



# **Environmental Science and Technology Department Annual Report 1994**

**Edited by A. Jensen, G. Gissel Nielsen, V. Gundersen,  
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## **Abstract**

The Environmental Science and Technology Department engage in research to improve the scientific basis for new methods in industrial and agricultural production. Through basic and applied research in chemistry, biology and ecology the department aspires to develop methods and technology for the future industrial and agricultural production exerting less stress and strain on the environment. The research approach in the department is predominantly experimental.

The research activities are organized in five research programmes and supported by three special facility units. In this annual report the main research activities during 1993 are introduced and reviewed in eight chapters. Chapter 1. Introduction. The five research programmes are covered in chapter 2-7: 2. Atmospheric Chemistry and Air Pollution, 3. Gene Technology and Population Biology, 4. Plant Nutrition and Mineral Cycling, 5. Trace Analysis and reduction of Pollution in the Geosphere, 6. Ecology, 7. Other Research Activities. The three special activity units in chapter 8. Special Facilities.

The department's contribution to national and international collaborative research projects and programmes is presented in addition to information about large research and development facilities used and managed by the department. The department's educational and training activities are included in the annual report along with lists of publications, publications in press, lectures and poster presentations at international meetings. Names of the scientific and technical staff members, visiting scientists, post. doctoral 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 engages in research to improve the scientific basis for new methods in industrial and agricultural production. Through basic and applied experimental research, the department aspires to develop methods and technology for the future industrial and agricultural production, exerting less stress and strain on the environment.

### 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, nutrient cycling, ecophysiology, marine and terrestrial ecology, radioecology and tracemetal ecology.

The department includes approximately 135 scientific and technical staff members. The research activities are organized into 5 research programmes and supported by 3 special facility units.

Dr. Arne Jensen is Head of Department.

### Research Programmes

Atmospheric Chemistry and Air Pollution.

Head: Dr. Ole John Nielsen.

Trace Analysis and Pollution in the Geosphere.

Head: Dr. Vagn Gundersen.

Gene Technology and Population Biology.

Head: Dr. Hanne Østergård.

Plant Nutrition and Nutrient Cycling

Head: Dr. Gunnar Gissel Nielsen.

Ecology.

Head: Dr. Asker Aarkrog.

### Special Facility Units

Growth chambers, Risø Environmental Risk Assessment Facility (RERAF), green houses and the experimental farm, Dyskørgaard.

Head: Dr. Vagner Haahr.

Risø High Dose Reference Laboratory.

Head: Dr. Arne Miller

Risø Integrated Environmental Facility (RIMI).

Head: Dr. Kim Pilegaard

The results of research and development are disseminated internationally 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, however, national and European research programmes, private foundations and commercial contracts also make a substantial contribution to the total budget of the department.

## 1.2 Research Programmes

### 1.2.1 Atmospheric Chemistry and Air Pollution

The effect of human activity on the global atmosphere has become increasingly evident during the last decades. Changes in atmospheric composition and chemistry influences both local, regional and global climate. Deposition of air-borne pollutants can give rise, either to direct injuries to plants and animals, or to indirect damage through bio-accumulation in ecosystems.

Atmospheric research in the department aims to establish a firm scientific basis for sensible and effective legislative measures to reduce the industrial and agricultural impact on the atmospheric environment. In order to model and pre-

dict 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 the influence of atmospheric processes, 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.

### **1.2.2 Gene Technology and Population 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 low input plant production, and will reduce a number of environmental problems related to modern high yield plant production.

A large proportion of the research effort, within plant biology and genetics, is devoted to the identification of genetic markers. 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. 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. The research involves inter-relationships between crop plants and weeds, and between crop plants and 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.

Experiments in population biology and theoretical studies of interactions between populations are important in the understanding of the ecosystems.

### **1.2.3 Plant Nutrition and Mineral Cycling**

The department aims to develop the scientific basis for low input in plant production based on biologically fixed nitrogen and enhanced phosphorus uptake mediated by VA-mycorrhiza, together with highly efficient nutrient assimilation by crop plants and effective nutrient recycling in the agro ecosystem.

The research provides basic scientific information about the mechanisms and processes involved in the root-microbe symbiosis in relation to carbon, nitrogen and phosphorus. The research emphasizes biological, physiological, biochemical and chemical processes involved in the transfer of plant nutrients through the Soil-Plant-Air-Continuum. The research also renders basic information about the processes involved in the turn-over of carbon, nitrogen and phosphorus in agro ecosystems helping to reduce losses of nutrients to the atmosphere, ground water or to streams and lakes.

The plant nutrition research involves five aspects: 1) research on symbiotic nitrogen fixation, which highlights the exchange of compounds between the host plant and the micro-symbiont across the membrane interface; 2) studies of the interaction between VA-mycorrhiza, plant roots and the rhizosphere; 3) studies on turn-over of nitrogen from crop residues and farmyard manure; 4) biological transfer of nitrogen from legumes to non-legumes; and 5) the effect of air pollution with ammonia on plants.

### **1.2.5 Trace Analysis and Reduction of Pollution in the Geosphere**

The professional image of the Chemistry Section has been considerably changed in 1994 caused by the re-forming of staff in 1993 and by the retirement of scientists in the Chemistry Section this year. After employment of new research scientists in 1994, advancements are achieved in the fields of organic analysis, upgrading of biomass and the transformation of organic matter in soil and water.

The research 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

of biomass. Wet oxidation readily solubilizes lignin in straw and the product is susceptible to enzymatic treatment. In the field of upgrading of biomass we aim at converting straw to ethanol by means of wet oxidation followed by fermentation. Converting of biomass by wet oxidation creates new applications for the degradation products and demands new methods for their characterization.

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. Development of a new gamma-ray-spectrometric method to estimate sedimentation rates on the seafloor has attracted considerable attention, and a Danish Center for Sediment Dating is planned for 1995.

An active part has been taken in the formation of the Danish R&D Center for Decontamination of Soils and Sediment, an umbrella organization between five environmental research institutions. The aim of the centre is to create and coordinate R&D activities in the field of decontamination.

In collaboration with the research programmes in ecology, genetics and plant nutrition within the department it is planned to expand the field of trace elemental analysis. With the purchase of a High Resolution ICP-MS instrument in 1995 the department will have excellent facilities to estimate oceanographic tracers as Pu and Tc in cooperation with the ecology programme.

Research on trace elements in plant materials grown on different soil types, using different methods of cultivation, is planned in cooperation with the plant nutrition research programmes on genetics and plant nutrition.

### 1.2.6 Ecology

Research within ecology and mineral cycling aims to improve the scientific basis and understanding of the impacts of environmental pollution by radionuclides and heavy metals on marine and terrestrial ecosystems with emphasis on the effect on natural and semi-natural ecosystems. Further, the research aims to establish a better understanding and knowledge about transport and the fate of pollutants by the use of

stable- and radioisotopes, and trace-metal techniques.

The ecological research focuses on six aspects: 1) 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 of the Baltic. Under the marine tracer studies the transfer of pollutants to the Arctic has been studied by using radioactive tracers discharged to the Irish Sea. 2) Contamination physics developing a basic knowledge and practical methods for decontaminating areas after the Chernobyl contamination. Further, 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. 3) Radioactive tracer techniques are used, in ecophysiological studies on lipid metabolism and copper toxicity to Rainbow trout and European eel. 4) Biosphere-atmosphere exchange fluxes of gaseous compounds ( $O_3$ ,  $NO_x$ ,  $CO_2$  and  $H_2O$ ) are studied by use of the eddy correlation method. 5) Research in radioecology comprising studies of the fate of  $^{137}Cs$  in marine ecosystems and Danish forest ecosystems. 6) Radioecological modeling concentrated on marine compartment models, and assessment of doses to man, from dumping of radioactive material in the Arctic Seas. Further, model calculations for the Baltic- and Mediterranean Sea were performed.

## 2 Atmospheric Chemistry and Air Pollution

### *Introduction (O.J. Nielsen)*

Because the biosphere cycles 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 effort 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.

### *Summary of Projects*

#### 2.1 The Gas Phase

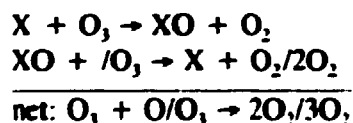
##### 2.1.1 Halogenated Compounds (O.J. Nielsen)

Recognition of the adverse effect of chlorofluorocarbon, CFC, release into the atmosphere has led to an international effort to replace CFCs with environmentally acceptable alternatives. In 1994 as part of the ongoing collaboration with

Ford Motor Company, we have published ~ 20 articles on the atmospheric chemistry of CFC substitutes, hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs), the environmental fate of intermediates and more stable atmospheric oxidation products. In 1994 we investigated the atmospheric chemistry of HCFC-123,  $\text{CF}_3\text{CCl}_2\text{H}$ , (Wallington *et al.* 1994a); methylchloroform,  $\text{CCl}_3\text{CH}_3$ , (Platz *et al.*, in press); HFC-152,  $\text{CFH}_2\text{CFH}_2$  (Wallington *et al.* 1994b); HFC-143a,  $\text{CF}_3\text{CH}_3$ , (Nielsen *et al.* 1994); HFC-272ca,  $\text{CH}_3\text{CF}_2\text{CH}_3$ , (Mogelberg *et al.* in press).

While it is well known that HFCs themselves do not react with ozone, questions have been raised over the last two years regarding the possibility that species formed during the atmospheric oxidation of HFCs could deplete stratospheric ozone. One way HFCs could impact stratospheric ozone would be if their degradation products participated in efficient catalytic ozone destruction cycles.

During the HFC atmospheric oxidation reaction, four groups of radicals are formed that could, in principle, impact stratospheric ozone ( $x=0,1,2,3$ ):  $\text{CF}_x\text{CO}_x$ ,  $\text{CF}_x\text{O}_x$ ,  $\text{FCO}_x$  (Wallington *et al.* 1994c), and  $\text{FO}_x$  (Sehested *et al.* 1994). These radicals could interact with stratospheric ozone directly in a catalytic process:



as  $\text{ClO}_x$ ,  $\text{BrO}_x$ ,  $\text{NO}_x$  and  $\text{HO}_x$  are known to do.

We have provided experimental evidence of efficient loss mechanisms for  $\text{CF}_3\text{C(O)O}$ ,  $\text{CF}_3\text{O}$ , and  $\text{FC(O)O}$  radicals and of their unreactivity towards ozone. This precludes any significant direct impact on the ozone layer associated with these radicals.

Consideration of the direct impact of  $\text{FO}_x$  radicals is complicated by the rapid interconversion between F, FO,  $\text{FO}_2$  and FNO (figure 2.1.1):

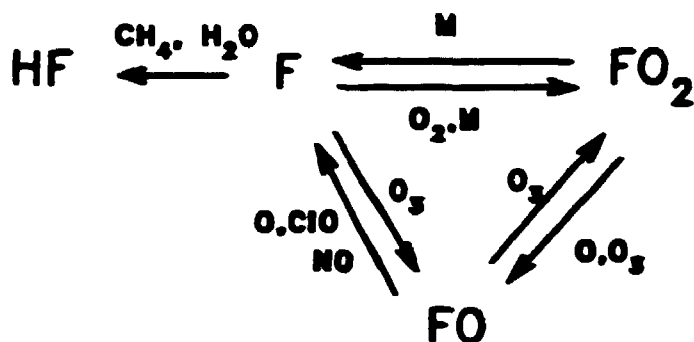
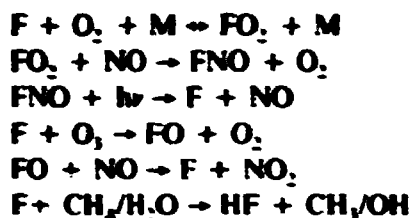
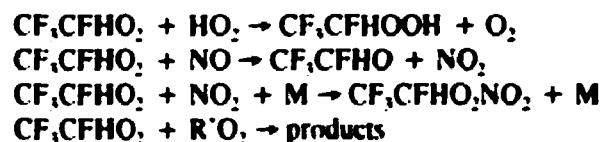


Figure 2.1.1.

FO and FO<sub>2</sub> radicals react extremely slowly with ozone and FO<sub>2</sub> radicals are efficiently lost via the reaction of F atoms with CH<sub>4</sub> and H<sub>2</sub>O. The direct impact FO<sub>2</sub> chemistry on stratospheric ozone has been addressed quantitatively by Sehested *et al.* (1994). While the efficiency of ozone destruction varies with altitude, the number of ozone molecules consumed per F atom was less than 3 at all altitudes.

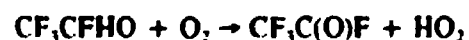
HFC-134a (1,1,1,2-tetrafluoroethane) is a substitute for CFC-12 in industrial refrigeration and automotive air conditioning units. An international research effort, presently investigating the environmental impact of HFC, release (e.g. HFC-134a) into the atmosphere.

The major loss process for HFCs in the atmosphere is the reaction with OH radicals, resulting in the generation of halogenated alkyl radicals which then react rapidly with O<sub>2</sub> to form peroxy radicals (RO<sub>2</sub>). In the atmosphere, RO<sub>2</sub> radicals react with HO<sub>2</sub>, NO, NO<sub>2</sub> or other peroxy radicals (R'O<sub>2</sub>), for example in the case of the peroxy radical derived from HFC-134a:



Results on the CF<sub>3</sub>CFHO<sub>2</sub> + NO<sub>2</sub> reaction has been published (Møgelberg *et al.* 1994a).

Trifluoroacetyl fluoride, CF<sub>3</sub>C(O)F, is formed during the atmospheric degradation of HFC-134a via reaction:



The atmospheric lifetime of CF<sub>3</sub>C(O)F has been estimated to be 5-15 days and is primarily determined by incorporation into rain-cloud-sea water where hydrolysis proceeds rapidly to produce CF<sub>3</sub>COOH. There is considerable uncertainty regarding the fate and environmental impact of CF<sub>3</sub>COOH. Evaporation of cloud droplets will release CF<sub>3</sub>COOH into the gas phase. The reaction of CF<sub>3</sub>COOH with OH radicals offers a potential degradation mechanism. The reaction of OH radicals with CF<sub>3</sub>COOH is expected to proceed via H-atom abstraction to give the radical CF<sub>3</sub>C(O)O, which undergoes rapid C-C bond scission to give CF<sub>3</sub> radicals and CO<sub>2</sub>. An accurate assessment of the importance of the reaction with OH as an atmospheric sink for CF<sub>3</sub>COOH, is hampered by the lack of kinetic data for this reaction. To remedy this situation we have performed absolute and relative rate studies of the reaction.

Two different experimental techniques were used to study the kinetics of the reaction of OH radicals with trifluoroacetic acid, CF<sub>3</sub>COOH. Using a pulse radiolysis absolute rate technique, rate constants at 315K and 348K were determined to be  $(1.6 \pm 0.4) \times 10^{-13}$  and  $(1.5 \pm 0.2) \times 10^{-13}$  cm<sup>3</sup>molecule<sup>-1</sup>s<sup>-1</sup>, respectively. Using a long path length FTIR relative rate technique a rate constant of  $(1.7 \pm 0.5) \times 10^{-13}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> was obtained at 296K. The reaction with OH radicals in the gas phase was estimated to account for 10-20% of the loss of CF<sub>3</sub>COOH. The major atmospheric fate of CF<sub>3</sub>COOH is rainout (Møgelberg *et al.* 1994b).

A review on the atmospheric chemistry and environmental impact of CFC replacements was published (Wallington *et al.* 1994d).

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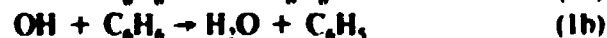
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### 2.1.2 Oxidation of Aromatics (P. Pugsberg, E. Bjergbakke, A.H. Sillesen)

Large amounts of aromatic hydrocarbons e.g. benzene and toluene are released into the atmosphere through automobile exhaust. These aromatic compounds are reactive in photochemical smog formation and the reaction products contribute to the increasing and severe air pollution in urban areas.

The chemical reaction mechanisms involved in the tropospheric oxidation of aromatic compounds are very complex, and detailed experimental investigations of the various intermediate species are required in order to identify the most important reaction path ways and products. We are engaged in a CEC-project, "CYTROXA" in collaboration with four other European research laboratories. The aim of the project is to investigate the reaction mechanisms involved in the tropospheric oxidation of aromatic hydrocarbons.

In our laboratory, we have studied the oxidation of benzene and toluene employing pulse radiolysis combined with time-resolved UV-spectroscopy. The tropospheric oxidation is initiated by the reaction with hydroxyl radicals giving rise to the formation of an addition complex. Thus, in the case of benzene we have observed transient absorption signals which we assign to hydroxycyclohexadienyl radicals produced in reaction (1a).



Under tropospheric conditions, reaction (1a) is the dominant channel while reaction (1b) is known to be important at high temperatures e.g. during combustion of benzene. The ultraviolet spectrum of hydroxycyclohexadienyl is presented in Figure 2.1.2.

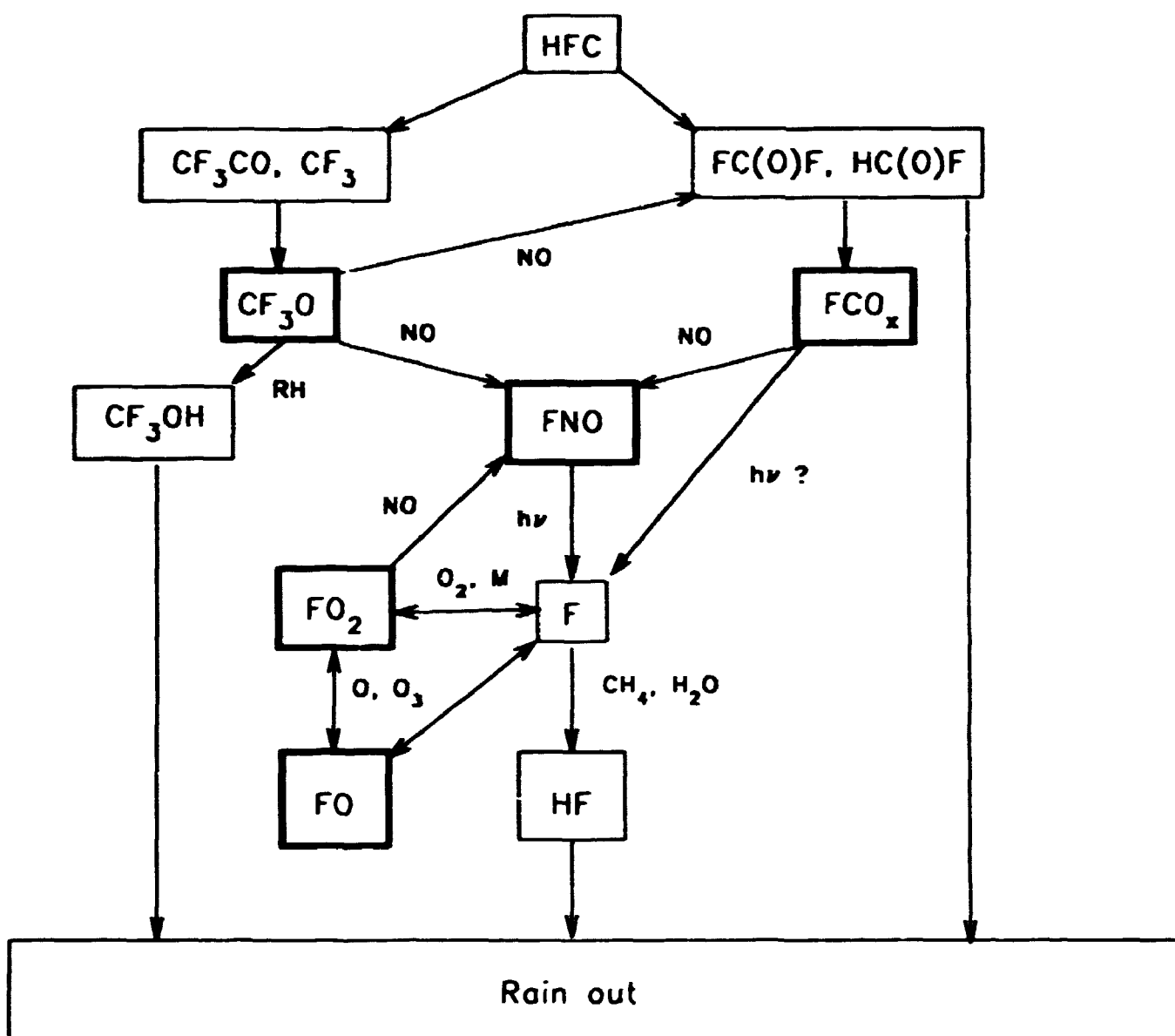
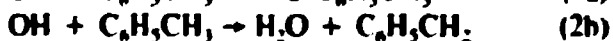
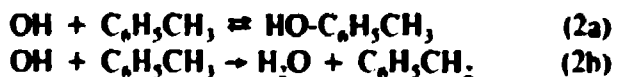


Figure 2.1.2.

In the case of toluene, we have observed competition between the addition reaction (2a) and the abstraction reaction (2b). In this case, however, the addition reaction is also the major channel under tropospheric conditions.



Recently, we have studied the reactions of hydroxycyclohexadienyl radicals with  $\text{O}_2$  and  $\text{NO}_2$ . Several reaction mechanisms have been proposed, based on the observed stable reaction

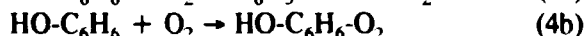
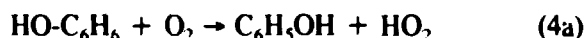
products, e.g. phenol and nitrobenzene. Based on direct spectrokinetic studies of the decay rate of  $\text{HO-C}_6\text{H}_5$ , we determined the absolute bimolecular rate constants for the reactions of this radical with  $\text{NO}_2$  and  $\text{O}_2$ .



Phenol and nitrobenzene were previously observed among the stable products by the photochemical oxidation of  $\text{C}_6\text{H}_6/\text{NO}_2$  mixtures.

However, since we did not observe the simultaneous formation of HO-C<sub>6</sub>H<sub>5</sub> or C<sub>6</sub>H<sub>5</sub>NO<sub>2</sub> in these direct experiments, it appears that the adduct formation (3c) is the main channel.

In the case of O<sub>2</sub> we have considered the reactions (4a) and (4b).

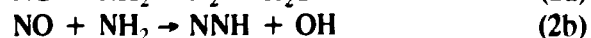
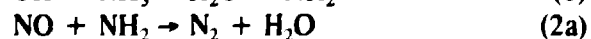


Also in this case, we find that the phenol formation is negligible compared with the adduct formation via reaction (4b). We also observed that by the reaction with oxygen, the spectrum of HO-C<sub>6</sub>H<sub>6</sub> was replaced by the spectrum of another transient species which we assigned to the peroxyradical HO-C<sub>6</sub>H<sub>6</sub>-O<sub>2</sub>. Thus, by our direct spectrokinetic studies we have been able to identify the most important path ways for the reactions of hydroxycyclohexadienyl radicals with NO<sub>2</sub> and O<sub>2</sub>. Much to our surprise, the reactions (3a), (3b) and (4a) which have been proposed in recent review articles appear to be of minor importance.

### 2.1.3 Chemistry of Nitrogen Oxides (*P. Pagsberg, E. Ratajczak, A.H. Sillesen*)

Emission of nitrogen oxides from power plants and automobiles is one of the most serious sources of air pollution, giving rise to "acid rain" and photochemical smog formation.

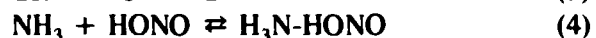
A lot of research has been devoted to the development of new technologies for the removal of nitrogen oxides in stack gases from power plants. A fairly efficient method, known as the "Thermal DENO<sub>x</sub> process" was developed by Lyon in 1975. Later, other methods have been developed, including selective catalytic reduction (SCR). The chemical reactions involved in the Thermal DENO<sub>x</sub> process are known to proceed via radical chain reactions initiated by the reaction of hydroxyl radicals with ammonia, which is added to the stack gases.



Recent computer modelling of the chemical reaction mechanisms involved in the Thermal

DENO<sub>x</sub> process has been quite successful. However, although more than 100 elementary reactions have been taken into account in the complete model, there are still major uncertainties regarding certain reactions and the efficiency of the chain reactions.

We have considered a possible alternative mechanism involving the same primary species, *i.e.* OH, NO and NH<sub>3</sub>.

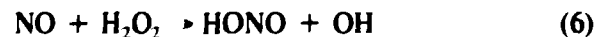


This alternative mechanism has not been investigated before and we thought that it might be of interest to study the reversible gas phase reaction (4), using infrared diode laser spectroscopy to monitor the kinetics of HONO during relaxation towards equilibrium.

We determined the equilibrium constant as a function of temperature to evaluate the thermochemistry involved, *i.e.* the reaction enthalpy, bond energy and heat of formation of the hydrogen bonded adduct (Pagsberg *et al.* 1994). The preliminary work was supported by a grant from the Ministry of Energy.

Recently we have re-established an experimental set-up for pulse radiolysis combined with infrared diode laser spectroscopy. Using this experimental technique, we should be able to study the kinetics of the reactions (3), (4) and (5) at elevated temperatures, where we expect to observe the thermal decomposition of the adduct, *i.e.* reaction (5).

The aim of these investigations is to develop a new DENO<sub>x</sub>-technology based on the chemical reaction mechanism described above. However, we want to replace reaction (3) with a suitable thermal reaction for the conversion of NO to HONO. We have carried out some preliminary experimental studies of the reaction (6), which is rather slow at room temperature.



At higher temperatures we expect to observe an increase in the rate of this reaction. In addition to reaction (6) we shall study other reaction mechanisms which may be used for the interconversion of NO to HONO.

## References

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## 2.2 The Liquid Phase (K. Sehested, J. Holcman)

The  $\text{NO}_3$  radical is an important atmospheric oxidant at night-time in the gas phase and may also be of importance in the aqueous phase. Its spectrum and rate of formation in the reaction  $\text{OH} + \text{HNO}_3$ ,  $k = (6.0 \pm 1.0) \times 10^7 \text{ M}^{-1}\text{s}^{-1}$  was determined in pulse radiolysis of 0.5 - 1 M nitric acid solution in competition with the reaction  $\text{OH} + \text{H}_2$  using the high pressure cell with 140 atm of  $\text{H}_2$ . The extinction coefficient was determined to  $\epsilon_{635} = 1250 \pm 100 \text{ M}^{-1}\text{s}^{-1}$  by numerical simulation from the radical G-values and the rate constants and from a competition of OH radicals for  $\text{HNO}_3$  and  $\text{HSO}_4^-$  using the extinction coefficient of  $\text{SO}_4^-$  as a relative measure.

The rate constants of the reactions  $\text{NO}_3 + \text{NO}_2$  and  $\text{NO}_3 + \text{HO}_2$  were measured in the high pressure cell using 140 atm of  $\text{H}_2$  or  $\text{O}_2$  or mixtures of  $\text{H}_2$  and  $\text{O}_2$ . The  $\text{NO}_3$  absorbances and kinetics were simulated applying the CHEMSIMUL programme and the rate constants were determined to be  $k(\text{NO}_3 + \text{NO}_2) = (1.7 \pm 0.2) \times 10^9$  and  $k(\text{NO}_3 + \text{HO}_2) = (3.0 \pm 0.5) \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ , respectively (Sehested *et al.*).

Methanesulfinic acid,  $\text{CH}_3\text{SO}_2\text{H}$ , an oxidation product from dimethyl sulfide, reacts with OH radicals at pH 7 forming  $\text{CH}_3\text{SO}_2$  radicals with a rate constant  $k = (6.0 \pm 1.0) \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ . The  $\text{CH}_3\text{SO}_2$  radical absorbs at 325 nm, with an extinction coefficient of  $900 \pm 100 \text{ M}^{-1}\text{cm}^{-1}$ , and disappears in a second order self-reaction with  $k = (1.0 \pm 0.2) \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ . This radical reacts with oxygen,  $k = (1.2 \pm 0.3) \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ , forming a peroxy radical which absorbs in the UV below 300 nm. The peroxy radical reacts in turn with methanesulfinic acid, reforming the  $\text{CH}_3\text{SO}_2$  radical whereby a chain oxidation of sulfinic acid takes place. During the course of the chain oxidation a peroxyacid, presumably methaneperoxymonosulfonic acid, is formed and accumulated. This acid absorbs UV

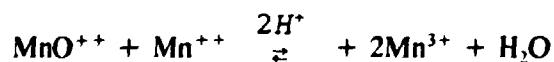
light and eventually decays by reaction with excess methanesulfinic acid  $k = 5 \times 10^3 \text{ M}^{-1}\text{s}^{-1}$ . The final product of the chain autooxidation is methanesulfonic acid. The chain is very efficient and proceeds until either oxygen or methanesulfinic acid is exhausted (Sehested and Holcman 1994).

Oxygen atom exchange in aqueous solution by the reactions  $\text{O}^- + \text{H}_2\text{O} \rightarrow \text{OH}^- + \text{OH}$  and  $\text{OH} + \text{H}_2\text{O} \rightarrow \text{H}_2\text{O} + \text{OH}$  were studied by measuring the oxygen isotope composition of  $\text{H}_2\text{O}_2$  and  $\text{O}_2$  produced by electron pulse irradiation and  $\gamma$ -irradiation of solutions of  $\text{N}_2\text{O}$  and  $\text{BrO}_4^-$  in water enriched with  $\text{H}_2^{18}\text{O}$ . The fraction of the reaction  $\text{O}^- + \text{H}_2\text{O} \rightarrow \text{OH}^- + \text{OH}$ , which takes place by hydrogen atom transfer is found to be  $0.22 \pm 0.02$  at  $22^\circ\text{C}$ , and to increase with temperature. The difference between the enthalpies of activation for hydrogen atom transfer and proton transfer is estimated to be  $16 \pm 2 \text{ kJ mol}^{-1}$  and the corresponding entropy of activation at  $22^\circ\text{C}$  to be  $44 \pm 8 \text{ J K}^{-1} \text{ mol}^{-1}$ . Assuming no interference from impurities, the rate constant for the exchange reaction  $^*\text{OH} + \text{H}_2\text{O} \rightarrow \text{H}_2^*\text{O} + \text{OH}$  is found to be  $(57 \pm 6) \text{ s}^{-1}$  at  $30^\circ\text{C}$  (Klänning *et al.* 1994), (cooperation with U. Klänning, Aarhus University).

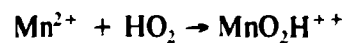
The temperature dependence of the rate constants, for the reactions of hydrated electrons with H atoms, OH radicals and  $\text{H}_2\text{O}_2$  was determined. The reaction with H atoms, studied in the temperature range  $20\text{-}250^\circ\text{C}$  gives  $k(20^\circ\text{C}) = 2.4 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$  and the activation energy  $E_A = 14.0 \text{ kJ mol}^{-1}$  ( $3.3 \text{ kcal mol}^{-1}$ ). For the reaction with OH radicals, the corresponding values are  $k(20^\circ\text{C}) = 3.1 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$  and  $E_A = 14.7 \text{ kJ mol}^{-1}$  ( $3.5 \text{ kcal mol}^{-1}$ ) determined in the temperature range  $5\text{-}175^\circ\text{C}$ . For reaction with  $\text{H}_2\text{O}_2$  the values are  $k(20^\circ\text{C}) = 1.2 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$  and  $E_A = 15.6 \text{ kJ mol}^{-1}$  ( $3.7 \text{ kcal mol}^{-1}$ ) measured from  $5\text{-}150^\circ\text{C}$ . Thus, the activation energy for all three fast reactions is close to that expected for diffusion controlled reactions. As phosphates were used as buffer system, the rate constant and activation energy for the reaction of hydrated electron with  $\text{H}_2\text{PO}_4^-$  was determined to  $k(20^\circ\text{C}) = 1.5 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$  and  $E_A = 7.4 \text{ kJ mol}^{-1}$  ( $1.8 \text{ kcal mol}^{-1}$ ) in the temperature range  $20\text{-}200^\circ\text{C}$  (Christensen *et al.* 1994), (cooperation with H. Christensen, Studsvik AB, Sweden).

The hydrated electron- and H-atom reduction processes of aqueous benzaldehyde and 2-, 3- and 4-chlorobenzaldehyde were studied by pulse radiolysis. The electron attachment occurs on the aldehyde group. In alkaline solutions the radical anions are formed by the reaction with  $e_{aq}^-$  as well as with  $(CH_3)_2COH$  and  $CO_2^-$  radicals. In acid solution, the protonated forms of these radicals are obtained,  $pK_a = 8.2-8.5$ . The rate constants for the reaction with  $e_{aq}^-$  have been determined to  $k(e_{aq}^- + C_6H_5CHO) = 2.4 \times 10^{10} \text{ dm}^3\text{mol}^{-1}\text{s}^{-1}$  and  $k(e_{aq}^- + ClC_6H_4CHO) = 2.2 \times 10^{10} \text{ dm}^3\text{mol}^{-1}\text{s}^{-1}$ . The electron transfer process from  $(CH_3)_2COH$  and  $CO_2^-$  radicals to the various benzaldehydes is much slower,  $k = (0.7-2.2) \times 10^8 \text{ dm}^3\text{mol}^{-1}\text{s}^{-1}$  and  $(5.4-16) \times 10^8 \text{ dm}^3\text{mol}^{-1}\text{s}^{-1}$ , respectively, depending on the position of the halide. The anion radicals of the chlorobenzaldehydes do not undergo intramolecular electron transfer and dehalogenation. This is confirmed by  $\gamma$ -radiolysis experiments, where no chloride and HCHO could be detected as final products (cooperation with N. Getoff, University of Vienna, Austria).

Ozone reactions with transition metal ions are very important for the oxidation processes in the atmosphere. The reaction with manganese in strong acid solutions has been studied by stopped-flow experiments. Manganese (II) forms manganese (III) by ozone oxidation, but it is proved that the first step is an oxygen atom transfer to form  $MnO^{++}$ , formally Mn(IV). The equilibrium reaction



is very fast and shifted to the right, favoring  $Mn^{3+}$ . The rate constant for the ozone reaction is determined to  $k(O_3 + Mn^{2+}) = 1.5-1.8 \times 10^3 \text{ M}^{-1}\text{s}^{-1}$ . The activation energy is  $40.0 \pm 2.0 \text{ kJ/mol}$  in the pH range 0-3. The manganese III reacts with  $H_2O_2$  with a rate of approximately  $4 \times 10^4 \text{ M}^{-1}\text{s}^{-1}$  forming the complex  $MnO_2H^{++}$ , which may also form in the reaction



These reactions are studied by pulse radiolysis, which has also yielded  $OH + Mn^{2+} \rightarrow Mn^{3+} + OH^-$  with a rate of  $k = 2 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$ . Reaction kinetics and spectra of the

various species are determined. The study is part of the EU contract: RENOX (Jacobsen 1994).

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## 2.3 Atmospheric Chemistry

### 2.3.1 Composition of Atmospheric Nitrogen Compounds (T. Nielsen)

As a contribution to the EUROTRAC-TOR project and to the Danish Centre of Air Pollution Processes under the Danish Environmental Research Programme, the relationships between ozone and the composition of the individual nitrogen compounds were investigated in collaboration with the National Environmental Research Institute in the period 25 May-30 June.

The concentrations and composition of the  $NO_x$  compounds ( $NO_x = NO_y - NO_x$ ) in the investigation were very similar to those observed earlier at a more remote site in southern

Scandinavia, Rörvik on the Swedish west coast (Ferm *et al.* 1984). Ferm *et al.* found a summer mean value of PAN to be  $0.38 \mu\text{gN m}^{-3}$  and of  $\text{HNO}_3$  + inorganic nitrate to be  $0.68 \mu\text{gN m}^{-3}$ , being very close to our values of 0.32 and  $0.61 \mu\text{gN m}^{-3}$ , respectively. Therefore, it is believed the observations in this investigation have general validity for southern Scandinavia. The influence by local sources on the  $\text{NO}_x$  levels at our site was reflected in the  $\text{NO}_2$  values. Ferm *et al.* found  $1.1 \mu\text{gN m}^{-3}$  of  $\text{NO}_2$ , while the  $\text{NO}_2$  concentration at our site was two times higher,  $2.3 \mu\text{gN m}^{-3}$ .

The relationships between the ozone air pollution level and the composition of total  $\text{NO}_y$  compounds (total  $\text{NO}_y = \text{NO} + \text{NO}_2 + \text{HNO}_3 + \text{PAN} + \text{PPN} + \text{inorganic nitrate} + 2 * \text{N}_2\text{O}_5 + \text{organic nitrates}$ ) are shown in Figure 2.3.1. The mean total  $\text{NO}_y$  was very similar for the four ozone category air pollution levels, being  $5.0 \mu\text{gN m}^{-3}$  at 20-30 ppb ozone,  $4.2 \mu\text{gN m}^{-3}$  at 30-40 ppb as well as 40-50 ppb and  $5.3 \mu\text{gN m}^{-3}$  at 50-60 ppb. The major feature in the relationship is the  $\text{NO}_x$  proportion decreases from 79% at 20-30 ppb ozone to 33% at 50-60 ppb, and the  $\text{NO}_2$  proportion increases from 21 to 67% with increasing ozone concentrations.

### *$\text{NO}_y$ composition compared to ozone category*

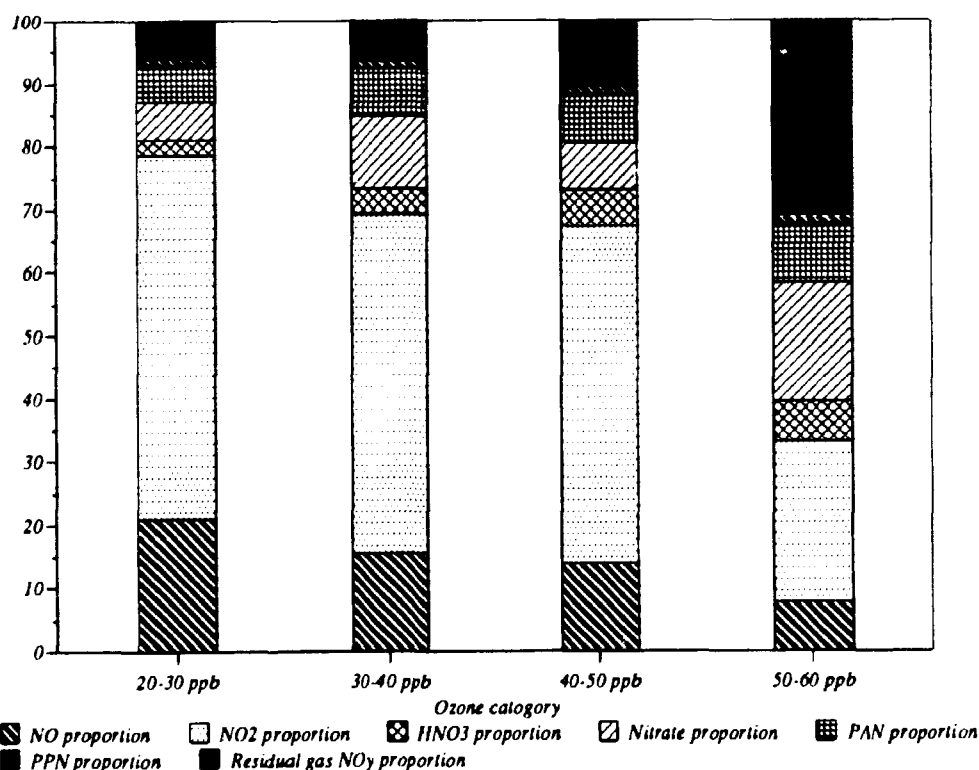
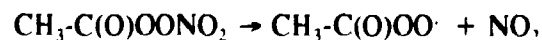


Figure 2.3.1. The figure shows the composition of total  $\text{NO}_y$  at different  $\text{O}_3$  levels.

The PAN/ $\text{NO}_2$  ratio decreased with the temperature ( $r = -0.54$ ,  $p < 0.01$ ), despite PAN ( $r = 0.53$ ,  $p < 0.01$ ) had a positive correlation with the ambient temperature. But the other  $\text{NO}_2$  compounds ( $\text{HNO}_3$  + inorganic nitrate ( $r = 0.60$ ,  $p < 0.001$ ) and residual gas  $\text{NO}_y$  (r.g.  $\text{NO}_y = \text{gas NO}_y - \text{NO} - \text{NO}_2 - \text{HNO}_3 - \text{PAN} - \text{PPN}$ ) (see the following section) ( $r = 0.61$ ,  $p < 0.001$ ) also had positive correlations with the

ambient temperature. The reason for the decrease of the PAN/(total  $\text{NO}_y$ ) ratio appears to be the thermolability of the peroxyacyl nitrates. An increase in the temperature from  $13^\circ\text{C}$  (mean temperature for 20-30 ppb ozone) to  $17^\circ\text{C}$  (mean temperature for 50-60 ppb ozone) increases the dissociation of PAN with a factor of 1.9:



The work has been presented by Nielsen *et al.* (1994).

## References

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### 2.3.2 Observations of unidentified Nitrogen Compounds (T. Nielsen)

As a contribution to the EUROTRAC-TOR project and to the Danish Centre of Air Pollution Processes under the Danish Environmental Research Programme the existence of some unidentified nitrogen compounds were observed in collaboration with the National Environmental Research Institute.

High concentrations of residual gas  $\text{NO}_y$  (residual gas  $\text{NO}_y = \text{gas NO}_y - \text{NO} - \text{NO}_2 - \text{HNO}_3 - \text{PAN} - \text{PPN}$ ) ( $1.5\text{--}2.1 \mu\text{gN m}^{-3}$ , 17-31% of total  $\text{NO}_x$ ) were observed in the periods 4-6 June and 9-11 June 1994 at 8<sup>00</sup> (see Figure 2.3.2). The  $\text{NO}_x/\text{NO}_y$  ratio varied from 0.33 to 0.66. Both periods were characterized by high pressure photochemical pollution and warm sunny weather and elevated daily ozone maximum values in the range 62-72 ppb. As shown in the figure, the 4-5 June and 9-10 June case studies were also characterized by elevated concentrations of other  $\text{NO}_x$  compounds, *e.g.* nitric acid and PAN. The photochemical pollution over the four days, was caused by the two high pressure systems, respectively, moving from Iceland to western Norway and from the Canary Islands to western France on 2-3 June. On 3 June the ozone maximum level was 48 ppb. On the 4th and 5th the high pressure systems covered Denmark. The air mass trajectory on the 4th started in Norway and during the transport the air masses were affected by photo-

24-h levels of  $\text{NO}_x$  compounds and  $\text{SO}_2$  in the periode 3 - 11 June

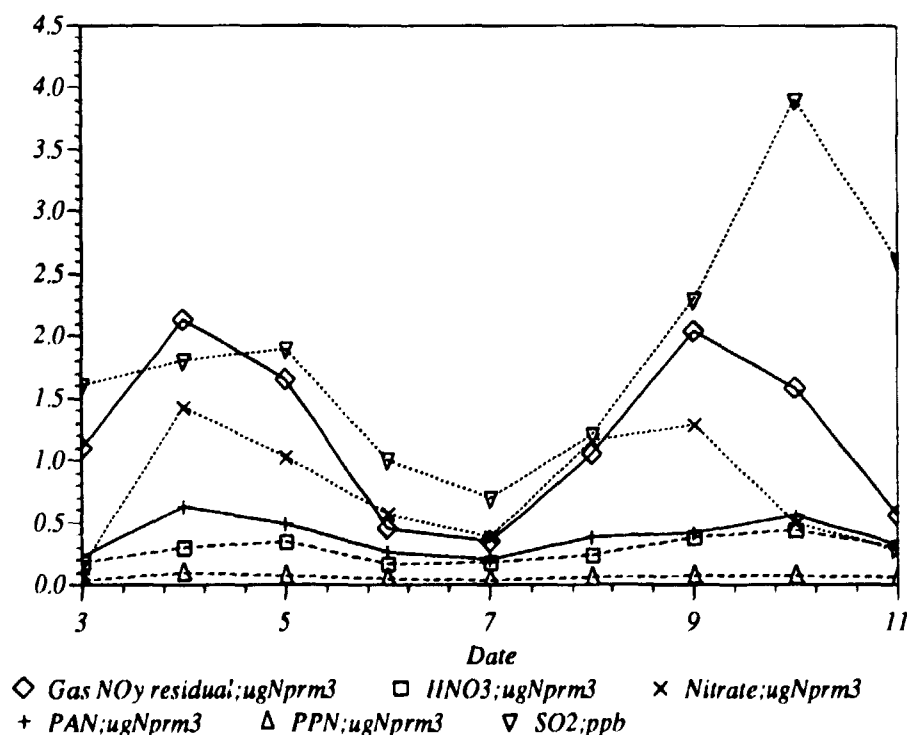


Figure 2.3.2. The figure shows the 24-h mean value variation of the  $\text{NO}_x$  compounds, residual gas  $\text{NO}_y$ ,  $\text{HNO}_3$ , particulate inorganic nitrate, peroxyacetyl nitrate (PAN) and peroxypropionyl nitrate (PPN), and  $\text{SO}_2$  in the period 3-11 June. The highest concentrations of the  $\text{NO}_x$  compounds were coincident with elevated levels of photochemical air pollution, *i.e.* on 4, 5, 9 and 11 June.

chemical processes in the high-pressure system. In the 5th sample, the air mass trajectory was very short and originated from the North Sea. On the 6-7 June, the high pressure system stabilized above south-west Brittany and the weather was determined by frontal systems from the north-west bringing clean air masses originating from the Atlantic Ocean and passing Scotland or the north of Scotland into Denmark. Figure 2.3.2 also shows decreasing air pollutant concentrations on the 6th and 7th. The ozone maximum levels had decreased to 48 and 43 ppb, respectively. On the 8th the ozone maximum level increased to 52 ppb. On the 8th and 9th, the high pressure system above south Brittany moved to south Sweden and further to the east on the 10th causing an increase in the occurrence of ozone and other photochemical oxidants. The wind speeds were relatively low, i.e. 2-3 m s<sup>-1</sup>, and the wind directions shifted. The air mass trajectories on the 9th were short. In the 10th sample, the air masses were characterized by warm continental polluted air from the south-east containing elevated concentrations of SO<sub>2</sub>. On the 11th, the ozone maximum level decreased to 60 ppb and the amount of residual gas NO<sub>y</sub> decreased to 0.6 µgN m<sup>-3</sup> (10% of total NO<sub>y</sub>) finishing the two high pressure photochemical polluted episodes.

NO, NO<sub>2</sub>, HNO<sub>3</sub>, PAN, PPN, inorganic nitrate and gas NO<sub>y</sub> was determined over 35 days in the period 25 May - 30 June. The mean total NO<sub>y</sub> was 4.3 ± 0.9 µgN m<sup>-3</sup>. The mean Σ(NO<sub>y</sub>)<sub>i</sub> was 4.0 ± 0.7 µgN m<sup>-3</sup>. The ratio Σ(NO<sub>y</sub>)<sub>i</sub>/NO<sub>y</sub> on 0.92 is not significantly different from 1.00. Nevertheless, it is assumed that the mean residual gas NO<sub>y</sub> value on 0.3 ± 0.2 µgN m<sup>-3</sup> and the ratio (residual gas NO<sub>y</sub>)/NO<sub>y</sub> on 0.07 has a physical meaning. The reasons for this are as follows:

- 1) Elevated concentrations at high pressure photochemical polluted episodes.
- 2) Significant positive and not negative correlations with all the "subtrahend components":
 

NO,	$r = 0.62, p < 0.001$
NO <sub>2</sub> ,	$r = 0.70, p < 0.001$
HNO <sub>3</sub> ,	$r = 0.81, p < 0.001$
PAN,	$r = 0.69, p < 0.001$
PPN,	$r = 0.54, p < 0.01$

- 3) Significant positive correlations with other atmospheric reaction products:
 

Formic acid,	$r = 0.53, p < 0.01$
Acetic acid,	$r = 0.55, p < 0.01$
- 4) Significant negative correlations with the indicator for clean marine air, methane sulphononic acid (MSA):
 

MSA,	$r = -0.40, p < 0.1$
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- 5) Significant positive correlation with an indicator for anthropogenic pollution, SO<sub>2</sub>:
 

SO <sub>2</sub> ,	$r = 0.72, p < 0.001$
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- 6) Significant correlations with meteorological parameters:
 

Wind-speed,	$r = -0.57, p < 0.001$
Temperature,	$r = 0.61, p < 0.001$
- 7) Analytical uncertainties are independent of point 1 - 6.
- 8) Organic nitrates are known to be formed by photooxidation reactions of NO<sub>x</sub> in laboratory experiments.
- 9) Observations in U.S.A. and Canada of a missing fraction, residual NO<sub>y</sub>, on 0.06 - 0.44.

The work has been presented by Nielsen *et al.*, and a paper (Nielsen, Egeløv, Granby and Skov: "Observations of particulate organic nitrates and unidentified components of NO<sub>y</sub>". is submitted for publication in *Atmos. Environ. Part A*).

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### 2.3.3. The Relationships between Particulate Organic Nitrates and the NO<sub>y</sub> Dose (T. Nielsen)

As a contribution to the EUROTRAC-TOR project and to the Danish Centre of Air Pollution Processes under the Danish Environmental

Research Programme the relationships between particulate organic nitrates and the  $\text{NO}_3$  dose were investigated in collaboration with the National Environmental Research Institute.

Twenty-one 24-h filter samples were collected in the period 23 March - 25 June and the content of particulate organic nitrate was determined.

At present, it is not known whether particulate organic nitrates (PON) are day-time produced by reaction of alkenes with  $\text{HO}^\cdot$  and/or night-time produced by reactions of  $\text{NO}_3$  with alkenes. Nevertheless, a most interesting correlation was observed between the 24-h levels of PON and the night  $\text{NO}_3$  dose. The night  $\text{NO}_3$  dose is the amount of  $\text{NO}_3$  formed in  $1 \text{ m}^3$  air during the night.

*Particulate organic nitrates ( $\text{ngN/m}^3$ )  
versus night  $\text{NO}_3$  dose ( $\mu\text{gN/m}^3$ )*

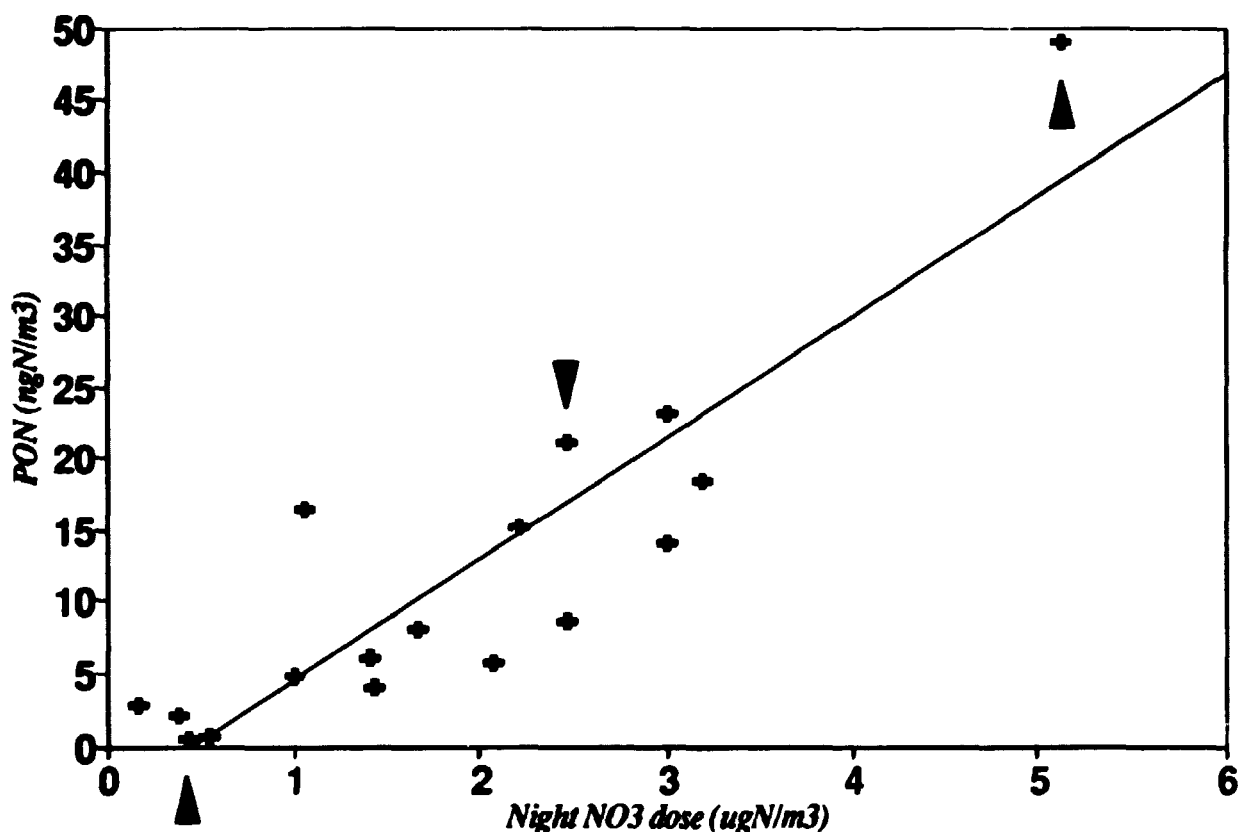


Figure 2.3.3. The figure shows the correlation between the 24-h mean levels of particulate organic nitrates (PON) and the night  $\text{NO}_3$  dose.

$\text{PON} (\text{ngN/m}^3) = (8.2 \pm 1.1) * (\text{night } \text{NO}_3 \text{ dose}) (\mu\text{gN/m}^3) - (3.6 \pm 5.8), r = 0.88, p < 0.001.$

The following samples, 26-27 April at 8<sup>00</sup> ( $49 \text{ ngN/m}^3$  PON), 10-11 June at 8<sup>00</sup> ( $21 \text{ ngN/m}^3$ ), and 21-22 June at 8<sup>00</sup> ( $0.5 \text{ ngN/m}^3$ ) were studied more detailed and is labeled with an arrow in the figure.

Some of the results were analyzed in more detail. High levels of PON were observed on 26-27 April at 8<sup>00</sup> ( $49 \text{ ngN/m}^3$ ), 13-14 May at 8<sup>00</sup> ( $35 \text{ ngN/m}^3$ ), and 10-11 June at 8<sup>00</sup> ( $21 \text{ ngN/m}^3$ ). In all three cases the weather was sunny and a high pressure system east of Denmark caused warm air masses to move from the

continent to Denmark. The air mass trajectories originated in a south-southeasterly direction. The episodes were associated with elevated levels of ozone with daily maximum values in the range of 66 - 76 ppb. In contrast to this a very low concentration of PON ( $0.5 \text{ ngN/m}^3$ ) was observed in the 21 June sample. The air mass

trajectory showed a marine origin from a north-westerly direction. The PON proportion of the NO<sub>3</sub> dose was much lower in the 21 June sample (0.09%), having elevated levels of wet sea-salt aerosols, than those in the 26 April (0.96%) and the 10 June samples (0.86%).

The work has been presented by Nielsen *et al.*, and a paper (Nielsen, Egeløv, Granby and Skov: "Observations of particulate organic nitrates and unidentified components of NO<sub>y</sub>", is submitted for publication in *Atmos. Environ. Part A*).

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### 2.3.4 Speciation of Diesel and Petrol PAH Traffic Contribution (T. Nielsen)

The PAH-rich diesel fuel contains a relatively high content of alkylated PAH compared to that of the parent PAH. The reason for this is that low temperature PAH formation (petrogenesis) produces mixtures enriched in alkyl-substituted PAH and other kinetically favored compounds in contradiction to high temperature processes (combustion and pyrolysis) encouraging the generation of unsubstituted (thermodynamically favored) compounds. The emission amount of PAH and mutagens, and the emission ratio of the alkylated PAH compared to the unsubstituted from diesel engines depends on the fuel composition, the PAH content and the PAH composition in the fuel and lubricant, and the engine operating conditions. Thus at low combustion temperature and low exhaust temperature the MePh/Ph ratio is high, while it decreases with increasing combustion and exhaust temperature. Nevertheless, compared to other sources, *e.g.* petrol engines, the MePh/Ph emission ratio is higher from diesel engines. At highway driving conditions, the MePh/Ph emission ratio from diesel engines is determined to be 4.5 and the ratio from petrol engines to 0.6. Considering the difference in the driving conditions between city traffic and roadway tunnel traffic, these ratios represent a lower limit value for city traffic.

Figure 2.3.4.1 shows the MePh to Ph ratio at different sites. The ratio values from this investigation are the ratio between the mean concentration of particulate MePh and that of particulate Ph. These values should be the same as the ratio between the mean concentration of total MePh and that of total Ph, as the gas to particle distributions of MePh and Ph have previously been found to be the same. The MePh/Ph ratio falls in the following order: Diesel exhaust gas (5.5), bus street (4.8), BS;WO (3.6), bus garage (2.0), BS;WE (1.8), CP;WO (1.6), petrol exhaust gas (0.7). (The abbreviations are explained in the text of Figure 2.3.4.1). The value of diesel exhaust gas of 5.5 was achieved from a Swedish bus during a test simulating driving in a European city. This value agreed reasonably with the value of 4.8 observed in a bus street. The advantages and disadvantages of applying field sampling and single engines in laboratory tests will be discussed later. The diesel exhaust gas value of 5.5 agreed even better if one compared it with the bus street value of the mean of the MePh/Ph ratio ( $5.4 \pm 1.7$ ). The fall of the MePh to Ph ratio in the range, BS;WO (3.6), BS;WE (1.8) and CP;WO (1.6), agreed with the expectations on the PAH traffic contribution in these three types of samples. The low MePh to Ph ratio observed in the bus garage samples appeared to be caused by other influences. The expression  $\text{dieselBeP} = \text{BeP} * ((\text{MePh/Ph} - 0.7)/(5.5 - 0.7))$  is, therefore, applied to evaluate the amount of BeP in air originating from diesel exhaust gases.

It appears reasonable to assume that contributions from long-range transport, power plants and heating sources are the same or almost the same in a city park area and in a busy street considering the distance between the two sites are only a few hundred meters. If one can neglect the influence of atmospheric chemical processes, deposition and resuspension processes, the only difference between the two sites is the distance to the traffic sources. Therefore, the PAH difference level between the two sites can be ascribed to originate only from traffic sources. In the following the PAH difference levels were utilized for the calculation of the diesel proportion of the total PAH traffic contribution.

**Diesel indicator ratio, MePh/Ph  
versus site or source**

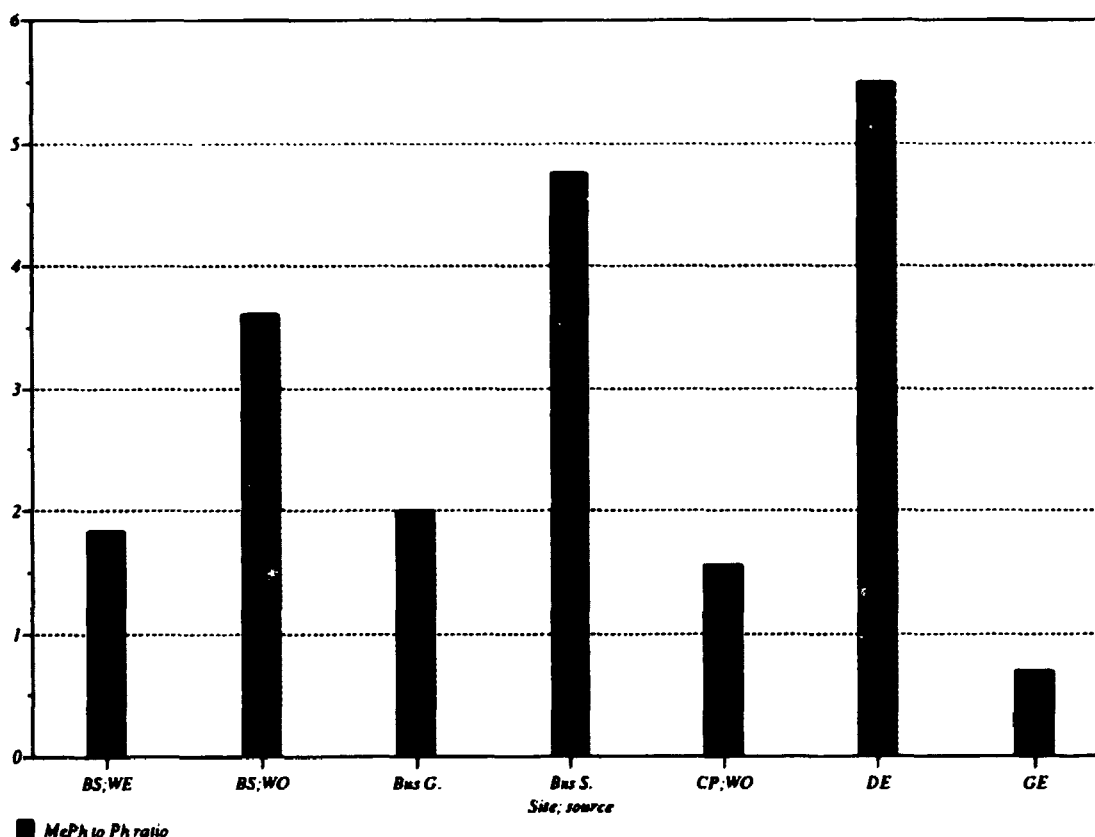


Figure 2.3.4.1. The diesel traffic indicator ratio, methylphenanthrenes to phenanthrenes ratio (MePh/Ph), at different sites or from different sources. BS;WE: Busy street, weekends, BS;WO: Busy street, working days, Bus G: Bus garage, Bus S: Bus street, CP;WO: City park, working days, DE: Heavy-duty diesel truck exhaust gas, GE: Petrol-powered vehicle exhaust gas.

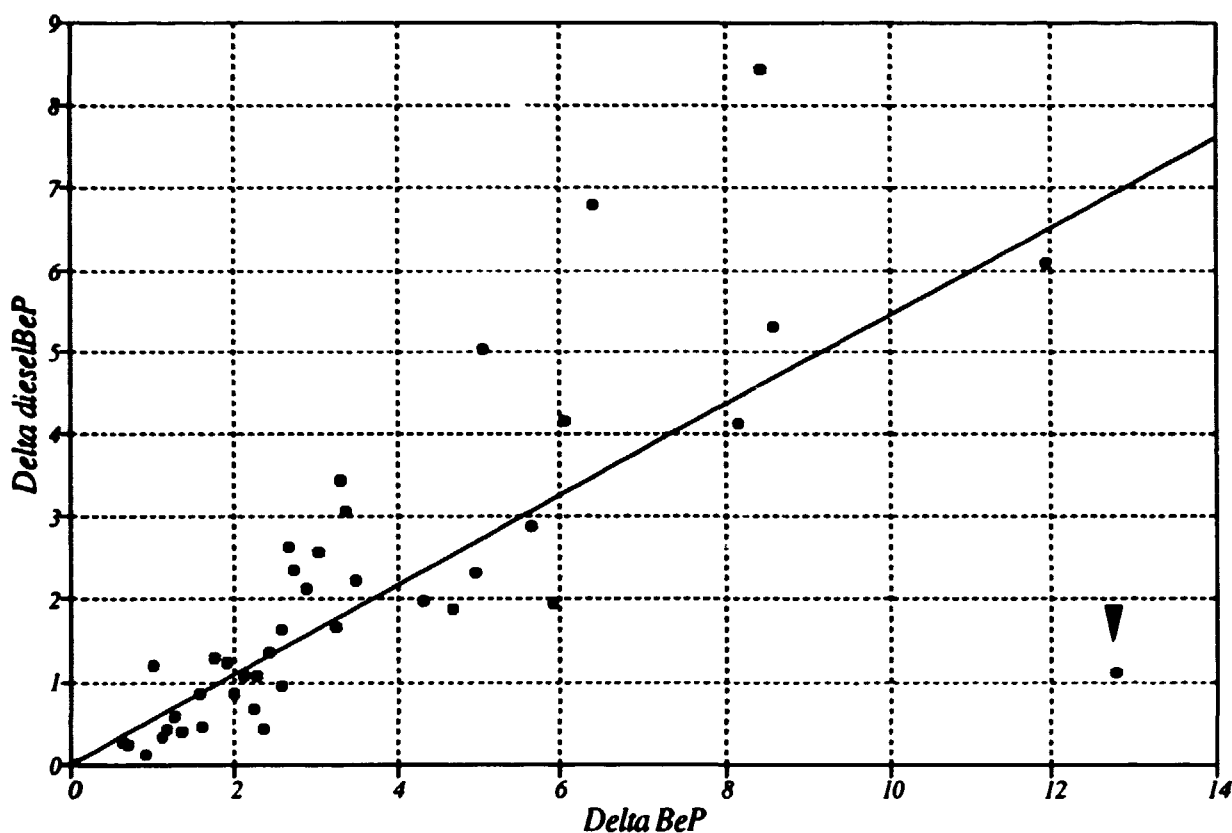
The advantage of the method is discussed as follows: The PAH composition differs from car to car and is dependent on driving conditions, fuel, lubricant and engine conditions. Therefore, it is an advantage the PAH has originated from the exhaust from a great number of cars driving in a pattern typical for city traffic.

The presumptions for the method are:

- 1) significant positive correlations of the individual PAH difference values, *i.e.*  $\Delta$ diesel-BeP and  $\Delta$ BeP in Figure 2.3.4.2,
- 2) traffic emissions are the major PAH source at the busy street sampling site.
- 3) atmospheric reactions have not changed the ratio between the level of MePh and that of Ph.
- 4) an adequate estimate of the MePh/Ph ratio in diesel exhaust gases.

Figure 2.3.4.2 shows the determination of the diesel BeP proportion of the total city traffic BeP contribution. In all the three tested modifications the correlation was significant ( $r = 0.69 - 0.86$ ,  $p < 0.001$ ). Concerning the third presumption as one can see in Figure 2.3.4.2, the MePh/Ph ratio during a long-range transport episode was extreme low suggesting degradation of MePh. The BeP diesel proportion is equal to the slope in the linear regression analysis. If one excludes the long-range transport episode in the analysis, the BeP diesel proportion changes to  $0.64 \pm 0.07$  from  $0.54 \pm 0.10$ . Concerning the fourth presumption, if one applies a value on 7.0 instead of 5.5 the slope changes to  $0.50 \pm 0.07$  instead of  $0.64 \pm 0.07$ . Thus, the analysis suggests that the BeP diesel exhaust contribution and the BeP petrol exhaust contribution is comparable.

### Correlation between delta dieselBeP and delta BeP



**Figure 2.3.4.2** Determination of the PAH (as benzo(e)pyrene (BeP)) diesel proportion of the total city traffic PAH (as BeP) contribution. The y-intercept value is forced to zero. The PAH diesel proportion = the slope =  $0.54 \pm 0.10$  ( $r = 0.69$ ,  $p < 0.001$ ).  $\Delta\text{BeP}$  = the difference between the BeP level in the busy street and that in the city park.  $\Delta\text{dieselBeP}$  = the difference between the estimated diesel traffic contribution to the BeP level in the busy street and that to the BeP level in the city park. If one excludes the long-range transport episode data, see later in this chapter, i.e. the point in the lower right corner from the correlation analysis, the PAH diesel proportion =  $0.64 \pm 0.07$  ( $r = 0.86$ ,  $p < 0.001$ ). If one also assumes an appropriate value for the diesel exhaust gas ratio between methylphenanthrenes and phenanthrene should be 7.0 instead of 5.5, the PAH diesel proportion =  $0.50 \pm 0.07$  ( $r = 0.81$ ,  $p < 0.001$ ).

The work was supported by the Danish Environmental Protection Agency and will be published in two reports in the beginning of 1995 (Nielsen, Poulsen, Larsen, Palmgren, Jensen, Jørgensen, Poulsen, Schramm and Tønnesen: "Traffic PAH and other mutagens in air in Denmark", and Nielsen, Jørgensen, Grundahl, Jensen, Nielsen and Tønnesen: "Traffic PAH and other air pollutants in the center of a large city").

## 2.4 Environmental Physical Chemistry

### 2.4.1 Development of Methods for the Estimation of 1-Octanol/Water Partition Coefficients

(C. Helveg, T. Nielsen)

In this project, methods for estimation of physical chemical properties of environmental importance for polar polycyclic organic material is developed and applied. This first part of the project deals with the 1-octanol/water partition coefficient ( $P_{ow}$ ).  $P_{ow}$  is used extensively in the evaluation of toxicity and partitioning behaviour in the environment of chemicals. The compounds chosen for this study are mainly azaarenes and the analogue PAH.

Two methods are currently being worked on, a chromatographic method and a so-called QSAR/QSPR method (quantitative structure activity/property relationship).

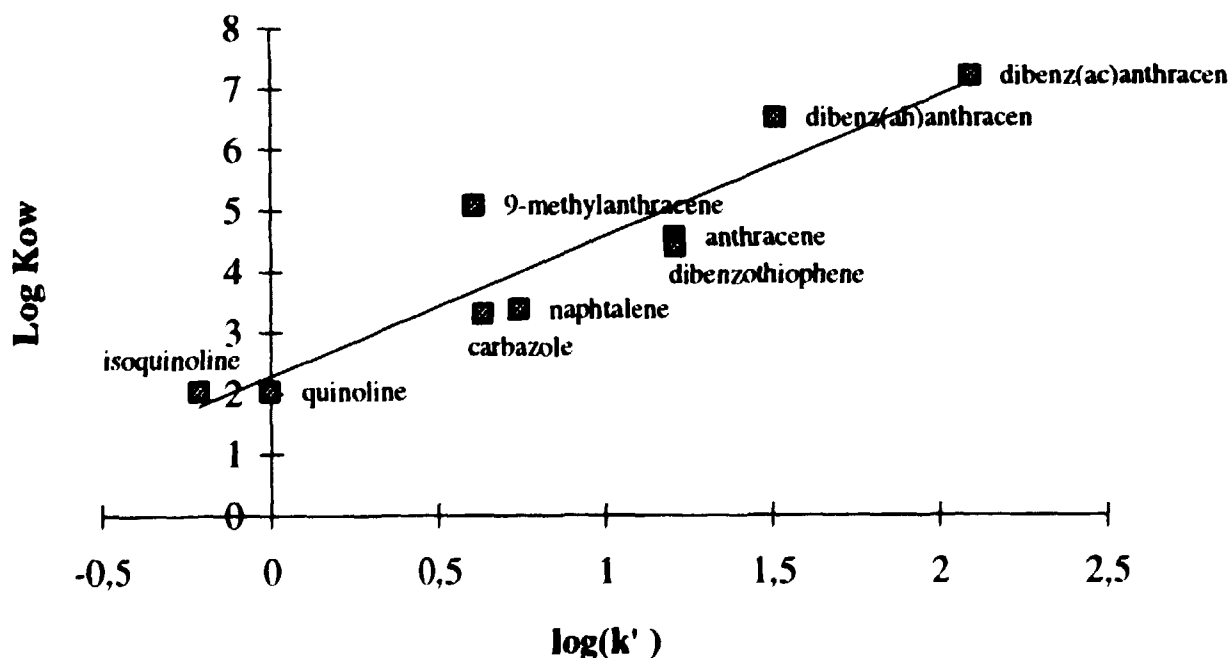
### Chromatographic Methods

A reversed phase high pressure liquid chromatography (RP-HPLC) method for the estimation of octanol-water partition coefficients, for polar polyaromatic organic compounds, is under development. The retention of a compound, on a chromatographic column, can be related linearly to the octanol water-partitioning coefficient of the compound under certain conditions. Several column materials, such as  $C_{18}$ ,  $C_8$  and Diol materials, are being tested and the results for the first  $C_{18}$  material are 80% completed and almost ready for evaluation.

As an example, the retention data for some compounds on a  $C_{18}$  column has been plotted against known  $K_{ow}$ 's. The eluent used here is a 65/35 methanol/water mixture.

As can be seen from the graph, the linear relationship is evident. The compounds, for which the results are shown here, are very heterogeneous and a perfect linearity was not expected. Application of eluents with a higher water content and extrapolation of data to 100% water, either volumetric or applying polarity data for the different solvent mixtures, will be tested.

ODS column, 65 % methanol



### ***Theoretical Methods***

Quantitative structure activity relationships (QSAR), based on the connection between the molecular structure and the physical-chemical properties of a compound, can be used to predict partition coefficients and aqueous solubility from structural data. A computer programme *matXcal*, for the calculation of several graph theoretical topological indexes, has been written and will be developed further.

The project is a contribution to the Danish Centre of Ecotoxicological Research under Danish Environmental Research Programme. Some of the results have been presented by Helweg and Nielsen (1994a and b).

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- Helweg, C., Nielsen, T. (1994b)* Polar polycyclic organic matter - particular azarenes - in contaminated soil. Annual Meeting in Danish Centre for Ecotoxicological Research, Kerteminde, Denmark, 10-22 Nov 1994.

# 3 Gene Technology and Population Biology

## Introduction (H. Østergård)

An understanding of interactions between plants and pathogens is important for developing strategies for a sustainable agriculture with reduced use of pesticides. A large part of our research is devoted to the establishment of genetic markers and analysis of genetic diversity. With these tools, the mechanisms of plant-pathogen interactions are studied, including evolutionary aspects and detection of gene products which are important for resistance or virulence. The plant-pathogen system, barley and barley powdery mildew (*Erysiphe graminis* f.sp. *hordei*) is used as a main model system for an obligate biotroph, but pathosystems, including oilseed rape are also studied (section 3.1).

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 plant improvement, can be greatly facilitated by the use of marker-assisted selection. In particular, the new methods for identifying molecular markers may help 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 regulation and expression of genes and characterization of gene products is important for developing plants with improved characteristics, e.g., a better quality of grain proteins or a higher level of resistance to pathogens. Studies of gene expression at the plant level taking genotype-environment interactions into account are essential for understanding the complicated processes leading to a functional plant. Barley and oilseed rape are the main crops of interest (section 3.2 and 3.3).

Studies of plant population biology are necessary for predicting the consequences of using new genotypes, e.g., genotypes possessing transgenes, as well as new species in agriculture. In this context, we are studying gene introgression from crop plants to their wild relatives to assess

the risks of releasing genetically modified plants. Further, the evolutionary processes imposed by interactions between crop plants and wild plant species, e.g. weeds, are being studied. Oilseed rape and wild *Brassica* species as well as ecosystems including cereal crops are used as model systems for these studies (section 3.4 and 3.5).

## Summary of Projects

### 3.1 The Barley/Barley Powdery Mildew (*Erysiphe graminis* f.sp. *hordei*) System and other Pathosystems

#### 3.1.1 Molecular Genetics of *Erysiphe graminis* f.sp. *hordei* (Egh) (H. Giese, S. Christiansen, A. Justesen)

##### *Isolation of an Avirulence Gene by Chromosome Walking*

A detailed linkage map of the Egh genome is constructed to gain knowledge on the fungal genome and to identify molecular markers that link to an avirulence gene. Two crosses between different isolates of the fungus have been carried out. The mapping populations segregate in 10 virulence loci. One population has been analysed using 160 RFLP and RAPD markers and the other using 125 markers. The RFLP markers typically cover multicopy sequences distributed throughout the fungal genome (Christiansen and Giese 1990). This makes it difficult to establish colinearity between the linkage groups derived from analysis of the different mapping populations. The same problem arises from the RAPD markers, as it is difficult to prove that a particular band represents an identical locus in the two populations. Some cDNA-derived RFLP markers which cover single copy genes are now included in the analysis to identify corresponding linkage groups. In addition, an RFLP marker and SCARs developed in laboratories in England

(J. Brown) and Switzerland (J. McDermot) will be included in the analysis to obtain common markers for different crosses. Cooperation has been established with the Zürich-group (M. Wolfe) in order to develop a common linkage map of the *Egh* genome based on 3 mapping populations. Two RFLP markers are linked to avirulence genes and will be used for chromosome walking.

A YAC library of the fungal genome has been constructed where the average insert size is 220kb (Borbye and Giese 1994). As the linked markers are about 10cM from the avirulence genes and we have estimated that 1cM corresponds to about 20kb DNA, we will need to identify overlapping YAC clones. This can be achieved by contig assembly using a highly repetitive SINE element characterized from the fungus (Rasmussen *et al.* 1993). This is done in cooperation with K. Edwards (Zeneca). Individual YACs are propagated, and DNA is prepared and cut with restriction endonucleases. Hybridization with the repetitive element yields fingerprints which can be assembled in contigs. In this way overlapping YACs can be assembled and selected for further analysis using the RFLP markers.

### *Transformation of Egh*

Functional characterization of potential cloned avirulence genes will require transformation and expression of these genes in *Egh* isolates carrying the corresponding virulence alleles. Pathogenicity tests on barley, carrying the corresponding resistance gene, should then result in an incompatible interaction.

Particle gun acceleration appears to be a possible way to transform *Egh* cells.  $\beta$ -glucuronidase (GUS) expression has been obtained in *Egh* mycelium cells growing on the barley leaf surface (Figure 3.1.1.1 - a and b) and in conidia (Figure 3.1.1.1 - c) when bombarding with a construction containing the *E. coli* GUS (Jefferson *et al.* 1987) gene regulated by the *Egh*  $\beta$ -tubulin promoter (Sherwood and Somerville 1990). Conidiophores are the most frequently hit cell types and this is an advantage with respect to stable transformation, as conidia are derived from these cells. This work has been performed in cooperation with S. Knudsen (Carlsberg Laboratories).



**Figure 3.1.1.** Expression of  $\beta$ -glucuronidase (GUS) in *E. graminis* cells after particle gun bombardment of mycelium growing on barley leaves (a and b) or conidia on a glass plate (c).

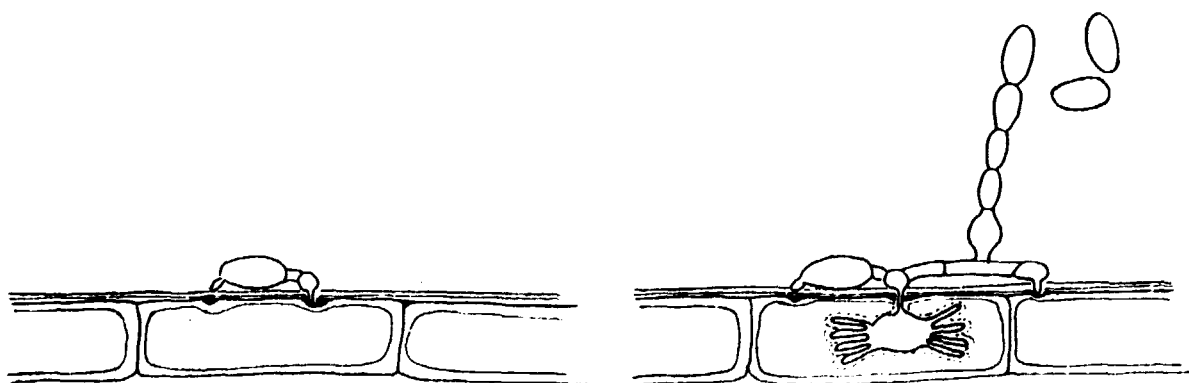
a) GUS expression in the basal cell, b) A group of GUS expressing hyphal cells, c) A conidium with a primary germ tube.

The number of GUS expressing cells obtained per shot is low, but can probably be improved by using a stronger promoter. Three heterologous promoters from two ascomycete fungi, *Aspergillus nidulans* and *Cochliobolus heterostrophus*, gave very low or no expression of GUS in *Egh*. Heterologous expression in ascomycete fungi has frequently been reported (Blakemore *et al.* 1989, Turgeon *et al.* 1985) and the result may indicate special gene regulation in obligate fungi.

In order to obtain a strong homologous promoter, we have isolated the *Egh* glyceraldehyde-3-phosphate dehydrogenase gene (GPD) which is now being characterized. The GPD gene is constitutively and highly expressed in the hyphae and the promoter will be used in the construction of a transformation vector.

#### **Isolation of putative pathogenicity genes of the obligate biotroph, *Erysiphe graminis* f.sp. *hordei***

Powdery mildew passes through several developmental stages during infection and colonization of the host. These stages are cytologically well characterized but remain to be investigated at the molecular level (Kunoh *et al.* 1977, Kunoh *et al.* 1978). The aim is to identify putative pathogenicity factors produced during the early infection stages of *Egh* (Figure 3.1.1.2.). Due to the obligate life style of *Egh*, isolation of proteins involved in pathogenicity is rendered difficult. Alternatively, the changes in gene expression during pathogenesis can be investigated.



**Figure 3.1.1.2.** After contact with the leaf surface, the conidium of *Egh* develops a primary germ tube which attempts to penetrate the host cell wall. This germ tube does not develop further, but shortly after, a second germ tube emerges and forms an appressorium. A penetration hypha developing from the appressorium penetrates the host cell wall. The plant cell responds to the germ tube by formation of a papillae. If the interaction between *Egh* and barley is compatible, a fully matured haustorium is formed and fungal growth continues.

In cooperation with S. Somerville (Michigan State University) a cDNA library has been constructed of RNA isolated from germinating conidia of *Egh*. By using subtractive hybridization and differential screening techniques, two cDNAs representing genes, which are differentially expressed during germination of conidia, were isolated and characterized. Northern analysis showed low expression in ungerminated conidia and an increased expression during germination. Expression could also be detected *in planta* during late stages of pathogenesis.

The corresponding genomic sequences, *gEgh7* and *gEgh16*, were isolated from a cosmid library and sequenced. The sequences did not show any significant similarities with sequences in the data bases (EMBL, Gene Bank, Swiss Prot.). The gene product, predicted by *gEgh7*, is rich in Pro-residues and possesses several peptide repeats indicating a structural function. The putative polypeptide, encoded by *gEgh16*, is rich in Ala- and Gly-residues, but the function of this protein is unknown. Further investigation of gene expression, during different developmental

stages, will provide more information about the pathogenicity of *Egh*.

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### 3.1.2 Epidemiology and Epidemiological

Parameters (H. Østergård, H.P. Jensen, C. Damgaard, M. Lyngkjær)

#### Histological and genetic studies on Mlo-virulent mildew

Mlo resistance is a highly effective resistance in barley determined by a single recessive gene. It prevents the barley powdery mildew fungus from penetrating the epidermal cell wall by depositing a large papilla beneath the site of penetration (Figure 3.1.2.1.); Skou *et al.* 1984. Only two powdery mildew isolates, a laboratory selected isolate (Schwarzbach 1979) and a Japanese isolate (Lyngkjær *et al.* 1994a, have been characterised as being able to overcome papilla resistance in Mlo-resistant barley and produce normal colonies in all types of epidermal cells. The genetics of virulence is under study by crossing these isolates with non-Mlo-virulent isolates and with each other. The mechanism which make it possible for these two isolates to deal with the papilla-response in Mlo-resistant barley is not known. Therefore, a histological examination was conducted (Lyngkjær *et al.* 1994b).



Figure 3.1.2.1. Normal sized papilla in a barley line with the Mlo susceptibility allele and an oversized papilla in a barley line with the mlo resistance allele.

Developmental stages of two near-isogenic powdery mildew isolates, GE3 (Mlo-avirulent) and a selected mutant HL3/5 (Mlo-virulent) (Schwarzbach 1979) were determined on epidermal tissue of primary leaves of a near-isogenic pair of barley lines, RISØ 5678R (Mlo-resistant) and RISØ 5678S (Mlo-susceptible) (Jørgensen

1975). In a time course study, initiation and termination of plant response and fungal development were determined at 3, 8, 12, 14, 16, 22, 28, 35 and 69 hours after inoculation using differential interference contrast optics and fluorescence.

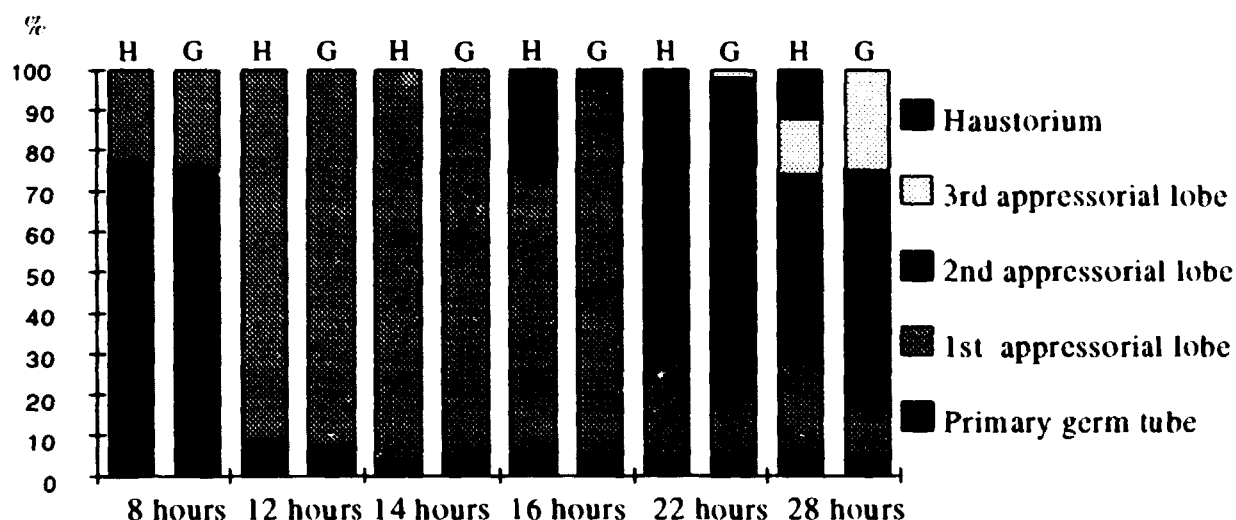


Figure 3.1.2.2. Percentage of mildew at each developmental stage between 8 and 28 hours after inoculation of the Mlo-resistant line. Bars noted H show the Mlo-virulent isolate, bars noted G show the Mlo-avirulent isolate.

On the Mlo-resistant line (Figure 3.1.2.2), the development of the two powdery mildew isolates was similar up to 14 hours after inoculation. At 16 hours, about 15% of the germinated spores of the Mlo-virulent isolate had penetrated the cell wall and started to produce haustoria. The remaining 85% of the spores failed to penetrate and developed a 2nd or 3rd appressorial lobe and died. Spores of the Mlo-avirulent isolate failed to penetrate and died after making a 2nd or 3rd appressorial lobe. From 22 to 69 hours, the Mlo-virulent isolate produced elongated secondary hyphae and micro-colonies at the penetrated cells.

Mlo-resistant barley responded to fungal penetration attempts by forming large papillae under the appressorial lobes. However, when inoculated with the Mlo-virulent isolate, plant cells beneath appressoria which succeeded in penetration, showed little or no cytoplasmic activity and papilla deposition. The percentage of interactions with the Mlo-virulent isolate developing haustoria or a 2nd appressorial lobe was the same for both barley lines. This indicates that development occurred with the same speed on both lines and that Mlo virulence is not just a matter of fast development. This leaves two possible explanations of Mlo virulence. It may either be due to no/late recognition of powdery mildew by the host or active inhibition by the Mlo-virulent isolate of the formation of papillae in the host cells.

#### Effects of Inoculum Density on Parasitic Growth

During an epidemic, changes in pathogen density occurs. In order to understand the influence of pathogen density on the interaction between barley powdery mildew and barley, different density- dependent growth models were investigated (Østergård 1994) and fitness components were estimated at different pathogen densities. Here we will briefly describe the empirical work (Damgaard and Østergård 1994).

Two types of data were obtained in the experiment, 1) infection efficiency in relation to inoculum density and 2) spore production in relation to colony density. Test pots were sown with the partial resistant barley cv. Pallas in a mildew-free growth chamber. Eight days later, the first leaf of 9-10 seedlings in each pot was horizontally attached to a plastic disk with the abaxial side upwards, and inoculated with spores from a recently sampled single-colony powdery mildew isolate and placed with constant light in a growth chamber at 15°C. Seedlings were infected with spores from 2, 5, 15, or 23 single colonies. This resulted in spore densities of 12, 32, 95 and 146 spores/cm<sup>2</sup>. The infection efficiency was estimated eight days after infection. Thirty seedlings with about 1.1, 2.8, and 9.0 colonies/cm<sup>2</sup>, respectively, were selected and spore production per colony per day was measured at day 8, 9, 10, 11 and 13.

As expected, infection efficiency decreased with inoculum density. However, contrary to our first expectations, colonies at high densities produced their spores earlier than colonies at low densities and had higher cumulative spore production and potential reproductive value. The differences in cumulative spore production and potential reproductive value were, however, not statistically significant.

During an epidemic, early released spores contribute more to an increased fitness than do later released spores. Consequently, "high" colony density has a positive effect on fitness.

We suggest that the positive effect of colony density on spore production is caused by insufficient capacity of the partial resistance mechanism to control infections at high densities. The exact mechanisms of partial resistance are unknown; however, one could speculate that the host plant has an upper limit on the amount of "resistance" for a given leaf, and that this upper limit is insufficient to control infections at high densities, either 1) because of resource allocation strategies, i.e. the plant does not invest energy in a leaf with many infections, or 2) because of a constant level of defence, due to self-toxicating side effects of an increased defence.

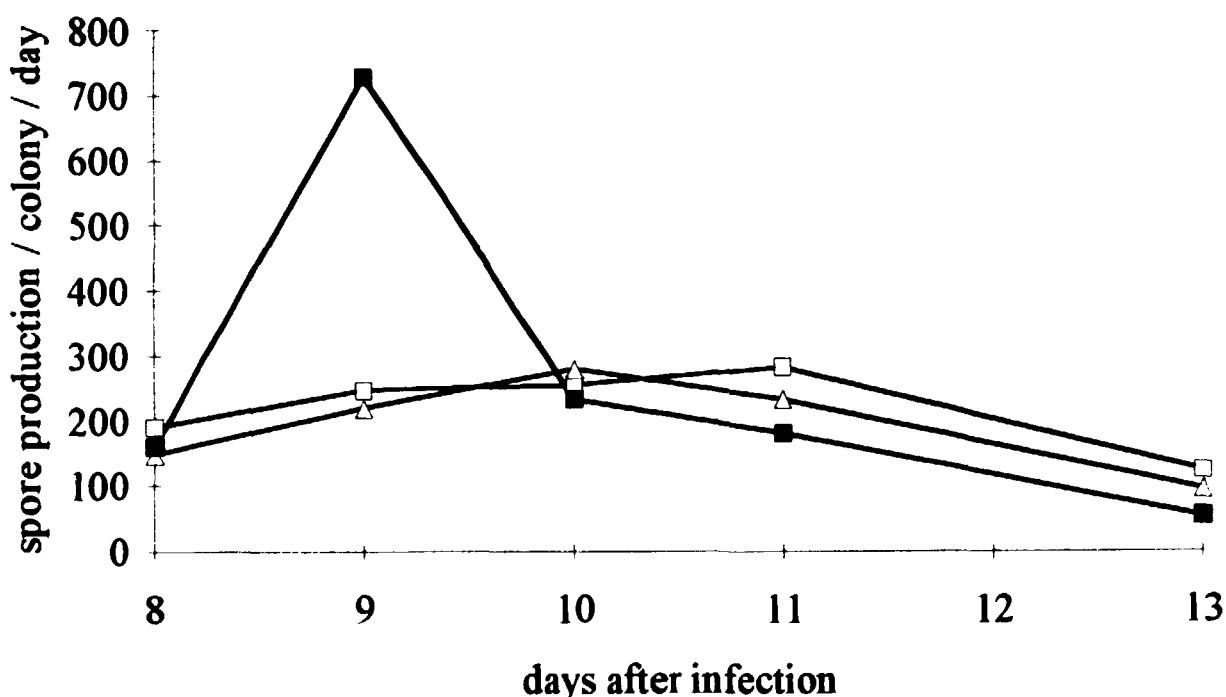


Figure 3.1.2.3. Spore production per colony per day. Open square: 1.1 colonies per cm<sup>2</sup>. Open triangle: 2.8 colonies per cm<sup>2</sup>. Closed square: 9.0 colonies per cm<sup>2</sup>.

#### **Population studies of the barley powdery mildew fungus**

Changes in frequencies of virulence genes in aerial populations of barley powdery mildew are being studied by analysing data from virulence surveys and by considering mathematical models in collaboration with M. Hovmøller, The National Institute of Plant Science and L. Munk, RVAU (Østergård and Hovmøller 1991, Hovmøller *et al.* 1993).

The most recent application has been to compare frequencies obtained by mobile and stationary sampling techniques. It is observed that estimates of virulence gene frequencies vary in time and space, since sampling of aerial populations will reflect the selection forces induced by the hosts of the spores sampled. Such sources will, to a large extent, be the field's "closest" to the point(s) of sampling, taking wind direction into account. This indicates the importance of defining aims and sources of virulence surveys.

Based on this work, a European collaboration on "Population studies of airborne pathogens on cereals as a means of improving strategies for disease control" has been initiated as COST-Action 817 with the head of section, Hanne Østergård, acting as chairman. The Action has participants from 11 European countries. The main items are 1) coordination of virulence and fungicide resistance surveys, 2) collaboration on field trials of variety mixtures, 3) common designations of resistance and virulence genes between researchers, breeders and extension services, 4) build up of a database on genetic markers of powdery mildew, and 5) collaboration on estimation and analysis of epidemiological parameters.

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### 3.1.3 Structure-Function Relationship of two Barley Peroxidases induced by *E. graminis* f.sp. *hordei* (S.K. Rasmussen)

It is well known that barley leaves produce papillae in the intercellular space on inoculation with spores of the powdery mildew fungus. The papillae can be detected after 8 hours following infection in normal barley varieties, and 2 hours earlier in barley lines carrying the *mlo* resistance gene (Skou *et al.* 1984). The papillae are primarily made up of callose synthesized by the membrane bound  $\beta$ -1,3-D-glucan synthase (Pedersen *et al.* 1993). The papillae also contain fluorescent phenolic compounds believed to crosslink the callose to form a rigid structure. Providing the depositions are made early, the papillae form a physical barrier against the penetrating hyphae. This may prevent the spores from establishing infections. At the same time as the papillae are formed, two new peroxidases can be detected at the mRNA and protein level (Thordal-Christensen *et al.* 1992, Kerby and Somerville 1992). The two peroxidases, Prx7 and Prx8, are likely to have different functions, since their amino acid sequences are less than 50% identical. Prx8 is extracellular and it is tempting to believe that this peroxidase catalyzes the crosslinking of phenolic compounds with the callose in the papillae. Prx7 have a C-terminal extension, which might act as a vacuolar targeting signal. The goal is to show the structure-function relationship of these two pathogen-related peroxidases in relation to the papillae deposition, as well as the targeting and function of the vacuolar peroxidase (Rasmussen *et al.* 1994). Transgenic tobacco plants were produced at Danisco Biotechnology A/S by *Agrobacterium*-mediated transfer of a Ti plasmid, carrying a construct of the barley Prx8-cDNA, under control of a 35S promoter, and made available to us. Our biochemical analyses have demonstrated that the

barley peroxidase Prx8 is also extracellular in tobacco plants with an isoelectric point pI 8.3 as expected. Furthermore, Prx8 is secreted in two molecular forms, one being glycosylated. The mechanism for this differential glycosylation, which has also been noted for barley seed peroxidase BP 1, is as yet unclear (Rasmussen *et al.* 1991). The genetic analyses of the transgenic tobacco plants, as well as of the changes in the interaction with the tobacco mildew fungus *Erysiphe cichoracearum*, is in progress. The current knowledge on plant peroxidases has been summarised by combining data collected from many different plant species (Welinder *et al.* 1993, for recent references). The systematic cloning and studies in heterologous systems of plant peroxidase genes will give a better understanding of the biological function of peroxidases in plants.

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## 3.1.4 Genetic Control of Defence Processes in Barley to Avirulent Powdery Mildew (J.H. Jørgensen)

A barley line with resistance gene *Mla12* was mutagenized, the M<sub>2</sub> generation inoculated with an avirulent powdery mildew isolate and 25 more or less susceptible mutants were selected (Torp and Jørgensen 1986). Twenty-two mutations had occurred in gene *Mla12* and three were in second-site suppressor genes. All 25 mutations modify the phenotypic expression of gene *Mla12* from an infection type 0 to infection types between 0-1 and 3-4 (Jørgensen 1988).

Over the past few years the three suppressor mutant lines have been crossed with seven near-isogenic lines with different powdery mildew resistance genes and one, M100, has been crossed with ten additional lines. Seedlings of parents, F<sub>1</sub> and F<sub>2</sub> were tested with powdery mildew isolates that possessed the appropriate avirulence and virulence genes. The segregation of phenotypes in F<sub>2</sub> disclosed that the three suppressor genes affected the phenotypic expression of three resistance genes, whereas that of four resistance genes remained unaffected. The suppressor gene in mutant M100 affected the phenotypic expression of nine of the ten additional resistance genes tested. It is suggested that the three suppressor mutant genes are mutationally modified genes involved in host defence processes. This implies that different resistance genes employ different, but overlapping spectra of defence processes against avirulent powdery mildew isolates.

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## 3.1.5 Effect of Powdery Mildew on Phenolic Compounds (H. Doll)

Our studies of the possible relationship between the content of putative phenolic compounds and the degree of partial resistance against powdery mildew showed significant effects of fungicide

treatment and nitrogen fertiliser on some of these compounds in field grown plants (Doll *et al.* in press). The effect of powdery mildew infection on phenolic components has been studied in a growth chamber in collaboration with B. Søgaard and H. Bay, RVAU. Two varieties with a respectively low and high degree of partial resistance were inoculated with powdery mildew four weeks after germination. The content of potential phenolic compounds was measured in leaf extracts by high performance liquid chromatography, which revealed 10 components present in significant amounts in both varieties.

Only leaf number five, which had just appeared at the time of inoculation, has been analysed so far. One component had increased by about 100% in infected plants compared to plants without mildew. Another compound had increased by about 30%, while two other putative phenolics had decreased in amount. The effects of powdery mildew were about the same 3 and 7 days after inoculation, and the two varieties responded similarly.

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### 3.1.6 Genetic Analysis of Resistance to *Leptosphaeria maculans* (stat. con. *Phoma lingam*) in Oilseed Rape (H. Giese, L. Butterworth)

In cooperation with D. Lydiate and R. Mitchen at the John Innes Centre, Norwich, two sets of *Brassica napus* lines have been established. The first is a recombinant inbred population resulting from an initial cross made between the European winter varieties 'Victor' and 'Tapidor'. The other is an introgression population originating from a synthetic *Brassica napus* and using 'Tapidor' as the recurrent parent. Further breeding with these populations is being carried out in an attempt to provide a greater understanding of the nature and function of both additional and the already existing resistance genes within *Brassica napus* to the fungal pathogen *Leptosphaeria maculans* (*Phoma lingam*). RFLP analysis of plant

DNA will enable the inheritance of a single gene determining resistance and a polygenically determined resistance to be followed and recorded.

RFLP and PCR markers already published will be utilised to characterize an extensive collection of isolates of *L. maculans* taken from both laboratory inoculum and from infected crops at various geographical locations within England and Denmark.

## 3.2 Gene and Chromosome Mapping in Plants

Genetic studies are greatly facilitated by the use of molecular markers such as RFLPs and RAPDs. Marker saturated linkage maps are important for the identification of genes with influence on quantitative traits and for chromosome walking. Estimation of variation in the gene background within and between species has also acquired an invaluable tool with the development of the RFLP and PCR techniques. Marker technology is used in genetic studies of barley, oilseed rape and Norway spruce.

Cloned repetitive sequences are used as markers on the barley chromosomes by *in situ* hybridization techniques. This technology allows localization of specific genes to the chromosomes. It is now possible to correlate estimated linkage distances to chromosomal distances, which is very important for chromosome walking procedures.

### 3.2.1. Gene Mapping (H. Giese, J. Jensen, B. Kjær, E. Skou)

#### Identification of Molecular Markers linked to Important Agronomical Traits

In collaboration with the Danish barley breeders, two barley mapping populations have been established. One population is derived from a cross between the spring barleys 'Alexis' and 'Regatta' and the other from a cross between the winter varieties 'Sonate' and 'Marinka'. Eighty out of the total of 220 lines from each cross are analysed with RAPD markers using the Operon primers. About 120 primers have been screened in each cross. Seventy RAPD markers have been mapped in the spring barley cross and 50 in the winter barley cross. The RAPD markers tend to

fall in clusters in certain chromosomal locations. For the complete linkage analysis of all 220 lines only the best markers in the different regions will be selected.

About six published RFLP markers will be included for each linkage group to ensure the correct chromosome designation. This will also allow comparison between different maps and map joining procedures. RFLP markers from North American/Canadian, German and English groups working on barley genetics will be included in the linkage analysis. Nine RFLP markers have been mapped in the spring barley cross. Another 20 RFLP markers have been analysed but showed no polymorphisms in the parents.

The spring lines have been analysed for a number of agronomic traits such as earliness, disease resistance and malting quality. These data will be included in the map and RAPD markers showing linkage may be converted into SCARs.

Linkage groups, containing the same RAPD markers estimated from three different mapping populations, were compared. These results indicate that the RAPD markers are inherited in a colinear fashion and that RAPD markers can be used across varieties. The amplified products of a few RAPD markers have been cloned with the intention of converting them into SCARs and to prove that the fragments are identical in different barley varieties. The overall distribution of RAPD markers in the barley genome were analysed in the cross between the varieties 'Vogelsanger Gold' and 'Alf' (Giese *et al.* 1994). The higher than expected frequency of linked RAPD markers in this study is in agreement with the results from the new crosses.

The Nordic Gene Bank has taken the initiative to support cooperation between the Nordic countries on the use of molecular markers in barley breeding. This has resulted in contacts between groups in Finland, Iceland, Norway, Sweden and Denmark. The two Danish barley mapping populations are being used as a basis for cooperation and the different countries are active in looking at different traits. Finland has their own mapping population but we have coordinated the use of markers which should permit comparison and joining. A meeting sponsored by the Nordic Council of Ministers, with participation of leading international barley

geneticists, gave a very good opportunity to discuss the Nordic initiative.

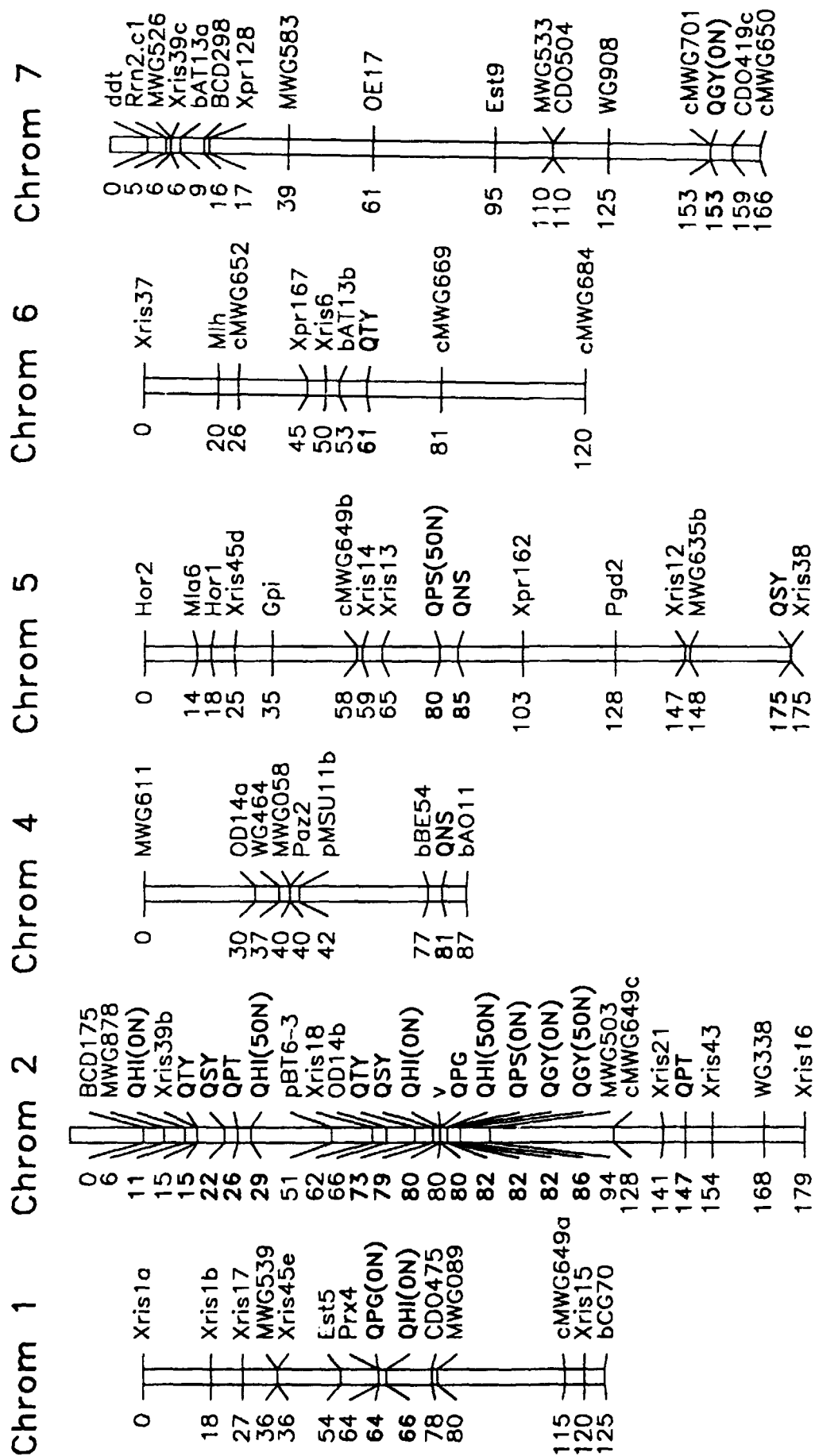
### ***Quantitative Trait Loci in Barley***

Most characters of agricultural crops show continuous variation. In spite of the importance of these characters, the knowledge of their genetic determination is poor. The inheritance is complex, usually assumed to involve several genetic factors that frequently interact with environmental effects. The genetic factors have generally not been resolvable individually, and little is known about the quantitative trait loci (QTLs) which underlie continuous variation. However, the use of genetic markers provides a powerful approach for studying quantitative traits and for locating individual genetic factors associated with the trait. Genetic linkage maps make it possible to evaluate the entire genome for QTLs.

We are mapping QTLs for various agronomic traits in four populations of chromosome doubled haploid lines (DH lines). One population has been evaluated for QTLs. The population consists of 79 DH lines produced by the Bulbosum method from F<sub>1</sub> plants of a cross between the two-rowed spring barley 'Tystofte Prentice' and the six-rowed winter barley 'Vogelsanger Gold'. Polymorphism, in the two parent varieties and in the DH lines, was studied for 85 markers including four morphological, eight isozyme, 70 RFLP and three RAPD markers. The estimated linkage map covered 1100 cM and corresponded to distances reported in other linkage maps of barley.

A range of agronomic traits was recorded in two years in replicated field trials with 'T. Prentice' and the 79 DH lines with no vernalization requirement. The agronomic traits included straw characters, earliness, yield and yield components, and content of nitrogen and phosphorus.

From one to four QTLs were found for each trait, except for the total amount of nitrogen accumulated in straw and grain. The individual QTLs explained from 13% to 80% of the variation between the DH lines. For many traits one or two QTLs explained more than 60% of the variation in the trait. A large part of the QTLs was found in both years with similar positions in the genome. However, QTLs for grain yield were found in different chromosomal regions in the two years.



**Figure 1:** Genetic linkage map of barley with locations of putative QTLs in the total DH population. Only QTLs which were significant when estimated simultaneously are shown. GY: grain yield, SY: straw yield, TY: total yield, NS: N % in straw, PG: P % in grain, PS: P % in straw, PT: total P content.

The majority of QTLs for different traits were clustered in a few segments in the genome. QTLs affecting different traits fell near one another more frequently than would be expected by chance. This suggests that the observed correlations between traits may partly be due to pleiotropic effects of single QTLs.

For most traits, a QTL was found near locus *v* (two-row/six-row spike) on chromosome 2. The chromosome segment had a large effect on thousand grain weight, number of kernels per ear, straw length, ear length, straw yield, and concentration of phosphorus in grain and straw. A pleiotropic effect of locus *v* could not be rejected and is likely.

Another group of QTLs was found near locus *Xris39b* on chromosome 2. The chromosomal segment had a large influence on heading date and straw diameter, and a smaller effect on straw length, ear length and straw yield. It is likely that the effects on quantitative traits in this segment are caused by a photoperiod sensitivity gene that has been located in this chromosomal region.

The DH lines were analysed for QTLs within the two-rowed and within the six-rowed lines. A number of different QTLs was found in the two groups, and a number of significant interactions was found between the QTL at locus *v* and other QTLs. In conclusion, different genes for quantitative traits are expressed in the two-rowed and in the six-rowed lines.

### ***Construction of a Linkage Map of Norway Spruce***

The reproductive system of conifers is custom designed for RAPD analysis, as the nuclei of the endosperm cells contain a chromosomal complement identical to that in the haploid megagametophyte. Enough DNA can be extracted from single endosperms to allow RAPD analysis. Thus it is possible to construct a complete linkage map on the basis of seeds from a single tree. A linkage map based on 80 seeds from one tree and about 90 RAPD markers has been constructed for Norway spruce. DNA extraction methods and RAPD conditions were refined and careful tests for reproducibility proved the system to be robust.

An RAPD-based linkage map published by an Italian group, was studied in an attempt to

merge the two maps. Information on RAPD markers and segregation data was exchanged and the identification of identical RAPD markers in the two materials established. RAPD markers could be transferred between the two mapping populations to allow joining of the two maps.

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### **3.2.2 Cytogenetics of Barley and related Species (I. Linde-Laursen, C. Pedersen)**

Modern plant breeding approaches, *e.g.* the use of transformation, require knowledge of the cytological positions of genes for traits of agronomic importance on the single chromosomes of a crop species. Presently, this information is best obtained through the application of *in situ* hybridization of DNA probes to the chromosomes of an organism at somatic metaphase. However, many agronomically important genes cannot be localized on the chromosomes in this way because of the lack of relevant probes or the small size of the locus in question,  $\leq 5$  kb (kilobases).

We have continued our efforts to optimize the *in situ* hybridization technique, especially with respect to the production of chromosome preparations with a high number of suitably contracted metaphase chromosomes. In our efforts to estimate the relationship between genetic and physical distances, we are focussing on DNA markers which can be mapped, both genetically by RFLP-mapping and physically by *in situ* hybridization to chromosomes. The B- and C-hordein genes provide such markers. We have estimated that a genetic distance of 1 cM corresponds to about 1 Mb (Megabase) in the region between the two hordein loci. This information is important for evaluating the chromosome walking strategy which is applied in attempts to clone a powdery mildew resistance gene in the *Mlu* region flanked by the hordein loci. Other common markers mapped are the *5S*rRNA locus on chromosome 1, the protein *Zx* locus on chromosome 4, the EM (early methionine-labelled) protein on chromosome 5, and the  $\alpha$ -amylase locus on chromosome 6. These markers are new

anchor sites for integrating the genetic and the physical chromosome map. All indicate that recombination is strongly reduced in the proximal part of the chromosome arms and increased in the distal part.

The chromosome complement of a number of wild relatives of cultivated barley belonging to the genus *Hordeum* (barley) contain fewer chromosome pairs with nucleolus organizers than expected from their ploidy level (Linde-Laursen *et al.* 1992). In the two North American taxa, the tetraploid *H. depressum* and the hexaploid cytotype of *H. brachyantherum*, the application of *in situ* hybridization with the wheat rDNA probe pTA71 revealed rDNA-carrying chromosomal segments without nucleolus-forming activity in addition to the segments at the nucleolar organizers. The locations of the former segments indicate that the two taxa derive from hybridizations among or within North American *Hordeum* species.

Giemsa C- and N-banding reveal the chromosomal location of the constitutive heterochromatin. The banding patterns produced can be used to identify species, chromosomes and chromosome arms. Application of the C-banding technique to the chromosome complements of all 32 *Hordeum* species has been used to establish karyotype evolution in the genus (collaboration with N. Jacobsen, RVAU, Copenhagen, and R. von Bothmer, Svalöv, Sweden). In *Festucopsis serpentina*, a *Triticeae* species from the Balkans, the C-banding patterns were rather similar to those produced in its previously studied nearest relative, *Peridictyon sanctum* (Seberg *et al.* 1991). However, differences in chromosome morphology indicate that the two species are not very closely related (collaboration with O. Seberg and S. Frederiksen, Copenhagen University).

Chromosome elimination takes place in many hybrids between cultivated barley (*H. vulgare*) and wild barley species, most often resulting in the production of haploids of the wild species. However, previous studies have shown that many plants produced from the cross *H. lechleri* (6x) x *H. vulgare* have partial elimination only of the *H. vulgare* chromosomes (Linde-Laursen and Bothmer 1991). Renewed chromosome counting of aneuploid 4- or 5-year old plants from the above cross shows that some of the plants now have a lower or higher chromosome

number thereby indicating instability for chromosome number.

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### 3.2.3 Gene and Chromosome Mapping in Oilseed Rape (R.B. Jørgensen)

One-hundred-and-six RAPD markers specific to the C-genome in a resynthesized oilseed rape were identified. The presence of these RAPD markers is being analysed in addition lines (2n=21-26, AA + one to six C-chromosomes), and six synteny groups of markers have been found. In a monosomic addition line (2n=21, AA + one C-chromosome), the alien C-chromosome harbours a gene that affect the oil contents of the seed. The gene has been linked close to two RAPD markers by intergenomic recombination. The project is carried out in collaboration with The Swedish University of Agricultural Sciences in Svalöv (Cheng *et al.* 1994). Localization of RAPD markers to the chromosomes of oilseed rape is relevant also to project 3.4.

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### 3.3 Expression and Regulation of Genes for Seed Quality (J. Jensen, S.K. Rasmussen)

#### Quality of the Barley Grain

The storage protein (hordein) from the 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. In addition, the modulation of the amino acid composition will lead to reduced nitrogen loss from monogastric animals. Five high-lysine barley mutants and a control were yield-tested in a three-year field experiment (1992-94). Three of the mutants showed a 14 to 30% higher level of lysine as compared to the mother variety 'Sultan', whereas the lysine content in two was similar to that of 'Sultan'. The threonine content also showed a markedly higher level in the three high-lysine mutants. Feeding experiments will be carried out in the coming year as part of a longterm collaboration with B. Eggum, Foulum. It is desirable to combine the high-lysine character with the resistance gene *mlo* towards the powdery mildew fungus in one barley variety. A number of chromosome-doubled haploids of crosses between 'Alexis' and two of the mutants have been produced and will be tested in the field in 1995.

Protein Z is a barley seed storage protein with a favourable lysine content. Another approach to balance the nutritional quality of the grain is to increase the gene copy-number of protein Z providing that a higher number of protein Z genes will lead to an increase in protein Z production and lysine content in the barley grain. Two protein Z genes Z4 and Zx have been cloned (Rasmussen 1993) and their promoters are being analysed in transgenic tobacco, *Nicotiana tabacum*. A fragment in the 5'-non-translated region, -596-0, of the protein Zx gene

is sufficient to drive the expression of a GUS reporter gene in tobacco seeds. Dissection of the Z4 promoter is in progress. These promoter elements will allow us to construct vectors for tissue-specific expression in plants.

#### Protein Z in other plants

The sequence analysis of barley protein Z4 showed, for the first time, that plants also express members of the mammalian serine proteinase inhibitor, serpin, superfamily (Hejgaard *et al.* 1985). Now a serpin has been purified from wheat grains (Rosenkrands *et al.* 1994) and the amino acid sequence deduced from its cDNA shows 70% identity to the barley proteins Z4 and Zx. The inhibitors form a loop at the carboxy-terminus which can dock into the reactive site of proteases. The amino acid sequence identity is 50% between serpin and Figure 3.3. The variation among the mammalian members is of a similar magnitude as that between plant members and their mammalian counterpart. The wheat serpin is an inhibitor of chymotrypsin, while the barley protein Z more resembles ovalbumin in its function. Both protein Z and ovalbumin serve as storage proteins to nourish embryos. Recombinant proteins of the barley and wheat serpins are produced in *E. coli*. Point mutations are introduced by means of protein engineering with the purpose of identifying residues, which are critical for inhibition of the target proteases. The work on the structure-function analyses of plant serpins is carried out in collaboration with J. Hejgaard, The Technical University of Denmark.

		P <sub>1</sub>
Con	.L..S.VFHK.FVEVNEEGTEAAA.T.....S....P..VDF.ANHPFLFLIRED..GVVLF.GHV.NP...S.	
WZ	GLRVSSVFHQAFVEVNEEGTEAAAST-AIKMVLQARPPSVMDFIADHPFLFLVREDISGVVLFMGHVVNPLLS	
Z7	GLYISSVFHKTFFVEVDEEGTKAGAATGDVIVDRSL---PIRMDFVANHPFLFLIREDIAGVVLFIGHVANPAVSS	
Zx	SLYVSSVFHKS.FVEVNEEGTEAAARTARVTLRSLPVEPVKVDVADHPFLFLIREDLTGVVLFVGHVFNPLVSA	
Z4.2	GLEISHVFHKS.FVEVNEEGTEAGASTVAMGVAMSMPLKVDLVDFVANHPFLFLIREDIAGVVVFVGHVFNPLISA	
ATI11	DLVSDAFHKAFLEVNEEGSEAAARSTAVVIAGRS-LNPNRVTFKANRPFLVFIREVPLNTIIFMGRVANPCVSA	
$\alpha_1$ AT	PLKLSKAVHKAVLTIDEKGTEAGAMFLEAIPMSI---PPGVKF--NKPFVFLMIEQNTKSPLFMGKVVNPTQK-	

Figure 3.3. Reactive center loop of serpins. The amino acid sequence of wheat WZ, barley Z4, Z7 and Zx is aligned with  $\alpha_1$ -antitrypsin and antithrombin. Con shows amino acids common between the inhibitors and the asterisk amino acids present in all serpins. P<sub>1</sub> marks the amino acid determining the specificity.

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### 3.4 Gene Dispersal in Relation to Risk Assessment (R.B. Jørgensen, T. Mikkelsen, L. Lundbo)

Cultivation of genetically modified plants may pose environmental risks. A transgenic crop may introduce the transgene to other species in natural or cultivated environments through hybridization with wild relatives. The impact of a transgene introgressed to a wild species is dependent on the transgenic character, as well as on the biology of the wild species (Jørgensen 1995). If a transgene provides an increased fitness to the crop plant, the transgenic crop may be able to invade natural ecosystems and affect their composition of species. These risks are assessed in an inter-institutional 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 (F.B. Christiansen) and RVAU (G.S. Poulsen). The industrial collaborators are Danisco (Denmark), Plant Genetic System (Belgium) and Monsanto Europe (Belgium). The purpose of the programme is to gain knowledge about transgenes, plants and their recipient ecosystem. This is obtained by studying fundamental mechanisms in plant population biology using 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 genes from oilseed rape (*B. napus*) to *B. campestris* in detail we are studying the inheritance of genetic markers in controlled crosses. In one cross of the type (*B. napus* x *B. campestris*) x *B. campestris* we obtained progeny of 92 plants. These plants were characterized with respect to 33 RAPD markers, which were shown to be specific to the oilseed rape parent of the cross. Most markers were transferred from the interspecific hybrid to the backcross progeny in a ratio of approximately 50%. A few markers had extreme (distorted) transmission frequencies.

Field trials with mixtures of non-modified oilseed rape and *B. campestris* produced 9-93% interspecific hybrids (Jørgensen and Andersen 1994). In 1994 hybridization and backcrossing were investigated in a field experiment with two lines of transgenic oilseed rape. Both lines were tolerant to the herbicide BASTA; one line was male-sterile, the other had a gene for restoration of fertility. Plots with the transgenic oilseed rape and *B. campestris* were grown to assess the interspecific hybridization between the species, and plots with transgenic interspecific hybrids and *B. campestris* were grown to assess backcrossing. We are now analysing the harvested seed. Preliminary results show that many interspecific, transgenic hybrids were produced as well as transgenic backcross plants of the type (*B. napus* x *B. campestris*) x *B. campestris* (Jørgensen et al. 1994). The presence of the transgene is verified by spraying with BASTA and PCR analysis.



Figur 3.4. BASTA tolerant plants from the field trial. *Brassica campestris*-like backcross plant (left); interspecific hybrid (*B. campestris*, ♀ x *B. napus*, ♂) (right).

In 1992, a 1:1 mixture of oilseed rape and *B. campestris* was sown together in the field. Since then, the population has maintained itself. In 1993, interspecific hybrids made up 7% of the population. 5% of the offspring plants from these interspecific hybrids were produced from natural backcrosses to *B. campestris*. In 1994 backcross plants occurred spontaneously in the field. The chromosome number was  $2n = 20-25$  in the analysed backcross plants with *B. campestris*. The segregation of 17 rapeseed-specific markers in the backcross plants showed that the more markers present, the higher the chromosome number.

Though *Brassica campestris* and *B. napus* hybridize and backcross in field experiments and controlled crossings, it is not known to what extent these processes (hybridisation and backcrossing) take place *in natura*. To address this question, we have collected wild Danish *B. campestris* and are presently investigating the genetic variation in this material with the RAPD technique. We have used the same RAPD primers on 18 *B. napus* cultivars, and by comparing marker patterns of the two species, we hope to be able to see signs of introgression from *B. napus* into *B. campestris*. The genetic variation within and between *B. campestris* populations is also characterised.

Preliminary results indicate that *B. napus* x *B. campestris* hybrid seeds have germination requirements other than *B. campestris* seeds. This could reduce the fitness of the hybrids under natural conditions and thereby limit the interspecific gene flow. In controlled crosses we have produced seeds from the combinations: *B. napus* x *B. napus*, *B. napus* x *B. campestris*, *B. campestris* x *B. napus* and *B. campestris* x *B. campestris*. The next step will be to compare the germination patterns of these seeds.

Detailed crossing experiments, with the purpose of estimating variation for fitness components in the species cross *Brassica napus* x *B. campestris* and in their hybrids, have been started. Varieties of *B. napus* and wild populations of *B. campestris* are crossed, and fruit set, seed set, and seed abortion are estimated. The hybrid seeds are then germinated and the resulting plants monitored for survival and flowering. After inter-crossing and back-crossing these plants, the resulting progeny are monitored for survival and reproduction. Possible differ-

ences among populations and varieties in their hybridisation ability may be detected. Additional experiments will test whether hybrid seeds are preferentially aborted in pods containing seeds sired by both intra-specific and inter-specific pollen.

### Gene dispersal from oilseed rape to *Brassica juncea*

Hybridization between oilseed rape and *B. juncea* was investigated in field experiments. The oilseed rape variety 'Drakkar' was sown in different mixtures with *B. juncea*. Seeds were harvested on the parental species and the frequency of hybrids estimated from species specific alleles in zymograms of phosphoglucumutase. The inheritance of 20 oilseed rape specific markers and a transgene was studied in the backcross *B. juncea* x (*B. juncea* x *B. napus*) (Freltho *et al.* 1994).

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## 3.5 Interactions between Cereals and Weeds (H. Doll)

Studies at Risø on the influence of weeds on cereals showed only negligible effects of herbicide treatments on grain yield in wheat and barley. However, weeds occurred sparsely in our experimental fields, which have been treated with herbicides for a long period.

A study of the competitive ability of barley varieties was therefore performed at a bindyna-

mically cultivated field, which was kindly provided by Axel Simonsen, Gl. Oremandsgård, Præstø. Twenty-five spring barley varieties, including varieties with reported good and poor competitive ability, were studied.

A large number of weed plants, 393 m<sup>2</sup> comprising ~ 28 species, were present in the plots. The average barley grain yield and weed biomass production were 460 and 18 g m<sup>-2</sup>, respectively. The quantity of weed biomass was much smaller than grain yield. It constituted only 2.3% of the total biomass production in the plots. Hence, barley had a good competitive ability against weeds in this experiment.

The grain and weed production of the individual varieties is shown in Figure 3.5. The weak negative correlation between grain yield and weed biomass is statistically significant. The variation in weed biomass production among the barley varieties was not significant, so no differences in the competitive ability of the barley varieties studied could be demonstrated.

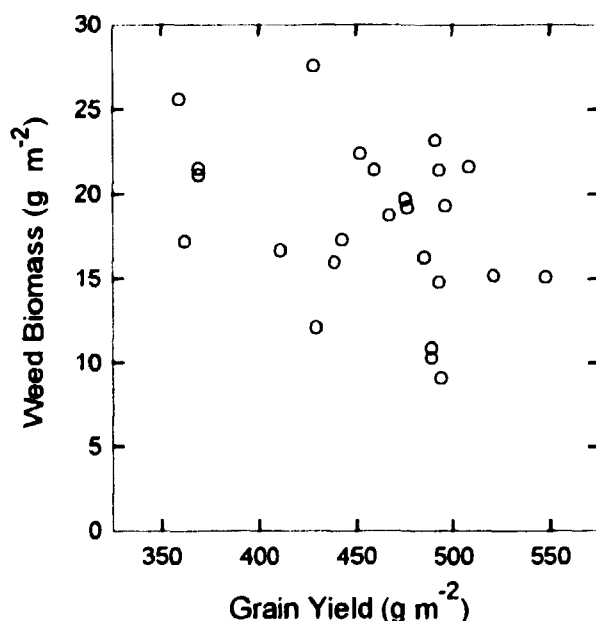


Fig. 3.5. Grain yield and weed biomass production in 25 spring barley varieties grown at a biodynamic farm with heavy weed infestation.

### 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 1994 a total of 1520 individual "experiments" were distributed.

## 4 Plant Nutrition and Nutrient Cycling

### *Introduction (G. Gissel Nielsen)*

This research programme comprises a number of projects that all contribute to a better understanding of the biological and chemical processes in the soil-plant-atmosphere system. The uptake processes must be controlled 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 reduced loss of nutrients to the aquatic and atmospheric environments.

Mutualistic symbioses between plant roots and microorganisms are directly involved in the nutrient uptake by plants. Nitrogen is provided by *Rhizobium* bacteria fixing atmospheric nitrogen in symbiosis with legumes. Our research in this area is particularly directed on studies of the exchange of signal components between bacteria and host plant across the peribacteroid membrane. The soil-plant transport of mineral nutrients, especially phosphorus, is mediated by arbuscular mycorrhizal fungi in symbiosis with most plant species. In our programme we deal with a number of aspects of the importance of mycorrhiza for plant growth such as the influence of soil-P status on the mycorrhizal transport of phosphorus, the efficiency of different fungi, and interactions with collembolans.

The soil microbial biomass is of fundamental importance to the mineralization of nutrients in plant residues and in animal manure. Special attention is directed towards processes involved in the cycling of nitrogen and turnover of organic matter. Nitrogen is essential for plants, but also a risk to the environment by leaching of nitrate and losses as volatile nitrogen compounds. The study of these processes will provide the basic information needed for economic and ecological sustainability of plant production.

Nitrogen is also absorbed from the air by the leaves, in some cases with a positive and some cases a negative effect for the plants. In our programme we are investigating root- and foliar uptake of different nitrogen compounds as a possible cause for the "red Norway spruce" a wide-spread disease in Danish plantations. We are looking in particular for disorder in the

balance of amino acids as an indicator for nitrogen malnutrition.

In order to fertilize the different parts of the fields in accordance with the natural variation in geology and fertility, a system was developed to measure continuously the grain yield and the position of the machinery in the field, so called computer-aided farming. We have the necessary equipment and are involved in a national programme studying and evaluating the system as the means to improved plant production.

In general, the programme of plant nutrition deals with fundamental processes in the turnover of nutrients in the soil-plant-air system. These processes govern the utilization of the nutrients and thereby the potential loss to the environment. Through close cooperation with other research institutes, covering research ranging from a very basic to a more approached level, our results contribute to the development of a sustainable plant production.

### *Summary of Projects*

#### **4.1 Mycorrhiza** (*I. Jakobsen, A. Johansen, J. Larsen, and S. Ravnskov*)

##### **4.1.1 Plant Roots and Hyphae of Mycorrhizal Fungi Compete for Soil Phosphorus**

The phosphorus (P) content in mycorrhizal plants results from the combined uptake of roots and their associated mycorrhizal fungi. We have attempted to measure the relative contribution of each component by means of a model growth system comprising a root-free hyphal compartment and a corresponding compartment containing both roots and hyphae. Phosphorus uptake from the two compartments was measured simultaneously by means of the two tracer isotopes  $^{32}\text{P}$  and  $^{33}\text{P}$ .

Previous results showed that the RIS 42 isolate of *Glomus caledonium* may transport just as much P to different host plants as the P trans-

port by roots and fungus in combination (Pearson and Jakobsen, 1993; Ravnskov and Jakobsen, in press). We suggested that the fungal P transport to the roots could decrease uptake by root tissues by feed-back regulation and consequently that the combined P uptake by roots and hyphae occurred primarily via the hyphae. A contrasting explanation would be that mycorrhizal fungi are of minor impact to P uptake at the relatively high root densities in the model systems.

We have now obtained evidence for competition for P between roots and mycorrhizal fungi. Subterranean clover was grown with RIS 42 in pots where a nylon mesh bag with  $^{32}\text{P}$ -labelled soil was inserted in the pot centre. Hyphae, but not roots, from the mycorrhizal plants grew into these bags. Some treatments also had plants growing inside the bags and the hyphal  $^{32}\text{P}$  transport out of them was much less than the  $^{32}\text{P}$  transport from bags with no plants. The inverse relationship between root length density inside the bags and the hyphal P transport out of the bags, confirms the general observation that effects of mycorrhizas on P uptake decrease with increasing root length density and disappear when P depletion zones around roots overlap. Mycorrhizas influence P uptake only when the fungi have access to P rich soil niches outside the P depletion zones.

These results suggest that the mycorrhizal fungus play a minor role in P uptake from the compartment of the model system containing mycorrhizal roots at a high length density. The model system is particularly useful for the direct measurement of the *potential* contribution to P uptake by the mycorrhizal fungus, and the model system has revealed that this fungal potential may be just as high as the potential root P uptake from a similar soil volume.

## References

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## 4.1.2 Utilization of Phosphorus in Organic Matter by Mycorrhizal Plants

Our understanding of mycorrhizal functioning requires an identification of the pools of soil P, which can be utilized by mycorrhizal fungi. Phosphorus in organic matter constitutes a large proportion of soil P and is potentially available to plants after mineralization. Previous investigations showing no effect of mycorrhizal fungi on levels of phosphatases in root-free soil compartments led to the suggestion that P mineralization is not directly influenced by these fungi. This has been confirmed in studies on the uptake of P from  $^{32}\text{P}$ -labelled organic matter by mycorrhizal and non-mycorrhizal subterranean clover.

The experiment included three levels of  $^{32}\text{P}$ -labelled plant material mixed into soil at three different supplies of P fertilizer. Mycorrhizas, with extraradical hyphae, became well established in inoculated plants, but they had no effect on the specific activity ( $^{32}\text{P}/^{31}\text{P}$  ratio) in the plants. Consequently, the mycorrhizal hyphae had no more direct access to the organic P than plant roots and we conclude that mycorrhizal fungi and plant roots obtain P from the same soil P pools (Joner and Jakobsen, in press). The major role of mycorrhizal fungi in the cycling of organic P is related to the close proximity of their hyphae to particles of soil organic matter. This close contact enables the hyphae to partially intercept the mineralized phosphorus from being fixed to soil particles, thereby becoming less available to plants.

## References

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## 4.1.3 Effects of Mycorrhizas on Nitrogen Uptake

The extraradical hyphae of mycorrhizal fungi may efficiently deplete the soil mineral N pool and influence the general turnover of N in soil (Johansen *et al.* 1994). This was revealed by studying the hyphal transport and soil depletion of  $^{15}\text{N}$ -labelled ammonium or nitrate supplied to

a root-free hyphal compartment confined by a fine nylon mesh. Information is also needed on effects of mycorrhizas on the depletion of an inorganic N source supplied directly to the rooting medium.

Cucumber plants were grown in symbiosis with *Glomus intraradices* or *G. clarum* or as non-mycorrhizal controls. Plants were initially supplied with 50 mg N and they received a second supply of 50 mg N kg<sup>-1</sup> soil 20 days after planting. One set of plants was harvested just before the second N supply and sequential harvesting was carried out during the following 20 days. Plant dry weights, total and mycorrhizal root lengths, and the content of KCl-extractable N were measured at each harvest.

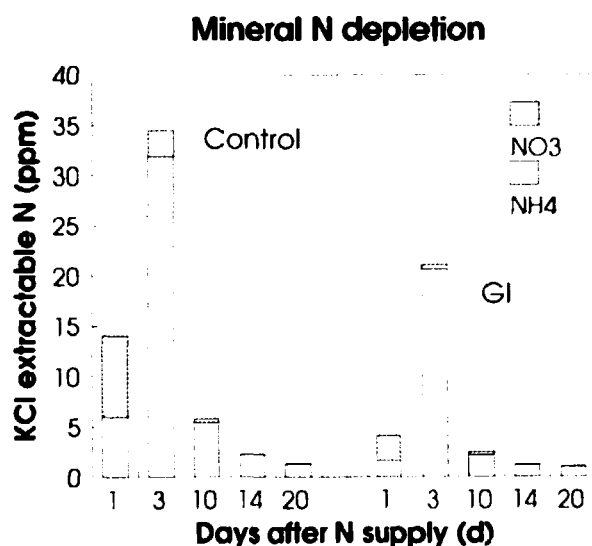


Figure 4.1.3. Soil mineral N concentration as affected by cucumber plants grown alone (control) or in symbiosis with the AM-fungus *G. intraradices* (GI) during 20 days of growth.

The soil mineral N content was considerably lower in pots with roots colonized by *G. intraradices* than in pots with non-mycorrhizal roots in one experiment (Figure 4.1.3.). Total root length was unaffected by mycorrhizal colonization. Soil mineral N content was not decreased by *G. intraradices* in two other experiments, but the total root length was generally decreased by the fungus. Colonization by *G. clarum* decreased both the soil mineral N content and the total root length as compared to the controls at all har-

vests. Although these results indicate a complex interaction between mycorrhizal fungi and their associated roots, they also suggest that mycorrhizal fungi may contribute significantly to the depletion of mineral N in soil where roots are also present.

## References

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### 4.1.4 Effect of Pesticides on Mycorrhizal Functioning

Pesticides used in agricultural systems may be harmful to the functioning of mycorrhizal fungi. A test system is required for the routine screening of these undesirable side effects of pesticides. The effect of the fungicide benomyl on the P transport by a mycorrhizal fungus was evaluated by means of a simple two-compartment test system. It comprised a root-free hyphal compartment where the direct effect of the fungicide on the fungal P transport was examined. Benomyl completely inhibited the fungal P transport, even at a concentration corresponding to the dosage recommended for agricultural use. We found the test system to be a promising tool in future risk assessments studies of pesticides, but further development is required.

### 4.1.5 Interactions between Fungivorous Collembolans and Mycorrhizal Fungi

In a time course study we examined the effect of yeast and fungivorous collembolans on the hyphal P transport of a mycorrhizal fungus. We also examined the effect of yeast and mycorrhizal mycelium on the reproduction and survival of the collembolans. The presence of yeast in the hyphal compartment increased both the collembolan population size and the hyphal P transport by three and five times, respectively. Collembolan numbers were not affected by the mycorrhizal mycelium, whereas collembolans influenced the hyphal P transport. The effect of the collembolans on the hyphal P transport depended on both the age of the fungi and the initial numbers of collembolans. A low population size resulted in a slight increase in the hyphal P transport, whereas high collembolan numbers decreased the

hyphal P transport. The fungal P transport was markedly reduced with time, reflecting a general decrease in the viability of the mycelium over a period of eight weeks.

## 4.2 Symbiotic Nitrogen Fixation

(L. Rosendahl, J. Christiansen, H. Feldner, A. Pedersen, I. Hansen)

Soil bacteria of the genus *Rhizobium* are capable of reducing atmospheric nitrogen into ammonia, provided the bacteria are supplied with the necessary energy and are maintained in a proper environment. Legumes are able to provide the conditions needed for nitrogen fixation in rhizobia by the establishment of a symbiotic relation. The *Rhizobium* bacteria inhabit root nodules which are formed as a response to specific signals exchanged between the symbionts. Within the nodules the bacteria transform into the nitrogen-fixing bacteroid stage, and the plants benefit from the symbiosis by receiving the fixed nitrogen.

Maintenance of an effective symbiosis is based on a continuous and carefully balanced exchange of molecular signals and metabolites between the symbionts. The communication is controlled in the interface between the symbionts, which consists of the plant-derived tissue specific peribacteroid membrane (PBM) and the peribacteroid space between this membrane and the bacteroid outer membrane. The crucial role of the interface in controlling the function of the symbiosis makes it an obvious target for research to extend our understanding of close associations between organisms in general. The legume-*Rhizobium* symbiosis performs a perfect model for such studies, as the PBM enclosed bacteroids, called "symbiosomes", are easily isolated from the nodules for investigations on the membrane interface.

We have established techniques for the isolation of symbiosomes from various legume nodules under anaerobic conditions, which allows maintenance of nitrogen fixation in the symbiosomes. These symbiosomes are used for studies on the passage of compounds from the plant to the bacteroids across PBM. The transport properties of the PBM may be affected by environmental stress as drought (Feldner *et al.* 1994). Drought-stress results in an accumulation of the

amino acid proline in plant tissue. Our recent results indicate, that bacteroids from drought-stressed legume nodules are superior to bacteroids from unstressed nodules in the utilization of proline for nitrogen fixation.

Auxins are a group of phytohormones which influence legume root nodule formation. Legume root nodules contain higher levels of auxin, primarily indole-3-acetic acid (IAA), than these in other plant tissue. Root nodule IAA originates from the plant meristem, but the rhizobia may also produce IAA. IAA alters the electrical potential of plasma membranes and activates the  $H^+$ -ATPase. PBM contains a plasma membrane-like  $H^+$ -ATPase that is essential in the transport properties of the membrane. Thus IAA may play an important role in the communication between the symbionts in established legume root nodules. IAA transport into plant cells is mediated by transmembrane diffusion and/or via a saturable  $H^+$ /IAA symport, whereas efflux occurs by an anion carrier as well as by diffusion. We have investigated the IAA transport properties of the PBM by recording the accumulation of  $^3H$ -IAA in isolated symbiosomes. We recorded a time-dependent increase in the radioactive labelling of the symbiosomes, which indicated uptake. A plot of  $1/V$  versus  $1/[S]$  for IAA indicated a biphasic uptake system. At low substrate concentrations there was a saturable uptake system with an apparent  $K_m$  of 59nM and a  $V_{max}$  of 0.83 pmol/min/mg protein. At high substrate concentrations, there was a nonsaturable accumulation of IAA.

PBM vesicles from pea and soybean root nodules were prepared by aqueous two-phase partitioning (dextran-PEG). The two-phase system facilitates isolation of vesicles with a defined orientation, and we have optimized the method to yield 100 $\mu$ g protein/g nodules of sealed primarily inside-out PBM vesicles. The sidedness of the vesicles was determined by latency of marker enzymes, and we recorded a latency of 1,3- $\beta$ -glucan synthase of 70-80% in the vesicle preparations (Christiansen *et al.* 1994). We confirmed the presence of a plasma membrane-like ATPase in pea PBM, but there is no evidence indicating the presence of other kinds of ATPases. Soybean PBM contains a tissue specific protein (nodulin-26), which has been suggested to be a PBM channel protein. Antibodies raised against a peptide homologous

to a conserved region of nodulin-26 (kindly provided by Professor D.P.S. Verma, Ohio State University) does not react with PBM or other root nodule fractions from pea, which may indicate that the proteins are lacking in pea nodules or that the homology to the corresponding pea PBM protein is low. The sealed inside-out PBM vesicles are currently being used in studies of transport of compounds from the bacteroid side to the plant cytoplasm across PBM.

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### 4.2.1 Nitrogen and Organic Matter Turnover in Agro-Ecosystems (E.S. Jensen, P. Sørensen, P. Ambus, F. Jørgensen)

The aim of our research is to improve the understanding of biological and chemical processes in nitrogen (N) and organic matter transformation in agro-ecosystems. This is the foundation in developing agricultural management methods to

optimize the supply of N to crop requirements and minimize the losses of nutrients from the agro-ecosystem. Major emphasis have been placed on the mineralization-immobilization turnover, plant uptake, denitrification and leaching of N after applying crop residues and animal manures to soils, and on symbiotic  $N_2$  fixation (SNF) by legumes.

Straw and other crop residues are the principal energy source for microbial N and carbon (C) transformation in agricultural soils. When cereal straw decomposes, the soil microbial biomass immobilizes ammonium and nitrate. Improved crop residue management, e.g. by using a more homogeneous distribution of the residues in the ploughlayer or reducing the residue particle size, potentially increasing the availability of C, may be a method to conserve N in the soil-plant system and reduce losses of N by leaching.

Experiments with pea straw showed that reducing the residue particle size increased the initial immobilization of N and decreased the rate of residue net-mineralization of N (Jensen 1994). Preliminary results from laboratory experiments with barley straw showed that the inorganic N in soil declined with 33% (Figure 4.2.1), when the straw particle size was reduced from 25 mm to < 3 mm under conditions where straw decomposition was not N-limited (Jensen and Ambus, in press).

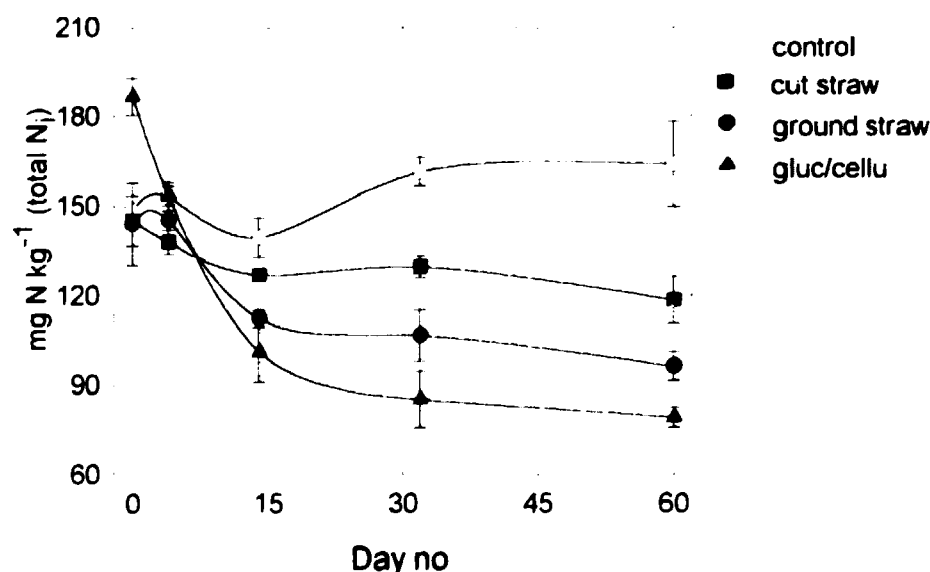


Figure 4.2.1. Effect of barley straw with different particle size (cut: 25 mm; ground: < 3 mm) and/or cellulose/glucose on inorganic soil N in repacked soil cores incubated at 15°C in the laboratory.

Barley straw incorporation in field plots in September increased the microbial biomass N in the spring, which indicated that N was conserved in the organic form (Jensen and Ambus, in press). The results showed that even if the straw had decomposed for more than 6 months, its decomposition still influenced N-cycle processes in soil in the spring. The remineralization of N and the effects on plant growth are being studied.

When perennial legume litter decomposes the mineralized N may reduce SNF in the legume. Incorporating increasing amounts of litter from the tropical legume *Pueraria phaseoloides* increased the amount of N<sub>2</sub> fixed as determined by <sup>15</sup>N isotope dilution technique (Østerby and Vesterager 1994). This unexpected effect was probably due to litter stimulating the growth of the legume, possibly because nutrients limiting growth became available during decomposition of the litter.

A research project on the interaction between SNF and animal manure as N-sources in grass-clover mixtures was initiated. The soil organic matter in field plots were successfully labelled with <sup>15</sup>N to determine clover SNF in the subsequent 2 years of growth.

Leaching of nitrate and volatilization of ammonia are often high in agro-ecosystems with intensive animal production, due to the production of large amount of animal manure. Research is needed to develop methods which can better predict the value of the organic nutrient fractions of manure as plant nutrients. Risø has developed <sup>15</sup>N techniques to study the transformation of organic N in animal manure (Sørensen *et al.* 1994). These techniques are now being utilized in a joint research project with The Danish Institute of Soil and Plant Science in Foulum. Experiments to determine the transformation of fresh and anaerobically stored urine in soil with different texture, showed that there was no effect of storage on net mineralization of urine N. The net mineralization of urine N was significantly higher in a soil with 4.5% clay compared to that in a sandy loam soil with 17% clay, because more urine N was immobilized in the microbial biomass in the latter (Sørensen, in press).

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### 4.2.2 Forest Decline and Ammonia (K.C. Engvild)

In Denmark, Norway spruce plantations are still severely damaged by the syndrome "red Norway spruce" or "røde rødgraner" causing premature felling of up to 10% of the trees on poor sandy soils. Contending hypotheses of possible causes include damage or overfertilization by airborne ammonia liberated from farms; damage by mild, windy winters on the spruce which normally require below -2°C in the month of January; damage by airborne sodium chloride in gales from the North Sea; lack or leaching of certain nutrients, such as K, Mg or Ca; as well as combinations of the various stresses.

We are investigating the ammonium hypothesis of Nihlgård (Nihlgård 1985) who thinks that the spruce is damaged by nitrogen overfertilization. Experiments by Saxe (Saxe 1993) on the content of mineral nutrients have shown little changes in damaged Norway spruce. We hope to use the content of free amino acids, particularly arginine and ornithine, as indicators that sick trees may be suffering from ammonium overload. Pot experiments over several years have shown repeatedly that the content of arginine and ornithine has increased more than 100 times in trees overloaded with ammonium nitrate or urea.

However, this response of arginine and ornithine increase comes either after nitrogen overloading or deficiency of phosphorus or potassium. So it is a relative phenomenon.

At first, trees that are fertilized heavily with nitrogen grow very well, with high biomass and a healthy dark green look. After one year the needles start browning and fall off. However, the symptoms not exactly the same as those of "red Norway spruce" where the needles turn red from the tip of the shoot.

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### 4.2.3 Are there Death Hormones in Pea? (K.C. Engvild)

Developing green peas contain a chlorinated indoleacetic acid derivative in quite large quantities, almost up to 0.1 gram per kg dryweight. This 4-chloroindoleacetic acid methyl ester is an intermediate between the ordinary auxins and the standard hormone herbicides. The chloroindole auxins are not found in pea before flowering nor in the mature seeds.

The substances were first isolated from hundreds of kg of pea seeds by J.P. Nitsch and his group in France (Gandar and Nitsch 1964) and by Marumos' group in Japan about 25 years ago (Marumo *et al.* 1968). I have developed methods for the identification and quantitative determination of the substances on 1-20 gram samples, using radioactive  $^{36}\text{Cl}$ , thin layer chromatography, autoradiography, and gas chromatography/mass spectrometry. Today the chloroindole auxins have been found by many groups in several countries. They are now recognized as a natural compound and not as an artifact. They are also present in *Vicia faba*, lens and lathyrus, closely related to pea, but with a single exception, have not been found in other species.

The substances are very strong plant growth hormones, causing strong elongation, bending, and rooting responses. However, pea cuttings, which form numerous roots after treatment, stop growth completely and the apical bud dies; the

cuttings develop large amounts of ethylene. Only after three weeks is growth resumed from the lowest adventitious bud.

Attempts to use the chloroindole auxins for other purposes, e.g. tissue cultures, had little success. The results with the dying cuttings made me wonder if the function of the chlorinated compounds in the developing peas is to kill the mother plant and cause all nutrients to be mobilized to the seeds, or in other words function as a death hormone or endogenous herbicide.

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### 4.3 Differentiation of Application of N-fertilizer (V. Haahr, A. Jensen)

Up to now, farmers are applying N-fertilizers by an even distribution over the individual fields with an amount recommended by The Farmers Union. This practice conflicts with the rather high variation of yield potential inside a field caused by soil fertility, topography and other varying parameters and it seems more rational to apply a differentiated amount of fertilizers proportional to the expected yield.

With modern techniques this is possible and at Risø we have practised this for two years and analyzed the importance of applying differentiated amounts of N-fertilizers to winter wheat. The yield potential was calculated by analyzing the organic amount of nitrogen, which can be mineralized during the growing period, N-min., in subfields based on iso-yield curves determined at the previous year's harvest.

The technique for analyzing the yield variation is a modern combine, a Danish "Dronningborg", equipped with a special device, "Foldmeter", which with the help of radiometric transmission, measures the yield continuously. The position is, at the same time, determined by the DGPS-technique global position satellites. Yield

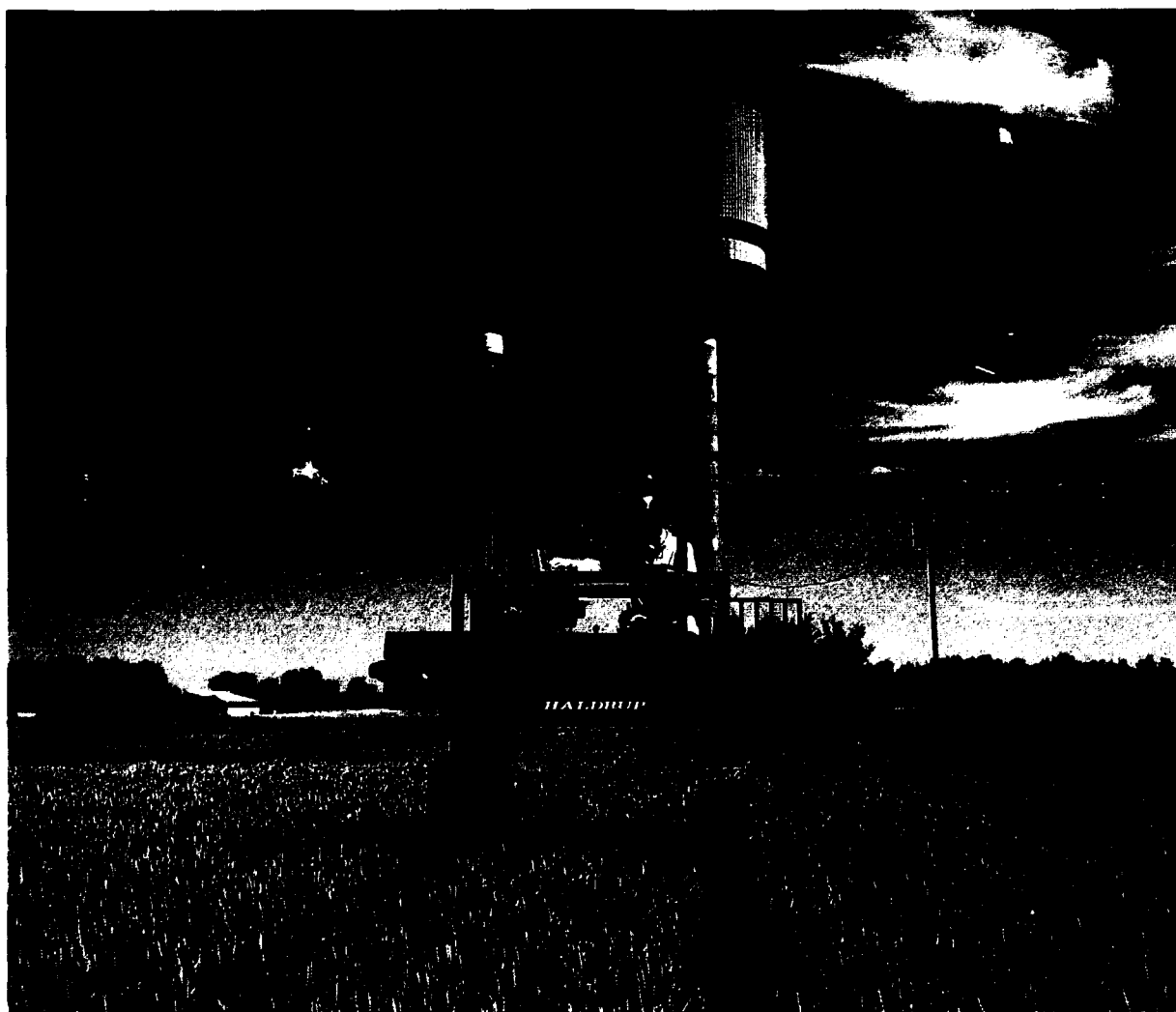
and position are registered every two seconds and results in about 1000 yield determinations per ha.

For the differentiation of fertilizer spreading, we used a commercial system, Agromatic/Elkjær, which can be programmed with the help of a normal PC and a special software.

The results from the two-year study have shown a significant grain yield improvement of about 2 hkg/ha, when a moderate amount of N-fertilizer is applied. At the normal recommended N rate no significant difference in yield was found. The importance for the environment, such as N-balance, is also being analyzed and will be reported later.

Measurements in the field also comprise light reflectance, infrared pictures taken from aircrafts and other physiological determinations of importance for yield determinations. Physical and chemical soil parameters are determined for every 35 x 35 m to a depth of 1 meter.

The experiments are performed in collaboration with The Institute of Plant and Soil Science at Foulum, and The Danish Agricultural Advisory Centre in Skejby, Aarhus.



*Figure 4.3. Measurements of plant biomass by use of remote sensing.*

## 5 Trace Analysis and Reduction of Pollution in the Geosphere

### *Introduction (V. Gundersen)*

The professional image of the Chemistry Section has changed considerably during 1994 due to retirement and employment of new scientists boosted organic analysis, the upgrading of biomass and the transformation of organic matter in soil and water.

In the field of upgrading biomass we participate in an EFP programme with the aim of converting straw into ethanol by means of wet oxidation followed by fermentation. The conversion of biomass by wet oxidation creates new applications for degradation products and demands new analytical methods for their characterization.

A new gamma-ray spectrometric method, dating sediments and estimating sedimentation rates on the seafloor, has been developed and has attracted considerable attention over the past year. A national centre for the dating of sediments will be established in the coming year.

The programme played an active role in the formation of the Danish R&D Center for Decontamination of Soil and Sediment. The Center is an umbrella organization, between five environmental institutions in DEG, aiming to create and coordinate R&D activities in the field of decontamination.

Cooperation with other programmes in the department has started in the field of trace elemental analysis. With the purchase of high resolution ICPMS equipment in 1995, the programme will have excellent facilities to estimate oceanographic tracers as Pu and Tc in cooperation with the Ecology programme. Estimation of trace elements in plant materials, as a consequence of the character of the soil, and the methods of cultivation, is a hopeful project in cooperation with the Section of Plant Nutrition made possible by the high resolution instrument.

We shall continue our efforts to balance our research activities between our strategic aims and possible financial support.

### *Summary of Projects*

#### 5.1 Chemical Modelling

##### **5.1.1 The Cooperative Effect of Carboxylic Acid Groups in Close Distance - as a Function of Ionic Strength (B.L. Jørgensen, B. Skytte Jensen)**

Different polycarboxylic acids are being investigated regarding the influence of the ionic strength/counter ions - in this case sodium ions. The purpose of the investigations is to describe how functional groups in close distance proximity affect one another. Carboxylic acid is used as example. Dissociation constants, found from potentiometric titrations performed with different ionic strength, are compared with proton affinities calculated with semiempiric quantum mechanical calculations (Figure 5.1.1.). The PC programme HyperChem™ was used for the calculations and geometric optimization was performed with the PM3 method (Stewart, 1989) in vacuum. Mellitic acid (benzene-hexacarboxylic acid) was the preferred model compound, but some dicarboxylic acids and other benzoic acid derivatives were also used.

The counter ions, together with the solvent, apparently have a decisive effect on the behaviour of the mellitic acid system, because there are distinctive differences between the theoretic calculations and the measured dissociation constants. There is apparently very little difference between the proton affinity of the third and fourth dissociated step of mellitic acid according the PM3 calculations. Also calculations with sodium ions present were performed as were some calculations with the acid dissolved in water (a periodic box).

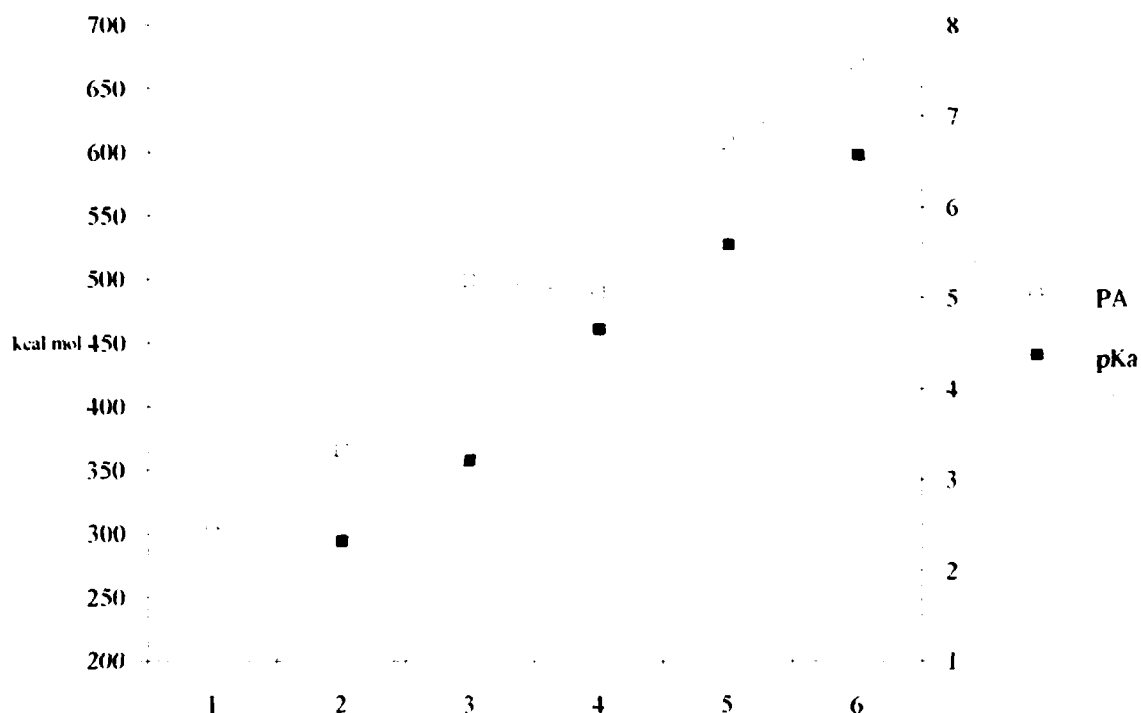


Figure 5.1.1. The calculated Proton Affinity (PA) for mellitic acid calculated with PM3 in vacuum and  $H_f = 367.2$  kcal/mol for  $H^+$  - compared with the pKa values measured for mellitic acid in water.

## References

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## 5.2 Applied Geochemistry

### 5.2.1 Dating of Recent Sediments by a New Gamma-spectrometric Technique (H. Kunzendorf)

By the analysis of natural and anthropogenic radioisotopes in marine sediments a historical sedimentation framework may be established. A new method, which in practical terms is an extension of an alpha-spectrometric technique previously developed at the former institution Isotopcentralen (Danish Natural Science Research Council funding), makes use of non-destructive gamma-ray spectrometry. Sediment cores of variable length are usually cut into 5 or 10 mm thick disks, dried and afterwards counted in a low-background facility. A prototype measuring instrumentation has been used to determine radioisotope contents in sediments from the Faroe continental margin, Skagerrak, Kattegat and Norwegian Trench areas. By its ease of opera-

tion and the possibility to determine a number of isotopes in the samples, the new technique is superior to the previous method. As a result of the measurements, average linear sedimentation and sediment accumulation rates (use of the constant initial concentration model) may be calculated and a sedimentation history (use of the constant rate of supply model) may then be estimated by using both the analytical and the sediment physical data. The new technique was presented at the 8th Danish Oceanographer's meeting in Odense (Kunzendorf 1994a) and described elsewhere (Kunzendorf 1994b). Because the new technique represents a prerequisite of all analytical work on marine sediments, the analytical strategy proposed was also presented at the recent annual Danish analytical chemistry meeting (Kunzendorf 1994c). After the sediment dating, the sediments may also be analysed for a number of selected chemical elements by radioisotope X-ray fluorescence for geochemical characterisation purposes.

Through the cooperation with Aarhus University a study of nutrient fluxes in coastal basins sediment accumulation data was achieved. The study included laboratory experiments for nutrient fluxes estimation. Two cores were dated from the western Kattegat area and these data were included in a contribution to the Baltic

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- Kunzendorf, H. (1994c). Low-energy gamma-spectrometry as a tool for marine chemical fluxes estimation. 3. Danske Symposium i Analytisk Kemi, 16-17/8, Københavns Universitet, Abstract, 1 p.
- Laima, M., Hansen, L.L., Christiansen, C., Kunzendorf, H. (1994). Nutrient fluxes in a coastal basin. 19th Conf. Baltic Oceanographers, 29/8-1/9 1994, Gdansk, Poland. Abstr. 1 pp.

### 5.2.2 European North Atlantic Margin Sediment Fluxes (H. Kunzendorf)

The MAST-2 project "European North Atlantic Margin (ENAM): sediment pathways, processes and fluxes" is a large-scale project involving 6 EU countries and Norway, with project coordination by GEOMAR (Germany). The 3 major objectives of the project are the determination of ocean margin sediment distribution (sediment fluxes), its chronology and the evaluation of past hydrographic regimes. Expected achievements of

the project are the definition of box models which define sediment flux patterns through glacial-interglacial cycles and their influence on the carbon cycle at the margins and through transport to the deep sea. Working areas are the Portuguese margin, the Faroe-Shetland Channel and the Norwegian Channel. Participation in the project is established through the Danish coordination (Geological Survey of Denmark) and involves the dating of recent sediments and geochemical studies of mainly rare earth elements. Sediment cores, recovered from several cruises in 1993, were analysed in 1994. The results of one year's work were presented at a project workshop in Portugal (Kunzendorf 1994).

Investigations in 1994 dealt with the dating of sediment cores from 2 stations in the Norwegian Channel (cores 16 and 18) and 3 cores from the Faroe continental margin (cores 25, 30 and 31). While the former cores, taken at water depths exceeding 350 m, show relatively low average sedimentation rates, 0.5 and 1.1 mm/year, respectively, a core from the Nolsoya Fjord (Faroe Islands) yields extremely high sedimentation rates, 6.4 mm/year. Cores 30 and 31 which are characterised by sand deposition in the upper core sections and by this reflect bottom current activity at present times, do not show any significant trend of unsupported lead-210 decrease with depth. As these cores could, therefore, not be dated it is also worthless to study their geochemistry.

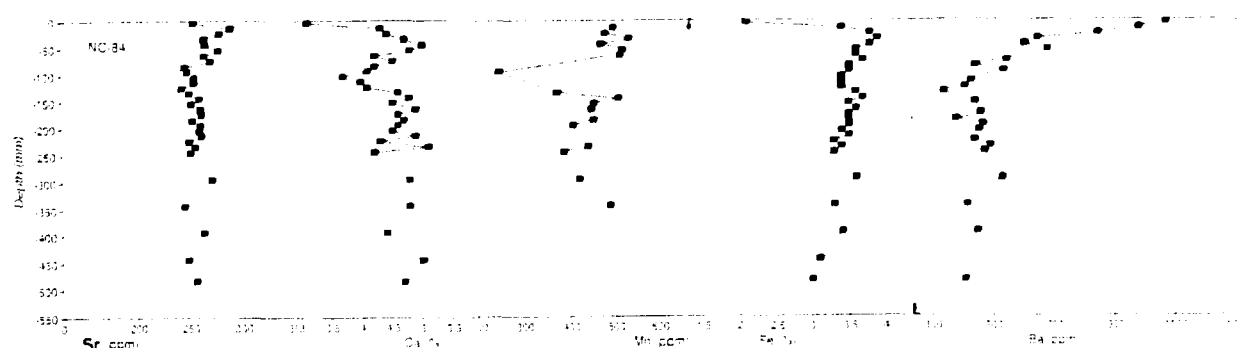


Figure 5.2.2. Distribution of selected metals along core ENAM-16.

The geochemical studies until now yielded two significant trends. Firstly, core 16 showed an anomalously high Ba concentration in the upper section. Through the dating of the core, by application of the constant rate of supply model, the start of Ba enrichment in the core could be estimated to be close to the forties with an almost linear increase from ~ 600-1800 ppm in present time sediments. At present, we have no definite explanation for the observed phenomenon, but pollution could be one of the possibilities. Secondly, the redoxcline is usually easily outlined by the sediment chemistry data as exemplified by the high manganese in, e.g., the upper 50 mm of core 18.

#### References

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### 5.2.3 Geochemical Mapping in the Skagerrak-Kattegat Area (H. Kunzendorf)

Sediment cores taken mainly from the Norwegian part of the Skagerrak area are presently being dated. Of the six cores taken in 1993, only four yielded significant data on the sedimentation history. Interestingly, although water depths are similar (> 300 m), the observed rates do vary significantly from about 1 to about 5 mm per year. The measurements also seem to show a clear dependence of the sedimentation rate on the hydrographic regime in the Skagerrak area. Judging from the few analysed cores, a central sediment transport channel may exist on the southwestern margin of the Norwegian Trough. Here sedimentation rates are highest. Because the historical modelling suggests a significant imprint of Sellafield-derived material especially in the high-sedimentation rate cores through increased Cs-137 contents, our data gathered until now, suggest an important sediment transport component from the southern North Sea into the Skagerrak and probably continuing into the Kattegat (Kunzendorf 1994; Kunzendorf *et al.* 1994). The sediment dating by radioisotopes is incorporated in the ongoing geochemical mapping efforts by the University of Bergen and the Geological Survey of Norway. Large-scale dispersion of heavy metals in the Skagerrak and

northern Kattegat have been outlined during recent years (Longva *et al.* 1994).

The work is carried out in collaboration with C. Christiansen, University of Aarhus, Denmark; O. Longva, The Geological Survey of Norway, Trondheim, Norway; and M. Paetzel, University of Bergen, Norway.

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### 5.3 Chemical Analysis

#### 5.3.1 Inductively Coupled Plasma Mass Spectrometry and Multivariate Calibration (A. Behrens)

Inductively coupled plasma mass spectrometry (ICPMS) has several advantages, e.g. multielement determination and low detection limits. For some of the elements, however, there are analysis difficulties because of spectroscopic interferences. These difficulties could be eliminated by using multivariate calibration, e.g. Partial Least Squares Regression (PLS). Another problem in ICPMS is non-spectroscopic matrix interferences. If non-spectroscopic interferences cause problems they might be solved by using reference materials as standards in the PLS model.

Gd is a rare earth element, which is very difficult to determine by ICPMS because of spectroscopic interferences. Figure 5.3.1. shows the prediction of Gd in reference materials by calibration with a single variable ( $^{157}\text{Gd}$ ), a PLS model based on aqueous standards, and a PLS model based on reference materials. Both PLS models are capable of eliminating spectroscopic interferences. It was not necessary to correct for non-spectroscopic matrix interferences in the PLS models, and therefore it is not possible to

conclude that the use of reference materials as standards eliminates the problem. The use of aqueous standards has some advantages. The concentration levels can be chosen freely, problems with covariation could be avoided, and a model based on aqueous standards can be adjusted more easily to determine the analyte in new types of samples.

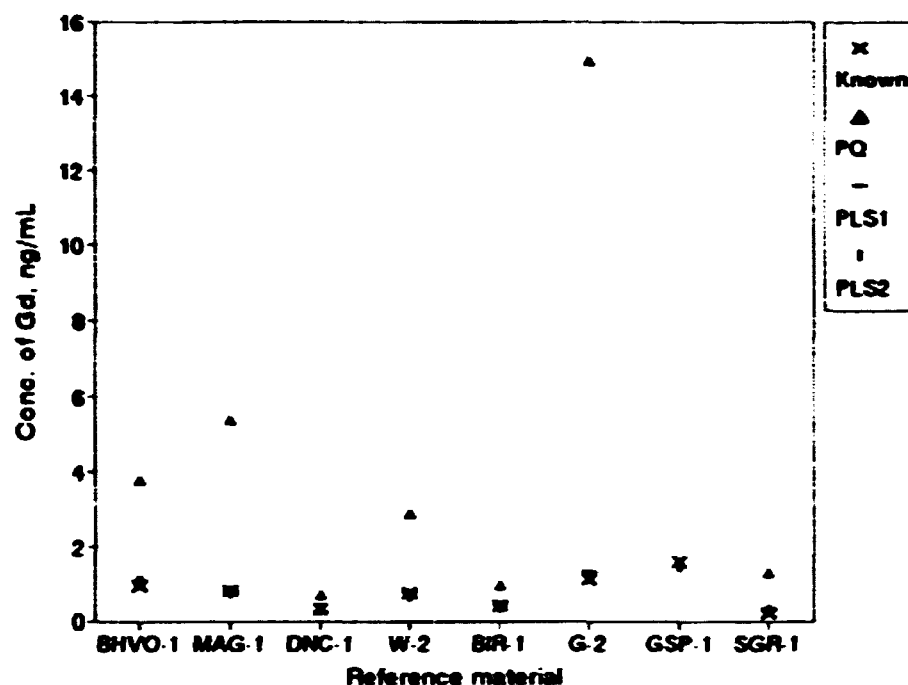


Figure 5.3.1. The predicted and known value of Gd in reference materials. PQ=calibration with a single variable ( $^{157}\text{Gd}$ ), PLS1= aqueous standards, PLS2=reference materials.

### 5.3.2 Chemical Analysis and Food Technology (P. Solgaard)

The inorganic part of FØTEK-1 project<sup>1)</sup> was divided into establishing the normal concentrations of toxic elements in organs and blood from cows and pigs, and on basis of this knowledge, to evaluate a fast and reliable analytical method to control the quality in an early stage of the production chain.

Cooperation between the Chemistry Section and Levnedsmiddelstyrelsens Centrallaboratorium was based on possession of both laboratories of instruments to perform ICPMS analyses, which obviously have the power to find the necessary basic information and the required qualities of the final method - fast, sensitive and multielemental.

The blood analyses were mainly dealt with in the Chemistry Section and results manifested the possibility of analyzing for elements Cu, Ni, Cd, Pb and even Cr, Se, As and Hg with detection limits approaching the ppb ( $10^{-9}\text{g/g}$ ) level after a fast digestion with organic base or with acid in a microwave oven.

The field of interest included filets of fish delivered by Nordsøcentret and preliminary results again gave promise for a reliable ICPMS method. The concentration of As was surprisingly measured to several ppm ( $10^{-6}\text{g/g}$ ) and the analysis was therefore under suspicion because of the possibility of heavy interference from ArCl. The use of HRICPMS - high resolution ICPMS - is an easy way to avoid such interference and this was demonstrated by the kind help of a Belgian laboratory as shown in Figure 5.3.2.1 and 5.3.2.2.

The work is carried out in cooperation with E. Larsen, Department of Combustion Research, Risø, J. Rud Andersen, Slagteriernes Forskningsinstitut; A. Büchert and S. Stürup, Levnedsmiddelstyrelsens Centrallaboratorium.

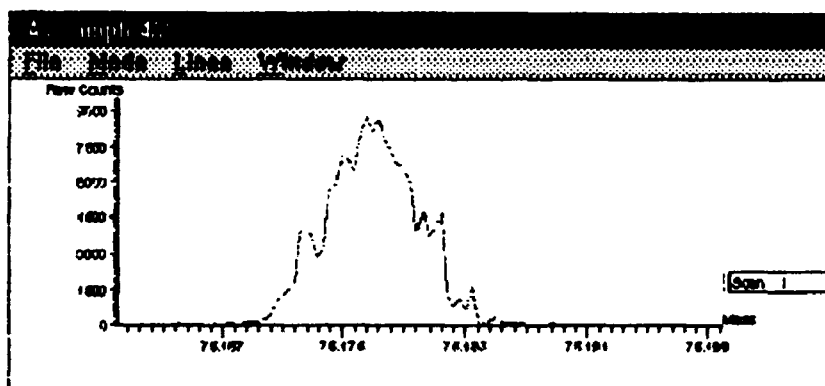


Figure 5.3.2.1. Sample

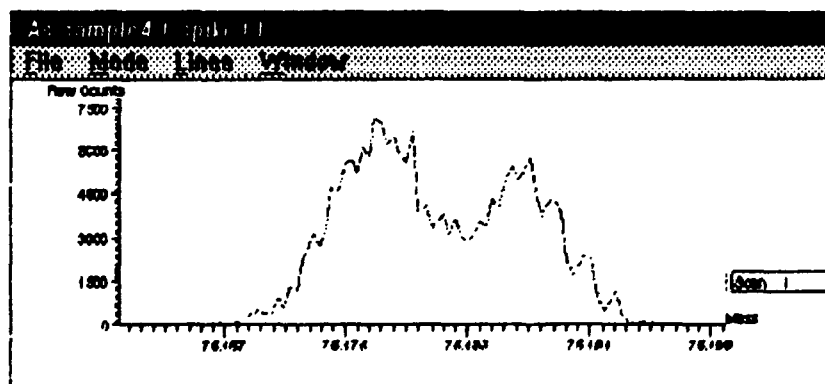


Figure 5.3.2.2. Sample spiked with Cl.

- 1) Project: Hurtigmatoder til restkoncentrationsbestemmelse i levnedsmidler (Quick methods for trace analysis on nutrition)

### 5.3.3 Chemical Analysis in Environment and Health (P. Solgaard)

Combustion is an important source of environmental impurity and projects to reduce the spread from energy works are being studied in the Department of Combustion Research<sup>1)</sup>. Many samples from different positions in the system, from the fire to the final release from the chimney, are brought to be analyzed for composition

of particles and concentrations of *e.g.* Cl in the air.

Samples of acid rain are still collected from several sites and hundreds are analysed by collaborations between DMU departments and the Chemistry Section. Included, are the establishment of recommended values of Nordic reference material.

Considerable work is performed investigating the effect on ground water from dumped contaminated materials in soil. Even here, the multi-element ICPMS method is of great help to scientists at the Danish Technical University in finding the percolation of toxic and other elements like Cr, Fe, Ni, Cu, Zn, Cd and Pb, and also having the chance of eliminating or reversing of

elements not looked for until now<sup>2)</sup>. Exciting prospects are brought forward, when impurities and health are combined. Smoking is, of course, known as unhealthy, but the high sensitivity of modern inorganic analysis performed in the Chemistry Section is necessary when measuring the dangerous effect of Cd to the unborn child of female smokers.<sup>3)</sup>

The work is carried out in cooperation with T.H. Christensen and Dorthe Lærke, Institute of Environmental Science and Engineering, Danish Technical University, M. Hovmand, National Environmental Research Institute, Denmark, H. Clausen, Gynækologisk-obstetrisk afdeling, Hvidovre Hospital, Denmark, P. Haid and P. Arendt Jensen, Department of Combustion Research, Risø.

- <sup>1)</sup> Project: Biomasses brændsels og fyrings-karakteristika (Characteristics of fuel and combustion of biomass)
- <sup>2)</sup> Project: Experimental evaluation of pollution of heavy metals in soil and ground water by metal recycling industry.
- <sup>3)</sup> Project: Stereologisk undersøgelse af placenta fra kvinder, der ryger under graviditeten (A stereological study of postmature placentae fixed by dual perfusion fixation)

#### 5.3.4 Reference Materials (P. Solgaard)

It is now recognized as very important to have excellent reference materials, with reliable concentration values, to be part of the analytical laboratory's means to get and maintain good precision and accuracy.

Among others, EU through their Measurements & Testing Department is engaged in this work. Many European laboratories are participating in Round Robin procedures as the first step in producing the right material, but the final analysis is performed by invited laboratories. In the final CRM482 certification of Lichen Reference material, the Chemistry Section participated and determined the concentration of As, Cd, Cu, Pb and Zn by ICPMS. During a workshop in Brussels, where these results were presented, the Chemistry Section and others predicted increase use of ICPMS or even better HRICPMS.

The work is carried out in cooperation with K. Heydorn, Isotop Laboratory, Risø National Laboratory, Denmark; P. Schramel, GSF, Neu-

herberg, Germany; S. Caroli, Instituto Superiore de Sanità, Rome, Italy; E. Blanco Conzales, Universidad de Oviedo, Spain; Ch. Barras, Lonza, Visp Switzerland; J.G. van Raaphorst, ECN, Petten, The Netherlands; R. Cornelis, L. Moens, Universiteit Gent, Belgium; J.L. Imbert, CNRS, Service Central d'Analyse, Vernaison, France; E. Orvini, Università de Pavia, Italy; S. Daniels, Acadia University, Wolfville, Canada; D. Richardson, Saint Mary's University, Halifax, GB.

#### 5.3.5 Enriched Stable Isotopes in Nutrition Research (P. Solgaard)

The publication of results from the project<sup>1)</sup> was started by forwarding manuscripts to international journals (Knudsen *et al.* in press). The successful cooperation is continuous on a new project<sup>2)</sup>, again using the superiority of ICPMS to take advantage of the use of enriched isotopes as tracers in investigation of human nutrition. The determination of <sup>70</sup>Zn - the best choice of tracer - is often difficult because of interference from Cl<sub>2</sub>, but experiments with careful digestion in a microwave oven with HNO<sub>3</sub> has eliminated the problem in normal fecal samples (Figure 5.3.5). Otherwise the laborious procedure of removal of Cl by chromatography had to be involved.

The work is carried out in cooperation with B. Sandström and E. Knudsen, Research Department of Human Nutrition, Royal Veterinary and Agricultural University.

- <sup>1)</sup> Project: Metodik til måling af tilgængelighed af sporelementer i levnedsmidler og kost (Methods for measurement of trace element accessibility in foodstuffs).
- <sup>2)</sup> Project: Mineralabsorptionsstimulerende komponenter i mælk. (Components in milk stimulating mineral absorption).

#### References

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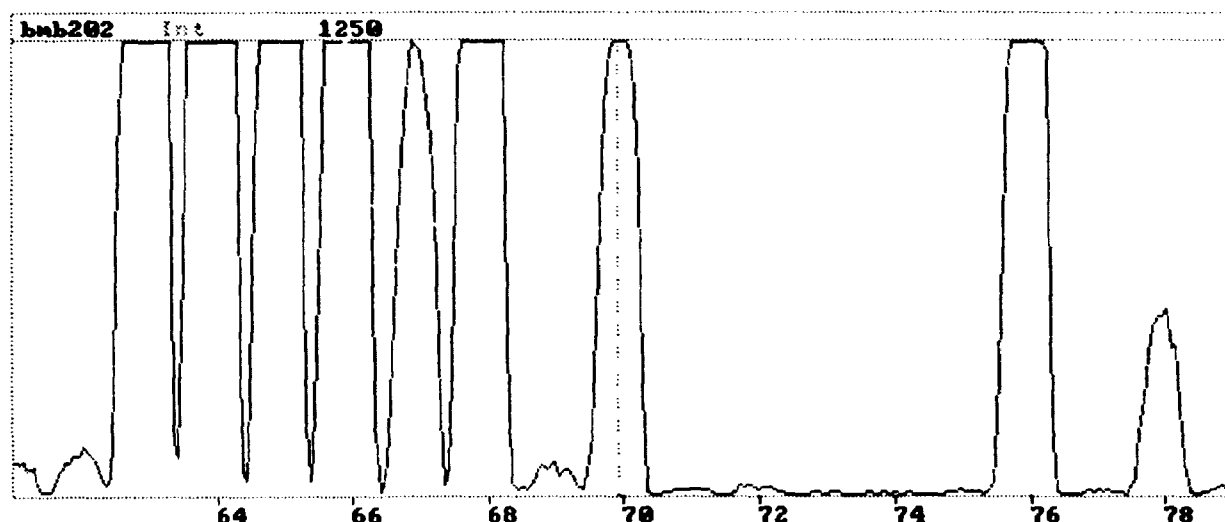


Figure 5.3.5. The spectrum shows the absence of  $^{37}\text{Cl}_2$  at amu 74 and consequently no interference from  $^{35}\text{Cl}_2$  on  $^{70}\text{Zn}$

## 5.4 Chemical processes in soil

### 5.4.1 Halogenation Processes in Forest Soils (C. Grøn)

Haloorganic chemicals of industrial origin, such as chlorinated solvents and pesticides, are considered contaminants of major environmental hazard in soils, groundwaters and waste waters. Regulatory measures planned to reduce production, use and emissions or to outline acceptable soil concentrations at contaminated/remediated sites require consideration. The production and degradation of haloorganic compounds taking place as natural processes in environment are also in need of regulation. The production of chloroform in spruce forest soils is one example of a natural halogenation process of environmental significance.

In uncontaminated soils, higher concentrations of chloroform have been found in soil air, than in ambient air (Frank *et al.* 1989; Hoekstra and Leer 1993) and chloroform has been detected in shallow, uncontaminated aquifers at forested sites during the Danish Groundwater Monitoring Programme. Investigations, by the Groundwater Research Centre at a Danish spruce forest site at Klosterhede in 1993, demonstrated profiles of soil air chloroform concentrations

(Figure 5.4.1.) which suggest production of chloroform in the top soil with diffusion to the atmosphere, as well as transport to the groundwater below (Grøn, in press; Grøn *et al.* 1994). Soil air concentrations up to  $\approx 30 \mu\text{g}/\text{m}^3$  and groundwater concentrations as high as  $2.7 \mu\text{g}/\text{L}$  were found.

An increase in the degree of halogenation of the dissolved organic matter observed in the soil water and 2,4,6-trichlorophenol detected in one soil water sample suggests that non-specific chlorination may have caused the chloroform production. Previously, chlorination activity in soils had been ascribed to the presence of chloroperoxidase-like enzymes (Asplund and Christiansen, 1993), and both chloroform production (Hoekstra and Leer 1993) and the incorporation of chloride into humic substances (Carlsen and Lassen 1992) had been demonstrated to result from chloroperoxidase activity. From soil samples taken in the autumn of 1994 at the Klosterhede site, chloroperoxidase-like activity could be extracted and characterized with respect to pH-optimum and chlorination/bromination capacity. The chloroperoxidase activity was highest in the litter layer, but measurable activity persisted through the A- and B-horizons and was even found in the C-horizon at 1.8 m below the surface (Table 5.4.1).

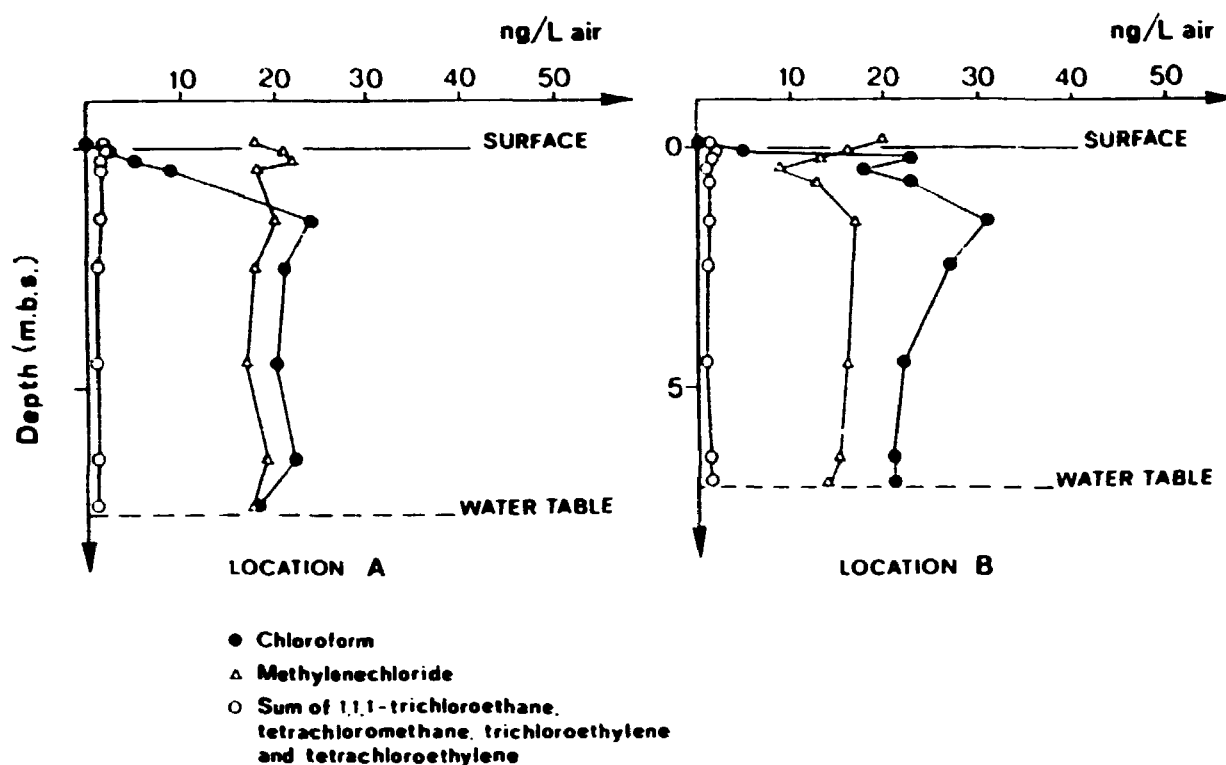


Figure 5.4.1. Distribution of soil air concentrations of chlorinated  $C_1$ - and  $C_2$ -compounds at two locations in Klosterhede<sup>3)4)</sup>

Table 5.4.1 Chloroperoxidase activity and pH optima in purified soil extracts from the two locations i Klosterhede.

	LOCATION A		LOCATION B	
	Chlorination activity (enzyme units)	pH optimum	Chlorination activity (enzyme units)	pH optimum
Litter	44 x 10 <sup>3</sup>	2.5	23 x 10 <sup>3</sup>	2.5
A-Horizon	2.8	3.0	4.5	4.0
B-Horizon	7.2	2.5	5.9	3.0
C-Horizon	10	4.0	5.3	3.5

One possible explanation of the results obtained at the Klosterhede site is, that soil microorganisms may produce and release chloroperoxidases. The enzymes can act as catalysts for the oxidation of otherwise refractory soil organic matter through the formation of hypochlorite from chloride and hydrogenperoxide present in the soil. The oxidation would not only produce soluble organic matter accessible to the microorganisms, but also halogenated organic compounds such as chloroform, chlorophenols and halogenated humic substances. Further investigations on the production of chlo-

roform and other trihalomethanes in forest soils are in progress.

The work is carried out in cooperation with M. Sindballe Poulsen, N & R Consult, Denmark; E Hoekstra, Department of Analytical Chemistry, Netherlands Organization for Applied Scientific Research, The Netherlands; F. Laturus, Department of Geology and Geotechnical Engineering, Groundwater Research Centre, Technical University of Denmark; G. Mehrtens, Alfred-Wegener-Institut für Polar- und Meeresforschung, Germany.

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## 5.5 Hydrothermal Processes

### 5.5.1 Hydrothermal Oxidative Decomposition of POM Components (A.B. Bjerre, A. Plöger, T. Nielsen, E. Sørensen)

Investigations on the decomposition of POM components have been carried out by hydrothermal oxidation, also called wet oxidation. The wet oxidation process is a high technology method decomposing toxic and hazardous compounds fatal to the environment *e.g.* in soil, waste water and sludge (Sørensen *et al.* 1990). The reaction takes place between molecular oxygen and an organic compound in aqueous solution at elevated temperature and pressure.

In this study the model substances for the preliminary tests were chosen to be:

Naphthalene (being the simplest PAH compound)  
Quinoline (being the simplest azarene)

Kinetic studies of these compounds are compared to kinetic studies of low molecular carboxylic acids, which are known intermediates and end products (Bjerre and Sørensen 1990; Bjerre and Sørensen 1992) from wet oxidation of many compounds. Some intermediates have been identified.

### Methods and materials

The autoclave used for the experiments is specially designed, developed and constructed at Risø National Laboratory (Bjerre and Sørensen 1992). The advantage with this autoclave is the very short heating up and cooling down characteristics which allow experiments on kinetic studies.

An analysis programme was carried out to analyze the components in question (Bjerre *et al.* 1994). Naphthalene was analysed by GC/MS after extraction by dichloromethane and with biphenyl as internal standard. Quinoline was analysed by GC/MS after extraction by dichloromethane and with biphenyl as internal standard or by deuterated quinoline. An HPLC analysis method has also been developed to determine quinoline in pure aqueous samples.

### Results and discussions

All experiments were carried out at 260°C, 20 bar O<sub>2</sub>. In Table 5.5.1, the rate constants for naphthalene, quinoline and a selection of low molecular carboxylic acids are shown listed according to decomposability (Table 5.5.1). The reactions were found to pseudo first order reactions and the rate constants were of the same levels as those of carboxylic acids, indicating that the transformation of POM in pure aqueous solution is slow. It is also seen that alkaline addition slows down the reaction rate. However, it has been observed that the same compounds in soil were readily removed by the method. This has led to a discovery which will probably increase the reaction rates of many organic compounds.

**Table 5.5.1.** Rate constants for naphthalene, quinoline and carboxylic acids

Component	k /min <sup>-1</sup>
acetic acid	0.0010
propionic acid	0.0022
butyric acid	0.0046
<b>Quinoline (neutral)</b>	<b>0.0058</b>
isobutyric acid	0.0067
<b>Naphthalene (alkaline)</b>	<b>0.0140</b>
formate ion	0.0356
<b>Naphthalene (neutral)</b>	<b>0.0384</b>
alpha-OH-isobutyric acid	0.1036
formic acid	0.2346

**Intermediates:**

The samples drawn from the autoclave experiments were esterified and analysed by GC/MS. So far, nicotinic acid is found to be the main product after decomposition of quinoline. Only phthalic acid corresponding to 5 ppm, has been identified as an intermediate from the experiment with naphthalene after 45 minutes.

**5.5.2 Bio-ethanol Production** (A.B. Bjerre, A. Plöger, A.S. Schmidt, E. Sørensen)

An alternative energy source to oil and coal is the micro-biological ethanol production from lignocellulosic material e.g. straw, wooden chips

etc. A new project has started in cooperation with the Danish Technical University developing a method for conversion of wheat straw to ethanol. Below 200°C, the wet oxidation method has proved to be an advantageous pre-treatment for the separation of the polysaccharid fractions resulting in cellulosic solid and water soluble hemicellulose (Bjerre *et al* 1994). At the same time, the lignin fraction is oxidized to low molecular carboxylic acids. The cellulosic solid was found to be enzymatically convertible to glucose. Figure 5.5.2 shows the influence of autoclave pretreatment on the following Enzymatically Conversion of Cellulose (ECC) to glucose.

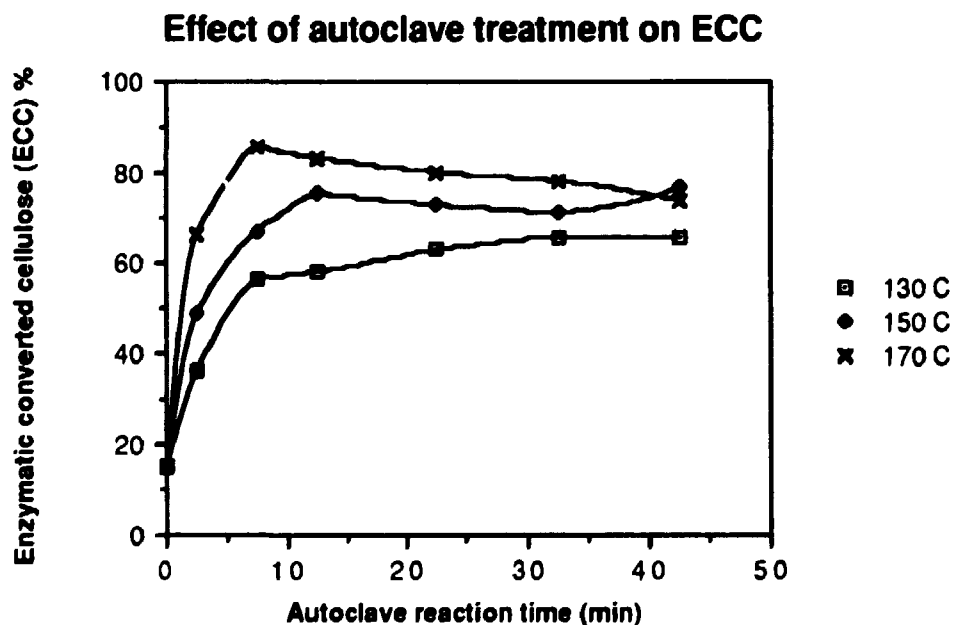


Figure 5.5.2. Effect of autoclave treatment on enzymatic conversion of cellulose products. Conditions for enzymatic treatment: 50°C, pH = 4.8, 24h incubation.

The project is carried out in cooperation with B. Ahring, Danish Technical University, Denmark.

The project is carried out in cooperation with B. Pallesen, Landskontoret for Planteavl, Denmark.

### 5.5.3 Production of Bio-fibres (A.B. Bjerre)

Flax is another example of lignocellulosic material. Pretreatment of flax by wet oxidation at alkaline conditions resulted in new fibres with very low contents of cement retarding components such as hemicelluloses and pectines providing a very high tensile strength (hemicellulose is known to increase the tensile strength) (Bjerre and Pallesen 1994). These new bio-fibres are neither hazardous to humans nor to environment and could become alternative composite materials e.g. chrysotile asbestos. Figure 5.5.3. shows the tensile strength of wet oxidized flax fibres compared to other pretreated flax fibres with much higher hemicellulose content.

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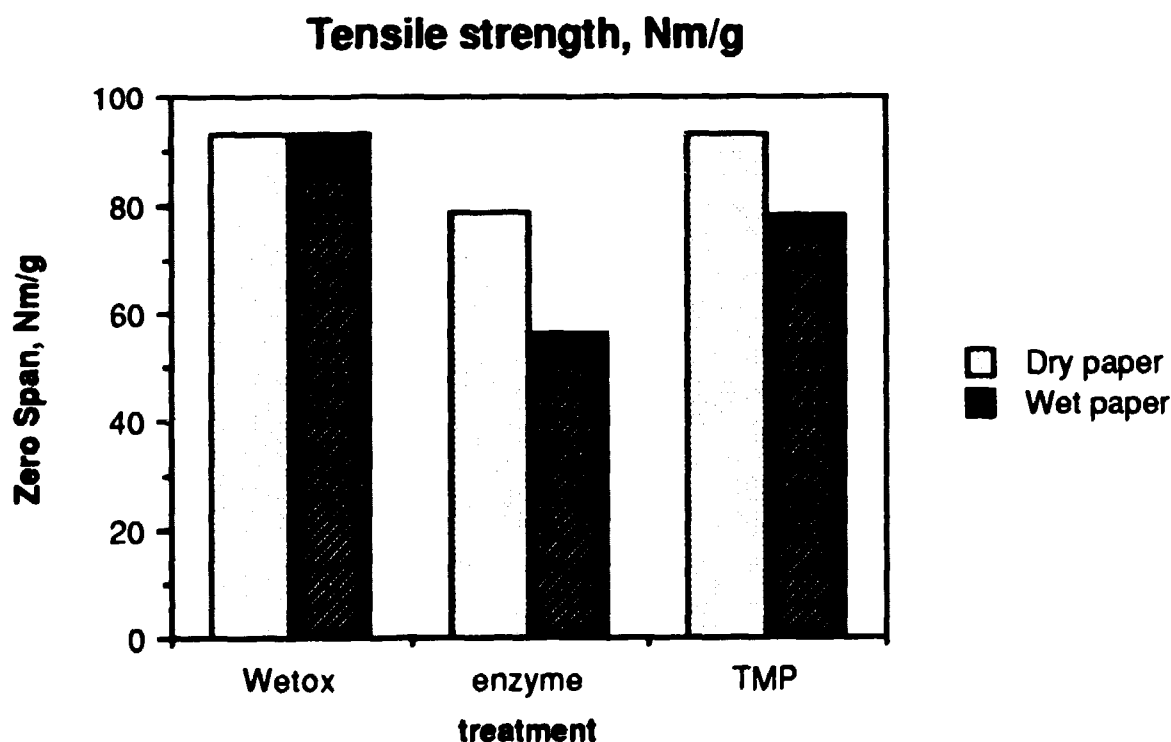


Figure 5.5.3. Tensile strength (Nm/g) of respectively wet oxidized, enzyme or TMP treated flax fibres.

## 6 Ecology

### *Introduction (A. Aarkrog)*

The Ecology programme works in six areas, each headed by a senior scientist.

In the biosphere-atmosphere exchange three field experiments were carried out in Falster, WestJutland and Lolland. Fluxes of gaseous compounds ( $O_3$ ,  $NO_x$ ,  $CO_2$  and  $H_2O$ ) were measured by the eddy correlation method. The flux of  $O_3$  was almost always downwards, whereas the flux of  $NO_2$  was both downwards and upwards. Both compounds showed diurnal patterns with the largest fluxes during daytime. It was found that stomatal uptake is an important parameter for deposition of  $O_3$ .

Work on the heavy metal deposition around the Maarmorliik mine and milling complex in Greenland from 1979 and 1990 was reported. It appeared that from 1979 to 1990, the lead contamination of lichen (*Cetraria*) decreased by a factor of two. The decrease was a result of the pollution abatement carried out at the mining complex.

In marine tracer studies, the transfer of pollutants to the Arctic have been studied. By using radioactive tracers, it was found that for each ton of a conservative pollutant discharged to the Irish Sea per year, 1-2  $ng\ m^{-3}$  is observed in the East Greenland polar water 7-10 years later.

In the CEC MAST programme, radionuclides discharged from La Hague in France were studied in the "European Coastal Current" from the English Channel to the Baltic Sea. Ten percent of the La Hague discharge is transported through Kattegat and one third of the inflowing Kattegat bottom water originates from the coastal current. This coastal transport is important, when contaminant transport is monitored.

The research on radioecological models has concentrated on marine models. A preliminary assessment of doses to man, from dumping of radioactive material in the Arctic Seas, has been carried out. Considering a "worst case" for the Russian sources in the Kara Sea, the resulting collective dose until the year 2040 was predicted to peak at value of about 2  $man\ Sv\ y^{-1}$ , which is more than four orders of magnitude lower than

the corresponding dose rate from natural radioactivity in seafood ( $^{210}Po$ ).

Model calculations were also made for the Baltic Sea (the MORS project) and for the Mediterranean Sea (the MARINA-MED project). In Baltic seawater the mean ratio between predicted and observed  $^{137}Cs$  concentrations was 1.2 with a geometric standard deviation of 1.2. The corresponding ratio in the Mediterranean Sea was 0.7.

In contamination physics, two major projects have been finalized. The first one dealt with the state of the environment in Belarus. It was concluded that, although Belarus received about 70% of the total Chernobyl contamination in the former Soviet Union, there may be even more pertinent environmental problems in this country. It was thus found that the quality of surface water and groundwater is threatened by discharges of untreated waste water and leaching from waste disposal sites. The soil is also often polluted by heavy metals from industries. Finally, the measurements of air quality in Belarus seem inadequate resulting in considerable uncertainties.

The studies of indoor deposition have been the other important effort. Indoor deposition is the most important process in reducing inhalation dose. However, it should be kept in mind that this deposition also contributes to the exposure of the occupants due to the gamma radiation from the deposited material.

The research within the field of ecophysiology are focusing on lipid metabolism and copper toxicity and metabolism in fish. Incorporation of radioactive precursors into fish gill membranes has been used to study the mechanism of biological adaption to changes in environmental salinity. Rainbow trout transferred from brackish to sea water, will synthesize an extra membrane phosphatidylethanolamine. This does not normally occur if they are instead transferred to fresh water. However, if the fish are stressed prior or during the transfer, the synthesis of phosphatidylethanolamine is initiated in any case.

The studies of copper metabolism in the European eel have revealed the  $^{64}Cu$  at low

concentrations and short exposure periods are bound mostly to a plasma-protein resembling ceruplasmin, which is also known to be responsible for copper transport in mammalian plasma.

The project domain on radioecology has comprised participation in three international studies: MARDOS, MARINA-MED and Task-force-4 of the IUR, and a Ph.D. project on radioecology of Danish forest ecosystems. In the MARDOS project, the total collective effective dose commitment from all sources over all years from  $^{137}\text{Cs}$  in the marine food stuff was estimated at 14000 man Sv corresponding to a half year's exposure from natural occurring  $^{210}\text{Po}$  in seafood. In the IUR study, seventeen radionuclides were identified as less known from a radioecological point of view.

In the project on forest radioecology studies of mushroom spores and  $^{137}\text{Cs}$  in faeces of roe deer confirmed that these animals eat fungi. Among the most commonly eaten species were the members of the *Boletaceae*.

## Summary of Projects

### 6.1 Biosphere - Atmosphere Exchange (K. Pilegaard)

#### 6.1.1 Fluxes of Gaseous Compounds

A number of projects (funded through RIMI, SMP/NECO and EEC) deal with the study of fluxes of gaseous compounds. The scientific methods and equipment are shared between the projects, and the projects are therefore described together.

Three field experiments were made in 1994. The first was in a beech forest at Corselitze on the island of Falster in April and May, the second was in Ulborg Plantation in western Jutland in June, and the third at the northwestern shore of Lolland at Vindeby in November. In all experiments fluxes were measured by the eddy correlation method, which requires very fast responding instruments ( $\sim 10$  Hz). In Corselitze and Ulborg the measurements comprised  $\text{O}_3$ ,  $\text{NO}_x$ ,  $\text{CO}_2$  and  $\text{H}_2\text{O}$ ; at Vindeby we only measured  $\text{NO}_x$ .

The purpose of the experiment in the beech forest (Corselitze) was to study the influence of the leaves on the fluxes. Therefore fluxes were measured during a period from 3 weeks before bud burst (which happened a few days around May 1st) to 3 weeks after. The flux of  $\text{O}_3$  was almost always downwards, whereas the flux of  $\text{NO}_2$  was mostly upwards. Both compounds showed diurnal patterns with the largest fluxes during daytime.

The effect of the beech leaves was seen most clearly in the fluxes of  $\text{CO}_2$  (Figure 6.1.1.), whereas the effects on the fluxes of  $\text{O}_3$  and  $\text{NO}_2$  were much less than expected. The diurnal pattern of the surface resistance to  $\text{O}_3$  indicates an influence of stomata, especially after bud burst. The reason for the absence of a strong difference in deposition of  $\text{O}_3$  before and after bud burst might be that  $\text{O}_3$  is taken up by vegetation on the forest floor (mainly by *Anemone nemorosa* in the April period) and removed by other means than stomatal uptake, such as destruction on leaf surfaces, deposition to soil and reaction with  $\text{NO}$ .

The upward flux of  $\text{NO}_2$  is most likely explained by the reaction of  $\text{O}_3$  with  $\text{NO}$ , emitted as a result of bacterial activity in the forest soil. The amount of  $\text{O}_3$  removed in this way is, however, only a small part of the total  $\text{O}_3$  flux. There seems to be a larger  $\text{NO}_2$  flux before bud burst than after. This might be either a result of lower bacterial activity in the second period due to the shadowing effect of the beech leaves, which leads to lower temperatures, or the result of uptake in the canopy.

The experiment in Ulborg was part of a series of experiments studying the fluxes in different seasons and relating the fluxes to meteorological and biological parameters. One of the most interesting findings of the experiment in 1994, is concerned with the understanding of deposition of  $\text{O}_3$ .

The measurements of fluxes of  $\text{O}_3$  and meteorological parameters were used for the calculation of aerodynamic resistance ( $r_a$ ), viscous boundary layer resistance ( $r_b$ ) and surface resistance ( $r_s$ ). The canopy stomatal resistance to  $\text{O}_3$  was calculated from measurements of the water vapour flux.

April 22-25, 1994

May 11-14, 1994

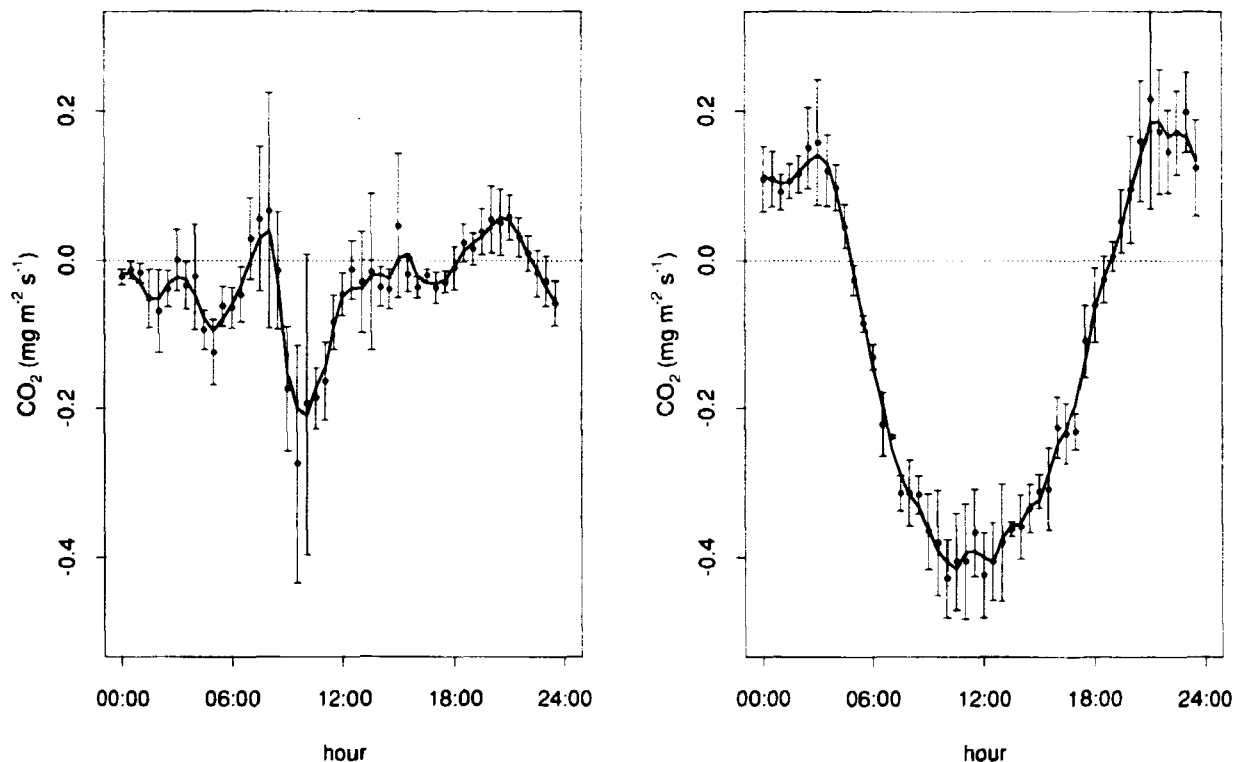


Figure 6.1.1. Diurnal variation of fluxes of  $\text{CO}_2$  over a beech forest at Corselitze before and after bud burst. The plots show means  $\pm$  standard error and a smoothed line.

The resistances showed a diurnal pattern with the lowest values in day-time. The surface resistance was highly dominating in day-time and the influence of meteorology low. In nighttime the surface resistance to  $\text{O}_3$  was lower than the canopy stomatal resistance. A low surface resistance was also found in winter-time, when the activity of the trees was low. The surface resistance increased when the trees were subject to water stress.

It was found that stomatal uptake is an important parameter for the deposition of  $\text{O}_3$ . However, other processes, such as destruction of  $\text{O}_3$  at surfaces, reaction with  $\text{NO}$  emitted from the soil, and reactions with radicals produced from VOC's emitted from the forest, must also be taken into consideration.

These projects contribute to EUROTRAC-BIATEX. At Risø, the projects are carried out as a collaboration between the Environmental Science and Technology Department and the

Meteorology and Wind Energy Department. The main national collaborators are the SMP/NECO partners. An EU-funded project is performed together with TNO (Delft, The Netherlands), UMIST (Manchester, Great Britain) and IFU (Garmisch-Partenkirchen, Germany).

### 6.1.2 Plant Uptake of Nitrogen Dioxide

In 1992, an experiment was initiated for studying the uptake of  $\text{NO}_2$  in Norway spruce (*Picea abies* L.). Small trees were grown in pots with  $^{15}\text{N}$  labeled fertilizer and exposed to different levels of  $\text{NO}_2$  in open top chambers. The experiment was continued in 1993 and the analyses were made in 1994. Preliminary results show that there is an increase in the uptake of  $\text{NO}_2$  directly from the air, when the air concentration increases. Results from the first year also show that the growth is stimulated by increased concentrations of  $\text{NO}_2$  in the air. The work is a joint

project with E.S. Jensen, Plant Nutrition Section.

### 6.1.3 Heavy Metal Deposition

Work on heavy metal deposition around the mining and milling complex Maarmorilik (Greenland) from 1979 to 1990 was compiled and published (Pilegaard 1994).

The deposition of heavy metals around the Pb-Zn mine in Maarmorilik (Greenland) was monitored during the years 1979-1990 by analysis of the concentrations in *in situ* lichens (*Cetraria nivalis* and *Umbilicaria lyngei*) and higher plants (*Rhododendron lapponicum*).

The concentrations of the metals Ag, As, Cd, Cu, Hg, Pb, Sb and Zn decreased with increasing distance from the mining and milling complex. The spread was most pronounced in the direction westwards from Maarmorilik. Exposed Pb-Zn mineralizations in the area were not found to influence the overall deposition pattern. It was also found that the transport of pollutants to higher altitudes was restricted.

The airborne pollution with Cd, Pb and Zn was monitored with suspended *Sphagnum*-bags during a period with ship-loading of concentrates and compared to a period without this activity. The results showed that there was a strongly increased deposition of airborne Cd, Pb and Zn during the period of ship-loading. The primary sources of pollution were the concentrate conveyor and the ship-loader. *Sphagnum*-bags were also used to monitor the effect of remedial actions carried out in the mining town.

Analysis of the concentrations of Pb in *Cetraria* during the years 1979 to 1990 showed that the pollution during the last years was only about half as large as that of the early years. This decrease is attributed to the pollution abatement carried out at the mining complex.

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## 6.2 Marine Tracers (H. Dahlgård)

### 6.2.1 Transfer to the Arctic

Controlled discharges of man-made radionuclides from nuclear reprocessing facilities, discharging to the British and the French coastal zones, have proved useful in tracing the long-distance transport and dilution of European coastal contaminants to the Barents Sea, the Kara Sea, the Arctic Ocean and the East Greenland Current. Figure 6.2.1 shows the major surface currents responsible for the transport of Sellafield and La Hague tracers to the Arctic, as well as an overview of transit times in years from Sellafield. The transfer is quantified by a Transfer Factor, calculated as the quotient between observed concentrations in the environment and an average discharge rate  $t$  years earlier, where  $t$  is the transport time.

A transfer factor of  $1-2 \text{ ng m}^{-3} / \text{ton yr}^{-1}$  (equivalent to  $1-2 \text{ Bq m}^{-3} / \text{PBq yr}^{-1}$ ) has been found for East Greenland Current Polar Water - a water mass reflecting contaminant levels in Arctic Ocean surface water. This value indicates that for each ton discharged to the Irish Sea per year,  $1-2 \text{ ng m}^{-3}$  is observed in the East Greenland Polar Water 7-10 years later. A similar magnitude for the transport of other near-conservative contaminants discharged to the European coastal zone probably occurs, *e.g.* in the ongoing Arctic Monitoring and Assessment work. Even non-conservative particle-reactive elements such as plutonium have now been traced from European coastal waters to the Arctic. Transfer factors to other areas are given in Table 6.2.1.

The radionuclide tracers provide a valuable opportunity to verify model calculations for the transfer of pollutants from the European coastal zone to the Arctic.

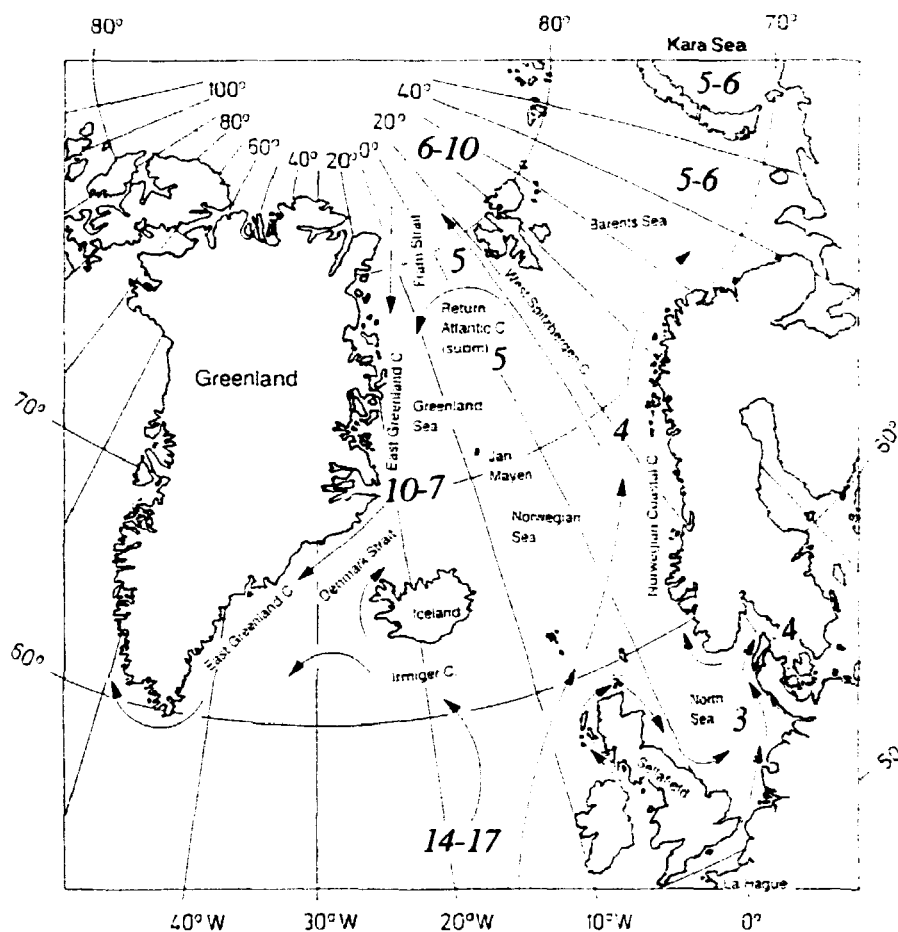


Figure 6.2.1. Major surface currents and transit times in years from Sellafield to different sea areas. Transit times for the La Hague discharge will be 2 years earlier.

Table 6.2.1. Transfer factors,  $TF = Bq\ m^3 / PBq\ yr^{-1} = ng\ m^3 / ton\ yr^{-1}$ , from Sellafield to various surface waters.

Location	Transport time years	TF $ng\ m^3 / ton\ yr^{-1}$
Kattegat*	4	15
N-W. Norwegian C.	3-4	10-50
S-SE Barents Sea	5-6	5-10
Kara Sea	5-6	5-10
W. Spitzbergen	~ 5	~ 5
Arctic Ocean	~ 6-10	~ 1-10
East Greenland C.	7-10	1-2
North Atlantic Current		
Farøe Islands	~ 14-17	~ 0.3

\*: TF from La Hague to Kattegat bottom water was  $\sim 75\ Bq\ m^3 / PBq\ yr^{-1}$  with a transport time of  $\sim 15$  months (Dahlgard *et al.*, in press b)

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### 6.2.2 Radioactive Tracers in Coastal Oceanography

The project "Studies on the transport of coastal water from the English Channel to the Baltic Sea using radioactive tracers", MAST-CT900052, under the EEC Marine Science and Technology programme, has been finalized by submitting a series of papers. Risø acted as coordinator. Other partners in the project were Institut de Protection et de Sûreté Nucléaire (IPSN), Cherbourg, France; Institut Français de Recherche pour l'Exploration de la Mer (IFREMER), Plouzané, France; Centre de Spectrométrie Nucléaire et de Spectrométrie de Masse, CNRS, Orsay, France; Ministry of Agriculture, Fisheries and Food (MAFF), Fisheries Research Lab, Lowestoft, U.K.; Netherlands Energy Research Foundation (ECN), Petten, Netherlands; Bundesamt für Seeschifffahrt und Hydrographie (BSH), Hamburg, Germany.

Radionuclides ( $^{99}\text{Tc}$ ,  $^{125}\text{Sb}$ ,  $^{90}\text{Sr}$ ,  $^{137}\text{Cs}$ ) discharged from La Hague in France have been used to trace advection and dispersion of water masses in the "European Coastal Current" from the English Channel to the Baltic. Time-series of radionuclide measurements in water samples taken in the English Channel, at the Netherlands coast, in the German North Sea sector and in Danish waters have been compared with reported discharge values. The prospects for using  $^{129}\text{I}$  measured by accelerator mass spectrometry (AMS) as an oceanographic tracer have been evaluated as positive. The  $^{99}\text{Tc}$  analytical procedure has been improved and background levels of  $^{99}\text{Tc}$ ,  $^{137}\text{Cs}$  and  $^{90}\text{Sr}$  in open North Atlantic seawater without influence from European discharges have been determined. An intercomparison programme has documented the quality of the measured  $^{99}\text{Tc}$  and  $^{125}\text{Sb}$  data. Transit times and transfer factors from La Hague to different locations in the study area were estimated. It is concluded that 10% of the La Hague discharge is transported through Kattegat and part of the inflowing Kattegat bottom water originates from the coastal current. Three fundamentally different numeric models have been further developed under the project. The measured data were then compared with values simulated by the 3 models. Models, as well as measured data, indicate that a close coastal transport, with longer transit times and often higher concentrations than seen in the open water main current, is taking place. This coastal transport is important when contaminant transport is monitored. It is concluded that the collected data give a unique opportunity to evaluate models on advection and dispersion of coastal water masses and contaminants. The database will be made available as a tool for the evaluation of such models. Figure 6.2.2. shows sampling locations and major transport routes.

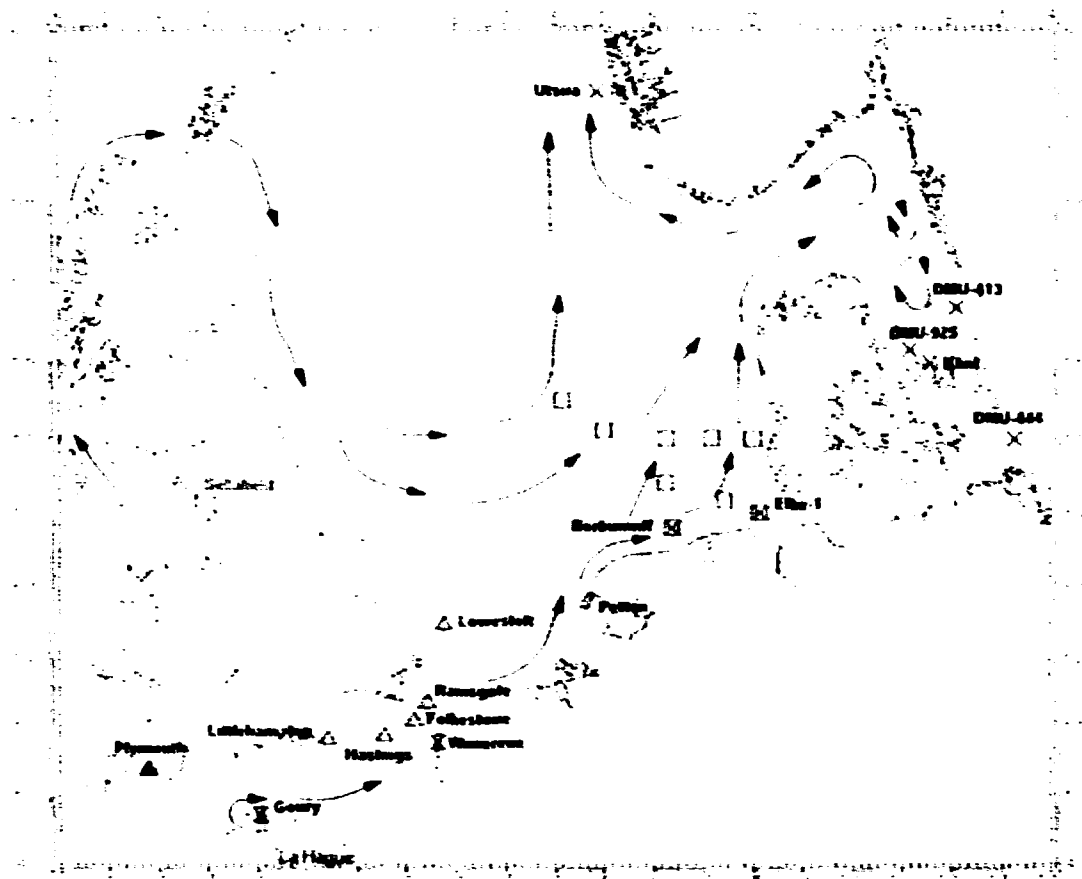


Figure 6.2.2. Map of the study area indicating time series stations where radionuclide concentrations have been measured. Transport routes for discharges from La Hague and Sellafield are indicated by arrows. \*: Discharge points at La Hague and Sellafield.

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### 6.2.3 <sup>210</sup>Po Pathways in Coastal Environments

Polonium-210 has been measured in Danish fish meat caught in the North Sea, the Kattegat and the Baltic in 1991 - 1994. Average values of 0.35, 0.65 and 0.96 Bq <sup>210</sup>Po kg<sup>-1</sup> fresh weight were observed for cod, herring and plaice fillets, respectively. The difference between species is statistically significant, whereas no effect of salinity could be observed. There is a high variation giving SD values in the range 70-100%.

*Mytilus edulis* soft parts were analyzed for <sup>210</sup>Po from 11 Danish locations ranging from full North Sea salinity to Baltic 8‰ water. Significantly increasing <sup>210</sup>Po concentrations with decreasing "condition index" was observed. Two former phosphate industry sites were not statistically different from the other locations. The average <sup>210</sup>Po concentration in the *Mytilus* soft parts was 149 Bq kg<sup>-1</sup> dry  $\pm$  55% SD (n=41).

The present levels of <sup>210</sup>Po in fish and mussels may represent a natural baseline.

The project is partly financed from the EC via contract no FI3P-CT92-0035. Other partners of the project are Rijksinstituut voor Volksgezondheid en Milieuhygiene (RIVM/LSO), The Netherlands; Institut de Protection et de Sûreté Nucléaire (IPSN), Laboratoire de Radioécologie Marine, France; Centro de Investigaciones Energéticas, Medioambientales y Tecnológicas (CIEMAT), Spain; Direcção General do Ambiente, Portugal; IAEA Marine Environment Laboratory, Monaco; Facultad de Física, Universidad de Sevilla, Spain; Radiological Protec-

tion Institute of Ireland, Ireland; Department of Zoology, Department of Zoology, University of Aberdeen, United Kingdom; Dep. Bio-Medical Physics and Bio-Engineering, University of Aberdeen, United Kingdom; Institute of Nuclear Techniques, Technical University of Budapest, Hungary.

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### 6.2.4 Nordic Radioecology

On Monday, 28th April, 1986, most Nordic radioecologists and health physicists realized the area was being contaminated by debris from a serious nuclear accident. The cloud from Chernobyl had already reached the Nordic countries on Sunday, 27th April, and contamination was to continue during May. Figure 6.2.4. shows the resulting ground deposition of <sup>137</sup>Cs in kBq m<sup>-2</sup> in the Nordic countries Denmark, Finland, Norway and Sweden. Off the map, the Chernobyl contamination on Iceland and Greenland was very low, whereas the deposition on the Faroe Islands was 0.6-4.5 kBq <sup>137</sup>Cs m<sup>-2</sup>.

The Nordic post-Chernobyl radioecology programme, RAD, was active during 1990 - 1993 under the Nordic Committee for Nuclear Safety Research, NKS. It consisted of four projects. The main radionuclides chosen for study were the two radiocaesium nuclides, <sup>137</sup>Cs and <sup>134</sup>Cs, because they appeared to be the most important contributors to doses to man after the Chernobyl accident, and because they are relatively simple to measure. However, a few results for <sup>90</sup>Sr and <sup>210</sup>Po were also reported.

RAD-1 (project leader E. Holm, Lund University, Sweden) had a multiple purpose: methodology, training, quality assurance and doses. Initially, a major task was to conduct a two-week post-graduate training course in various aspects of radioecology. The course included 20 lectures by various Nordic radioecologists (Holm, 1994). An exchange programme permitting, preferentially, young scientists to stay for one or two weeks at another Nordic laboratory, e.g. to

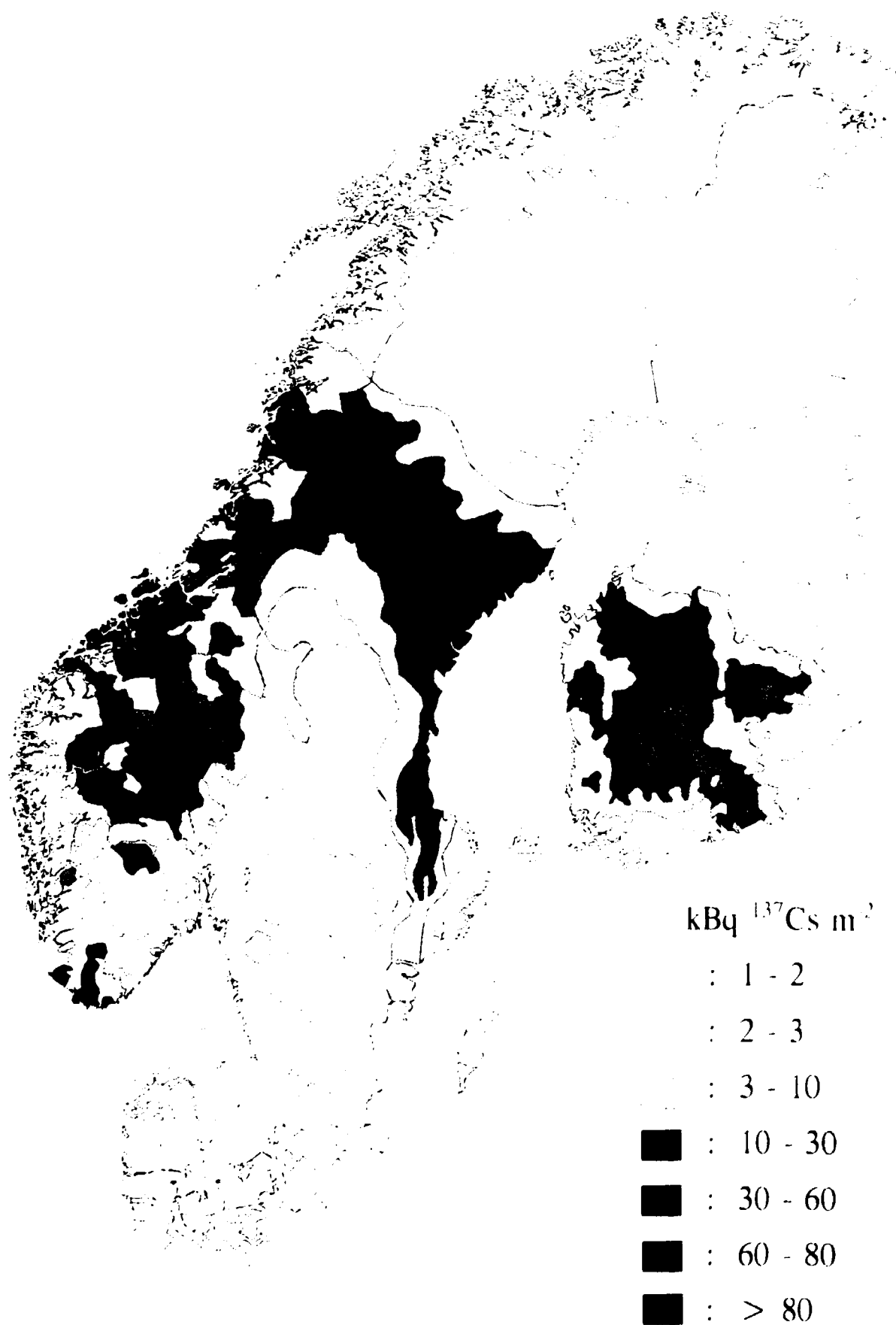


Figure 6.2.4. Ground deposition of  $^{137}\text{Cs}$ ,  $\text{kBq m}^{-2}$ , in Denmark, Finland, Norway and Sweden resulting from the Chernobyl accident.

adopt a new radiochemical method, was also conducted by RAD-1. Three separate programmes on quality assurance were carried out. Of these, the intercomparison of nine large, stationary air samplers and the intercalibration of 20 Nordic whole-body counting systems are especially remarkable. Finally, RAD-1 was responsible for dose assessments, based partly on the results produced in the three other RAD projects.

**RAD-2:** Aquatic ecosystems (project leader M. Notter, National Swedish Environmental Protection Board, Solna, Sweden) mainly concerned Nordic lakes, as the major problems in aquatic environments after the Chernobyl accident appeared in fresh-water systems. However, two minor projects were run in the marine environment.

**RAD-3:** Agricultural ecosystems (project leader P. Strand, Norwegian Radiation Protection Authority, Østerås, Norway) focused on various aspects of Nordic agriculture in relation to nuclear contamination: annual crops, cows' milk, grazing sheep and on countermeasures. RAD-3 also included a study of physico-chemical forms and a model study.

Finally **RAD-4:** Forest and alpine ecosystems (project leader A. Rantavaara, Finnish Centre for Radiation and Nuclear Safety (STUK), Helsinki, Finland) concerned the natural terrestrial environment which, like the freshwater environment, appeared to surprise the authorities with high and variable radionuclide levels after the Chernobyl accident. RAD-4 studied radio-caesium transfer from soil to plants and fungi, game animals, the reindeer foodchain and boreal forests in general.

## References

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## 6.3 Radioecological Models

(S.P. Nielsen)

Compartment (box) models are useful in connection with studies of the behaviour of radionuclides in the environment. These models may be linked closely to basic data obtained from observations, thereby ensuring that the model predictions reflect reliable representations of environmental conditions. Compartment models have been applied for the prediction of the dispersion of radionuclides in the marine environment for a number of regions.

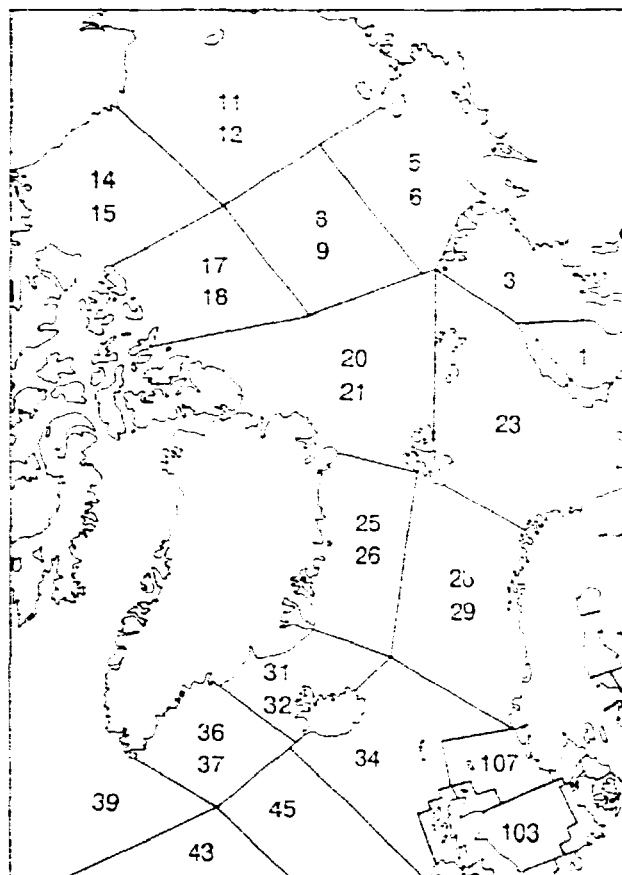
The marine box models include dispersal of radionuclides by advection and mixing due to water movement as well as scavenging of particle-bound radionuclides from the water column to the sediment surface. The transfer of radionuclides in the sediment includes mixing due to diffusion and bioturbation as well as burial due to sedimentation.

### 6.3.1 Arctic Ocean

A box model covering the Arctic Ocean, including the North Atlantic, has been developed based on a 3D World Ocean general circulation model (Chartier 1993) and a box model for the North-East Atlantic coastal waters (Nielsen 1994). The Arctic model is being used for an assessment of potential doses to man from the dumping of radioactive material by the former Soviet Union in the shallow waters of the Arctic Seas.

The present version of the model includes 134 boxes of which those in the Arctic Ocean are shown in Figure 6.3.1.1.

The contamination of radionuclides in fish, crustaceans and molluscs is calculated from the concentrations in filtered seawater in the different water regions. For this purpose, concentration factors obtained from the Marina study (CEC 1990) for biological material are used. Data for the catch of seafood in the various regions have been compiled from the Marina study supplied with FAO statistics obtained from the IAEA MARDOS project which deals with a global assessment of doses to man from radioactivity in the marine environment.



**Figure 6.3.1.1. Regions in the Arctic Ocean covered by the box model. The numbers refer to water boxes.**

A preliminary assessment of doses to man from dumping of radioactive material in the Arctic Seas has been carried out based on estimates of the source terms derived from the Yablokov report (Yablokov 1993). For a worst-case scenario, instant releases have been assumed for all radionuclides irrespective of their containment at the time of dumping. The releases are dominated by spent nuclear fuel in dumped reactors from nuclear submarines and the LENIN icebreaker. Table 6.3.1.1 shows the total releases assumed into the Kara and Barents Seas.

Collective doses to the world population from the consumption of fish, crustaceans and molluscs were calculated with the model. The graph in Figure 6.3.1.2 shows the resulting collective dose rate predicted until year 2400 including the contributions from each radionuclide. It is noted that the collective dose rate is predicted to peak at a value of about 2 manSv y<sup>-1</sup> which is more than four orders of magnitude lower than the corresponding dose rate from natural radioactivity (<sup>210</sup>Po) in seafood (of the order 10<sup>5</sup> manSv y<sup>-1</sup>). The predicted collective dose rate from the dumpings of radioactive materials in the Arctic Seas integrated over 1000 years is about 200 mansieverts.

**Table 6.3.1.1. Total integrated releases (TBq) into the Kara Sea and the Barents Sea assumed for the calculations.**

	<sup>3</sup> H	<sup>60</sup> Co	<sup>90</sup> Sr	<sup>137</sup> Cs	<sup>239</sup> Pu	<sup>241</sup> Am
Kara Sea	11000	4300	11000	11000	43	850
Barents Sea	70	70	70	70	0	0

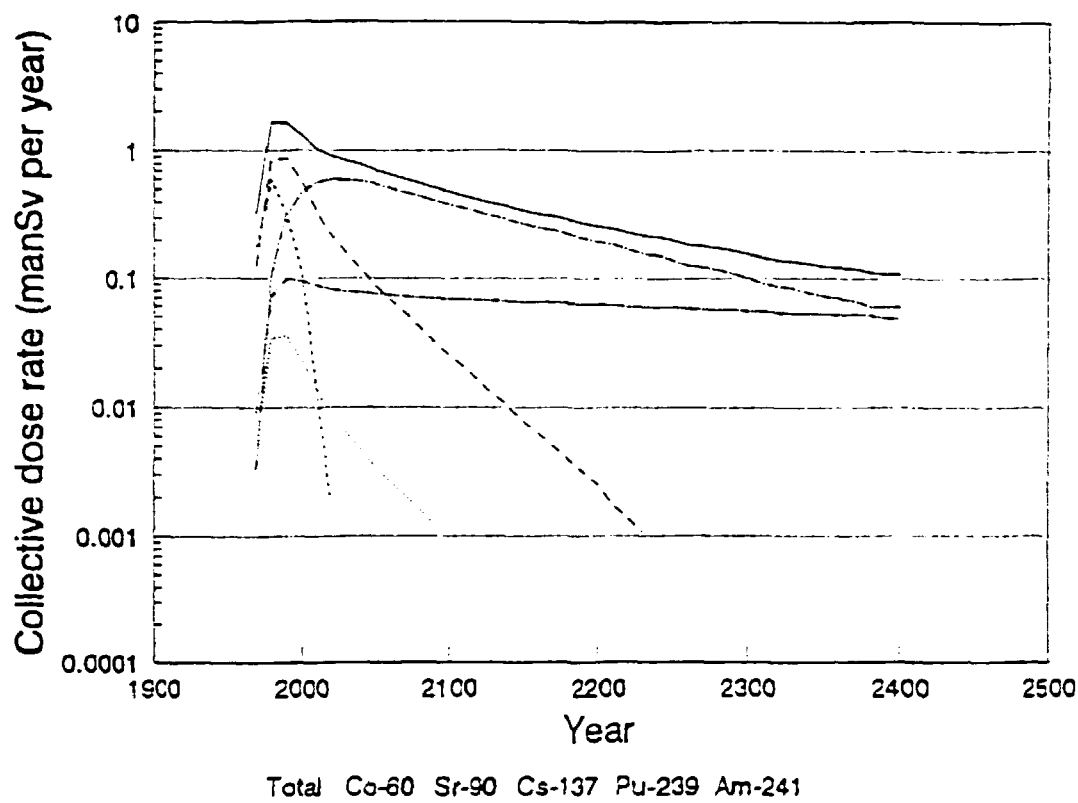


Figure 6.3.1.2. Collective dose rates (mansieverts per year) calculated until year 2400 for a worst-case scenario showing the contributions from the different radionuclides.

## References

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## 6.3.2 Baltic Sea

The marine box model covering the North-East Atlantic coastal waters (Nielsen, in press) includes the Baltic Sea and the model reliability for this region has been tested using data for Cs-137 and Sr-90 for the time period 1950-1991. The regions covered by the model in the Baltic Sea area are shown in Figure 6.3.2.1.

Model predictions were compared with observed concentrations of Cs-137 and Sr-90 in water and surface sediments. For that purpose, the following sources of radioactive contamination into the Baltic Sea were considered: fallout from atmospheric weapons testing, fallout from the Chernobyl accident, discharges to sea from the European reprocessing plants Sellafield in the UK and La Hague in France, and routine releases from the nuclear installations bordering the Baltic Sea area. The indirect transfer of radionuclides to sea via river runoff has also been taken into account. Table 6.3.2 gives total discharges of Cs-137 and Sr-90 to the Baltic Sea for the time period 1950-1994 used for the calculations.

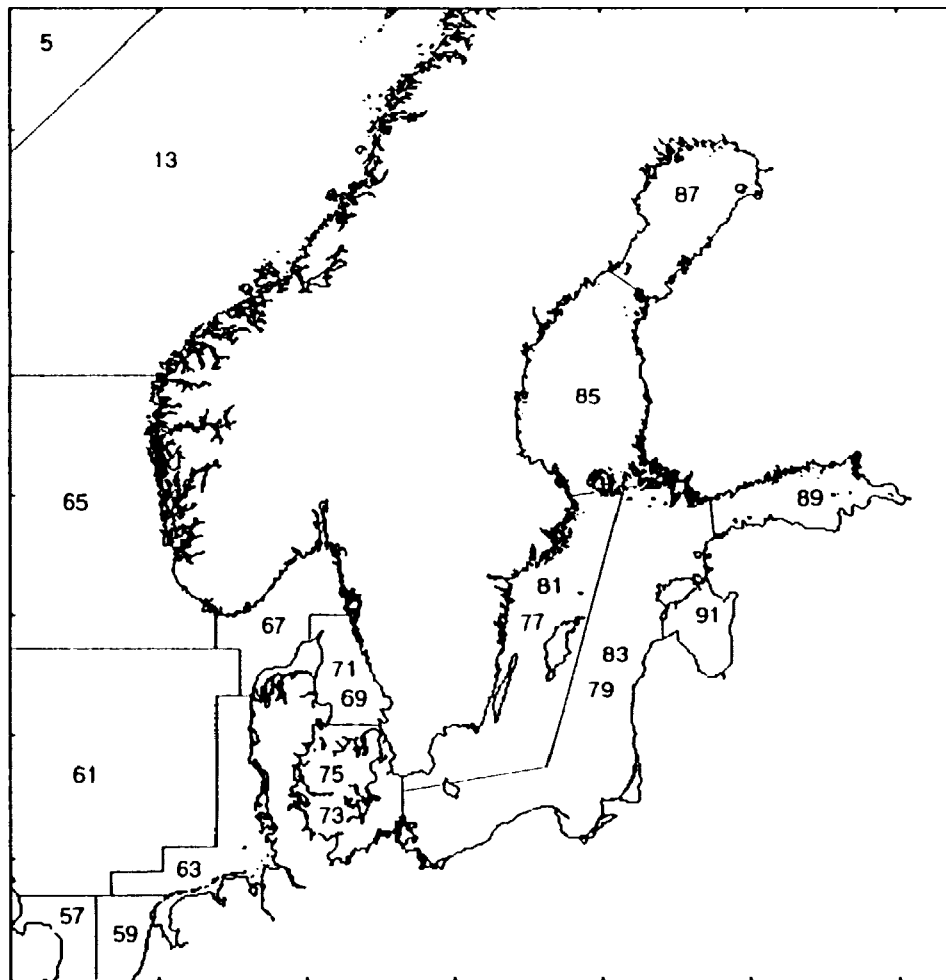


Figure 6.3.2.1. Regions around the Baltic Sea covered by the marine box model. The numbers of the water boxes are indicated.

Table 6.3.2. Discharges of Cs-137 and Sr-90 to the Baltic Sea in 1950 to 1994 used for the model calculations.

Source	Cs-137 (TBq)	Sr-90 (TBq)
Weapons fallout, direct deposition to sea	1780	1130
Weapons fallout, river runoff	70	410
Chernobyl fallout	4500	90
European reprocessing	380	70
Nuclear installations	1.7	0.014
Total	6732	1700

The reported discharges of Cs-137 and Sr-90 from Sellafield and La Hague have been used (BNFL 1993; CEC 1990) as input to the model. However, only a small fraction of these discharges reaches the Baltic Sea. The input to the Baltic Sea has been estimated from the model calculations, which indicate that about 4% of the discharges from Sellafield are transferred to Kattegat compared to about 8% of the discharges from La Hague. The relative transfer of Cs-137 is lower (about 10% relative difference) than that of Sr-90 because of the chemical differences that result in a higher transfer to sediments of Cs-137 than of Sr-90. Due to the efficient mixing of the upper and lower waters in the Kattegat and the Belt Sea, the main part of the activity of these radionuclides from the two reprocessing plants return to the Skagerrak and only about 1% of the discharges of Cs-137 and Sr-90 are estimated to be transferred to the Baltic Proper.

The observed data have become available from a number of sources including the data base organised by the Helsinki Commission (HELCOM). Since 1984, the countries around the Baltic Sea have reported data to HELCOM annually on observed levels of radionuclides in

seawater and sediments. Figure 6.3.2.2 shows a comparison between predicted and observed inventories of Cs-137 in seawater and sediments in the Baltic Sea. It is noted that there is a good agreement for the water data prior to 1986 after which the model overestimates the water levels. This could indicate a different (faster) rate of transfer from the water to the sediments of the Cs-137 from the Chernobyl fallout compared to that from the atmospheric fallout from the nuclear weapons testing. This is in qualitative agreement with the comparison between the observed and predicted sediment concentrations after the Chernobyl accident. For all the water inventory data (n=32) there is good agreement between the predicted and the observed inventories with a geometric mean predicted-to-observed (P/O) ratio of 1.2 with a geometric standard deviation of 1.2. For the sediment data there is a reasonable agreement between observations and predictions, but the number of observations are few (n=6). The geometric mean of the P/O ratios for the sediment inventory data is 0.9 with a geometric standard deviation of 1.7.

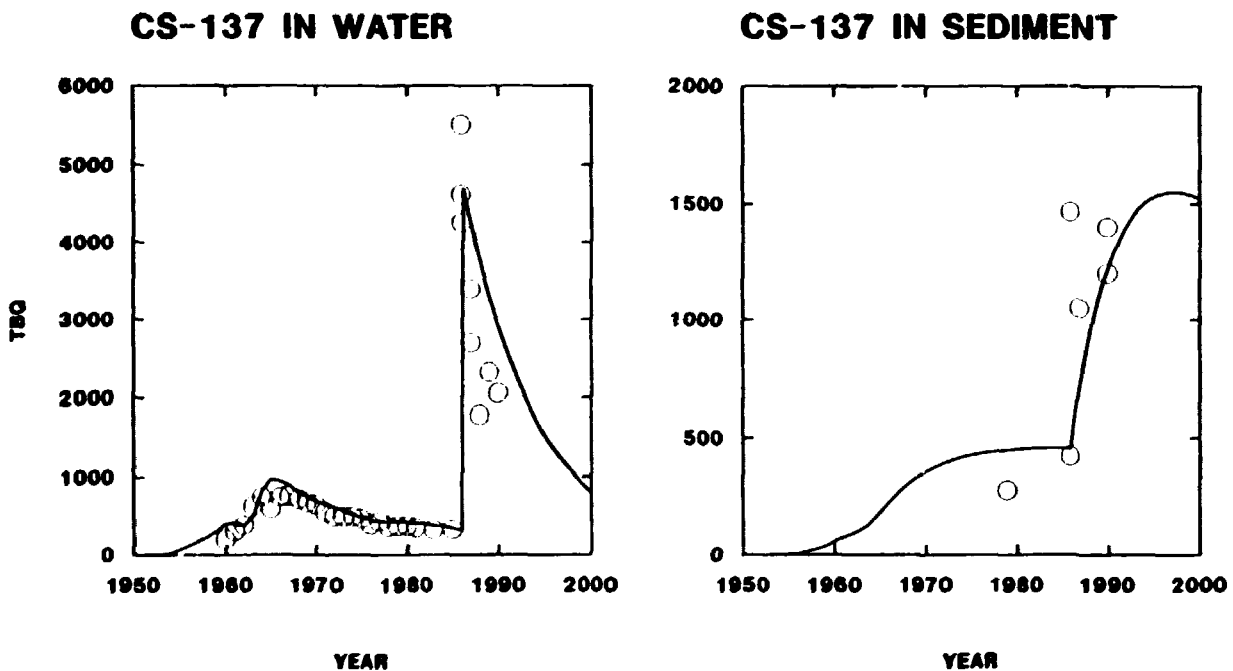


Figure 6.3.2.2. Comparison of predicted and observed inventories of Cs-137 in Baltic seawater and sediments. The full lines show the predicted levels and the circles show the annual arithmetic mean values of the observed levels.

Collective doses to man from ingestion of Cs-137 and Sr-90 in seafood from the Baltic Sea have been calculated with the model. The calculations are based on 1991 fishery statistics from ICES (1993) and it has furthermore been assumed that the annual harvest of marine produce has remained unaltered throughout time. The results for the collective dose rates are shown in Figure 6.3.2.3 which gives the collective dose rate broken down in components according to the sources. The collective dose rate is estimated to reach a maximum of about 42 manSv y<sup>-1</sup> in the 1960's before 1986 where the collective dose rate peaks at about 160 manSv y<sup>-1</sup> due to the Chernobyl accident. The time course of the dose rate from weapons fallout is predicted to be reduced at a rate slower than that from the other sources after year 2000 due to inflow of radionuclides to the Baltic Sea from the North Atlantic via the North Sea. The corresponding collective dose rate from natural radioactivity (Po-210) in seafood is estimated to be about 200 manSv y<sup>-1</sup>.

## References

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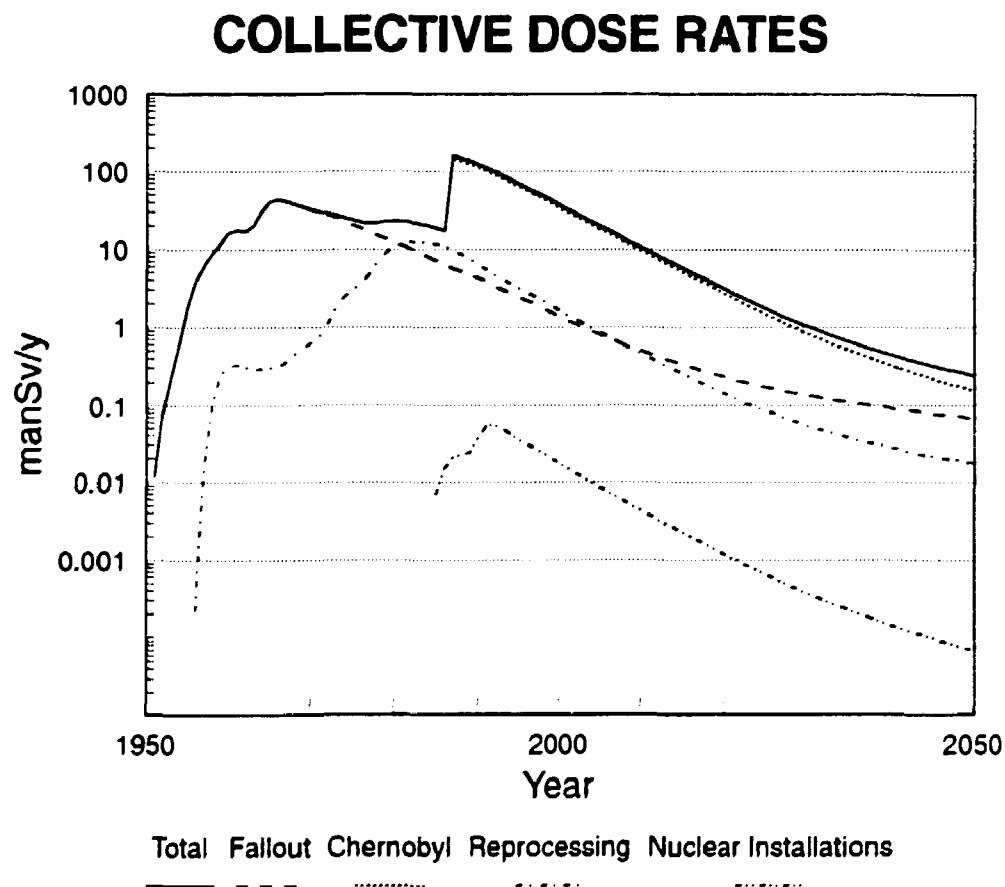


Figure 6.3.2.3. Collective dose rates (manSv y<sup>-1</sup>) to members of the public from the ingestion of Cs-137 and Sr-90 in seafood from the Baltic Sea according to sources.

### 6.3.3 Mediterranean Sea

The Commission of the European Communities has carried out a project MARINA-MED to examine the overall radiological impact on the population of the CEC Member States from natural and man-made radionuclides in the Mediterranean Sea. Four working groups covered the items: 1) Sources of radioactivity in the Mediterranean waters, 2) Environmental measurements and critical group dose assessments, 3) Survey of quantities and use of marine products, and 4) Collective dose assessment. The work was published in a CEC report (CEC 1994) and presented at a seminar in Rome 17-19 May, 1994.

A box model for the Mediterranean Sea was developed by Chartier (Chartier 1994) and used for the assessment of collective doses; a benchmark exercise was carried out (Cabianca *et al.* 1994) to ensure the correct implementation. Good agreement was found between three different implementations of the model. The area and sub-regions covered by the model are shown in Figure 6.3.3.1.

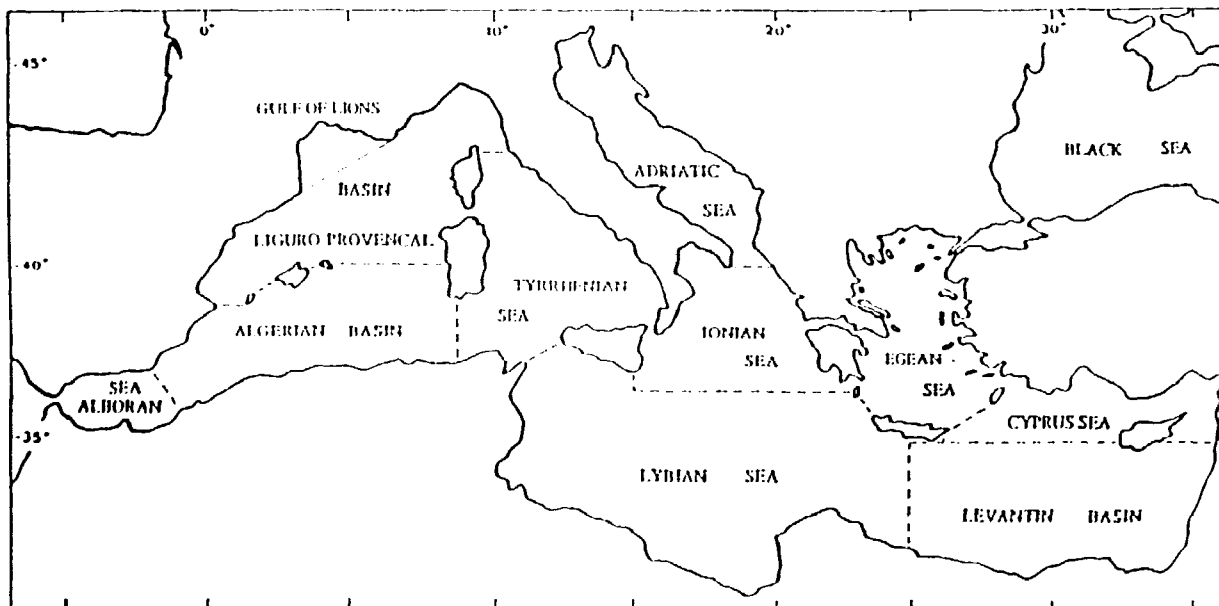


Figure 6.3.3.1. Map of the Mediterranean Sea showing the sub-regions covered by the model.

A comparison has been carried out (Nielsen 1994) between the predictions of Cs-137 in water and sediments in the Mediterranean Sea calculated with the box model and environmental measurements from 1981 to 1993 made in Italy, Greece, Spain, France, Croatia, Ukraine and Rumania (Aarkrog 1994).

The input of Cs-137 to the Mediterranean Sea from atmospheric nuclear weapons fallout, is taken into account based on measured data from Denmark modified with the latitudinal dependency. The following Cs-137 input from Chernobyl fallout was used: 0.9 TBq in the Liguro-Provençal Basin, 0.6 TBq into the Tyrrhenian Sea, 1.9

TBq into the Adriatic Sea, 0.6 TBq into the Ionian Sea and 2.4 TBq into the Black Sea. Furthermore, the discharges of Cs-137 from Marcoule into the Gulf of Lions have been taken into account.

The results of the model calculations of Cs-137 concentrations in seawater for the time period 1950 to 2000 are shown in Figure 6.3.3.2 which includes annual averages of the observed data in the different regions of the Mediterranean Sea obtained from the MARINA-MED Working Group II on measured levels of Cs-137 (Aarkrog 1994).

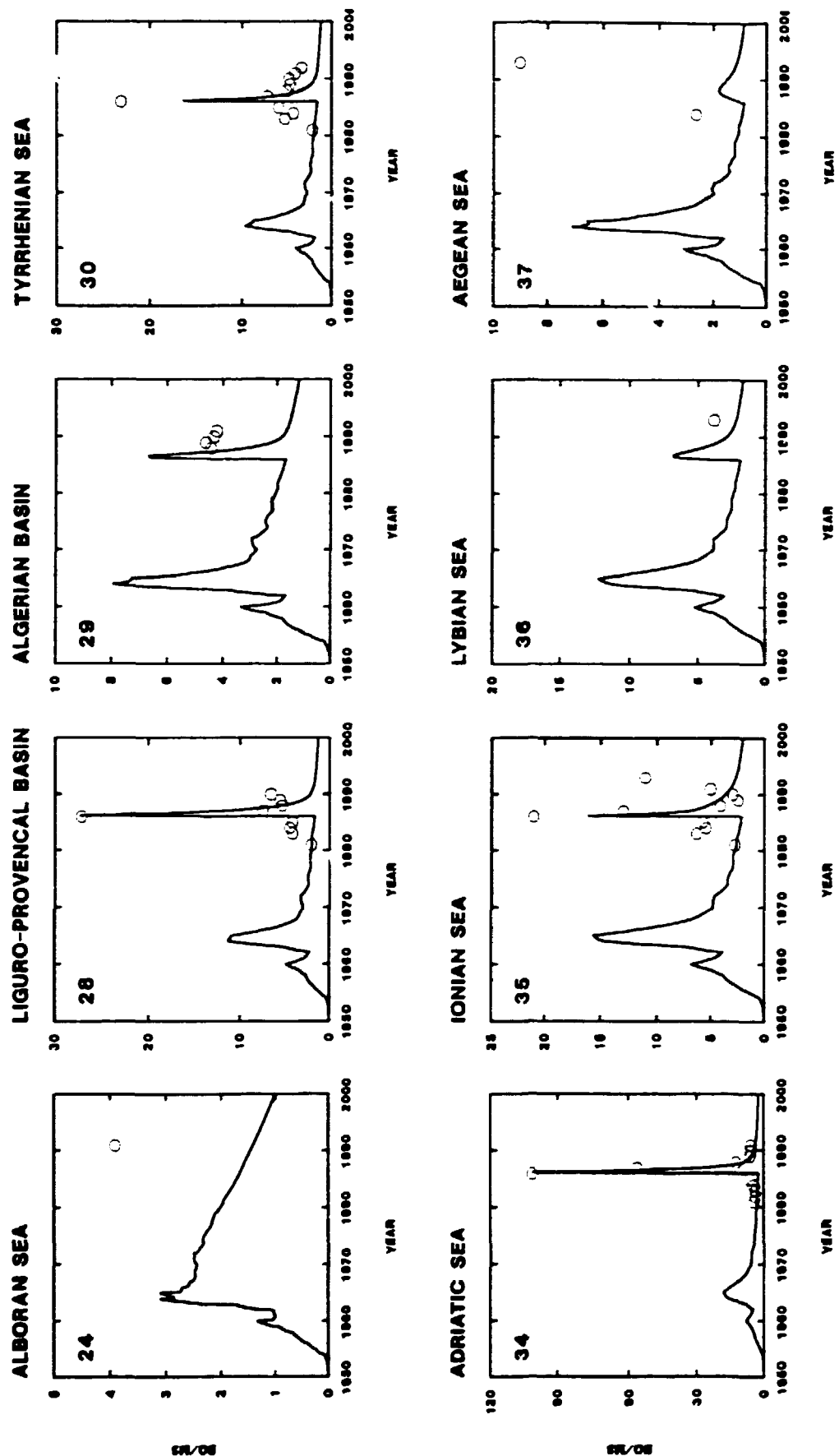


Figure 6.3.3.2. Predicted and observed concentrations of Cs-137 in seawater (Bq m<sup>-3</sup>) in regions of the Mediterranean Sea.

A quantitative comparison of the predicted and measured data in terms of an overall predicted-to-observed (P/O) ratio for the seawater data gives a mean value of  $0.7 \pm 13\%$  (1 SE,  $n=62$ ), and a mean value of  $0.4 \pm 23\%$  (1 SE,  $n=49$ ) for the sediment data. However, the observed data may be biased towards the high side, due to the general omission of data lower than detection limit for the calculation of annual averages. For the sediment data there is, furthermore, an unresolved question of how well the average sediment depths compare between the model assumptions and the observations. The concentrations of Cs-137 in surface sediments for the model calculations are based on a sediment depth of 0.1 m, but it is not clear if this is also the case for the sediment data. If the measured sediment data represent smaller average depths than 0.1 m, this may explain the differences, since the concentration of Cs-137 generally decreases exponentially with depth in sediments.

For the purpose of radiological risk assessments, it may be concluded that the model is an adequate tool for the prediction of the dispersion of Cs-137 in the Mediterranean Sea.

## References

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## 6.3.4 Radiological Exemption Applied to Sea Disposal

The International Atomic Energy Agency (IAEA) has been requested by the Contracting Parties to the Convention on the Prevention of Marine Pollution by Dumping of Wastes and Other Matter, London Convention 1972, to advise the Contracting Parties with respect of defining quantitatively the exempt levels, *i.e.* the radioactive levels below which material may be considered "non-radioactive" for the purposes of the Convention (IMO 1985).

Risø has carried out calculations for the IAEA to identify the exempt levels based on generic assessments for bulk material disposed into the sea by the following three practices:

- disposal into coastal waters through pipelines,
- disposal into coastal waters from vessels and platforms defined as "dumping" in the London Convention 1972,
- deep sea disposal: dumping from vessels or platforms of material in a manner that restricts its release to the deep ocean floor.

From a radiation protection standpoint there are three basic criteria for determining whether or not a practice can be a candidate for exemption:

- individual risks must be sufficiently low as not to warrant regulatory concern,
- the collective radiological impact must be sufficiently low as not to warrant regulatory control,
- exempted practices and sources must be inherently safe with no appreciable likelihood of scenarios that could lead to failure to meet the two other criteria.

The individual dose criterion is based on risk-based considerations and on natural-background-radiation considerations. It is concluded that an individual dose in the order of  $10 \mu\text{Sv y}^{-1}$  is appropriate as the individual (critical group) criterion for an exempt practice. For the collective dose criterion, it is concluded that for continuing practices, a commitment of about 1 manSv per year could be considered a trivial collective dose for exemption purposes. This figure was derived from the cost of a formal optimization analysis and represents a level at

which further efforts to reduce dose do not provide benefits commensurate with the cost of the assessment. Furthermore, a criterion of 100 mSv y<sup>-1</sup> for the protection of marine fauna has been adopted as a trivial dose for biota when considering deep ocean disposal. For inputs of radioactivity in coastal waters where humans and fauna are located in the same environment, the system for limiting the exposure of man ensures that an adequate level of protection of fauna is obtained.

Calculations have been made for a selection of radionuclides covering physical and chemical properties which represent classes of nuclides, thereby providing confidence that groups of nuclides with different characteristics have been

considered. The physical and chemical properties include half life, distribution coefficient ( $k_d$ ), biological concentration factor, and radiation type and energy. The following artificial radionuclides were selected: <sup>3</sup>H, <sup>14</sup>C, <sup>35</sup>S, <sup>51</sup>Cr, <sup>60</sup>Co, <sup>65</sup>Zn, <sup>90</sup>Sr, <sup>99</sup>Tc, <sup>106</sup>Ru, <sup>110m</sup>Ag, <sup>131</sup>I, <sup>137</sup>Cs, <sup>192</sup>Ir, <sup>237</sup>Np, <sup>239</sup>Pu, <sup>241</sup>Am and <sup>241</sup>Pu. These nuclides include some naturally-occurring radionuclides - <sup>3</sup>H and <sup>14</sup>C - to which have been added other important radionuclides <sup>210</sup>Pb, <sup>226</sup>Ra, <sup>228</sup>Ra and <sup>230</sup>Th.

Preliminary results of the calculations are shown in Tables 6.3.4.1 - 6.3.4.3 which give the ranking of the radionuclides for each practice in terms of the concentrations rounded to one order of magnitude.

Table 6.3.4.1. Ranking of radionuclides for discharges via pipelines.

Exempt concentration (Bq kg <sup>-1</sup> )	Nuclides
10 <sup>-3</sup> - 10 <sup>-2</sup>	<sup>14</sup> C
10 <sup>-2</sup> - 10 <sup>-1</sup>	<sup>239</sup> Pu, <sup>241</sup> Am, <sup>210</sup> Pb
10 <sup>-1</sup> - 10 <sup>0</sup>	<sup>60</sup> Co, <sup>226</sup> Ra, <sup>237</sup> Np, <sup>230</sup> Th, <sup>228</sup> Ra
10 <sup>0</sup> - 10 <sup>1</sup>	<sup>65</sup> Zn, <sup>106</sup> Ru, <sup>110m</sup> Ag, <sup>241</sup> Pu
10 <sup>1</sup> - 10 <sup>2</sup>	<sup>137</sup> Cs, <sup>192</sup> Ir
10 <sup>2</sup> - 10 <sup>3</sup>	<sup>90</sup> Sr, <sup>99</sup> Tc, <sup>131</sup> I
10 <sup>3</sup> - 10 <sup>4</sup>	<sup>51</sup> Cr
10 <sup>4</sup> - 10 <sup>5</sup>	<sup>35</sup> S
10 <sup>5</sup> - 10 <sup>6</sup>	<sup>3</sup> H

Table 6.3.4.2. Ranking of radionuclides for dumping in coastal waters.

Exempt concentration (Bq kg <sup>-1</sup> )	Nuclides
10 <sup>0</sup> - 10 <sup>1</sup>	<sup>14</sup> C
10 <sup>1</sup> - 10 <sup>2</sup>	<sup>60</sup> Co, <sup>65</sup> Zn, <sup>110m</sup> Ag, <sup>237</sup> Np, <sup>239</sup> Pu, <sup>241</sup> Am, <sup>210</sup> Pb, <sup>226</sup> Ra, <sup>228</sup> Ra
10 <sup>2</sup> - 10 <sup>3</sup>	<sup>106</sup> Ru, <sup>131</sup> I, <sup>137</sup> Cs, <sup>192</sup> Ir, <sup>241</sup> Pu, <sup>230</sup> Th
10 <sup>3</sup> - 10 <sup>4</sup>	<sup>51</sup> Cr, <sup>99</sup> Tc
10 <sup>4</sup> - 10 <sup>5</sup>	<sup>90</sup> Sr
10 <sup>5</sup> - 10 <sup>6</sup>	
10 <sup>6</sup> - 10 <sup>7</sup>	<sup>35</sup> S
10 <sup>7</sup> - 10 <sup>8</sup>	<sup>3</sup> H

Table 6.3.4.3. Ranking of radionuclides for deep sea dumping.

Exempt concentration (Bq kg <sup>-1</sup> )	Nuclides
10 <sup>1</sup> - 10 <sup>2</sup>	<sup>14</sup> C, <sup>60</sup> Co, <sup>110m</sup> Ag, <sup>226</sup> Ra
10 <sup>2</sup> - 10 <sup>3</sup>	<sup>65</sup> Zn, <sup>106</sup> Ru, <sup>131</sup> I, <sup>137</sup> Cs, <sup>192</sup> Ir, <sup>237</sup> Np, <sup>239</sup> Pu, <sup>228</sup> Ra
10 <sup>3</sup> - 10 <sup>4</sup>	<sup>51</sup> Cr, <sup>241</sup> Am, <sup>210</sup> Pb
10 <sup>4</sup> - 10 <sup>5</sup>	<sup>230</sup> Th
10 <sup>5</sup> - 10 <sup>6</sup>	<sup>90</sup> Sr, <sup>99</sup> Tc, <sup>241</sup> Pu
10 <sup>6</sup> - 10 <sup>7</sup>	
10 <sup>7</sup> - 10 <sup>8</sup>	<sup>35</sup> S
10 <sup>8</sup> - 10 <sup>9</sup>	<sup>3</sup> H

Some of these exempt concentrations are considerably more restrictive than the exempt activity concentrations to be found in the Basic Safety Standards (The International Basic Safety Standards for Protection Against Ionizing Radiation and for the Safety of Radiation Sources (BSS); IAEA 1994). The main reason for this difference is that the exemption values from the BSS are derived in relation to relatively small sources and practices. Sea disposal practices involve large-scale movement of bulk materials (e.g. the total mass disposal rate from all pipelines of a single nation is at the order of 10<sup>12</sup> kg y<sup>-1</sup>).

The above results are preliminary and may have to be adjusted and supplemented with data for additional radionuclides depending on comments to the IAEA.

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## 6.4 Contamination Physics (J. Roed)

### 6.4.1 The State of the Environment in Belarus

With support from the National Agency of Environment Protection, Riso National Laboratory in collaboration with Danish Toxicology Centre and the Association of Danish Boiler Owners has carried out a project with the objective of describing the state of the environment in Belarus. The project was carried out in close association with the State Committee for Ecology (Belarus) and with assistance from Dørstøjtjenika (Belarus).

The Chernobyl accident has had an enormous impact on the Republic of Belarus as about 70% of the contaminated land in the former USSR lies in this Republic. Nearly all reported investigations on the impact of the contamination from the Chernobyl accident have solely dealt with radiation. In this investigation, we have had the unique opportunity to compare the impact of the different kinds of pollution including radioactive contamination from Chernobyl.

By far the majority of the administrators in Belarus consider the task of dealing with the repercussions of the Chernobyl accident to be a most urgent environmental problem. However, our priority after having performed the investigation is not necessarily the same.

The intensive industrial and agricultural exploitation over the last decades has its impacts on the environment; furthermore the situation has been aggravated by the transboundary pollution from the neighbour countries, both from the heavy industry and from the Chernobyl accident. At the same time, Belarus is in a very difficult transition period, characterized by the transition towards an independent republic and market economy. Combined with the present economic recession, this brings difficult social conditions for a large part of the population in Belarus. The industrial plants are worn down and affected by the lack of raw materials. Large reorganizations and investments are necessary to secure supplies to the society and to reduce emissions and environmental impacts.

The State environmental policy has been laid down in a newly approved law. It is a framework law with many good intentions, but only a follow-up by concrete Statutory Orders with subsequent implementation and enforcement will ensure these intentions.

Many data are available on environmental impacts and public health in the form of registration of measured data or calculations. It is not always possible to ascertain what the data have been based on. Contradictory data or data which cannot immediately be related to internationally approved correlations are seen (Falster *et al.*).

If the efforts are to be goal- and priority oriented, it is absolutely necessary with open, accessible and internationally applicable data to illustrate the state of the environment and public health in Belarus.

This would help to differentiate between the various impacts on the environment and humans; e.g. pollution, bad social conditions, incorrect exploitation of the resources or radioactive contamination.

There is enough space and teaching capacity at the institutes of higher education to ensure an up-to-date ecology education, but on the organizational level the higher education institutes should prepare more goal-oriented tuition in ecology and pollution reducing techniques. In the first few years, it will be necessary to transfer up-to-date know-how and educational material to universities and polytechnical institutes.

The industrial sector is in great need of practically all kinds of pollution-combating techniques and treatment plants. Due to the limited financial resources it is to be expected that this modernization will stretch across many years. An obvious start would be to limit the use of resources, as this may often be self-financing and at the same time reduce the pollution correspondingly.

Measurements of the atmospheric air quality are made manually and only cover short measuring periods of 20 minutes maximum 4 times a day. The applied measuring methods give considerable uncertainties in the results. There are undoubtedly local problems with the air quality, but a more detailed evaluation and follow-up will require modern automatic equipment and processing of data according to international guidelines.

With regard to waste, it is necessary to construct several waste-treatment plants, and for dangerous waste in particular, combating measures should be introduced immediately.

The quality of surface water and groundwater is threatened by discharges of untreated waste water and leaching from dumping grounds and waste disposal sites. There is a great need to expand the capacity of the water-treatment plants and limit the industrial discharges of water into the aquatic environment. Follow-up measures will require an increase of the present sampling equipment.

Pollution of the soil by heavy metals derived from discharges of polluted water and air is rather common in polluted industrial areas. In the case of radioactive contamination, the hitherto applied measures should be re-evaluated, and a long-term strategy for future use of the areas should be made with the aim of determining activities for the decontamination and disposal of materials contaminated by radiation.

The ongoing activities to reduce the use of pesticides and fertilizers should be encouraged.

As a result of the study the three institutes involved have identified a number of fields which we find should have priority. These fields are the following, in random order:

- 1) Measures to reduce the consequences of the Chernobyl accident.
- 2) Energy saving.
- 3) Measuring techniques and equipment.
- 4) Compilation and processing of large quantities of data.
- 5) Waste treatment.
- 6) Waste water-treatment
- 7) Pollution-reducing measures.
- 8) Transfer of know-how.

The group feels convinced that it is advisable to initiate a number of smaller, easy-to-study, demonstration projects as soon as possible, so that useful experience can be gained quickly in Belarus.

As Belarus is a fairly small country situated not far from Denmark, these projects could be started in close collaboration between Danish and Belarussian enterprises and in this context Risø National Laboratory and other institutes dealing with the environment could have an important role to play, as consultants or by patting directly involved in the projects.

It is important to underline that the earlier these projects are carried out, the more positive impact will they have. This is not at least true when the projects are about mitigating the consequences of the Chernobyl accident.

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## 6.4.2 Indoor Deposition

The object of investigation of indoor deposition in houses is to find out by which degree staying indoors during an air-pollution episode will influence the impact of that episode on people.

People inside a building will normally obtain some protection against air pollution originating outside. This is the result of physical and chemical processes. Both filtration in cracks, crevices and pores through which air penetrates and the deposition on floors, walls, ceilings and furniture of the pollution that penetrates inside will contribute towards reducing the inhalation dose. The processes which reduce the inhalation dose can, in the case of pollution from radioactive material, also contribute to the exposure of the occupants because of the gamma radiation from the trapped and deposited material.

Earlier investigations (Roed and Cannell 1987) have indicated that deposition is the most important process in reducing inhalation dose.

The new investigations have, therefore, concentrated on finding indoor deposition parameters from a spectrum of different particle sizes.

The particle has been tagged with rare earth, so that neutron activation will make it possible to count them as radioactive particles. A concentration of the particles is introduced into the room under consideration, then the air-exchange  $\lambda_r$  (fraction of air exchanges per unit time) and the aerosol concentration as a function of time is measured. From this, the rate coefficient of deposition  $\lambda_d$  (fraction of aerosols deposited per unit time) can be found, and from  $\lambda_d$  and the dimension of the rooms, the deposition velocity can be calculated.

The result of the measurements in four different houses is summarized in Table 6.4.2. (Lange 1994)

Table 6.4.2. Measurements of indoor Deposition Velocities in four houses. First two columns show size and geometric standard deviation (GSD), of the test aerosol. The next two columns give the average deposition to all surfaces measured in three different test houses. The number in parenthesis gives the number of tests for that condition.

Size [ $\mu\text{m.}$ ]	GSD []	Avg. $v_d$ Unfurnished [ $10^{-4}\text{m/s}$ ]	Avg. $v_d$ Furnished [ $10^{-4}\text{m/s}$ ]
0.5	1.60	$0.61 \pm 0.08$ (2)	$0.82 \pm 0.08$ (6)
2	1.48	$1.13 \pm 0.16$ (5)	$1.36 \pm 0.5$ (5)
3	1.20	$1.33 \pm 0.37$ (2)	2.25 (1)
4	1.07	$2.42 \pm 0.17$ (5)	$3.11 \pm 0.6$ (5)
5.5	1.18	$3.03 \pm 0.04$ (2)	3.24 (1)

The results are in good agreement with the theory, as the obtained deposition velocities increase with increasing particle size and the deposition velocity in furnished houses are higher than in unfurnished houses.

## References

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## 6.5 Ecophysiology (H.J.M. Hansen)

We study the metabolism of osmoregulation and ambient heavy metal uptake by aquatic vertebrates *in vivo*. The work is done in collaboration with P. Rosenkilde, The August Krogh Institute, University of Copenhagen.

### 6.5.1 Adaptation to Changes in Ambient Salinity

Recent work on lipid metabolism in toad (*Bufo bufo*) skin has shown (Hansen *et al.* 1994) a formation of extra phosphatidylethanolamine (PE) when toads, pre-adapted to Ringer solution (isosmotic brackish water), were transferred to

fresh water. This did not occur when they were pre-adapted to fresh water and stayed in fresh water. We suggest that the formation of PE is involved in a stabilisation of the integral membrane proteins that implement compensating ion transport through the skin, following changes in ambient salinity (i.e. brackish  $\rightarrow$  fresh water).

Similar experiments with rainbow trout (*Oncorhynchus mykiss*) pre-adapted to isosmotic brackish water and subsequently transferred to either fresh or sea water showed again (Hansen and Rosenkilde 1994, Hansen *et al.*, in press) that the formation of PE was connected to osmoregulation. In this case extra PE was formed in osmoregulating tissue (gills as well as esophagus) when trout went from brackish water to a higher salinity, but not when they went to a lower salinity. Parallel to the results on toad skin (Hansen *et al.* 1994), the formation of PE observed in sea water could indicate compensating ion transport; this was not seen in fresh water, apparently because the fish - unlike toads - did not experience an osmotic challenge under these circumstances.

We assayed membrane lipid biosynthesis by the incorporation of both the radioactive precursors  $^{32}\text{P}$ -phosphate and  $^{14}\text{C}$ -acetate. This enabled us also to show (Hansen and Rosenkilde 1994; Hansen *et al.*, in press) that the formation of extra PE involved a separate turnover of phospholipid polar headgroups, independent of what happened to the rest of the lipid molecules within the membrane core.

## References

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- Hansen, H.J.M., Rosenkilde, P. (1994) Lipid metabolism in fish gills. Is phosphatidylethanolamine an endogenous regulator of membrane transport? Oral presentation at FEBS special meeting *Biological membranes*, Helsinki/Espoo, Finland, June 26 - July 1, 1994.
- Hansen, H.J.M., Olsen, A.G., Rosenkilde, P. Formation of phosphatidylethanolamine as a putative regulator of salt transport in the gills and esophagus of the rainbow trout (*Oncorhynchus mykiss*). *Comp. Biochem. Physiol.* (in press)

### 6.5.2 Effect of Ambient Copper

The primary site of sublethal copper toxicity to rainbow trout has been shown (Laurén and McDonald 1987) to be the ion transport mechanism of the gills. To what degree does this affect gill lipid metabolism?

Recent work (Hansen *et al.* 1994a) has shown that rainbow trout exposed to  $\text{Cu}^{2+}$  in brackish water at levels up to 0.8 ppm for 4 days experienced a drop up to 8% in plasma  $\text{Na}^+$  24 h after transfer to clean fresh water. If they remained in (now clean) brackish water, nothing special was seen; if instead they were transferred to sea water, plasma  $\text{Na}^+$  went up, but remained independent of previous  $\text{Cu}^{2+}$  treatment. Equivalent assays of gill lipid metabolism showed a marked degradation of membrane lipids after transfer to sea water, in this case correlating to previous  $\text{Cu}^{2+}$  treatment. Both plasma  $\text{Na}^+$  and gill lipid metabolism were thus influenced by  $\text{Cu}^{2+}$  treatment, but there was no evident connection between the two effects.

Further experiments (Hansen *et al.* 1994b) have shown that when the exposure to  $\text{Cu}^{2+}$  is prolonged to 12 days, the overall effect is reduced; i.e. the trout experience an acclimation to copper. This applies as well to plasma  $\text{Na}^+$  as to lipid metabolism, not only in gill tissue but also in the esophagus.

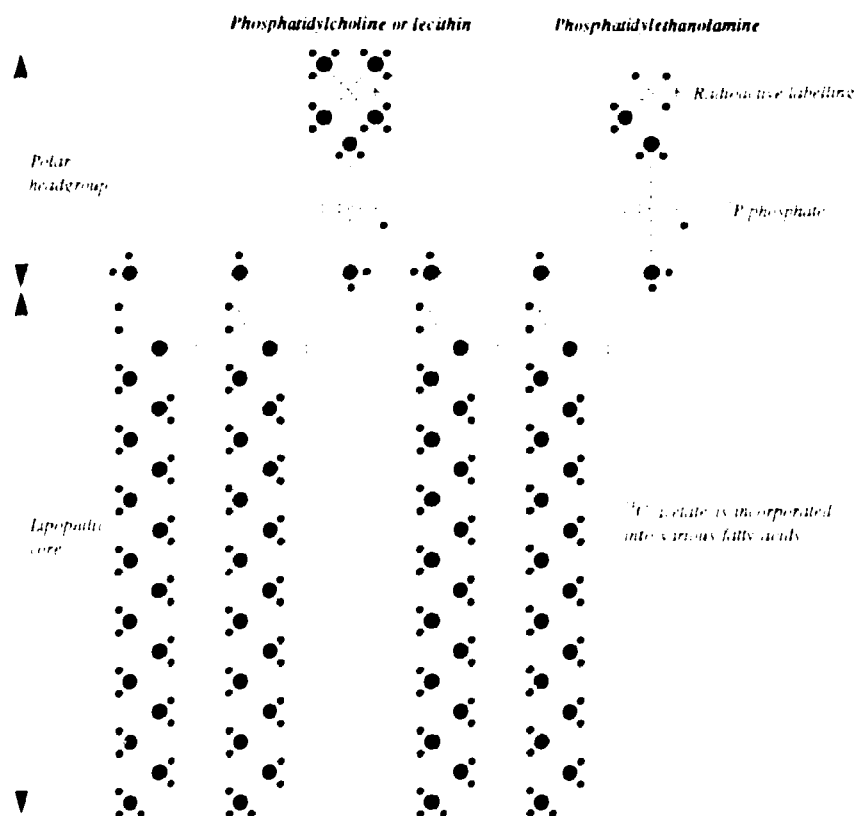


Figure 6.5. Phospholipid structure. The difference between phosphatidylcholine and phosphatidylethanolamine is just three methyl ( $\text{CH}_3$ ) groups.

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### 6.5.3 Copper Metabolism in Fish

Recent work on the acute uptake and turnover of radioactive  $^{64}\text{Cu}$  by the European eel (*Anguilla anguilla*) following prolonged exposure to stable  $^{63}\text{Cu}$  at sublethal levels has shown (Grosell *et al.* 1994a, b, c) an apparent stimulation of copper excretion. What is the mechanism involved?

Further experiments have covered  $^{64}\text{Cu}$  measurements in 7 different tissues. They have shown that the excretion of copper takes place in the liver via the bile bladder to the gut. We have developed a method of determining  $^{64}\text{Cu}$  in individual proteins and salts of blood plasma and bile, based on the automatic scanning of SDS-PAGE polyacrylamide gels, after electrophoresis, with a special low-level beta counter (Bøtter-Jensen *et al.* 1977). This has revealed that  $^{64}\text{Cu}$ , at low concentrations and short exposure periods, is bound mostly to a plasma-protein resembling ceruloplasmin, which also is known to be responsible for copper transport in mammalian plasma (Cousins, 1985; Harris, 1991). At higher concentrations, however, or longer periods of exposure,  $^{64}\text{Cu}$  was found in almost all plasma-protein fractions. We were furthermore able to show that all  $^{64}\text{Cu}$  excreted by the eels during acute exposure was bound to the bile salts and not to bile proteins, as seen in most investigated mammals (Cousins 1985; Harris 1991).

## References

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## 6.6 Radioecology (A. Aarkrog)

This project domain comprises participation in a number of international projects (MARDOS, MARINA-MED, "Less Wellknown Radionuclides") and M. Strandberg's Ph.D. project on radioecology of Danish forest ecosystems.

### 6.6.1 MARDOS (IAEA)

MARDOS was a five year Coordinated Research Programme of the IAEA. The full title of the programme was: Sources of radioactivity in the marine environment and their relative contributions to overall dose assessment from marine radioactivity. Sixteen countries from all parts of the world (except Africa) participated. The scientific secretariat was provided by the Marine Environment Laboratory in Monaco (A. Sanchez and P.P. Povinec). The participants were R. Jeffree (Australia); I. Cunha (Brazil); J.N. Smith

(Canada); Li Pingyu (China); A. Aarkrog (Denmark), chairman of MARDOS; S. Charmasson (France); H. Nies (Germany); R. Delfanti (Italy); E. Duran (Philippines); R. Bojanovski (Poland); A.O. Bettencourt (Portugal); A. Bologa (Romania); E. Holm (Sweden); S. Mahapanyawong (Thailand); D. Swift (UK) and H.D. Livingston (USA).

The collective doses from the natural occurring  $^{210}\text{Po}$  and from the anthropogenic  $^{137}\text{Cs}$  from consumption of marine foods in 1990 were estimated for the world population. Two methods were applied. One was based upon measured water concentrations and the respective concentration factors for fish and shellfish. The other method used measured levels in fish and shellfish.

The collective effective dose commitment for  $^{137}\text{Cs}$  in marine food in 1990 was 160 man Sv with an estimated uncertainty of 50%. The corresponding dose from  $^{210}\text{Po}$  was 30000 man Sv with an estimated uncertainty of a factor of 5.

Considering the total collective effective dose commitment from all sources over all years from  $^{137}\text{Cs}$  in marine food stuffs, it becomes 14000 man Sv. Global fallout from nuclear weapons testing contributed to about 65%, discharges from nuclear reprocessing in western Europe (Sellafield) to 20% and the Chernobyl accident to 15%.

## References

IAEA-MEL (1994): Sources of radioactivity in the marine environment and their relative contributions to overall dose assessment from marine radioactivity (MARDOS). Final report of the CRP. IAEA-MEL-R2/94, June 1994, 50 p.

### 6.6.2 MARINA-MED (CEC-DGXI)

MARINA-MED was a CEC project dealing with the impact of radioactivity in Mediterranean waters. The project was a continuation of a similar project (MARINA) carried out 1985-1990 for the NE-Atlantic. MARINA-MED run from 1992 to 1994 (cf. also 6.3.3).

One of the four working groups of MARINA-MED dealt with the reporting of available  $^{137}\text{Cs}$  and  $^{210}\text{Po}$  data in seawater, sediments, fish and shellfish from the Mediterranean Sea. The participants in this group were A. Angelopoulos and H. Florou (Greece); D. Calmet

(France); R. Delfanti, S. Piermattei and S. Risica (Italy); L. Romero (Spain); and A. Aarkrog (Denmark), chairman of the group.

It was found that until 1986 the Mediterranean  $^{137}\text{Cs}$  concentrations in sea water, fish, shellfish and sediments normally showed only minor local variations. However, after the Chernobyl accident in 1986, a patchy deposition pattern of the fallout was reflected in the various samples. In 1990 most levels were back to pre-Chernobyl concentrations, the Mediterranean means for sea water then were:  $5.7 \text{ Bq } ^{137}\text{Cs m}^{-3}$ , fish:  $0.4 \text{ Bq kg}^{-1}$ , shellfish:  $0.3 \text{ kg}^{-1}$  and sediments:  $6.5 \text{ Bq kg}^{-1}$ . The concentrations in the Black Sea were an order of magnitude higher, mainly due to influence from the Chernobyl accident.

The Mediterranean mean individual effective dose received from Chernobyl  $^{137}\text{Cs}$  in marine foods is approximately  $0.5 \mu\text{Sv}$ . The annual dose received from  $^{210}\text{Po}$  in marine foods was  $33 \mu\text{Sv}$ . The doses to a hypothetical critical individual in the Mediterranean were estimated to be an order of magnitude higher than those of the general population.

## References

CEC (1994) The radiological exposure of the population of the European Community from radioactivity in the Mediterranean Sea. Project "MARINA-MED" (in press)

### 6.6.3 Less Commonly Considered Radionuclides (IUR)

The International Union of Radioecologists (IUR) established in 1992 is a task-force-group (TF4) with the purpose of identifying radionuclides which were less well studied from a radioecological point of view and which might be of actual or potential relevance. The taskforce consisted of C. Vandecasteele (Belgium); G. Lindner (Germany); E. Holm (Sweden), A. Korotkov (Ukraine) and A. Aarkrog (Denmark), chairman of the group.

Each radionuclide was listed and characterised by physical parameters (half-life, decay, sources etc.) by source term parameters (environmental concentrations), radioecological parameters (TF,  $K_d$ , CF), health physics parameters (ALI) and specific problems/properties.

In order to rate the radioecological importance of the various radionuclides three so-called radioecological indices:  $R_T$ ,  $R_M$  and  $R_F$  have been applied.

$R_T$  is the terrestrial radioecological index:

$$\log \frac{TF(\text{plant soil})}{ALI}$$

where TF (plant soil) is the transfer factor from soil to grass of the radionuclide in question given as  $Bq\ kg^{-1}$  dry weight/ $Bq\ kg^{-1}$  dry weight of soil (0-20 cm layer) and ALI is the annual limit of intake of the radionuclide

$R_M$  is the marine radioecological index:

$$\log \frac{CF(\text{marine fish/seawater})}{K_d(\text{marine sediments}) \times ALI}$$

where CF(marine fish/seawater) is the concentration factor for marine fish for the radionuclides in question given as  $Bq\ kg^{-1}$  fresh weight/ $Bq\ l^{-1}$  seawater, and  $K_d$  is  $Bq\ kg^{-1}$  dry weight of sediments/ $Bq\ l^{-1}$  seawater.

$R_F$  is the freshwater radioecological index

$$\log \frac{CF(\text{freshwater fish/freshwater})}{K_d(\text{freshwater sediments}) \times ALI}$$

The following radionuclides are given top priority for future radioecological studies of wellknown radionuclides:  $^{35}S$ ,  $^{63}Ni$ ,  $^{79}Se$ ,  $^{93}Mo$ ,  $^{103}Ru$ ,  $^{106}Ru$ ,  $^{110m}Ag$ ,  $^{109}Cd$ ,  $^{126}Sn$ ,  $^{125}I$ ,  $^{129}I$ ,  $^{210}Pb$ ,  $^{210}Po$ ,  $^{227}Ac$ ,  $^{231}Pa$ ,  $^{237}Np$  and  $^{252}Cf$ .

## References

IUR Report of IUR task-force-group TF4 on the behaviour of less commonly considered radionuclides (in press).

### 6.6.4 Mushrooms Spores and $^{137}Cs$ in Faeces of the Roe Deer (M. Strandberg)

This study is part of a Ph.D. project on the radioecology of Danish forest ecosystems. The study was carried out with H. Knudsen, University of Copenhagen.

Levels of  $^{137}Cs$  in meat, faeces and feed of Danish roe deer were measured and faecal samples were studied under the microscope for the occurrence of fungal spores.

It was confirmed that the roe deer eats fungi, as spores from a great variety of species and genera were observed. Among the most commonly eaten species were members of the *Boletaceae*. In particular, the bay bolete *Xerocomus badius* seems to be preferred. Increased autumnal  $^{137}Cs$  concentrations in the meat of the fallow deer (*Cervus dama*) indicated that these peak values could be due to ingestion of mushrooms.

The method has to be further developed in order to quantify the spores. Better knowledge of the levels in the different mushroom species is also needed. However, the increasing amount of *Xerocomus badius* with an increased concentration of  $^{137}Cs$  indicated that the ingestion of this species in 1992 was the explanation of the relatively high levels of radiocaesium in the roe deer in Tisvilde that year.

The significant differences between the  $^{137}Cs$  levels in meat from Tisvilde and Gribskov are explained by the fact that some of the Gribskov animals, in contrast of the Tisvilde animals, get some of their feed from the surrounding agricultural areas.

## References

Strandberg, M., Knudsen, H. (1994) Mushroom spores and  $^{137}Cs$  in faeces of the roe deer. J. Environ. Radioactivity 23, 189-203.



Figure 6.6.4. Fungal spores in faeces of roe deer from Tisvilde, *Xerocomus badius* (1250 $\times$ )

## 7 Other Activities

### 7.1 Photochemistry and Photophysics

#### 7.1.1 Electronic States of Polyenes (R. Wilbrandt)

International collaboration with groups in Italy, The Netherlands, Poland and the USA has continued.

Investigations of the mechanisms of photoisomerization of polyenes have been continued. In particular, the optical spectroscopy of a **conformationally locked hexatriene** (1,2-divinylcyclopentene) has been compared with that of Z-1,3,5-hexatriene. As expected from theory, an increase in triplet lifetime by a factor 20 was demonstrated for this molecule and it was thus confirmed that the deactivation of the  $T_1$  state of 1,3,5-hexatriene occurs via a twisted intermediate. This work has been published (ten Wolde *et al.* 1994).

Furthermore, the **lowest triplet state of stilbene** and three of its specially synthesized isotopomers were studied both experimentally and theoretically. The main issue in these studies was the question of whether the  $T_1$  potential energy surface has a minimum at planar and/or twisted geometries. We were able to definitely demonstrate, from resonance Raman spectroscopy, that the spectroscopically observed molecules are planar in  $T_1$ , but could not rule out the additional presence of "dark" twisted forms. This work has been published (Langkilde *et al.* 1994).

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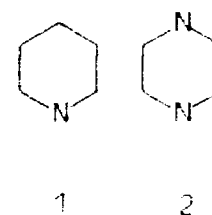
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#### 7.1.2 Ions and Free Radicals (R. Wilbrandt)

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 of importance for conducting polymers under stable conditions by resonance Raman spectroscopy in low temperature glasses was continued, 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 strongly overlaps the studies of macrocyclic compounds.

Some 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. This work has led to a publication (Langkilde *et al.* 1994).

In collaboration with A.M. Brouwer in Amsterdam, we have continued a time-resolved resonance Raman and a theoretical *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 transient species in polar solution by laser photolysis.



Piperidine (1) and  
piperazine (2)

The resonance Raman spectra of these compounds are of excellent quality, yield a great amount of detail and allow 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 dimethylpiperazine radical cation has been published (Brouwer *et al.* 1994).

One of our other important projects was to study short-lived species of importance in the photoconductivity of conducting polymers such as polyacetylene. Such species include the hexatriene radical cation, but also other radical anions, cations and free radicals of conjugated polyenes. We succeeded to get the first resonance Raman spectra of the radical cation of trans and cis-1,3,5-hexatriene. This project is carried out as a Ph.D. project by T. Keszthelyi from Hungary and has been published (Keszthelyi *et al.* 1994). This work has been extended to include the study of diene radical cations.

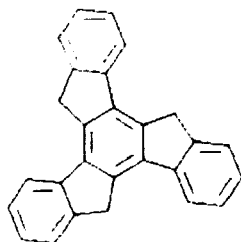
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### 7.1.3 Photochemistry and Photophysics of Macrocyclic Compounds (R. Wilbrandt)

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

1) In a Ph.D. project by J. Frederiksen and in collaboration with N. Harrit, Copenhagen University, we continued our studies of the photophysical, photochemical and spectroscopic properties of the polynuclear aromatic molecule **truxen**. This is a



Truxen

large molecule, suggested and studied previously as possible ferromagnetic material in the context of organic supraconductivity. 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 and fluorescence quantum yields have been found.

2) In collaboration with the Polish group of Professor Grabowska and A. Mordzinski in Poland and of Professor Adamowicz in USA, we have continued investigations of **photochromism by intramolecular proton transfer**. Intramolecular proton transfer can, if it is coupled 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. This work has led to three publications (Mordzinski *et al.* 1994a; Mordzinski *et al.* 1994b; Kownacki *et al.* 1994).

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### 7.1.4 Theoretical *ab initio* Calculations (R. Wilbrandt)

With the general availability of both semi-empirical and *ab initio* programs, 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 semi-empirical or *ab initio* methods at a level which at least yields a qualitatively meaningful picture. The main problems on the one hand, are still computations on large molecules, 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 Danish national supercomputers and have initiated various theoretical *ab initio* calculations in order to reach a better understanding of our observed vibrational spectra of short-lived intermediates. Many of these calculations form part of the above mentioned work.

#### 7.1.5 Establishment of a Center of Laser Chemistry and Molecular Dynamics

(R. Wilbrandt)

The Danish Natural Science Research Council has decided to establish and support a "Center of Laser Chemistry and Molecular Dynamics" for a five-year period from February 1, 1994 with Professor G. Due Billing, Copenhagen University, as head of the centre. The photochemistry and photophysics group is part of this centre. This implies more extensive national collaboration with groups from Copenhagen University, the Technical University at Lyngby, Odense University and Aarhus University in the general area of laser chemistry and chemical reactivity.

## 7.2 Dosimetry and Industrial Irradiation

### 7.2.1 Risø High Dose Reference Laboratory (HDRL) (A. Miller)

During 1994, the following reports and certificates were issued:

1. Irradiation at cobalt-60 gamma-cell of dosimeters or samples	5
2. Irradiation at 10 MeV electron accelerator of dosimeters or samples	3
3. Issue of calorimeters	10
4. Issue of dichromate reference dosimeters	9
5. Issue of FWT-60 reference dosimeters	5
6. Measurement of irradiation facility parameters	4
7. Measurement of dose distribution in irradiated products	30

The traceability for both gamma and electron dosimetry is derived from the National Physical Laboratory, UK. After acceptance of the polystyrene calorimeters by our accrediting body DANAK, these calorimeters now serve as reference dosimeters in the electron dosimetry traceability chain. The present polystyrene calorimeters are only valid at 10 MeV electron irradiation, and although they may be used at energies down to 4 MeV, we have started development of calorimeters which may be used at an energy range of 1 - 10 MeV.

An electron spin resonance spectrometer (Bruker EMS 104) was acquired and we are working to establish the alanine/ESR dosimeter under the DANAK accreditation.

Also this year two one-week training courses were organized with the title: *Validation and routine control of electron-beam sterilization*. The recent approval of the EU-directive of the manufacture of medical devices means that national legislation in the EU member countries will have to be changed to adhere to these directives, and the increased emphasis on documentation and quality control has heightened an interest in these courses.

### 7.2.2 Industrial Irradiation (A. Miller)

Irradiation of products at the 10 MeV electron accelerator for sterilization and for material modification has continued two days a week. The product irradiation is carried out in collaboration with the Danish industrial irradiation facilities.

Work has been initiated to establish certification of the quality control for the product irradiation according to the ISO-9002 standard.

### 7.3 MODECS (B. Skytte Jensen)

In 1994, MODECS arranged a one-day meeting on *"Light and Molecules"* and a two-day meeting with the title *"From Oligomers to Polymers, The Influence of Shape and Size on Functional Properties"*. Both meetings, with internationally renowned specialists as main-speakers, were very successful.

Aims for 1995 and 1996 are in progress, but the topics for the meetings have not yet been chosen.

MODECS has, in 1994, sponsored a visit for a scientist to a microsymposium on Supramolecular Chemistry in Hamburg, supported the ongoing Ph.D. study and contributed to the purchase of an advanced molecular modelling programme.

By the end of 1994, the responsibility for the administrative and planning activities of MODECS will be transferred from the Environmental Science and Technology Department to the Department of Solid State Physics, Materials Chemistry Group.

## 8 Special Facilities

### 8.1 10 MeV Linear Electron Accelerator (*J. Fenger*)

The accelerator has been in operation for a normal number of hours. Half of the time is allocated for commercial product irradiation and the remainder for experiments. The operation has been trouble free.

The main thyatron in the high voltage modulator was replaced medio 1994 with another type. The original American ITT has caused many problems in the daily operation. The new one is an English EEV type and so far, the operation has been satisfactory. The expected lifetime is in the range of 10,000 hours, and the price is 100,000 DKK.

The cooling tower for the accelerator was partly renewed and renovated. The original one was installed in 1977. The total price was 75,000 DKK. Two third of this, 50,000 DKK, was paid by the Risø fund for building maintenance work.

### 8.2 Pilot Plant for Wet Oxidation (*V. Gundersen*)

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 (*K. Pilegaard*)

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, and scientists

from the Meteorology and Wind Energy Department.

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 (*V. Huuhr*)

In 1994, the economic result of the farm was not satisfactory because of a severe summer drought resulting in a low harvest yields.

Around 25 ha have been utilized for research and demonstration in a project with differentiated application of N-fertilizers.

### 8.5 Open Top Chamber Facility (*V. Huuhr*)

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 Riso Ecological Risk Assessment Facility, RERAF (K. Nilsson)

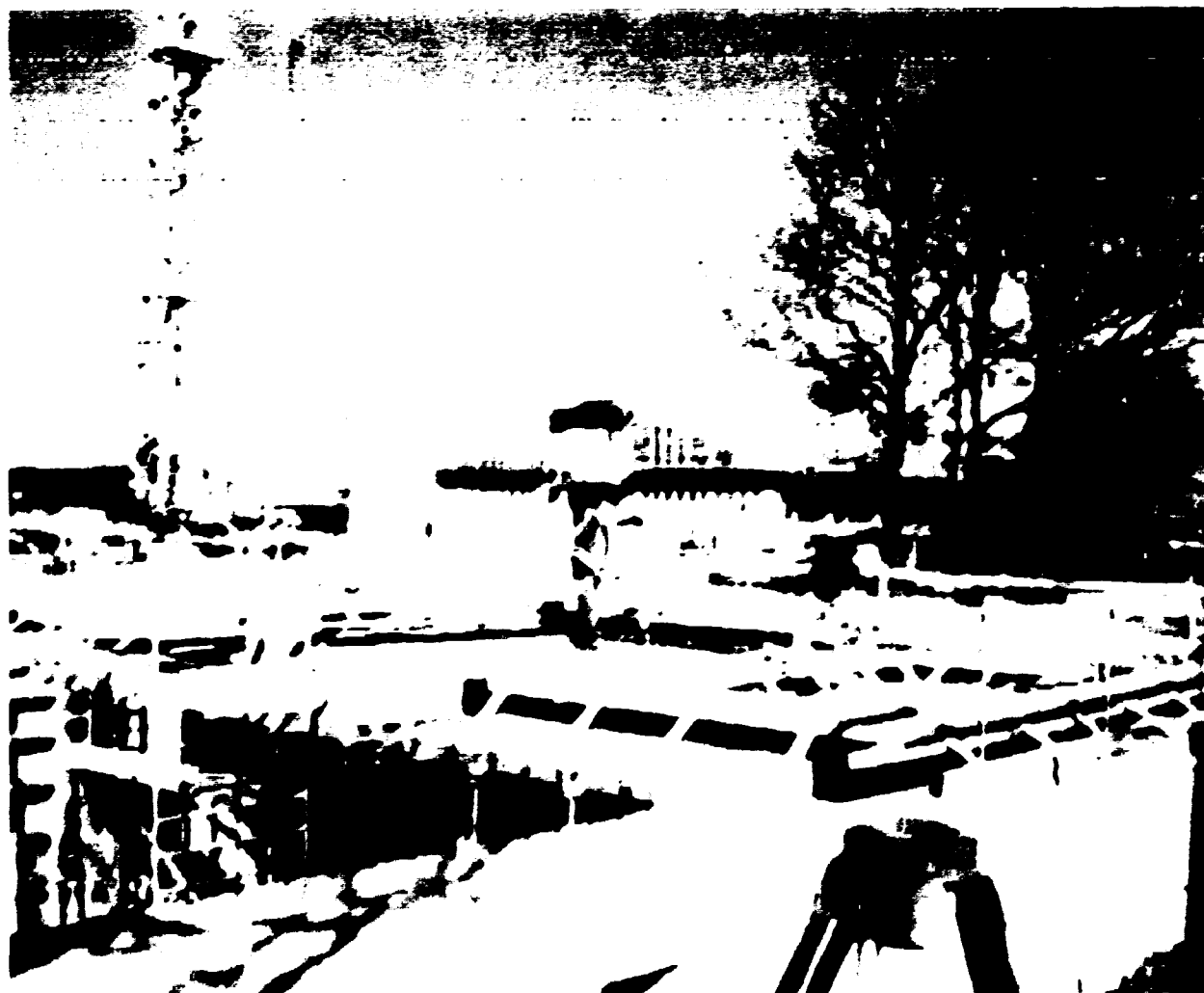
In the RERAF-facility, physical, chemical and biological conditions existing in nature will be simulated with good approximation, and RERAF is intended to become one of the most advanced systems for conducting a wide range of experiments associated with the environment.

The detailed plans for building the RERAF-facility were finalized during 1994, and at the end of the year, the construction of RERAF1 was started.

RERAF1 will embody a total of 6 growth chambers (4 × 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. Atmospheric air and/or special mixtures of gasses such as nitrogen, oxygen, carbon dioxide or air pollutants such as ozone, NO<sub>x</sub> and SO<sub>x</sub> can be supplied. The chambers will have mobile light roofs with high pressure Hg lamps, giving a maximum photonflux of approximately 1000  $\mu\text{mol m}^{-2} \text{s}^{-1}$ . The chambers will be certified for experiments with radioisotopes and transgenic organisms. Each of the growth chambers can be connected with a 3 meter deep root compartment with separate temperature controls.

Versatility has been the major guideline in planning the RERAF-facility where the latest developments within analytical chemistry and computer technology will be combined with advanced plant growth facilities with separate root and shoot compartments. It will be possible to operate, and independently control, experimental conditions of both above- and below-ground parts of model ecosystems.



## 9 Publications

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- Mikkelsen, T.R., Andersen, B., Hansen, S., Jørgensen, R.B. Can transgene escape from oilseed rape (*Brassica napus*) to the weedy species *Brassica campestris*. 4th International Congress of Plant Molecular Biology, Amsterdam, The Netherlands 19-24 Sep 1994. Poster.
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- Miller, A. Dosimetry systems: Properties, calibration, traceability, uncertainties. Workshop on Industrial Gamma and Electron Beam Processing: Process Control and Dosimetry, Sao Paulo, Brazil, 9-13 May 1994.
- Miller, A. Process validation for electron accelerator facilities. Workshop on Industrial Gamma and Electron Beam Processing: Process Control and Dosimetry, Sao Paulo, Brazil, 9-13 May 1994.
- Miller, A. Uncertainty of dose measurements in radiation processing. 8th "Tihany" Symposium on Radiation Chemistry, Hungarian Chemical Society, Balatonszéplesi, Hungary, 3-8 Sep 1994.
- Miller, A. Documentation requirements for radiation sterilization. 9th International Meeting on Radiation Processing, Istanbul, Turkey, 11-16 Sep 1994.
- Miller, A. Polystyrene calorimeter for electron beam dose measurements. 9th International Meeting on Radiation Processing, Istanbul, Turkey, 11-16 Sep 1994.
- Miller, A. Documentation requirements derived from the new CEN and ISO standards on radiation sterilization. 8th International Conference MEDICAL PLASTICS'94, Götterburg, Sweden, 4-6 Oct 1994.
- Miller, A. Polystyrene calorimetry for dose measurements and calibration at industrial electron accelerators. NPL Calorimetry Workshop, National Physical Laboratory, Teddington, UK, 12-14 Oct 1994.
- Mogelberg, T.E., Nielsen, O.J., Sehested, J. Absolute rate constants for the reactions of CF<sub>3</sub>CFHO<sub>2</sub> with NO<sub>2</sub> and CF<sub>3</sub>COOH with OH. Nordic Network Meeting on Atmospheric Chemistry, Helsingør, Denmark, 19-21 Aug 1994. Abstract available.
- Mogelberg, T.E. Laboratory studies of the reaction of peroxy radicals with NO<sub>2</sub>. 12th Polish-Danish Symposium on Radiation Chemistry, Institute of Physical Chemistry, Polish Academy of Sciences, Madralin, Poland 4-7 Jun 1994.
- Mogelberg, T.E., Sehested, J., Nielsen, O.J., Wallington, T.J. A kinetic study of the reaction of hydroxyl radicals with CF<sub>3</sub>COOH at different temperatures. Annual Meeting of the Danish Chemical Society at the University of Odense, Denmark, 14 Jun 1994.
- Mogelberg, T.E. Degradation of HFCs in the atmosphere. Friday Seminars, Autumn 1994, Department of Life Science and Chemistry Roskilde University, Denmark, 18 Nov 1994.
- Nielsen, O.J. Riso - Status and future plans. Nordic Network Meeting on Atmospheric Chemistry, Helsingør, Denmark, 19-21 Aug 1994.
- Nielsen, O.J. Degradation of CFC and HFC compounds in the atmosphere. AG-konference om nye isotemidler, Sønderborg, Denmark, 15 Dec 1994.
- Nielsen, O.J. Atmospheric Degradation of HCFCs and HFCs. 12 Polish-Danish Symposium on Radiation Chemistry, Institute of Physical Chemistry, Polish Academy of Sciences, Madralin, Poland, 4-7 Jun 1994.
- Nielsen, O.J., Ellermann, T., Wallington, T.J. Studies of the gas phase atmospheric oxidation of dimethyl sulfide. Annual meeting of the Danish Centre for Atmospheric Research (DCAR), Copenhagen, Denmark, 2 Feb 1994.
- Nielsen, O.J., Sehested, J., Wallington, T.J. Reactions of NO with a series of peroxy radicals in the gas phase at 298 K. Annual meeting of the Danish Centre for Atmospheric Research (DCAR), Copenhagen, Denmark, 2 Feb 1994.
- Nielsen, O.J., Sehested, J., Ellermann, T. Atmospheric chemistry of HFCs. Annual meeting of the Danish Centre for Atmospheric Research (DCAR), Copenhagen, Denmark, 2 Feb 1994.
- Nielsen, O.J., Sehested, J., Gønborg, E., Wallington, T.J., Hurley, M.D. Atmospheric chemistry of HFC-143a. Annual meeting of the Danish Chemical Society at the University of Odense, Denmark, 14 Jun 1994.
- Nielsen, S.P. Beregning af strålingsdoser fra radioaktivt affald dumpet i Barents- og Karahavet. 8 Danske Havforskermede, Odense, Denmark, 25-27 Jan 1994.
- Nielsen, S.P. A preliminary assessment of potential doses to man from radioactive waste dumped in the Arctic Sea. Seminar on Dumping of Radioactive Waste in the Kara and Barents Seas, Norwegian Radiation Protection Authority, Østerås, 18 Feb 1994.
- Nielsen, S.P. Radiocological studies of semi-natural ecosystems. CEC Seminar on Semi-Natural Ecosystems, Brussels, Belgium, 21-25 Apr 1994.
- Nielsen, S.P. Quality assurance of radioanalytical data from Riso National Laboratory. Seminar of EC MORS, Helsinki, Finland, 30 May - 3 Jun 1994.
- Nielsen, T. Determination of air pollution components in the atmospheric boundary layer. Annual meeting of the Danish Centre for Atmospheric Research (DCAR), Copenhagen, Denmark, 2 Feb 1994.
- Nielsen, T., Egeløv, A.H., Grønby, K., Skov, H. Do vapor phase organic nitrates make up a significant

- part of the content of  $\text{NO}_x$  compounds in the atmosphere? Nordic Network Meeting on Atmospheric Chemistry, Helsingør, Denmark, 19-21 May 1994.
- Nielsen, T. Sammensætning af kvælstofforbindelser i atmosfæren - Findes der en ukendt gruppe af kvælstofforbindelser? 3. Danske Symposium i Analytisk Kemi, Københavns Universitet, H.C. Ørsted Institutet, Copenhagen, Denmark, 16-17 Aug 1994.
- Nielsen, T., Egelev, A.H., Granby, K., Skov, H. The influence of ozone on the  $\text{NO}_x$  composition. 9th TOR Workshop, Forschungszentrum Jülich, Germany, 18-20 Oct 1994.
- Pagsberg, P. Spectroscopy and kinetics of free radicals of importance in atmospheric chemistry. University of Linköping, Sweden, 3 Jun 1994.
- Pedersen, C. Relationship between recombination estimates and physical distances on the chromosomes of barley. Nordic Course in Plant Biotechnology, SLU, Uppsala, Sweden, 2-10 May 1994. Poster.
- Pedersen, C. Chromosome identification in barley and related species using a microsatellite sequence. 2nd International Triticeae Symposium, Logan, Utah, USA, 20-24 Jun 1994. Poster.
- Pedersen, C., Linde-Laursen, I. Genome and chromosome identification in *Triticeae* species by *in situ* hybridization with the GAA satellite. Kew Chromosome Conference IV, Royal botanic Gardens, Kew, England, 30 Aug - 2 Sep 1994. Poster.
- Pedersen, C., Linde-Laursen, I. Estimating relationship between the physical and genetic distances at the *Hor1* and *Hor2* loci of barley by two-colour fluorescent *in situ* hybridization. IVth workshop of the Nordic Genome Initiative "Beyond mapping single genes" Helsinki, Finland, 3-5 Sep 1994. Poster.
- Pilegaard, K. SMP/NECO deposition (oral presentation in Danish). Joint meeting of NECO and Health, Risø National Laboratory, 24 Mar 1994.
- Pilegaard, K. Deposition studies in SMP/NECO (oral presentation in Danish). Annual meeting, Danish Centre of Atmospheric Research, 2 Feb 1994.
- Pilegaard, K. Eddy-correlation flux measurements in Ulborg (oral presentation in Danish), NECO and Health workshop, Mønsted Laboratory, 20-21 Sep 1994.
- Pilegaard, K. Deposition of ozone and nitrogen compounds to terrestrial ecosystems (oral presentation in Danish). Seminar in Environmental Science and Technology Department, Risø National Laboratory, 6 Oct 1994.
- Pilegaard, K. Deposition of nitrogen oxides and ozone to Danish forest sites. Speciality Conference: Acid Rain Research, Do we have enough answers? S'Hertogenbosch, Holland, 10-12 Oct 1994.
- Pilegaard, K. SMP/NECO deposition projects. Meeting for the contact group for the Danish Centre of Research in Terrestrial Ecosystems. Lyngby, Denmark, 30 Nov 1994.
- Platz, J., Sehested, J., Nielsen, O.J. Atmospheric chemistry of  $\text{CCl}_3\text{CH}_3$ . Annual Meeting of the Danish Chemical Society at the University of Odense, Denmark, 14 Jun 1994.
- Platz, J., Nielsen, O.J., Sehested, J., Wallington, T. UV absorption spectra and kinetics of the degradation products of methylchloroform in the atmosphere. 3. Danske Symposium i Analytisk Kemi, Københavns Universitet, H.C. Ørsted Institutet, Copenhagen, Denmark, 16-17 Aug 1994.
- Platz, J., Sehested, J., Nielsen, O.J., Wallington, T.J. Atmospheric degradation of  $\text{CH}_3\text{CCl}_3$ . Nordic Network Meeting on Atmospheric Chemistry, Helsingør, Denmark, 19-21 Aug 1994. Abstract available.
- Plöger, A. Oprensnings- og analysemetode til HPLC-bestemmelse af monosakkarider med RI-detektion. Risø National Laboratory, Denmark, 2 Nov 1994.
- Rasmussen, S.K., Kjær, B., Petersen, C., Sørensen, L.D., Jensen, J. Barley serpins: Physical and genetic mapping and characterization of structural genes. 4th International congress of plant molecular biology, Amsterdam, Holland, 19-24 Jun 1994. Poster.
- Ravnkov, S. Functional compatibility in arbuscular mycorrhizas measured as hyphal P transport to the plant. Fourth European Symposium on Mycorrhizas, Granada, 11-14 Jul 1994.
- Roed, J., Andersson, K.G. Development of a Strategy for Decontamination of an Urban Area, CNEN/GSF/IAEA/CEC. International Workshop on Scientific bases for decision making after a radioactive contamination of an urban environment. Rio de Janeiro, Goiânia, Brazil, 29 Aug - 2 Sep 1994.
- Roed, J., Andersson, K.G. Early measurements in Scandinavia following the Chernobyl Accident. International Workshop on Scientific bases for decision making after a radioactive contamination of an urban environment. Rio de Janeiro, Goiânia, Brazil, 29 Aug - 2 Sep 1994.
- Rosendahl, L. Biological Nitrogen Fixation: Physiological and Biochemical Aspects. Institut for Jordbrugsvidenskab, U. Copen, (Ph.D. kursus), 19 May 1994.
- Sehested, J.  $\text{C}_3\text{C}$  reactions in the atmosphere. 12th Polish-Danish Symposium on Radiation Chemistry. 12th Polish-Danish Symposium on Radiation Chemistry. Institute of Physical Chemistry, Polish Academy of Science, Madralin, Poland, 4-7 Jun 1994.
- Sehested, J. Pulse radiolysis and FTIR studies of the atmospheric chemistry of halogenated compounds. Trombay symposium on radiation and photochemistry. Bhabha Atomic Research Centre, Bombay, India. 17-21 Jan 1994. Abstract available.
- Sehested, J., Nielsen, O.J. Studies of the reaction of  $\text{CF}_3\text{O}_2$  and  $\text{CF}_3\text{O}$  radical with  $\text{NO}$  at 295 K. Annual meeting of the Danish Centre for Atmospheric Research (DCAR), Copenhagen, Denmark, 2 Feb 1994.

- Sehested, J., Nielsen, O.J., Wallington, T.J.* Atmospheric chemistry of  $\text{CF}_3\text{CO}_2$  radicals. Nordic Network Meeting on Atmospheric Chemistry, Helsingør, Denmark, 19-21 Aug 1994. Abstract available.
- Sehested, J., Nielsen, O.J., Wallington, T.J.* Atmospheric chemistry of  $\text{CF}_3\text{C}(\text{O})\text{O}_2$  radicals: Kinetics of their reaction with  $\text{NO}_2$  and kinetics of the thermal decomposition of the product  $\text{CF}_3\text{C}(\text{O})\text{O}_2\text{NO}_2$ . 13th International Symposium on Gas Kinetics, University College Dublin, Ireland, 11-16 Sep. 1994. Abstract available.
- Sehested, K.* Formation and decay of peroxonitrous and peroxonitric acid in aqueous solutions. 12th Polish-Danish Symposium on Radiation Chemistry. Institute of Physical Chemistry, Polish Academy of Sciences, Madralin, Poland, 4-7 Jun 1994.
- Sehested, K., Holcman, J.* A pulse radiolysis study of the OH radical induced autoxidation of methanesulfonic acid. 8th "Tihany" Symposium on Radiation Chemistry. Hungarian Chemical Society. Balatonszéplak, Hungary, 3-8 Sep 1994.
- Sehested, K., Løgager, T., Holcman, J., Nielsen, O.J.* Formation and reactions of the  $\text{NO}_3$  radical in aqueous solution. Annual meeting of the Danish Centre for Atmospheric Research (DCAR), Copenhagen, Denmark, 2 Feb 1994.
- Solgaard, P.* Prøveoplukning i mikrobølgeovn og bestemmelse af sporelementer i fisk ved ICPMS. Levnedsmiddelstyrelsen, Copenhagen, Denmark, 15 Nov 1994.
- Sørensen, P.* The fate of  $^{15}\text{N}$ -labelled animal manure in soil. Afdeling for Planteernæring og Jordbundsvidenskab, Kiel University, Germany, 30 Nov 1994.
- Wilbrandt, R.* Resonance Raman spectroscopy of chemical intermediates. LASER'94, Dansk Optisk Selskab. Dansk Fysisk Selskab, Odense, Denmark, 12-13 Apr 1994. Abstract available.
- Wilbrandt, R.* Resonance Raman spectroscopy of chemical intermediates. 12th Polish-Danish Symposium on Radiation Chemistry "Transient Ionic Species and Excited Molecules in Radiation Chemistry and Spectroscopy", Warszawa, Poland, 4-7 June 1994.
- Wilbrandt, R.* Experimental and theoretical resonance Raman spectra of open-shell systems. European Research Conference on Theoretical Models of Chemical Reactivity. San Feliu de Guixols, Spain, 8-13 Sep 1994.
- Wilbrandt, R.* The structure of chemical intermediates by resonance Raman spectroscopy combined with ab initio calculations. Roskilde University Friday Seminars, Autumn 1994, Department of Life Sciences and Chemistry. Roskilde, Denmark, 2 Dec 1994.
- Østergård, H.* A model for density dependent regulation of a pathogen population. 7th International workshop on Epidemiology of Plant Diseases, Papendal, Holland, 10-15 Apr 1994.
- Østergård, H.* Gene-for-gene coevolution of cultivated barley and powdery mildew. XV Meeting of the Scandinavia Association of Geneticists, Aarhus, Aug 1994.
- Østergård, H.* Models for growth of a mixture of isolates. 3rd Cereal Mildew workshop (Cost-Action 817), Kappel am Albis, 5-10 Nov 1994.
- Østergård H., Damgaard, C.* Epidemiologiske modeller for meldugvækst. Dina-seminar, The Royal Veterinary and Agricultural University, Copenhagen, 31 May 1994.

## 10 Papers Accepted for Publication

- Ambus, P. Patterns of  $N_2O$  and  $CH_4$  fluxes along topographic gradients in Danish ecosystems. - Journal of Environmental Quality.
- Dahl, S.W., Rasmussen, S.K., Hejgaard, J. Subcloning and production of barley serpins in *E. coli*. Proc. 3rd International Symposium on Perspectives on Protein Engineering.
- Dahlgård, H. Radioactive tracers as a tool in coastal oceanography: an overview of the MAST-52 project. Journal of Marine Systems.
- Dahlgård, H., Herrmann, J., van Weers, A.W., Masson, M., Ibbett, R.D., Chen, Q. Quality assurance of the oceanographic tracers technetium-99 and antimony-125: intercomparisons and recovery tests. Journal of Marine Systems.
- Dahlgård, H., Herrmann, J., Salomon, J.C. A tracer study of the transport of coastal water from the English Channel through the German Bight to the Kattegat. Journal of Marine Systems.
- Dahlgård, H., Chen, Q., Herrmann, J., Nies, H., Ibbett, R.D., Kershaw, P.J. On the background level of  $^{99}Tc$ ,  $^{90}Sr$  and  $^{137}Cs$  in the North Atlantic. Journal of Marine Systems.
- Dahlgård, H. Transfer of European coastal pollution to the Arctic: Radioactive tracers. Marine Pollution Bulletin.
- Damgaard, C., Østergård, H. Density dependent growth of powdery mildew on a partial resistant barley variety: infection efficiency and spore production. Proceedings of 3rd Cereal Mildew workshop (Cost-Action 817), Kappel am Albis, 5-10 Nov 1994, Kluwer Academic Press.
- Doll, H., Søgaard, B. Klinte - en gammel ukrudtsplante med nye muligheder. Jord og Viden.
- Doll, H., Holm, U., Søgaard B., Bay, H. Phenolic compounds in barley varieties with different degree of partial resistance against powdery mildew. International Scientific Symposium: Natural Phenols in Plant Resistance, 13-17 September 1993, Freising-Weihenstephan, Germany.
- Giese, H., Hippe-Sandwald, S., Somerville, S., Weller, J.P. Chapter 21, *Erysiphe graminis*, The Mycota. K. Esser and P.A. Lemke (eds), In: Volume VI "Plant Relationships". G. Carroll and P. Tudzynski (eds).
- Grøn, C. AOX in Groundwater. Proceedings of the International Conference on Naturally Produced Organohalogens, Delft, 14-19 Sep 1993.
- Hansen, H.J.M., Olsen, A.G., Rosenkilde, P. Formation of phosphatidylethanolamine as a putative regulator of salt transport in the gills and esophagus of the rainbow trout (*Oncorhynchus mykiss*). Comp. Biochem. Physiol. B.
- Hovmøller, M.S., Munk, L., Østergård, H. Comparison of mobile and stationary spore sampling techniques for estimating virulence frequencies in aerial barley powdery mildew populations. Plant Pathol.
- Hummelshøj, P., Pilegaard, K., Jensen, N.O. (1994) Flux measurements of  $O_3$  and  $NO_2$  over a regrown wheat field. In: Proceedings of the EUROTRAC Symposium '94. P. Borell (ed). SPN Academic Publishing bv., The Hague, The Netherlands.
- Jakobsen, I. Transport of phosphorus and carbon in VA mycorrhiza. In: Mycorrhiza: Function, Molecular Biology and Biotechnology. B. Hock and A. Varma (eds).
- Jensen, B.K., Jensen, E.S., Magid, J. Decomposition of  $^{15}N$ -labelled ryegrass in soils from a longterm field experiment with different manuring strategies. Biological Agriculture and horticulture 3.
- Jensen, E.S. Cycling of grain legume residue nitrogen. Biological Agriculture and Horticulture.
- Joner, E., Jakobsen, I. Utilization of P from organic matter by mycorrhizal subterranean clover (*T. subterraneum* L.) at low root length densities. Plant and Soil.
- Joner, E., Jakobsen, I. Growth and extracellular phosphatase activity of arbuscular mycorrhizal hyphae as influenced by soil organic matter - Soil Biology and Biochemistry
- Joner, E., Magid, J., Gahoonia, T., Jakobsen, I. Phosphorus depletion and activity of phosphatases in the rhizosphere of mycorrhizal and non-mycorrhizal cucumber (*Cucumis sativus* L.) - Soil Biology and Biochemistry.
- Jørgensen, R.B., Andersen, A., Landbo, L., Mikkelsen, T. Spontaneous hybridization between oilseed rape (*Brassica napus*) and weedy relatives. Acta Horticulturae.
- Knudsen, E., Jensen, M., Solgaard, P., Sørensen, S.S., Sandström, B. Zinc absorption estimated by fecal monitoring of zinc stable isotopes validated by comparison to whole body retention of zinc radioisotopes in humans. The Journal of Nutrition
- Lyngkjær, M., Østergård, H., Munk, L. Papilla formation in leaves of Mlo-resistant barley attacked by Mlo-virulent powdery mildew. Proceedings of 3rd Cereal Mildew workshop (Cost-Action 817), Kappel am Albis, 5-10 Nov 1994, Kluwer Academic Press.
- Masson, M., van Weers, A.W., Groothuis, R.E.J., Dahlgård, H., Ibbett, R.D. Time series for sea water and seaweed of Tc-99 and Sb-125 originating from releases at La Hague. Journal of Marine Systems.

- Møgelberg, T.E., Nielsen, O.J., Sehested, J., Wallington, T.J., Hurley, M.D. Atmospheric chemistry of HFC-272a: Spectrokinetic investigation of the  $\text{CH}_3\text{CF}_2\text{CH}_2\text{O}_2$  radical, its reactions with NO and  $\text{NO}_2$ , and the fate of the  $\text{CH}_3\text{CF}_2\text{CH}_2\text{O}$  radical. *J. Phys. Chem.*
- Nielsen, S.P. A box model for North-East Atlantic coastal waters compared with radioactive tracers. *Journal of Marine Systems.*
- Olsson, P.A., Bååth, E., Jakobsen, I., Söderström, B. The use of phospholipid and neutral lipid fatty acids to estimate biomass of arbuscular mycorrhizal fungi in soil. *Mycological Research.*
- Pedersen, C. Relationship between recombination estimates and physical distances on the chromosomes of barley. Conference booklet. Nordic Course in Plant Biotechnology. The Swedish University of Agricultural Sciences, Uppsala (S), 2-10 May 1994.
- Pedersen, C., Linde-Laursen, I. Visualization of hordeins and telomeric repeats by two-colour fish to barley chromosomes. In: "Beyond mapping single genes" Conference booklet. 4th workshop of the Nordic Genome Initiative, Helsinki, Finland, 3-5 Sep 1994.
- Platz, J., Nielsen, O.J., Sehested, J., Wallington, T.J. Atmospheric chemistry of 1,1,1-trichloroethane: UV spectra and self-reaction kinetics of  $\text{CCl}_3\text{CH}_2$  and  $\text{CCl}_3\text{CH}_2\text{O}_2$  radicals, kinetics of the reactions of the  $\text{CCl}_3\text{CH}_2\text{O}_2$  radical with NO and  $\text{NO}_2$ , and the fate of the alkoxy radical  $\text{CCl}_3\text{CH}_2\text{O}$ . *J. Phys. Chem.*
- Pilegaard, K., Jensen, N.O., Hummelshøj, P. Deposition of nitrogen oxides and ozone to Danish forest sites. In: Proceedings of the Speciality Conference: Acid Rain Research. Do we have enough answers? T. Schneider (ed.). Elsevier.
- Ravnkov, S., Jakobsen, I. Functional compatibility in arbuscular mycorrhizas measured as hyphal P transport to the plant. *New Phytologist.*
- Sehested, K., Holcman, J. A pulse radiolysis study of the OH radical induced autoxidation of methanesulfonic acid. *Radiat. Phys. Chem.*
- Sørensen, P., Jensen, E.S. Mineralization-immobilization and plant uptake of nitrogen as influenced by the spatial distribution of cattle slurry in soils of different texture. -- Plant and Soil
- Sørensen, P., Jensen, E.S. Mineralization of carbon and nitrogen from fresh and anaerobically stored sheep manure in soils of different texture. *Biol. Fertil. Soil.*
- Wallington, T.J., Schneider, W.F., Møgelberg, T.E., Nielsen, O.J., Sehested, J. "Atmospheric Chemistry of  $\text{FCO}_x$  Radicals: Kinetic and Mechanistic Study of the  $\text{FC(O)O}_2 + \text{NO}_2$  Reaction". *Int. J. Chem. Kinet.*
- Wallington, T.J., Schneider, W.F., Szente, J.J., Maricq, M.M., Nielsen, O.J., Sehested, J. "Atmospheric chemistry of FNO" and  $\text{FNO}_2$ : Reactions of FNO with  $\text{O}_3$ ,  $\text{O}(^3\text{P})$ ,  $\text{HO}_2$ , and HCl and the reaction of  $\text{FNO}_2$  with  $\text{O}_3$ ". *J. Phys. Chem.*
- Østergård, H. Gene-for-gene coevolution of cultivated barley and barley powdery mildew (Abstract). XV Meeting of the Scandinavian Association of Geneticists. *Hereditas.*
- Østergård, H. Models for growth of a mixture of isolates. Proceedings of 3rd Cereal Mildew workshop (Cost-Action 817), Kappel am Albis, 5-10 Nov 1994, Kluwer Academic Press.

# 11 Education

## 11.1 Doctorates

*Engvild, K.C.* (Dr.Scient. Thesis), 1994: "The Chloroindole Auxins of Pea, Strong Plant Growth Hormones or Endogenous Herbicides?". Risø National Laboratory and University of Roskilde, 120 p.

## 11.2 Titles of Honour

*Pagsberg, P.* has received an Honorary Doctorate at Technical University, Linköbing, Sweden.

## 11.3 Ph.D. Theses

*Kjær, B.J.*, 1994. Use of molecular markers to identify quantitative trait loci in barley. Ph.D. Thesis, Risø National Laboratory and Royal Vet. and Agricultural University, Copenhagen, 114 p.

*Lange, C.*, 1994: The Protective Value of Houses. Indoor Deposition. Ph.D. Thesis, Risø National Laboratory and Technical University, Copenhagen, 116 p.

*Løgager, T.*, 1994. A study of aqueous phase reactions relevant for atmospheric chemistry. Ph.D. Thesis, Risø National Laboratory and University of Copenhagen, 115 p.

*Sehested, J.*, 1994. Atmospheric chemistry of hydrofluorocarbons and hydrochlorofluorocarbons. Ph.D. Thesis, Risø National Laboratory and University of Copenhagen, 120 p.

## 11.4 M.Sc. Theses

*Ravnkov, S.*, 1994: Functional compatibility in arbuscular mycorrhizas. Risø National Laboratory and University of Copenhagen, 29 p.

*Østerby, S. and Vesterager, J.M.*, 1994: Symbiotic N<sub>2</sub> fixation by the cover crop *Pueraria phaseoloides* as influenced by litter mineralization. Risø National Laboratory and Royal Vet. and Agricultural University, Copenhagen, 52 p.

## 11.5 B.Sc. Theses

*Eskelund, L.*, 1994: Arbuscular mycorrhizas. Risø National Laboratory and Royal Vet. and Agricultural University, Copenhagen, 38 p.

*Nørgaard, A.*, 1994: DNA-sekventering af en chymotrypsin inhibitor fra hvide serpin familien. Risø National Laboratory and Denmark's Academy for Engineering, 71 p.

## 11.6 External Examiners

*Aarkrog, A.* First opponent at Per Strand's Dr.philos thesis at Oslo University, Jan 28, 1994.

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

*Giese, H.* Censor in plant science, The Royal Veterinary and Agricultural University, Copenhagen.

Censor in biology, Aarhus University.

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

*Hansen, H.J.M.* Censor at Odense University.

*Haahr, V.* Censor in plant crop husbandry at The Royal Veterinary and Agricultural University.

*Jakobsen, I.* Censor in soil microbiology at The Royal Veterinary and Agricultural University.

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

*Jørgensen, J.H.* Censor in plant science, The Royal Veterinary- and Agricultural University, Copenhagen.

*Jørgensen, R.B.* Censor in Biology, Aarhus University.

Censor at Industrial Research Education - Ph.D. Marianne Madsen: Pajbjerg (Aarhus University).

*Linde-Laursen, I.* Censor, Institute of Genetics, University of Lund, Sweden.

Censor in genetics, Section of Genetics, The Royal Veterinary- and Agricultural University, Copenhagen.

*Nielsen, O.J.* Censor in kinetic studies on the reaction of ozone with alkenes and haloalkenes at the University College Dublin, Ireland.

*Nielsen, O.J.* Censor in fluxes of nitrous oxide between soils and the atmosphere. The University of Copenhagen.

*Pilegaard, K.* Censor in environmental science at the Technical Universities in Denmark.  
Censor in biology at Danish Universities.

*Rasmussen, S.K.* Censor in plant science, Department of Plant Biology, The Royal Veterinary- and Agricultural University, Copenhagen.

Censor, Slagteriskolen in Roskilde.

*Wilbrandt, R.* Censor in synthesis and spectroscopy of configurationally locked conjugated trienes at the University of Leiden, The Netherlands.

Censor at Ph.D. exam, Odense University.

*Østergård, H.* Censor at Institute of Genetics and Ecology, Aarhus University.

## **11.7 External Teaching**

*Aarkrog, A.* Lectured 20-25 February 1994 in Radioecology on Medical College of St. Bartholomew's Hospital. University of London.

## 12 Exchange of Scientists

- Abdel-Fattuh, A.A.-H.**, IAEA-Stip., National Center for Radiation Research and Technology, Cairo, Egypt (8 months).
- Annum, K.**, University of Bern, Switzerland (1 week).
- Anestasi, C.**, University of York, England (2 week).
- Bajdor, K.**, Industrial Chemistry Research Institute, Warsaw, Poland (8 weeks).
- Bird, D.**, University of York, England (1 week).
- Bobrowski, K.**, Institute of Biochemistry & Biophysics, Warsaw, Poland (2 weeks).
- Brouwer, F.**, University of Amsterdam, The Netherlands (2 weeks).
- Brown, J.**, JI Centre for Plant Science Research, Cambridge Laboratory, England (1 week).
- Cheng, B.F.**, Svalöv/Weibull, Sweden (1 week).
- Christensen, H.**, Studsvik AB, Nyköping, Sweden (1 week).
- Davydov, Y.**, Institute of Radioecological Problems Academy of Sciences, Belruss (1 week).
- Deichman, V.**, Royal Vet. and Agricultural University, Denmark (1 week).
- Demeter, A.**, Central Research Institute for Chemistry of the Hungarian Academy of Sciences (1 week).
- Daashjerg, K.**, University of Aarhus, Denmark (2 months).
- Felsenstein, F.G.**, Technische Universität München, Freising, Germany (2 weeks).
- Finlayson-Pitts, B.**, University of California, Irvine, USA (1 week).
- Forsberg, S.**, Sweden, (1 week).
- Galkin, G.**, A.A. Bochvar All-Russia Scientific Research Institute of Inorganic Materials, Russia (4 weeks).
- Geppert, W.D.**, Institute für Strahlenchemie, Vienna, Austria (5 weeks).
- Getoff, N.**, University of Vienna, Austria (4 weeks).
- Grahowska, A.**, Polish Academy of Sciences, Warsaw, Poland, (1 week).
- Heathfield, A.E.**, University of York, England (3 weeks).
- Hickel, B.**, CNRS, SACLAY, France (1 week).
- Ikram, A.**, Microbiol. Division, The Rubber Research Institute of Malaysia (RRIM) (3 weeks).
- Itenov, K.**, Statens Planteavlfsforsøg, Afd. for Korn, Frø- og Industriafrøder, Denmark (1 week).
- Junovský, J.**, Nuclear Research Institute, Rez, Czech Republic (4 weeks).
- Jestin, I.M.**, University of Bordeaux, France (9 months).
- Johansen, A.**, Visiting scientist at Department of Microbial Ecology, University of Lund (4 months).
- Johansen, L.**, Pajbjergfonden, Denmark (1 week).
- Joner, E.**, Agricultural University of Norway (4 weeks).
- Kuchuro, I.**, Institute of Physiology, Academy of Sciences, Belruss (1 week).
- Kjærgård, G.**, Statens Planteavlfsforsøg, Afd. for Korn, Frø- og Industriafrøder, Denmark (1 week).
- Kling, M.**, Inst. of Microbiology, Swedish Agricultural University, Uppsala, Sweden (3 months).
- Kownacki, K.**, Polish Academy of Sciences, Warsaw, Poland (2 weeks).
- Langer, S.**, University of Gothenburg, Sweden (2 weeks).
- Lannou, C.**, INRA, France (1 week).
- Lee, S.-B.**, Crop Experimental Station, Suwon, Korea (3 weeks).
- Ljungström, E.**, University of Gothenburg, Sweden (2 weeks).
- Lu, B.-R.**, International Rice Research Institute (IRRI), Philippines (1 week).
- Lydiate, L.**, John Innes Institute, England (1 week).
- McLaughlin, W.L.**, National Institute of Standards and Technology, USA (2 weeks).
- Mithen, R.**, John Innes Institute, England (1 week).
- Obata, Kazuichi**, Japan Atomic Energy Research Institute. (3 months).
- Oester, B.**, Westfälische Wilhelms-Universität, Münster, Germany (1 week).
- Pitts, Jr., J.**, University of California, Irvine, USA (1 week).
- Postek, R.**, Narodowa, Warszawa, Poland (1 week).
- Ratajczak, E.**, University of Wroclaw, Poland (3 months).

- Solar, S.*, University of Vienna, Austria (3 weeks).
- Strzelczak-Burlinska, G.*, Institute of Biochemistry & Biophysics, Warsaw, Poland (2 weeks).
- Sucević, Z.*, Ruder Bosković Institute, Zagreb, Croatia (8 weeks).
- Sudin, M.N.*, Microbiol. Division, The Rubber Research Institute of Malaysia (RRIM) (2 weeks).
- Sørensen, P.*, Visiting Research Fellow at CSIRO, Division of Soils, Australia (4 months).
- Tichelen, K. van*, Instituut voor Plantkunde, Kardinaal Mercierlaan 92, Belgium (1 week).
- Togawa, O.*, Tokai Research Establishment, Japan Atomic Energy Research Institute (1 year).
- Voronik, N.*, Institute of Radioecological Problems Academy of Sciences, Belruss (4 weeks).
- Wallington, T.*, Ford Motor Co., Dearborn, USA (2 weeks).

## 13 Main Cooperative Projects

Risø project coordinators are marked with \*  
Principal investigators are marked with \*\*

Arctic Monitoring Assessment Programme (AMAP). *A. Aarkrog*.

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

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

Pathways of radionuclides emitted by non-nuclear industries ( $^{210}\text{Po}$ ,  $^{210}\text{Pb}$ ). EU project in collaboration with partners in Netherlands, Ireland, France, Spain, Portugal and UK. *H. Dahlggaard*.

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. Dahlggaard, S.P. Nielsen*.

Nordic Radioecology Cooperation (NKS/ECO). ECO1 - Marine Radioecology; ECO2 - Terrestrial Radioecology. *H. Dahlggaard, S.P. Nielsen, Morten Strandberg*.

Transuranics in the Marine Environment. EU project in collaboration with partners in Ireland, U.K., France, Spain, Italy, Sweden and Norway. *H. Dahlggaard, 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). *S.P. Nielsen*.

Exemption of radiation sources and practices from regulatory control for disposal into the marine environment. International Atomic Energy Agency, Vienna. *S.P. Nielsen*.

Modelling of the radiological impact of radioactive waste dumping in the Arctic seas. International Atomic Energy Agency, Vienna. *S.P. Nielsen*.

Dumping of radioactive material in the Barents and Kara Seas. Radiation Protection Authority of Norway. *S.P. Nielsen*.

Uptake of Nitrogen compound by above ground plant parts. Collaborator: National Environmental Research Institute DK. *K. Pilegaard*.

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*.

Risø's integrated environmental project (RIMI). *K. Pilegaard\*, O.J. Nielsen, T. Nielsen, P. Solgaard*.

EU-project on Deposition in Urban Areas. Collaborators: UKAEA, Harwell, GSF, München. *J. Roed*.

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

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

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

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

Mapping of the pollution situation in Byelorussia. Collaborator: Danish Toxicology Center. *J. Roed, K. Andersson*.

NKS-Project BER 6. Countermeasures. Collaborators: SSI, Stockholm, SIS, Oslo, STUK, Helsinki and Swedish University of Agricultural Science, Uppsala. *J. Roed, K. Andersson*.

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*.

Implementation of wet oxidation techniques to decontaminate polluted materials in cooperation with Conor Pacific Environmental Technologies Inc. *A.B. Bjerre, E. Sørensen, V. Gundersen\**.

Conversion of Biomass. EFP-project. Collaborator: Technical University of Denmark, *A.B. Bjerre\*, Emil Sørensen*.

Test runs of catalyst productions. *B. Bukholt, V. Gundersen\**.

The Isotope Geochemistry of Humic Groundwaters. National Hydrology Research Institute, Environment Canada. *C. Grøn\**.

Ultrafiltration in Drinking Water Treatment of Humic Waters. Department of Chemical Engineering, Technical University of Denmark and Dow Danmark A/S. *C. Grøn\**.

Structures and Reactivity of Organic Matter in Aquifers. Department of Geology and Geotechnical Engineering, Technical University of Denmark, as part of research programmes within the Strategic Environmental Research Programme (SMP) and a Danish Natural Sciences Research Council (SNF) programme. *C. Grøn\**.

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 Risø). *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\**.

FØTEK. Collaborators: Levnedsmiddelstyrelsens Centrallaboratorier and others. *P. Solgaard\**.

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

EF-akvasystem. Determination of Al. *P. Solgaard*.

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

Uncertainties in the Modelling of Migration Phenomena. 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\*\**.

Euromet. Collaboration with National Physical Laboratory, UK on calibration and measurements of ionizing radiation. *A. Miller.*

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.*

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.*

Danish Environmental Research programme (SMP). Heterogeneous processes. *O.J. Nielsen.*

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

Atmospheric chemistry of alternative fuels. Collaborators: Ford Motor Company, Detroit, USA, and University of Gothenburg. *O.J. Nielsen.*

DCAR-MST-Traffic-PAH. Collaborators: National Environmental Research Institute, Institute of Toxicology, Dk-Technics, Office of Copenhagen of Environmental Surveillance, Meteorology and Wind Energy Department. *T. Nielsen\*\*.*

EMEP-Long Range Transport of Nitrogen Compounds and Photochemical Oxidants. National Collaborators: National Environmental Research Institute, Meteorology and Wind Energy Department. *T. Nielsen\*\*.*

EUROTRAC-DCAR-TOR. National Collaborators: National Environmental Research Institute, Meteorology and Wind Energy Department. *T. Nielsen\*\*.*

NMR-Photochemical oxidants. National Collaborators: National Environmental Research Institute, Meteorology and Wind Energy Department. *T. Nielsen.*

SMP-Atmospheric Nitrogen Compounds Composition. Collaborators: National Environmental Research Institute. *T. Nielsen\*\*.*

SMP-POM Physical Environmental Chemistry. Collaborators: Institute of Toxicology, Department of Solid Phase Chemistry and Physics, Department of Combustion. *T. Nielsen\*\*, A.B. Bjerre, C. Helweg, G. Gissel-Nielsen, B. Skytte Jensen, H. Kunzendorff, E. Sørensen.*

EU-project "CYTROXA" on atmospheric chemistry of aromatic hydrocarbons. Collaboration with four European laboratories. *P. Pagsberg.*

EU-project on Removal and interconversions of oxidants in the atmospheric aqueous phase (RINOXA). *K. Sehested\*.*

Danish Natural Science Research Council: Collaboration within "Center for Molecular Dynamics and Laser Chemistry". *G. Due Billing\*\*, K. Mikkelsen, S. Keiding, N. Bjerre, O. Sonnich Mortensen, F. Jensen, N. Engholm Henriksen, F. Yssing Hansen, C. Nyeland, R. Wilbrandt\*.*

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

Intramolecular proton transfer. Collaborators: Polish Academy of Sciences, Warsaw, Poland, University of Arizona, USA. *R. Wilbrandt\*, A. Mordzinski\*\*, K. Kownacki\*\*, A. Grabowska, A. Adamowicz\*\*.*

Radical cations of donor-acceptor systems. Collaborator: University of Amsterdam, The Netherlands. *R. Wilbrund\**, *A.M. Brouwer\*\**.

Polyene triplet states. Collaborators: State University of Leiden, The Netherlands. *R. Wilbrund\**, *H.J.C. Jacobs\*\**, *A. ten Wolde*.

The triplet state of stilbenes. Collaborators: University of Bologna, Italy. *R. Wilbrund\**, *G. Orlandi\*\**, *F. Zerbetto\*\**, *F. Negri*.

The benzyl radical and its derivatives. Collaborators: Industrial Chemistry Research Institute, Poland, University of Bologna, Italy. *R. Wilbrund\**, *K. Bajdor\*\**, *G. Orlandi\*\**.

The photochemistry and photophysics of truxene. Collaborator: Copenhagen University, (Ph.D. project J. Frederiksen). *R. Wilbrund\**, *N. Hurrit*, *K. Bechgaard*.

Radical cations of polyenes. Collaborator: Harvey Mudd College, USA. *R. Wilbrund\**, *R.J. Cave*, *T. Keszthelyi\*\**.

EU project on the ammonium hypothesis of spruce decline. Subcontract to the National Forest and Nature Agency. *K.C. Engvild*.

Computer Aided Farming (CAF). Collaborator: Foulum Research Station, Research Centre of Agriculture, Skejby. *V. Huahr*, *A. Jensen*.

SJVF project "Soil Microbiology". Collaborator: The Royal Veterinary and Agricultural University, Copenhagen, University of Lund. *I. Jakobsen*.

NKJ project "Utilization of mycorrhizas in sustainable agriculture". Collaborators: Agricultural University of Norway, Agricultural Research Centre of Finland, *I. Jakobsen*.

Pesticide research: Effects of pesticides on decomposition and growth processes in the root zone. Collaborators: University of Copenhagen, Royal Veterinary and Agricultural University, Danish Institute of Plant and Soil Science, National Environmental Research Institute, *I. Jakobsen*.

Nutrient transport in VA mycorrhizas. Collaborators: INRA, Dijon, France; The University of Western Australia. *I. Jakobsen*.

Evaluating the role of legume cover crops in the nitrogen nutrition of rubber 1989-1994. CE project under The International Scientific Cooperation Programme. Collaborator: The Rubber Research Institute of Malaysia, Kuala Lumpur. *I. Jakobsen*, *E.S. Jensen\**.

Danish Strategic Coordinated Environmental Research Programme: Influence of crop residue particle size and spatial distribution in soil on the mineralization-immobilization turnover, plant uptake and losses of nitrogen. 1992-1996. Collaborators: Danish Centre for Root Zone processes, nutrient losses from agro-ecosystem and processes in riparian areas. *E.S. Jensen\**, *P. Ambus\*\**.

Research Programme: Ecological Farming: Symbiotic nitrogen fixation in biologically cultivated clover-grass fields. 1993-1997. Collaborators: The Royal Veterinary and Agricultural University, Copenhagen, and Research Centre Foulum. *E.S. Jensen\**, *F.B.V. Jørgensen\*\**.

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

Compound exchange in symbiotic nitrogen fixation. Collaborator: B.U. Jøchimsen, University of Aarhus. *L. Rosendahl*.

Research programme: Sustainable Agriculture Project: Cycling of nitrogen from animal manure and plant residues. 1992-1996. Collaborator: Department of Plant Nutrition and -Physiology, Danish Research Service for Plant and Soil Science. *P. Sørensen\*\**, *E.S. Jensen\**.

Interaction between crop plants and weeds. Collaborator: B. Søgaard, 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. Søgaard, The Royal Veterinary and Agricultural University. *H. Dull\**.

Genetic markers for embryogenesis in barley. Collaborators: University of Copenhagen; D. Bowles, Leeds University, U.K. *H. Giese\*, E.T. Larsen*.

Linkage map of the barley genome. Collaborators: The Royal Veterinary and Agricultural University; the Danish plant breeding stations: Abed, Sejet, Pajbjerg; European and American barley geneticists. *H. Giese\*, J. Jensen, L. Petersen, S.K. Rasmussen*.

Molecular genetics of *Erysiphe graminis* f.sp. *hordei*, the causal agent of barley powdery mildew. Collaborators: Danish Plant biotechnology Research Center; The Royal Veterinary and Agricultural University; J. McDermott, ETH Zentrum, Zürich. *H. Giese\*, M. Lyngkjær, S. Christiansen*.

Oilseed Rape Initiative. Collaborators: O. Rasmussen, University of Aarhus, B. Eggum, Foulum Research Station; J. Schjørring, The Royal Veterinary and Agricultural University; P. Ulvskov, Research Centre for Plant Protection. *H. Giese*.

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

Improvement of protein quality in barley. Collaborator: B.O. Eggum, Foulum Research Station; J. Hejgaard, Technical University of Copenhagen. *J. Jensen, S.K. Rasmussen\**.

Evaluation of cereal genetic resources in the Nordic Gene Bank. Collaborators: Nordic Gene Bank, Alnarp, and the Agricultural University, Sweden; Boreal Plant Breeding, Finland; SFL Apelsvoll, Norway. *J.H. Jørgensen*.

New sources of powdery mildew resistance genes in barley. Collaborators: Three Danish cereal breeding companies. *J.H. Jørgensen, H.P. Jensen*.

Risk assessment of genetically modified plants. Collaborators: Patrick Rüdesheim, PGS, Belgium; A. Buchter-Larsen, Maribo Seed; G.S. Poulsen, The Royal Veterinary and Agricultural University; F.B. Christiansen, Aarhus University. *R.B. Jørgensen\*, H. Østergård\*, T. Mikkelsen, L. Landbo, T. Hunser*.

Polyplloid *Hordeum* species. Collaborators: R. von Bothmer, Department of Crop Genetics and Breeding, The Swedish University of Agricultural Sciences, Svalöv, Sweden. *I. Linde-Laursen*.

Recombination estimates and physical/chemical distances on the chromosomes. Collaborators: The Royal Veterinary and Agricultural University. *I. Linde-Laursen, H. Giese, C. Pedersen*.

Resistance response-genes in barley. Collaborators H. Thordahl-Christensen, David Collinge, The Royal Veterinary and Agricultural University, Copenhagen. *S.K. Rasmussen*.

Protein engineering of plant serpins. Collaborators: A. van Dijk, Heikeken Leiden, Holland, J. Hejgård, Technical University of Denmark. *S.K. Rasmussen\*, S.W. Dahl*.

Molecular strategies for improving crop protection. Collaborators: K.G. Welinder, Copenhagen University, J. Hejgård, Technical University of Denmark, J. Mundy, Carlsberg Laboratory, *S.K. Rasmussen\*, P.W. Jensen*.

Biotechnological frame work programme for disease resistance in plants. Collaborator: The Royal Veterinary- and Agricultural University, Copenhagen. *S.K. Rasmussen\*, Brian K. Kristensen*.

Barley Serpins. Collaborators: J. Hejgård, Technical University of Denmark. *S.K. Rasmussen, L.D. Sørensen, A. Nørgaard, S.W. Dahl*.

Linkage map of Norway spruce. Collaborator: H. Wellendorf, The Arboretum, Hørsholm. E. Skov\*, H. Giese.

COST 817: Population biology of airborne pathogens on cereals. Collaborators: M. Hovmøller, Bent Nielsen, Research Centre for Plant Protection, and L. Munk, The Royal Veterinary and Agricultural University. H. Østergård, J.H. Jørgensen, H.P. Jensen, M. Lyngkjær, C. Damgaard.

## 14 Guest Lectures

*Dr. R. von Bothmer*, Department of Crop Genetics and Breeding, Swedish University of Agricultural Science, Svalöv, Sweden: "Genetiske resourcer og deres anvendelse i planteforædlingen".

*Dr. J. Brown*, John Innes Centre for Plant Science Research, Norwich, UK: "Molecular and cellular aspects of the barley-mildew interaction".

*Dr. S. Christensen*, Department of Weed Control, Flakkebjerg, Denmark: "Afgødernes udnyttelse af lysenergi. Optagelse og udnyttelse af lys i hvedesorter bestemt ved telemåling".

*Dr. D.B. Collinge*, The Royal Veterinary and Agricultural University, Copenhagen, Denmark: "Defense mechanisms in barley".

*Dr. H. Dalbøge*, Novo Nordisk A/S, Symbion, Denmark: "Isolering af svampeenzymgener ved ekspressionskloning i gær".

*Dr. S. Duke*, United States Department of Agriculture, ARS, Mississippi, USA: "Trends in transgenic crop research in the USA, biological considerations and risk assessment".

*Dr. B. Eggum*, Foulum Research Station, Denmark: "Proteinkvalitet i cerealier med fokus på højlysin byg".

*Dr. F.G. Felsenstein*, Department of Agronomy and Plant Breeding, TU Munich-Weihenstephan, Germany: "Investigations on virulence and fungicide sensitivity of cereal powdery mildews at Weihenstephan".

*Professor B. Finlayson-Pitts*, University of California, Irvine, USA: "Heterogeneous" reactions in the lung: A possible key to the understanding of the effects of inhaled ozone".

*Professors B. Finlayson-Pitts and J.N. Pitt, Jr.*, University of California, Irvine, USA: "Future perspectives in air pollution research".

*Dr. C. Hammer*, University of Copenhagen, Denmark: "Measurements and results from GRIP (Greenland Ice Cove Project)".

*Dr. K. Hjortsholm*, Sejet Plant Breeding, Denmark: "Bæredygtig planteforædling".

*Dr. A.L. Jensen*, Foulum Research Station, Denmark: "Et modelbaseret beslutningsstøttesystem til kontrol af meldug".

*Dr. B. Krebs*, Institute of Genetic and Ecology, University of Aarhus, Denmark: "Ecological genetics of resistance to high temperature stress".

*Dr. L. Lange*, Novo Nordisk, Denmark: "Mikrobielle fungicider".

*Dr. E. Ljungström*, University of Göteborg, Sweden: "On the importance of nitrate radical reactions in Scandinavia".

*Dr. B. Nielsen*, Danish Institute of Plant and Soil Science, Lyngby, Denmark: "Fungicidanvendelse og fungicidresistens".

*Dr. B. Oeser*, Münster, Germany: "*Claviceps purpurea*: Host parasite interaction".

*Dr. Th. Pedersen*, H.C. Ørsted Institute, Copenhagen, Denmark: "Om måling af søjler og profiler af atmosfæriske molekyler og partikler." (Measurement of particles in the atmosphere).

*Professor J.N. Pitts, Jr.*, University of California, Irvine, USA: "Role of atmospheric transformations in California's novel strategies for the control of two major environmental problems: (1) Ozone, and (2) The "Med Fly".

*Professor J.N. Pitts, Jr.*, University of California, Irvine, USA: "Atmospheric transformations and health risks assessments for indoor air pollutants, PAH and diesel exhaust: A California perspective."

*Dr. T. Schwarzacher*, Karyobiology Group, John Innes Centre, Norwich, UK: "Genomic *in situ* hybridization".

*Dr. O. Seberg*, University of Copenhagen, Denmark: "Molekyler og morfologi: Kan vi se skoven for bare træer".

*Dr. D. Simpson*, Department of Physiology, Carlsberg Laboratory, Denmark: "Transport and targeting of hordeins in barley endosperm".

*Dr. P. Steen*, Maribo Seed Danisco, Denmark: "Status for field trials at Maribo Frø with transgenic crops".

*Dr. J. Stehr*, University of Minnesota, USA. "The Isotopes of Ozone: Why Can't This Molecule Just behave Itself?."

*Dr. M.M. Svenning*, University of Tromsø, Norway: "Indigenous *Rhizobium* isolates described by REP- and ERIC-primers".

*Dr. I. Thingstrup*, University of Copenhagen, Denmark: "Detektion of mykorrhizasvampe".

*Dr. T.J. Wallington*, Ford Motor Company, Dearborn, USA: "Atmospheric chemistry of CFC replacements: An assessment of their environmental impact."

*Dr. S. Widell*, University of Lund, Sweden: "The plasma membrane-associated cytoskeleton in plants".

## 15 Committee Membership

### 15.1 National

*Aarkrog, 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.

*Giese, H.* The Danish Agricultural and Veterinary Research Council.  
Board of The Institute of Forest and Landscape.  
Board of Danish Polar Center.  
Danish Society for the Conservation of Nature, Committee for Environmental Issues.

*Gissel-Nielsen, G.* Vice chairman of The Danish Agricultural and Veterinary Research Council.  
Danish Academy of Technical Sciences.  
Governing board of Danish Institute of Plant and Soil Science.  
Danish Society for the Conservation of Nature, Committee for Environmental Issues.  
Danish Space Committee, Commission for remote sensing.

*Gundersen, V.* Board of Society of Chemical Engineers in DIF Deputy Chairman.

*Gundersen, V.* Working Committee for Chemical Technology, Environment and Safeguard.

*Jensen, A.* Member of the board of directors for Pajbjergfonden, Denmark.  
DCAR, Danish Center of Atmospheric Research.  
DaFoLa, Danish Center for Forest and Landscape Ecosystem Research.  
Invited member of The Rockwool Foundation Research Unit discussion group "how to value "nature" in environmental policy".  
Chairman of the evaluation panel concerning aquatic and terrestrial ecotoxicology in The Danish Environmental Research Programme.  
Chairman of the steering committee for the international evaluation of the Danish university educations in biology.  
Member of The Danish Academy of Technical Sciences.  
Censor in biology at all Danish universities.

*Jensen, E.S.* Member of evaluation committee for Ph.D. thesis in Plant Nutrition and Soil Fertility, Royal Vet. and Agricultural University.

*Jørgensen, J.H.* Dansk Genbanknævn.

*Miller, A.* Danish Medical Device Association (DMDA). Sterilization committee.  
Danish Standards Association. Committee S 259 on Sterilization of Medical Equipment. (Chairman).

*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. (Chairman).

National Strategy for Danish Agricultural Research Working Group on Forest and Landscape.

Committee on the national strategi for public agricultural research. Subgroup on forest and landscape.

*Solgaard, P.* Dansk Standard S-168 - Vandundersøgelser.

*Østergård, 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.

Koordineringsgruppen for resistens og virulens i korn og kornsygdomme.

### 15.2 International

*Aarkrog, A.* IAEA VAMP programme (Acting chairman).

IAEA VAMP terrestrial working group (chairman).

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-ECO Programme.

AMAP drafting group on Radioactivity Assessment.

- EF MARINA MED programme (Chairman of the datagroup).
- IUR taskforce No. 4 (Chairman).
- IUR taskforce No. 6 (Chairman).
- Programme Committee for International Conference on "Environmental Radioactivity in the Arctic". Oslo, Norway, August 1995.
- Programme Committee for the Marina-Med symposium in Rome 17-19 May 1994.
- Editorial board of Journal of Environmental Radioactivity.
- Bjerre, A.B.** IEA - Bioenergy agreement Task XIII. Bioconversion activity. Alternative member of committee.
- Engvild, K.C.** Member of Journal Committee of 'Physiologia Plantarum'.
- Gissel-Nielsen, G.** OECD committee for plant/soil/microbial interactions.
- Grøn, C.** Member of CEN TC 230/WG 1/TG 8 working on the European Standard for the AOX method.
- Board member of the Nordic branch of the International Humic Substances Society.
- Referee for Water Research and for Waste Management and Research.
- Member of the Organizing Committee for Nordic Meetings on Organic Micropollutants.
- Jakobsen, I.** Management committee for COST Action 8.21: Arbuscular mycorrhizas in sustainable soil-plant systems.
- Jensen, A.** Member of an EEC expert panel for the collaboration on higher educations between European countries and USA.
- Jensen, B. Skytte.** 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'. Sectionboard for Soils and Fertilizers, Scandinavian Association of Agricultural Scientists.
- Opponent and member of evaluation committee for Ph.D. thesis, Department of Soil Science, Swedish University of Agricultural Science.
- Member of Terminal Project Evaluation Committee for UNDP/FAO project in India, New Delhi.
- Jensen, J.** International coordinator, barley chromosome 5; International Barley Nomenclature Committee.
- Jørgensen, J.H.** Editorial board of 'Euphytica'. International coordinator for disease and pest resistance genes in barley.
- Working group cereal, Nordic Gene Bank (Chairman).
- Kunzendorf, H.** Editorial Board of 'Marine Georesources and Geotechnology'.
- Linde-Laursen, I.** Editorial Board of 'Plant Systematics and Evolution'.
- Miller, A.** American Society for Testing and Materials: Subcommittee E10.01: Dosimetry for Radiation Processing.
- Radiation Sterilization Ordentlich Publishers (Israel) (Editorial Board).
- 9th Int. Meeting on Radiation Processing, Istanbul 1994 (Programme Committee).
- Radiation Physics and Chemistry. Editor-in-Chief.
- Third International Workshop on Dosimetry for Radiation Processing (organized by ASTM), Ste. Adele, Canada, 1-6 October 1995. Organizing Committee.
- 4th International Symposium on ESR Dosimetry and Applications. Munich, Germany, 15-19 May 1995. International Advisory Committee.
- International Atomic Energy Agency. Member of Advisory Group on International Dose Assurance Service.
- International Electrotechnical Commission (IEC), Subcommittee 15B, Working Group 2 on Endurance Tests, Radiation. Corresponding member.
- Organisation Internationale de Metrologie Legale (OIML). TC-15, Measuring measurements for ionizing radiation. Member.
- Nielsen, O.J.** EUROTRAC International Executive Committee.
- COST-611 Working Party 2 Steering Committee, Atmospheric and Photochemical Processes.
- Steering Committee for NORSAC (Nordic Symposia 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)

- (Chairman) Baltic Marine Environment Protection Commission, Helsinki Commission (HELCOM).
- Nielsen, T.* The board of Nordic Society of Aerosols (NOSA).
- Roed, J.* The Group on in-situ measurements (ICRU).
- IAEA and EEC VAMP Project Urban Group. (Chairman).
- The Fuel Cycle Safety Group (OECD).
- Wilbrandt, R.* Member of the panel for the professorship of Chemical Dynamics, University of Lund, Sweden.
- 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**

**Biological Nitrogen Fixation in Scandinavian Agriculture, 26-28 May 1994 (*E.S. Jensen*).**

**Organic Micropollutants in Uncontaminated Air, Soil and Groundwater (in Danish). Copenhagen, 26 October, 1994 (*C. Grøn* and *R. Greulich*, *H. Gädda* and *B. Nyeland*).**

**Molecular Genetics and Breeding of Barley in Scandinavia, 31 October - 1 November 1994 (*H. Giese*).**

**Training course on Validation and Process Control for Electron Beam Sterilization, Risø 22-26 August and 14-18 November 1994 (*A. Miller*).**

**Workshop on future resistance and virulence studies in relation to cereal variety testing in Denmark, 8 December 1994 (*J. Helms Jørgensen*).**

## 17 Personnel

The list also includes short term employees

*Head of Department*

Arne Jensen

### 17.1 Scientific staff

Aarkrog, Asker  
Ambus, Per  
Andersen, Kirsten  
Andersson, Kasper  
Bjerghakke, Erling  
Bjerre, Anne Belinda  
Chen, Qiangjiang  
Christiansen, Solveig Krogh  
Dahlgaard, Henning  
Damgaard, Christian  
Doll, Hans  
Engvild, Kjeld C.  
Fenger, Jørgen  
Giese, Henriette  
Gissel Nielsen, Gunnar  
Grøn, Christian  
Gundersen, Vagn  
Hansen, Heinz H.  
Hansen, Knud Bent  
Hauser, Thure  
Holcman, Jerzy  
Haahr, Vagner  
Jakobsen, Iver  
Jensen, Erik Steen  
Jensen, Hans Peter  
Jensen, B. Skytte  
Jensen, Jens  
Johansen, Anders  
Jørgensen, Dorthe Heidi  
Jørgensen, Jørgen Helms  
Jørgensen, Rikke Bagger  
Kunzendorf, Helmar  
Kure, Martin  
Lange, Christian  
Linde-Laursen, Ib  
Lynggård, Bent  
Miller, Arne  
Nielsen, Harly Alex Møller  
Nielsen, Ole John  
Nielsen, Sven P.  
Nielsen, Torben  
Nilsson, Karen

Olesen, Anne Bjerring  
Pagsberg, Palle  
Pedersen, Susanne  
Pilegaard, Kim  
Plöger, Annette  
Rasmussen, Søren Kjærsgård  
Ravnskov, Sabine  
Roed, Jørn  
Rosendahl, Lis  
Sehested, Jens  
Sehested, Knud  
Sillesen, Alfred Heegaard  
Solgaard, Per  
Sørensen, Emil  
Sørensen, Peter  
Wilbrandt, Robert  
Østergård, Hanne

### 17.2 Technical Staff

Andersen, Bente  
Andersen, Heidi Bøje  
Andersen, Lis Brandt  
Andersen, Margit Elm  
Bitsch, Gunnar  
Bjerg, Flemming  
Brandstrup, Oda  
Brink-Jensen, Merete  
Baade-Pedersen, Pearl  
Christensen, Tove  
Clausen, Jytte  
Clemmensen, Heidi  
Corfitzen, Hanne  
Djurdjevic, Stanko  
Ebbling, Elise  
Edwards, Henrik  
Eriksen, Kim  
Fernqvist, Tomas  
Gade, Poul  
Green, Jytte  
Gudiksen, Peter  
Gundersen, Pernille  
Hansen, Carl

Hansen, Elly  
 Hansen, Ina  
 Hasselbalch, Finn  
 Henriksen, Ebbe  
 Hubert, Line  
 Ibsen, Elly  
 Jensen, Ellen Møller  
 Jensen, Karen Mandrup  
 Jensen, Rie Højgaard  
 Johansen, Torben  
 Jørgensen, Vibeke  
 Karlsen, Aage  
 Kavukis, Nick  
 Kjølhede, Alice  
 Koutras, Charlotte  
 Kristiansen, Bo  
 Larsen, Erik Engholm  
 Larsen, Fritz  
 Larsen, Ingelis  
 Larsen, Inge Merete  
 Larsen, Aase Neve  
 Lilholt, Ulla  
 Lindskou, Fini  
 Lærkholm, Peter  
 Madsen, Michael Birch  
 Meltofte, Liselotte  
 Nielsen, Anders Bjergskov  
 Nielsen, Jette Bruun  
 Nielsen, Karen Wie  
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 Nielsen, Svend  
 Oldager, Alf G.  
 Olsen, Anette  
 Olsen, Inge  
 Olsen, Svend K.  
 Prip, Henrik  
 Rønnebech, Kit  
 Sillesen, Anerikke  
 Svaneborg, John  
 Sølvholm, Elsebeth  
 Sørensen, Lisbeth Dahl  
 Sørensen, Peter Fl.  
 Sørensen, Poul  
 Thomsen, Michael H.  
 Tung, Tran Duc Tuan  
 Vestesen, Hans  
 Vinther, Lis  
 Weinreich, Ulla  
 Wojtaszewski, Hanne

### 17.3 Office Staff

Andersen, Annie Senten  
 Bay, Kirsten  
 Bækmark, Anni  
 Frandsen, Anette  
 Jakobsen, Inger  
 Jensen, Hanne  
 Kornerup, Berit  
 Kristensen, Ingrid  
 Krogh, Helle  
 Madsen, Ruth  
 Petersen, Lis  
 Rasmussen, Hanne  
 Vedsø, Nanna

### 17.4 Ph.D. Students

Behrens, Annette  
 Butterworth, Lisa A.  
 Christiansen, Jens  
 Dahl, Søren Weis  
 Frederiksen, John Myhre  
 Grosell, Martin  
 Helweg, Christian  
 Jacobsen, Frank  
 Justesen, Annemarie F.  
 Jørgensen, Finn  
 Jørgensen, Birgitte Lund  
 Kaszthelyi, Tamas  
 Kjær, Birgitte  
 Landbo, Lars  
 Lange, Christian  
 Larsen, Else Toftdahl  
 Larsen, John  
 Lyngkjær, Michael  
 Mikkelsen, Thomas  
 Møgelberg, Trine  
 Pedersen, Carsten  
 Ravnskov, Sabine  
 Sehested, Jens  
 Skov, Elise  
 Strandberg, Morten

### 17.5 M.Sc. Students

Christiansen, Lars  
 Fatum, Peter  
 Feldner, Helle

Forsting, Peter  
Gamborg, Elisabeth  
Jensen, Peter Westphal  
Johansen, Benja  
Kramer, Linda  
Kristensen, Brian K.  
Larsen, Karina Block  
Madsen, Niels Lolck  
Nielsen, Harly Alex Møller  
Pedersen, Annette  
Platz, Jesper  
Prior, Susanne  
Sletsgaard, Jan  
Sørensen, Lisbeth Dahl  
Vesterager, Jens  
Winther, Tomas Schou  
Østerby, Susanne

## **17.6 B.Sc. Students**

Barnkob, Chatrine  
Bouakaz, Lamine  
Brandt, Jan  
Christensen, Sanne Bove  
Eskelund, Lise  
Gelskov, Sara  
Harder, Helle  
Nørgaard, Anette  
Petersen, Lars  
Schneider, Kenn

## **17.7 Apprentices**

Andersen, Mette Kuhlmann  
Carlsen, Heidi Desireé  
Hansen, Heidi Lærkeberg  
Hassel, Maja  
Jørgensen, Christina Toftlund  
Jørgensen, Iben  
Lind, Lene Engelbrecht  
Rasmussen, Charlotte Holte  
Schjönning, Liza  
Sonberg, Tina

## 18 Acronyms

AAS	Atomic Absorption Spectrometry
ALI	Annual Limit of Intake
AMAD	Activity Median Aerodynamic Diameter
AMAP	Arctic Monitoring and Assessment Programme
BCR	Community Bureau of Reference
BIATEX	Biosphere-Atmosphere Exchange of Pollutants
BMC	Baltic Marine Cooperation
BNFL	British Nuclear Fuels Ltd.
BSS	Basic Safety Standards
CAT	Center for Advanced Technology
CEC	Commission of European Communities
CEN	European Standard Organization
CF	Concentration factor ( <i>e.g.</i> Bq kg <sup>-1</sup> fish : Bq l <sup>-1</sup> water)
CGC	Management and Coordination Advisory Committee (CEC)
CIS	Commonwealth of Independent States
CISMI	Center for Interdisciplinary Studies of Molecular Interactions
COST	European Cooperation in the Field of Scientific and Technical Research
CRP	Coordinated Research Programme (IAEA)
DANAK	Danish Accreditation Scheme
DCAR	Danish Centre for Atmospheric Research
DEG	Danish Environmental Group
DF	Decontamination Factor
DGXI	General Directorate No 11 (CEC, Luxembourg)
DH	Chromosome-doubled Haploid
DIA	Denmark's Academy for Engineering
DIF	Dansk Ingeniørforening
DMU	National Environmental Research Institute
DNA	Dioxyribonucleic acid
ECC	Enzymatically Conversion of Cellulose
Egh	<i>Erysiphe graminis</i> f.sp. <i>hordei</i>
EMBL	European Molecular Biology Laboratory
EMEP	European Monitoring Environmental Programme
ETV	Electro Thermal Vaporisation
EUROTRAC	European Experiment on Transport and Transformation of Environmental Relevant Trace Constituents of Anthropogenic and Natural Origin
FAO	United Nations Food and Agriculture Organization
FIA	Flow Injection Analysis
FTIR	Fourier Transform Infrared
FYM	Farm Yard Manure
FØTEK	Fødevareteknologi
GC/MC	Gas chromatography and mass spectrometry
DGPS	Differential Global Position System
GMP	Genetically Modified Plants
GPD	glyceraldehyd-3-phosphate dehydrogenase
GSF	Gesellschaft für Strahlen - und Umweltforschung
GUS	β-glucuronidase
HDRL	Risø High Dose Reference Laboratory
HELCOM	Helsinki Commission
HPLC	High Performance Liquid Chromatography

<b>HRICPMS</b>	<b>High Resolution Inductively Coupled Plasma Mass Spectrometry</b>
<b>IAA</b>	<b>Indole-3-acetic acid</b>
<b>IAEA</b>	<b>International Atomic Energy Agency</b>
<b>IC</b>	<b>Ion Chromatography</b>
<b>ICES</b>	<b>International Council for the Exploration of the Seas</b>
<b>ICPMS</b>	<b>Inductively Coupled Plasma Mass Spectrometry</b>
<b>ICRU</b>	<b>International Commission on Radiological Units</b>
<b>IEC</b>	<b>International Electrotechnical Commission</b>
<b>IFU</b>	<b>Institut für Umweltforschung</b>
<b>IMO</b>	<b>International Maritime Organization</b>
<b>IUR</b>	<b>International Union of Radioecologists</b>
<b>K<sub>d</sub></b>	<b>Distribution coefficient between sediments and water (Bq kg<sup>-1</sup> sediment : Bq l<sup>-1</sup> water)</b>
<b>K<sub>m</sub></b>	<b>Michaelis-Menten constant</b>
<b>MARDOS</b>	<b>IAEA CRP on "Sources of Radioactivity in the Marine Environment and their Relative Contributors to Overall Dose Assessment from Marine Radioactivity"</b>
<b>MARINA-MED</b>	<b>Overall Radiological Impact on Population of Member States of Natural and Manmade Radionuclides Present in the Mediterranean</b>
<b>MAST</b>	<b>Marine Science and Technology Programme (under CEC)</b>
<b>MEL</b>	<b>Marine Environmental Laboratory, IAEA, Monaco</b>
<b>MODECS</b>	<b>Molecular Design of Chemical Systems</b>
<b>MORS</b>	<b>Group of Experts Monitoring of Radioactive Substances in the Baltic Sea.</b>
<b>MST</b>	<b>Miljøstyrelsen</b>
<b>NECO</b>	<b>Nitrogen Ecology (SMP project)</b>
<b>NKJ</b>	<b>Nordisk Kontaktorgan for Jordbrugsforskning</b>
<b>NKS</b>	<b>Nordic Nuclear Safety Project (RAD)</b>
<b>NLVF</b>	<b>Norway Agricultural Research Council</b>
<b>NMR</b>	<b>Nordisk Ministerråd</b>
<b>NPP</b>	<b>Nuclear Power Plant</b>
<b>ODP</b>	<b>Ozone depletion potential</b>
<b>OECD</b>	<b>Organisation for Economic Cooperation and Development</b>
<b>OIML</b>	<b>Organisation Internationale de Metrologie Legale</b>
<b>PAH</b>	<b>Polycyclic Aromatic Hydrocarbons</b>
<b>PBM</b>	<b>Peribacteroid membrane</b>
<b>PBS</b>	<b>Peribacteroid space</b>
<b>PCR</b>	<b>Polymerase Chain Reaction</b>
<b>PEG</b>	<b>Polyethyleneglycol</b>
<b>PFGE</b>	<b>Pulse Field Gel Electrophoresis</b>
<b>PLS</b>	<b>Partial Least Squares Regression</b>
<b>PM3</b>	<b>Parametric Method Number 3</b>
<b>PMC</b>	<b>Pollen Mother Cell</b>
<b>POM</b>	<b>Polycyclic Organic Matter</b>
<b>PON</b>	<b>particulate organic nitrates</b>
<b>QSAR/QSPR</b>	<b>Quantitative Structure Activity/Property Relationship method</b>
<b>QTL</b>	<b>Quantitative Trait Loci</b>
<b>RAD</b>	<b>Radioecology Programme (under NKS)</b>
<b>RADPATH</b>	<b>Biological Pathways of Artificial Radionuclides (under CEC)</b>
<b>RAPD</b>	<b>Random Amplified Polymorphic DNA Technique</b>
<b>RERAF</b>	<b>Risø Ecological Risk Assessment Facility</b>
<b>RFLP</b>	<b>Restriction Fragment Length Polymorphism</b>
<b>RIMI</b>	<b>Risø Intergrated Environmental Project</b>
<b>RP-HPLC</b>	<b>phase high pressure liquid chromatography method</b>

<b>RVAU</b>	<b>The Royal Veterinary and Agricultural University</b>
<b>SCAR</b>	<b>Sequence characterized amplified reaction</b>
<b>SCR</b>	<b>Selectiv catalytic reduction</b>
<b>SINE</b>	<b>Short interspersed nuclear element</b>
<b>SIS</b>	<b>Statens Inst. for Strålehygiene (Statens Strålevern) (Norge)</b>
<b>SJVF</b>	<b>The Veterinary and Agricultural Research Council</b>
<b>SNF</b>	<b>Symbiotic Nitrogen Fixation</b>
<b>SMP</b>	<b>Strategisk Miljøforskningsprogram</b>
<b>SSI</b>	<b>Statens Strålskyddsinstitut (Sverige)</b>
<b>STUK</b>	<b>Strålsäkerhetscentralen (Finland)</b>
<b>TF</b>	<b>Transfer factor (eg. Bq kg<sup>-1</sup> per Bq m<sup>-2</sup>)</b>
<b>TOR</b>	<b>Tropospheric Ozone Research</b>
<b>TNO</b>	<b>Nederlands Organization for Applied Scientific Research</b>
<b>TRACT</b>	<b>Transport of Pollutants over Complex Terrain</b>
<b>UKAEA</b>	<b>United Kingdom Atomic Energy Authorities</b>
<b>UMIST</b>	<b>University of Manchester, Institute of Science and Technology</b>
<b>V<sub>max</sub></b>	<b>Maximum velocity</b>
<b>VAM</b>	<b>Vesicular-Arbuscular Mycorrhiza</b>
<b>VAMP</b>	<b>Validation of Model Project (under IAEA)</b>
<b>VOC</b>	<b>Volatile organic carbon</b>
<b>YAC</b>	<b>Yeast Artificial Chromosome</b>

## Title and author(s)

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167

## Abstract (Max. 2000 characters)

The Environmental Science and Technology Department engage in research to improve the scientific basis for new methods in industrial and agricultural production. Through basic and applied research in chemistry, biology and ecology the department aspires to develop methods and technology for the future industrial and agricultural production exerting less stress and strain on the environment. The research approach in the department is predominantly experimental.

The research activities are organized in five research programmes and supported by three special facility units. In this annual report the main research activities during 1993 are introduced and reviewed in eight chapters. Chapter 1. Introduction. The five research programmes are covered in chapter 2-7: 2. Atmospheric Chemistry and Air Pollution, 3. Gene Technology and Population Biology, 4. Plant Nutrition and Mineral Cycling, 5. Trace Analysis and reduction of Pollution in the Geosphere, 6. Ecology, 7. Other Research Activities. The three special activity units in chapter 8. Special Facilities.

The department's contribution to national and international collaborative research projects and programmes is presented in addition to information about large research and development facilities used and managed by the department. The department's educational and training activities are included in the annual report along with lists of publications, publications in press, lectures and poster presentations at international meetings. Names of the scientific and technical staff members, visiting scientists, post. doctoral fellows, Ph.D. students and M.Sc. students are also listed.

## Descriptors INIS/EDB

AIR POLLUTION; ATMOSPHERIC CHEMISTRY; CHEMICAL ANALYSIS; CONTAMINATION; DISEASE RESISTANCE; ECOLOGY; ECOSYSTEMS; GENETICS; GEOCHEMISTRY; NUTRIENTS; NUTRITION; PLANTS; PROGRESS REPORT; RADIOECOLOGY; RADIONUCLIDE MIGRATION; RESEARCH PROGRAMS; RISØ NATIONAL LABORATORY

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