. Doll.

Efficiency of partial mildew resistance in barley and correlation with secondary metabolites in the leaves. Collaborator: B. Sogaard, The Royal Veterinary and Agricultural University. H. Doll*


Molecular genetics of Erysiphe graminis f.sp. hordae, the causal agent of barley powdery mildew. Collaborators: Danish Plant biotechnology Research Center: The Royal Veterinary and Agricultural University; J. McDermott, ETH Zentrum, Zurich. H. Giese, M. Lyngeby, L. Borbye, M. Rasmussen, S. Christiansen.

Genetic variation between cotton varieties. Collaborator: The Royal Veterinary and Agricultural University. H. Giese, B. Kolling.


QTLs (Quantitative Trait Loci) in barley. Collaborator: The Royal Veterinary and Agricultural University. J. Jensen, B. Kjær.


Biotechnological framework programme for disease resistance in plants. Collaborator: The Royal Veterinary and Agricultural University, Copenhagen. S.K. Rasmussen.


Oil Seed Rape Initiative. Collaborators: O. Rasmussen, University of Aarhus, B. Eggum, Fou lum Research Station; J. Schjorring, The Royal Veterinary and Agricultural University; P. Ulyskov, Research Centre for Plant Protection, H. Giese.
14 Guest Lectures

Dr. A. Bjørnstad, Institutt for Plantekultur, NLU, Norway: "Dihaploider i byg og hvede sammenlignet med konvensionelle afkomstlinjer".

Dr. A.H.D. Brown, CSIRO, Australia: "Wild relatives-source of and sink for crop genes".

Dr. C.E. Dotuka, Dept. of Biology, Nuclear Research Center, Athens, Greece: "Beneficial effects of biological nitrogen fixation on the elemental chemical composition of plants".

Dr. W.T. Frankenberger, Jr., Department of Soil & Environmental Sciences, University of California, Riverside, USA: "Microbial production of plant hormone and their influence on plant growth".

Professor N. Getoff, Institut für Theoretische Chemie und Strahlenchemie der Universität Wien, Austria: "Application of Radiation Chemistry. Methods for Solving Environmental Problems".

Dr. G.P. Glashy, University of Sheffield, England: "Scenarios at the Cretaceous-Tertiary boundary".

Dr. K. Kerby, Elmhurst College, USA: "Characterization of a pathogen-related peroxidase gene from barley."

Dr. J. McDermott, ETH Zürich, Switzerland: "Genetic variation in populations of Erysiphe graminis f.sp. hordei in Europe: RAPDs, SCARs and VNTRs."

Dr. S. McDow, North Carolina University, USA: "Quantum yields and mechanisms for decay of polycyclic aromatic hydrocarbons in the presence of selected compounds detected in combustion aerosols particles."

Dr. S. Pelger, Lunds Universitet, Sverige: "The evolution and organization of the hordein gene family."

Dr. D.M. Sylvia, Department of Soil and Water Science, University of Florida, Gathersville, USA: "Importance of arbuscular mycorrhizal fungi in restoration ecology."

Dr. M. Vircavs, Nuclear Research Centre, Latvian Academy of Sciences: "Preconcentration of heavy metal traces from natural waters using the coprecipitation with organic disulphides."

Dr. M. Vircavs, Nuclear Research Centre, Latvian Academy of Sciences: "Neutron activation analysis used in solving environmental problems."

Dr. K. Währman, Department of Population Biology, University of Tübingen, Germany: "Thoughts on risk assessment of deliberate release of transgenic organisms."
15 Committee Membership

15.1 National

Aurkrog, A. Danish National Council for Oceanology.
Danish reference group for CEC's MAST programme.
Danish reference group for CEC's Radiation protection Programme.
Danish AMAP steering group (expert on radioactivity).
Dahlgaard, H. Greenland Sea Project, Danish Working Group.
Giese, H. The Danish Agricultural and Veterinary Research Council.
Board of The Institute of Forest and Landscape.
Giesel-Nielsen, G. Vice chairman of The Danish Agricultural and Veterinary Research Council.
Danish Academy of Technical Sciences.
Board of the National Research Service for Soil and Plant Sciences.
Jørgensen, J.H. Dansk Genbankverkn.
Koordineringsgruppen for resistens og virulens i korn og kornsygdomme.
Miller, A. Danish Medical Device Association (DMDA). Sterilization committee.
Nielsen, O.J. The National Committee for The International Geosphere-Biosphere Programme (IGBP).
Pilegaard, K. Danish Centre for Atmospheric Research (DCAR) Working Group on effects.
Pilegaard, K. National Strategy for Danish Agricultural Research Working Group on Forest and Landscape.
Wilbrandt, R. Member of "bedømmelsesudvalg" for Søren Hassings Ph.D. grad. Odense University, 1993.
Østergaard, H. Programme Committee for Biotechnology Programme "Risk of introducing genetically modified plants into the environment" (head of programme).
Danish reference group for OECD's "Security in Relation to Biotechnology".
Ph.D. uddannelseskomiteen, RVAU.

15.2 International

Aurkrog, A. IAEA CRP MARDOS (Chairman).
IAEA VAMP programme. (Acting chairman of terrestrial group).
CGC for CEC's Radiation Protection Programme, including ad hoc CGC for CHECIR and advisory committee "Radiation Protection" (CGC-10) for Fourth Framework Programme.
Reference group NKS-RAD Programme.
EF MARINA MED programme (Chairman of the datagroup).
IUR taskforce No. 4 (Chairman).
International group for the evaluation of the Norwegian Research Programme on Radioactive Fallout.
Evaluation committee for dr. philos thesis at Oslo University.
Programme Committee for International Conference on "Environmental Radioactivity in the Arctic and Antarctic". Kirkenes, Norway, Aug 1993.
Programme committee for International Symposium on "Radiological aspects related to remediation and restoration of radioactive contaminated sites". Antwerp, Belgium, Oct 1993.
Board of censors for dr. scient thesis at Agricultural University of Norway.
Editorial board of Journal of Environmental Radioactivity.
Engvild, K.C. Member of Journal Committee of "Physiologia Plantarum".

Gissel-Nielsen, G. OECD committee for plant-soil microbial interactions.

Kuntendorf, H. Editorial Board of 'Marine Georesources and Geotechnology'.


Jørgensen, I. Management committee for COST Action 810: The role of VA-mycorrhizae in transformation of matter in the soil and their importance for plant nutrition and plant health.

Jensen, B. Skjøtt. Working Groups within the EEC R&D Programme Management and Storage of Radioactive Waste (MIRAGE) in the subcommittees CHEMVAL, COCO, and Natural Analogues.

Member of WP Geological Disposal of Radioactive Waste. The Editorial Board of "Waste Management".

Jensen, E.S. Editorial Board of 'Plant and Soil'.

Section board for Soils and Fertilizers. Scandinavian Association of Agricultural Scientists.


Jorgensen, J.H. Editorial board of 'Euphytica'.

International coordinator for disease and pest resistance genes in barley.

Working group cereal, Nordic Gene Bank (Chairman).

Linde-Laursen, I. Editorial Board of 'Plant Systematics and Evolution'.


Radiation Physics and Chemistry (Pergamon Press) (Editorial Board).

Radiation Sterilization Ordentlich Publishers (Israel) (Editorial Board).

9th Int. Meeting on Radiation Processing, Istanbul 1994 (Programme Committee).

Nielsen, O.J. COST-611 Concertation Committee on Physico-Chemical Behaviour of Atmospheric Pollutants.


Steering Committee for NORSAC (Nordic Symposium on Atmospheric Chemistry).

Nielsen, S.P. International Committee on Radionuclide Metrology.

Articles 35 and 36 of the Euratom Treaty (Environmental Monitoring).


Group of experts on Monitoring of Radioactive substances in the Baltic Sea (MORS).

Nielsen, T. The board of Nordic Society of Aerosols (NOSA).


IAEA and EEC VAMP Project Urban Group, (Chairman).

The Fuel Cycle Safety Group (OECD).


Sixth International Conference on Time-resolved Vibrational Spectroscopy, Berlin 1993 (Organization Committee).

Medlem af bedømmelsesudvalg til professorat in Physical Chemistry, Lund University.

Østergård, H. COST, chairman of Management Committee "Population studies of airborne pathogens on cereals as a means to improve strategies for disease control".

16 Seminars Organized


Training course on Process Control and Validation of Electron Beam Sterilization, Risø, 1-5 November and 22-26 Nov 1993 (A. Miller).

17 Personnel

The list also includes short term employees.

Head of Department
Anne Jensen

17.1 Scientific Staff

Aarkrog, Asker
Anderson, Arna J.
Anderson, Kasper
Bergbakke, Erling
Biere, Anne Belinda
Christiansen, Solveig Krogh
Dahlgaard, Henning
Doll, Hans
Engvild, Kjeld C.
Egger, Jørgen
Giese, Henriette
Gissel Nielsen, Gunnar
Gundersen, Vagn
Hansen, Heinz H.
Hansen, Knud Bent
Holm, Jerzy
Holm, Ulla
Haahr, Vagner
Jakobsen, Iver
Jensen, Erik Steen
Jensen, Hans Peter
Jensen, B. Skytte
Jensen, Jens
Johansen, Anders
Jorgensen, Jorgen Helms
Jorgensen, Rikke Bagger
Kunzenort, Helmar
Kure, Martin
Linde-Laursen, Ib
Lynggaard, Bent
Michelsen, Lars
Miller, Arne
Nielsen, Sven P.
Nielsen, Ole John
Nielsen, Harley Alex Møller
Nielsen, Torben
Nilsson, Karen
Pagsberg, Palle
Petersen, Karin Kirke
Pilegaard, Kim
Qiangjiang, Chen
Rahimpour, Reza
Rasmussen, Esben Lindegård
Rasmussen, Soren Kjærgaard
Roed, Jorn
Rosendahl, Lis
Sehested, Knud
Sillefsen, Alfred Heegaard
Søgaard, Per
Sørensen, Peter
Sørensen, Emil
Theilade, Bohl
Torp, Jan
Wilbrandt, Robert
Østergaard, Hanne

17.2 Technical Staff

Andersen, Bente
Andersen, Esther
Andersen, Lis Brandt
Andersen, Margit Elm
Bitsch, Gunnar
Brandstrup, Oda
Brink-Jensen, Merete
Buade-Pedersen, Pearl
Christensen, Tove
Clausen, Jytte
Corfitzen, Hanne
Djurdjevic, Stanko
Dyrgaard-Jensen, Lone
Ebling, Elise
Eriksen, Kim
Fernqvist, Tomas
Gade, Poul
Green, Jytte
Gudiksen, Peter
Hansen, Carl
Hansen, Torben Heien
Hansen, Ina
Hansen, Elly
Hasselbalch, Finn
Hedeboe, Finn
Henriksen, Ebbe
Holm Jensen, Anne Grethe
Holmgaard, Anne
Haugaard, Henrik
Ibsen, Elly
Jensen, Ellen Møller
Jensen, Hanne
Jensen, Karen Mandrup
Johansen, Torben
Pedersen, Jørgen E.
Jørgensen, Vibeke
Jørgensen, Ole
Karlsen, Aage
Kjølbye, Alice
Kristiansen, Bo
Larsen, Erik Engholm
Larsen, Aase Neve
Larsen, Inge Merete
Larsen, Ingelis
Larsen, Hanne Egerup
Larsen, Fritz
Lilliolt, Ulla
Lindskou, Fini
Madsen, Michael Birch
Meltote, Liselotte
Nielsen, Ivar Rønn
Nielsen, Vagn Aage
Nielsen, Svend
Nielsen, Jette Bruun
Nielsen, Karen Wie
Nielsen, Jette Bruun
Oldager, Alf G.
Olsen, Inge
Olsen, Anette
Olsen, Svend K.
Prip, Henrik
Rasmussen, Charlotte
Schjørmann, Birgit Roy
Sillesten, Anrikkke
Sorensen, Poul
Vestesen, Hans
Vinthner, Lis
Weinreich, Ulla
Wojtaszewski, Hanne
Yu, Yixuan

17.3 Office Staff

Andersen, Annie Senten
Bay, Kirsten

Barkmark, Anni
Brandt, Anette
Hansen, Vivi
Jalkelsen, Inger
Kornetup, Berit
Kristensen, Ingrid
Krogh, Helle
Madson, Ruth
Petersen, Lis
Rasmussen, Hanne

17.4 Ph.D. Students

Behrens, Annette
Borbye, Lisbeth
Christiansen, Jens
Dahl, Søren Weis
Frederiksen, John Myhre
Justesen, Annemarie
Jørgensen, Birgitte Lund
Kjær, Birgitte
Landbo, Lars
Lange, Christian
Larsen, Else Tofudahl
Larsen, John
Lyngkjær, Michael
Lyngkær, Tine
Markert, Frank
Mikkelsen, Thomas
Ovesen, Birgitte Neergaard
Pedersen, Carsten
Rasmussen, Merete
Sehested, Jens
Skov, Elise
Strandberg, Morten
Sorensen, Peter

17.5 M.Sc. Students

Christiansen, Lars
Falkenberg-Klok, Jens
Feldner, Helle
Forsting, Peter
Jensen, Birgitte Kudahl
Kolling, Bent
Larsen, Karina Block
Madson, Niels Lolck
Pedersen, Annette
Ravnkov, Sabine
17.6 B.Sc. Students

Andersen, Martin
Nielsen, Anders Bjergskov
Nielsen, Maj Britt

17.7 Apprentices

Hansen, Sanne
Hansen, Vivi
Hass, Maja
Jørgensen, Iben
Ladefoged, Tine
Larsen, Nille Birkensk
Lind, Lene Engelbrect
Linde-Nielsen, Pia
Møller, Margit
Olsen, Susanne Oxholm
Pedersen, Dorte Juul
Poulsen, Maj-Britt Tveen
Rasmussen, Charlotte Holte
Schionning, Liza
Thomson, Susanne
Tran Duc Tuan Tung
### 18 Acronyms

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Definition</th>
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<tbody>
<tr>
<td>AAS</td>
<td>Atomic Absorption Spectrometry</td>
</tr>
<tr>
<td>AMAD</td>
<td>Activity Median Aerodynamic Diameter</td>
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<tr>
<td>BCR</td>
<td>Community Bureau of Reference</td>
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<td>BIATEX</td>
<td>Biosphere-Atmosphere Exchange of Pollutants</td>
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<td>BMC</td>
<td>Baltic Marine Cooperation</td>
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<td>CAT</td>
<td>Center for Advanced Technology</td>
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<tr>
<td>CEC</td>
<td>Commission of European Communities</td>
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<td>CEN</td>
<td>European Standard Organization</td>
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<tr>
<td>CGC</td>
<td>Management and Coordination Advisory Committee (CEC)</td>
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<tr>
<td>CIS</td>
<td>Commonwealth of Independent States</td>
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<tr>
<td>CISME</td>
<td>Center for Interdisciplinary Studies of Molecular Interactions</td>
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<tr>
<td>CRP</td>
<td>Coordinated Research Programme (IAEA)</td>
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<tr>
<td>DANAK</td>
<td>Danish Accreditation Scheme</td>
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<tr>
<td>DCAR</td>
<td>Danish Centre for Atmospheric Research</td>
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<tr>
<td>DF</td>
<td>Decontamination Factor</td>
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<tr>
<td>DHI</td>
<td>Chromosome-doubled Haploid</td>
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<td>DIA</td>
<td>Denmark’s Academy for Engineering</td>
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<td>DNA</td>
<td>Deoxyribonucleic acid</td>
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<td>EMEP</td>
<td>European Monitoring Environmental Programme</td>
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<tr>
<td>ETV</td>
<td>Electro Thermal Vaporisation</td>
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<tr>
<td>EUROTRAC</td>
<td>European Experiment on Transport and Transformation of Environmental Relevant Trace Constituents of Anthropogenic and Natural Origin</td>
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<tr>
<td>FIA</td>
<td>Flow Injection Analysis</td>
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<td>FTIR</td>
<td>Fourier Transform Infrared</td>
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<td>FYM</td>
<td>Farm Yard Manure</td>
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<td>FOTEK</td>
<td>Fødevareteknologi</td>
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<td>DGPS</td>
<td>Differential Global Position System</td>
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<td>GMP</td>
<td>Genetically Modified Plants</td>
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<tr>
<td>GSF</td>
<td>Gesellschaft für Strahlen - und Umweltforschung</td>
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<tr>
<td>HDRL</td>
<td>Riso High Dose Reference Laboratory</td>
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<td>HELCOM</td>
<td>Helsinki Commission</td>
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<td>HPLC</td>
<td>High Performance Liquid Chromatography</td>
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<td>IC</td>
<td>Ion Chromatography</td>
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<tr>
<td>IAEA</td>
<td>International Atomic Energy Agency</td>
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<tr>
<td>ICPMS</td>
<td>Inductively Coupled Plasma Mass Spectrometry</td>
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<tr>
<td>ICRU</td>
<td>International Commission on Radiological Units</td>
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<tr>
<td>IUR</td>
<td>International Union of Radioecologists</td>
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<tr>
<td>MARDOS</td>
<td>IAEA CRP on “Sources of Radioactivity in the Marine Environment and their Relative Contributors to Overall Dose Assessment from Marine Radioactivity”</td>
</tr>
<tr>
<td>MARINA-MED</td>
<td>Overall Radiological Impact on Population of Member States of Natural and Manmade Radionuclides Present in the Mediterranean</td>
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<tr>
<td>MAST</td>
<td>Marine Science and Technology Programme (under CEC)</td>
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<tr>
<td>MODECS</td>
<td>Molecular Design of Chemical Systems</td>
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<tr>
<td>MORS</td>
<td>Group of Experts Monitoring of Radioactive Substances in the Baltic Sea</td>
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<td>MST</td>
<td>Miljøstyrelsen</td>
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<td>NECO</td>
<td>Nitrogen Ecology (SMP project)</td>
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<td>NKS</td>
<td>Nordic Nuclear Safety Project (RAD)</td>
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<td>NLFV</td>
<td>Norway Agricultural Research Council</td>
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<td>NMR</td>
<td>Nordisk Ministerråd</td>
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<td>Acronym</td>
<td>Description</td>
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<tr>
<td>NPP</td>
<td>Nuclear Power Plant</td>
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<td>ODP</td>
<td>Ozone depletion potential</td>
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<tr>
<td>OECD</td>
<td>Organisation for Economic Cooperation and Development</td>
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<tr>
<td>PAH</td>
<td>Polycyclic Aromatic Hydrocarbons</td>
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<tr>
<td>PBM</td>
<td>Peribacteroid membrane</td>
</tr>
<tr>
<td>PBS</td>
<td>Peribacteroid space</td>
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<tr>
<td>PCR</td>
<td>Polymerase Chain Reaction</td>
</tr>
<tr>
<td>PEG</td>
<td>Polyethylene glycol</td>
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<tr>
<td>PFGE</td>
<td>Pulse Field Gel Electrophoresis</td>
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<tr>
<td>PMC</td>
<td>Pollen Mother Cell</td>
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<tr>
<td>POM</td>
<td>Polycyclic Organic Matter</td>
</tr>
<tr>
<td>QTL</td>
<td>Quantitative Trait Loci</td>
</tr>
<tr>
<td>RAD</td>
<td>Radioecology Programme (under NKS)</td>
</tr>
<tr>
<td>RADPATH</td>
<td>Biological Pathways of Artificial Radionuclides (under CEC)</td>
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<tr>
<td>RAPID</td>
<td>Random Amplified Polymorphic DNA Technique</td>
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<tr>
<td>RERAF</td>
<td>Riso Ecological Risk Assessment Facility</td>
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<td>RFLP</td>
<td>Restriction Fragment Length Polymorphism</td>
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<td>RIMI</td>
<td>Riso Integrated Environmental Project</td>
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<td>RVAU</td>
<td>The Royal Veterinary and Agricultural University</td>
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<td>SCR</td>
<td>Selective catalytic reduction</td>
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<td>SINE</td>
<td>Short Interspersed Repetitive Element</td>
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<td>Statens Inst. for Strålehygiene (Statens Strålevern) (Norge)</td>
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<td>Transport of Pollutants over Complex Terrain</td>
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<tr>
<td>UKAEA</td>
<td>United Kingdom Atomic Energy Authorities</td>
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<td>UMIST</td>
<td>University of Manchester, Institute of Science and Technology</td>
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<td>VAM</td>
<td>Vesicular-Arbuscular Mycorrhiza</td>
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<td>VAMP</td>
<td>Validation of Model Project (under IAEA)</td>
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<td>YAC</td>
<td>Yeast Artificial Chromosome</td>
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