

# **INTERNATIONAL LABORATORY OF MARINE RADIOACTIVITY**

## **Biennial Report 1983-1984**



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The International Laboratory of Marine Radioactivity operates under a tripartite agreement between the International Atomic Energy Agency, the Government of the Principality of Monaco and the Institut Océanographique (Paris). The Laboratory is situated in the Musée Océanographique in Monaco.

**INTERNATIONAL LABORATORY OF MARINE RADIOACTIVITY:  
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The Monaco Laboratory Staff in front of  
the Oceanographic Museum Building

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## 1. General Aspects of the Laboratory Operations

### 1.1 Status of the Laboratory

The existence of the International Laboratory of Marine Radioactivity at Monaco is based on a Tripartite Agreement between the International Atomic Energy Agency, the Government of the Principality of Monaco and the Oceanographic Institute (Paris) at Monaco, which was originally signed in 1961 and has been renewed several times since. The last renewal was made in 1981, covering a period of three years until June 1984.

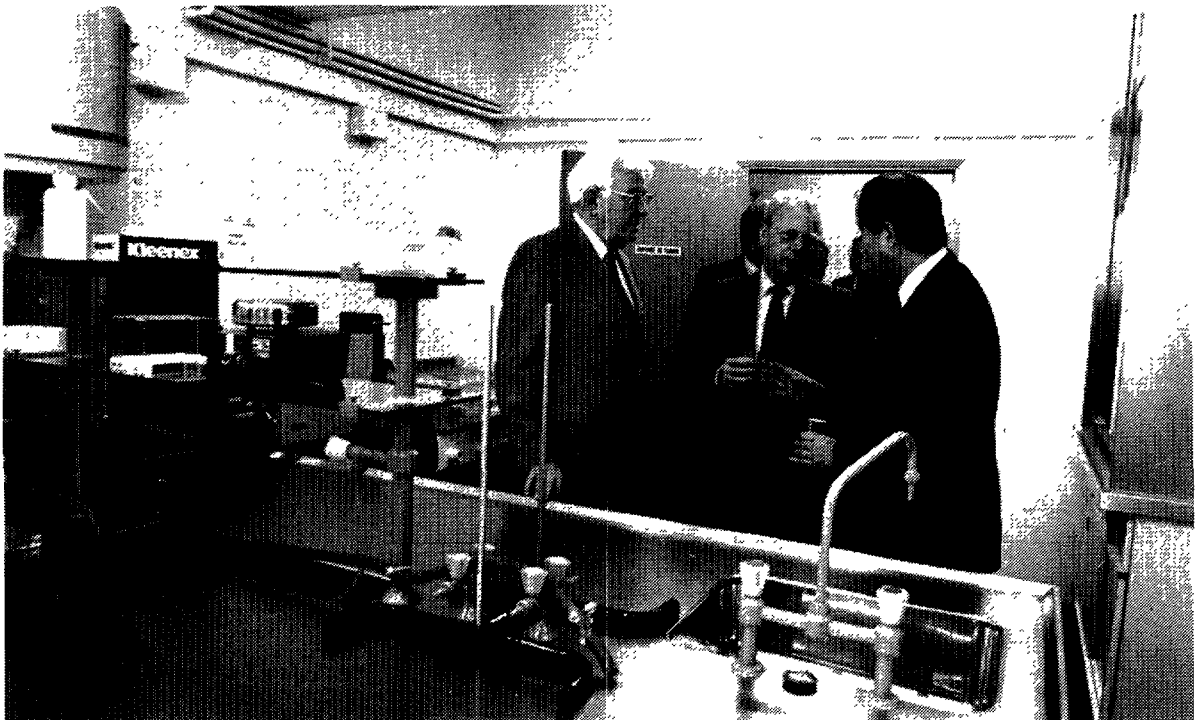
Meanwhile, the Monegasque Government expressed their desire to maintain the Laboratory in Monaco and to negotiate a seat agreement which would accommodate the Laboratory on a more permanent basis. In June 1982, negotiations on the seat agreement commenced at an administrative level and several contacts have been made since that time. The fundamental difference between the present tripartite agreement and the future seat agreement lies especially in the articles concerning the applications of the privileges and immunities for the Laboratory's staff, which are now to be cleared by the French authorities. This clearance ensures more appropriate and universal application of these articles. Although a substantial progress in drafting the seat agreement was achieved by the parties concerned, official clearance procedures had not been completed by June 1984. At the IAEA Board Meeting held in June 1984, therefore, it was recommended to extend the existing tripartite agreement for another year.

### 1.2 New Laboratory premises

Based on an offer made by the Government of Monaco in March 1982, the Laboratory was given additional laboratory space measuring approximately 350m<sup>2</sup> in the "Aigue Marine" Building at Fontvieille as well as a warehouse measuring approximately 70m<sup>2</sup> along the Old Port of Monaco. The inauguration of these new premises took place in March 1983 in the presence of H.E. Mr. J. Herly, Minister of State representing the Government of Monaco and Prof. M. Zifferero, Deputy Director General representing the IAEA (Figs. 1.1 and 1.2). Thus, the problem of shortage of space in the Laboratory which had persisted for several years was substantially relieved. Considering the radioprotection aspects of the laboratory operation, scientific units not using radioisotopes were transferred to the new premises. The new laboratory space represents a 50% increase compared to that in the Oceanographic Museum (approximately 700m<sup>2</sup>) and this enabled the Laboratory to accept more experts,



**Fig. 1.1** Prof. M. Zifferero addressing at the Inauguration of the "Aigue Marine" Premises.



**Fig. 1.2** H.E. Mr. J. Herly, Minister of State and H.E. Mr. R. Biancheri, Minister Plenipotentiary, both from the Government of the Principality of Monaco, inspecting the new laboratory installations.

fellowships and trainees from the Member States in the field of marine radioactivity studies as well as in marine non-nuclear pollution studies. The serious efforts made by the Monegasque authorities to realise this enlargement of the Laboratory are cordially appreciated and acknowledged.

### 1.3 Staffing and the structure of the Laboratory

A list of the staff of the Laboratory during 1983-1984 is given in Appendix 1. Three groups, the Biology, Chemistry and Geochemistry, continued to be responsible for carrying out scientific and technical operations of the Laboratory during this period. The leaders of the Chemistry and Geochemistry Group were replaced respectively by Dr. E. Holm (from Sweden) and Dr. N.E. Whitehead (from New Zealand). Dr. F. Azam (from U.S.A.) stayed for about a year during 1983 in the Biology Group for initiating microbiological studies at the Laboratory, while Dr. J. Derenbach (from FRG) and Dr. B. Hargrave (from Canada) contributed to the research programmes as Government-sponsored Experts respectively in the Chemistry and Biology Groups. In May 1984, Dr. S. Aston (from U.K.) was recruited in order to implement the new UNEP project "Development, Testing and Intercalibration of Guidelines and Reference Methods for Marine Pollution Studies" and he was also charged with coordinating other relevant aspects of UNEP projects carried out in the Laboratory. The Laboratory's involvement in several UNEP sponsored projects inevitably necessitated recruiting a number of temporary staff, but the number of established posts in the Laboratory for the General Service Staff seems still too low, compared with that of the Professional Staff.

As shown in Appendix 1, the Laboratory received a number of scientific experts, fellowships and trainees from 22 Member States.

### 1.4 Scientific programmes

In order to review the scientific programmes of the Laboratory in the light of their relevance to the IAEA's general scope and direction, a meeting of senior consultants was convened in March 1984. The consultant group was composed of specialists familiar with the marine radioactivity problems from the Federal Republic of Germany, Finland, France, India, United Kingdom and United States of America. The representatives of the Department of Research and Isotopes and the Department of Nuclear Energy and Safety from IAEA Vienna as well as those of the Government of Monaco and Oceanographic Institute at Monaco also took part in the meeting. In addition, the representatives of the United Nations Environmental Programme and the Intergovernmental Oceanographic Commission of the

United Nations Educational, Scientific and Cultural Organizations were present in the discussions on the future role of the Laboratory within the framework of international marine programmes implemented by these organisations.

The Group reviewed the scientific activities, budget, structure and external relations of the Laboratory. The Group considered that the scientific activities of the Laboratory fall into the following areas:

1. Method development, intercalibration and training;
2. Research on radionuclides in the marine environment; and
3. Scientific and technical service to other international programmes in relation to radioactive and non-radioactive pollution.

After examining in detail each scientific task included in the proposed projects, the Group made the following recommendations:

(1) Following the review of the Laboratory's activities we recommend that the present allocation of resources between the above three major programme areas be maintained.

(2) The Laboratory's activities in intercalibration, method developments and training, have justifiably earned an excellent reputation in this area. We recommend that these programmes continue as indicated.

(3) We recommend that research related to the Agency's responsibilities in the field of radiological protection and radioactive waste management in the marine environment continues to be the primary role for the Laboratory.

- We recommend that the closest collaboration and cooperation is maintained between the Laboratory and relevant staff in Vienna to maximize the effectiveness of the Laboratory's own activities and thus its contribution to IAEA programmes.

- We recommend that the Laboratory takes fuller account of the value of mathematical modelling in the determination of its research priorities, as well as the contribution that the Laboratory's own activities can make to dose assessment modelling.

- We recommend that the Laboratory should develop the capability for data compilation and review related to radioactivity in the marine environment.

(4) We recognize that if there should be further expansion in the non-nuclear area this could result in an impact on the IAEA nuclear

related programmes and a shift away from the primary role of the Laboratory. We recommend that the IAEA examine the implications of the proposed acquisition of a UNEP supported GC/Mass Spectrometer at the Laboratory, in light of the above statement.

(5) We feel that staff continuity and discretionary research are very important factors in maintaining the effectiveness of programmes and the scientific calibre of the Laboratory. We recommend that these matters be given serious consideration.

Taking the comments made by the Consultant Group at the meeting into account, scientific activities of the Laboratory were shifted to accommodate the recommendations in a most effective manner, by phasing out some tasks, combining and simplifying or changing the emphasis on other tasks. The proposed scientific programmes for 1985-1986 are given in Table 1.1.

Following up the Consultant Group's recommendations, the Programme Co-ordination Committee on the Waste Management/Monaco Laboratory activities met in October 1984 at Vienna. The scientific programmes proposed for 1985-1986 as presented in Table 1.1 were discussed and the Committee approved the general lines of the programme proposed. As to the Co-ordinated Research Programme (Task IIe), it was pointed out that the scope seems somewhat premature and further focusing of the objectives to be achieved by the programme is necessary before launching the programme. It was also emphasized that the Task II f "Compilation and evaluation of input of radionuclides into the marine environment" will be useful to the Waste Management Programme as well as to the activities carried out by the United Nations Scientific Committee for the Effects of Atomic Radiation.

Although the resources in the Laboratory were rearranged during the course of 1984 in order to pursue effectively the tasks listed in Table 1.1, the scientific tasks carried out in 1983-1984 and presented in Chapters 2-5 of the present report are not exactly the same as presented in the Table 1.1.

Most of the results of these studies were published in the open literature. A list of the Laboratory's publications is given in Appendix 2.

#### 1.5 Co-operation with Member States and other organizations

Under the participation of 14 institutions from 11 countries a Co-ordinated Research Programme on the "Behaviour of Long-lived Radionuclides associated with the Deep-Sea Waste Disposal of Radioactive

Table 1.1 Scientific Programmes of the International Laboratory of Marine Radioactivity for 1985-1986

PROGRAMME: RADIOACTIVE WASTE MANAGEMENT

Sub-programme: International Laboratory of Marine Radioactivity

Project I. Technical Support for Marine Radioactivity Monitoring and Investigation

- Task Ia Development of methods for radionuclide measurements
- Task Ib Analytical quality assurance service
- Task Ic Training in radionuclide measurements and tracer experiments
- Task Id Consultation to national laboratories on monitoring of radioactivity in the marine environment.

Project II. Data Collection for Evaluation of Environmental Impacts of Radionuclide Releases into the Marine Environment

- Task IIa Assessment of the vertical flux of radionuclides associated with particules
- Task IIb Bioaccumulation, transfer and transport of radionuclides through marine food chains
- Task IIc Comparative studies of the fate of radionuclides released into different marine environments
- Task IID Behaviour of radionuclides in sediments and across the water/seabed interface
- Task IIe Co-ordinated Research Programme: Methods and strategies of monitoring radionuclide releases in coastal marine environments (tentative)
- Task IIIf Compilation and evaluation of input of radionuclides into the marine environment

Project III. Contribution of International Marine Pollution Monitoring and Research

- Task IIIa Intercalibration of non-nuclear pollutant measurements
- Task IIIb Training in pollutant measuring techniques
- Task IIIc Transport, fate and effects of specific marine pollutants
- Task IIId Development and testing of reference and new methods for pollutant measurements
- Task IIIe Technical co-operation in pollutant measurements
- Task IIIIf Instrument maintenance services

Wastes" continued to be organized by the Laboratory during the period 1983-1984. This programme was completed by holding the final meeting in November 1984. A final report of the results achieved within the programme will be published in the IAEA's Technical Document Series.

The Laboratory also participated in the IAEA Co-ordinated Research Programmes on "Study of Radioactive Materials in the Baltic Sea" and "Role of Sediments in Transport and Accumulation of Radionuclide in Waterways" organized respectively by the Division of Nuclear Safety and Division of Nuclear Fuel Cycle of the IAEA. In the former programme 12 laboratories participated from 8 Baltic countries and the Laboratory was



charged with the responsibility for organizing intercalibration exercises of radionuclide measurements and evaluating their results.

Within the framework of the IAEA's Analytical Quality Assurance Service Programme, the Laboratory actively collaborated with a number of national institutions from all over the world by organizing several intercalibration exercises for radionuclide measurements as well as those for non-nuclear pollutants such as heavy metals and chlorinated hydrocarbons. In 1983-1984 two worldwide intercalibration exercises were completed for a sediment sample and a seawater sample and the most probable values for several radionuclides were obtained with their confidence limits. These samples are being distributed on request as certified standard reference materials for the purpose of analytical quality control in interested national laboratories. Several intercalibration exercises by using samples such as seaweed, mussels, marine sediments, etc. were also carried out during this period, with the participation of more than 80 institutions from approximately 30 countries.

The Laboratory was also invited to participate in national scientific programmes, such as VERTEX Programme sponsored by the US National Science Foundation, ECOMARGE Programme sponsored by French PIROCEAN, TEMPARC Programme sponsored by the Danish Riso National Research Centre, etc. In these programmes useful data for the Laboratory's programme were collected in collaboration with national laboratories. In return the Laboratory contributed its scientific expertise for the execution of the whole programmes. In order to further reinforce scientific collaboration with national institutions, the Laboratory staff took part in several seminars, conferences, workshops, etc. which were organized at national and international levels. These attendances are listed in Appendix 3.

Based on the agreement for co-operation on marine environmental problems concluded in 1981, the Laboratory continued to collaborate with the United Nations Environmental Programme (UNEP) in the implementation of its Regional Seas Programmes such as the Mediterranean Action Plan, Kuwait Action Plan, West and Central African Action Plan, etc. The Laboratory provided its expertise in the analytical method development, intercalibration and training for non-nuclear pollutant measurements. In the Kuwait Region the Laboratory assisted some countries in obtaining base-line data for selected pollutants in their coasts, while maintenance services for atomic absorption spectrometers, gas chromatographs, current meters, etc. distributed to several national research centres were provided in the Mediterranean Region. A new UNEP project on "Development, Testing and Intercalibration of Guidelines and Reference Methods for Marine Pollution Studies" was launched in May 1984.

The Laboratory also continued its co-operation with the Nuclear Energy Agency of the Organization for Economical Co-operation and Development (NEA/OECD) on the scientific investigation of the NEA Northeast Atlantic Dumpsite for Radioactive Wastes. The Laboratory was charged with the responsibility for the intercalibration of low-level measurements of radionuclides within the framework of the NEA Co-ordinated Research and Environment Surveillance Programme (CREPS).

Attendance by the Laboratory staff at meetings organized by these international organizations are also listed in Appendix 3.

#### 1.6 Direct assistance received from Member States

The largest contribution to the Laboratory's programme received directly from the Member States during the period 1983-1984 is obviously the New Laboratory Annex at "Aigue Marine" from the Monegasque Government. In addition to the enlarged laboratory space, the Laboratory enjoyed free electricity and water supply, cleaning services, fire security installations, etc. borne exclusively by the Monegasque Government. As in the past, the Laboratory received the continuing support of the Monegasque Government and Oceanographic Institute at Monaco respectively in the form of a cash contribution and of contributions in kind, such as space, boat time, electricity, library, cleaning services, etc.

In 1984, the Government of the Federal Republic of Germany offered an Expert cost-free to the IAEA, who could assist the research work carried out in the Laboratory. Due to this arrangement Dr. J. Derenbach from Kiel University joined in the Organic Chemistry Unit and participated fully in the execution of the scientific programmes of this unit.

Several staff members also participated during this period in diverse oceanographic cruises organized by national institutions in Canada, France, USA, etc. in order to achieve effectively the scientific objectives of the Laboratory's programme. The costs of such cruises were borne by national funds. These oceanographic cruises are listed in Appendix 4.

All these contributions have been essential for the operation of the Laboratory. The government authorities which made these contributions are cordially acknowledged and thanked.

## 2. Methods Development and Analytical Quality Assurance for Radionuclide Measurements

### 2.1 Determination of radium isotopes in solid samples by alpha-spectrometry (R. Bojanowski)

Radium belongs to the most frequently measured natural radionuclides and is among one of the earliest measured in the human environment. The continuing interest in radium measurements stems from the relatively high radiotoxicity of radium itself and its volatile decay product, radon. There are a number of analytical techniques for radium determination, the most frequently used being gamma-spectrometry and alpha-scintillation. For many environmental applications these are neither sufficiently sensitive nor capable of furnishing the result rapidly. As both techniques rely on measuring its decay products via a volatile component, serious problems arise from calibration and background variations, which often leads to large uncertainties as demonstrated by our recent intercomparison exercises.

In the preceding report (IAEA, 1983) a method was described for direct radium measurement in natural waters using a combination of ion-exchange and alpha-spectrometry techniques. However, this sensitive method was not well suited for solid samples due to low recoveries and poor quality of discs which rendered the alpha-spectra difficult to resolve.

This difficulty was overcome to some extent by introducing two specific separations steps which effectively eliminate the bulk of interfering elements in ion exchange purification (Fig. 2.1). The overall recovery has now improved substantially attaining 60% on the average. The main losses occur at the stage of electrodeposition and further improvement is expected by optimizing the plating conditions. The method was tested on a number of reference materials and was proved to be accurate. It can be applied to rock, sediment and biological samples and is particularly suitable for samples of plankton, suspended matter, fecal pellets, etc., for which the quantity of material is limited.

#### Reference

IAEA (1983). International Laboratory of Marine Radioactivity  
Biennial Report 1981-1982, IAEA TECDOC-297, Vienna, pp. 18-20.

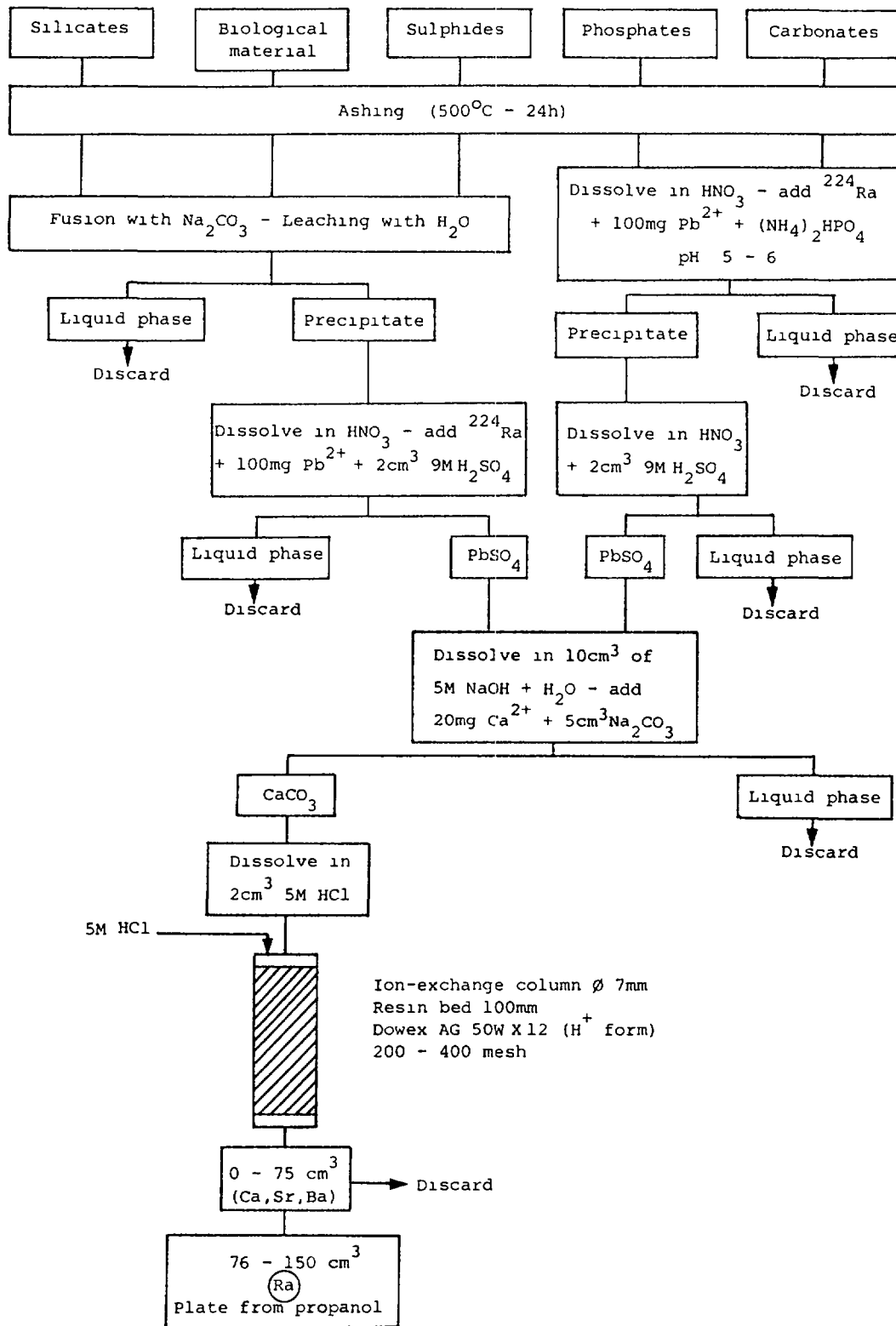


Fig. 2.1 Analytical scheme for the determination of radium in solid samples.

## 2.2 A radiochemical method for determining $^{227}\text{Ac}$ in sediments

(R. Bojanowski, E. Holm, N. Whitehead and P. Parsi)

Actinium-227, a member of  $^{235}\text{U}$  family, is formed by alpha decay of its long-lived predecessor  $^{231}\text{Pa}$ . As a naturally occurring homologue of trivalent man-made transuranium elements, it offers an interesting possibility to study their comparative geochemical behaviour in relation to disposal and containment of highly radioactive wastes at selected dump sites. Such studies are difficult to perform at present, due to the lack of well-established analytical methods for determining actinium at its very low environmental levels.

An attempt to develop a radiochemical method for measuring  $^{227}\text{Ac}$  primarily in sediments has been successful. As the radiation characteristics of  $^{227}\text{Ac}$  (99% of which decays by beta emission), offer no advantage for differentiating this isotope from other radionuclides by traditional radioanalytical techniques, a recourse must be made to measure its short-lived daughter  $^{227}\text{Th}$  which has a characteristic alpha emission. However, due to the complex energy spectrum observed, the  $^{227}\text{Th}$  cannot be measured directly on the isolated thorium fraction by alpha-spectrometry. In our method, a sample solution is first passed through an anion exchange resin Dowex AG1 X8 in 9 M HCl to remove U and Pa isotopes, followed by two sequential passages through similar columns in 8 M  $\text{HNO}_3$  for removal of thorium isotopes. The eluate is then spiked with  $^{230}\text{Th}$  and put aside for at least a month for the in-growth of  $^{227}\text{Th}$ . Subsequent column separation of thorium isotopes and plating from sulphate electrolyte at pH 2.4 yields sources virtually free of interfering nuclides and spike recovery is consistently over 90%. The method was tested on sediment samples with known amounts of  $^{227}\text{Ac}$  and was proved to give correct results within  $\pm 10\%$  at an activity level of 5 mBq/g. A substantial improvement was achieved lately by isolating the actinium on Dowex AG50 X8 in 3M  $\text{HNO}_3$  which specifically separates this element. The  $^{227}\text{Ac}$  is then determined from the sum of its decay products  $^{227}\text{Th} + ^{223}\text{Ra}$  by alpha-spectrometry. Recovery is monitored by the  $^{225}\text{Ac}$  milked from  $^{229}\text{Th}$ .

2.3 Development of radiochemical methods for determining  $^{99}\text{Tc}$  and  $^{237}\text{Np}$  (E. Holm, S. Ballestra, G. Barci\*, J. Gastaud and J.-J. Lopez)

During the past years there has been a great interest in analysing actinides in the marine environment in view of their radiotoxicity, their long half-lives and the possibility of using them as tracers for biological and geochemical processes in the marine environment.

Procedures for radiochemical separation and alpha-spectrometry of plutonium and americium developed earlier in our laboratory have been adopted by national institutions in several Member States. There is, however, a need for simplifying these methods as they are time consuming. This can be done partly by adopting sequential procedures for these radionuclides which include those for natural actinides as well as for technetium and/or neptunium. For some types of samples more rapid extraction procedures may be adopted.

In view of the need for radioprotection related to radioactive waste disposal into the deep-sea the most important radionuclides to be considered are  $^{237}\text{Np}$  and  $^{99}\text{Tc}$ . Very few radioecological studies in the marine environment have been performed on these isotopes due to analytical difficulties involved in measuring them (low specific activity and/or pure beta particle emitters).

During 1984, a method for determining  $^{99}\text{Tc}$  in environmental samples was established. The method is based on the extraction of technetium from a sulphuric acid medium by TBP and its back-extraction with sodium hydroxide solution. Technetium is electroplated onto stainless steel discs. The radiochemical yield is determined by the use of  $^{99}\text{Tc}^{\text{m}}$  (half-life: 6 h) obtained from  $^{99}\text{Mo}$  (half-life: 67 h). After decay of  $^{99}\text{Tc}^{\text{m}}$ ,  $^{99}\text{Tc}$  is counted by a multi-GM anticoincidence gas-flow counter.

There is a need for analysing  $^{99}\text{Tc}$  in environmental waters, but this requires a very large sample volume (up to 1000 l). The feasibility of such analysis by reducing and precipitating technetium in large-volume water samples is now being investigated. The possibility of using stable Re as a radiochemical yield determinant is also being tested given that the preconcentration procedures are usually carried out on board ship during relatively long cruises.

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\* Department of Chemistry, University of Nice, Nice, France.

We have participated in an international intercalibration exercise (of a sample of vegetation) for  $^{99}\text{Tc}$  measurements organized by the U.S. Environmental Measurement Laboratory in New York with excellent results. A new intercalibration on a soil sample from the same laboratory is now under way. We have also organized an intercalibration exercise for radionuclide measurements using a Baltic seaweed sample, AG-B-1,  $^{99}\text{Tc}$  measurements are included in this intercalibration exercise.

A method for measuring  $^{237}\text{Np}$  in environmental samples has also been established. The method is based on separation of Np (+IV) on an anion exchanger from hydrochloric acid medium. Finally neptunium is purified by extraction with TTA. As a radiochemical yield determinant  $^{239}\text{Np}$  (half-life: 2.35 d), milked from  $^{243}\text{Am}$ , has been used. The measurement of  $^{239}\text{Np}$  can be performed either by gamma-spectrometry or by beta-counting.

At present we are also investigating the possibilities of using  $^{235}\text{Np}$  (half-life: 400 d) as a radiochemical yield determinant. This increases the time available for the radiochemical separations. However,  $^{235}\text{Np}$  decays almost exclusively by electron capture in the L and M shells. Only 2 disintegrations out of 100 take place as capture in the K shell, giving characteristic K X-rays of U at 95 and 99 keV. In a lower energy region, however, L X-rays and M X-rays are much more abundant. Therefore, the measurements of  $^{237}\text{Np}$  can be performed at an energy range of 15-18 KeV (by L X-rays) with a n-type high-pure Ge-detector, planar Ge-detector or a GM gas-flow counter.

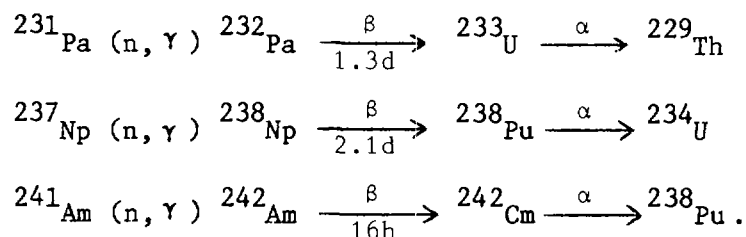
#### 2.4 An attempt at improving actinide analysis by neutron activation (N.E. Whitehead, E. Holm and J. Veselsky\*)

It is customary in many laboratories to isolate alpha-emitting nuclides from environmental samples using complex chemical techniques, electroplate them onto stainless steel, and count them using surface barrier detectors. The background of these detectors is so low that very low activities may thus be measured. However, a counting time of a week or longer may be needed for quantitatively measuring Pa, Np, Pu or Am. This tends to restrict investigations to regions where concentrations of these radionuclides are high due to radioactive effluent releases from reprocessing facilities, etc.

Calculations show that neutron activation may offer possibilities for increase in sensitivity for measuring these isotopes. The relevant transformations are:

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\*Seibersdorf Laboratory, IAEA, Vienna, Austria.



In each example the initial product of neutron capture, decays rapidly into an alpha emitting isotope with half-life significantly shorter than the original target isotope. Calculation shows that an increase of an order of magnitude or more of sensitivity should be reasonably expected by either beta or alpha counting.

However, it is inconvenient to subject to neutron activation the electroplated disk, because a very large activity of  $^{60}\text{Co}$  would be produced. A substitute material must be found which is also a good conductor of electricity but which does not yield a highly radioactive product on neutron irradiation.

A very high purity graphite and high purity aluminium were irradiated for two days under a neutron flux of  $2 \times 10^{13} \text{ n cm}^{-2} \text{ sec}^{-1}$  at the Austrian Reactor Research Centre at Seibersdorf. The activities of the irradiated samples decreased to relatively low levels over the succeeding weeks. Examination of these samples showed that the irradiation resulted in large amounts of beta-emitting short-lived activation products. Initial beta activity was about  $10^5$  cpm which is likely due to traces of  $^{60}\text{Co}$ ,  $^{65}\text{Zn}$ ,  $^{51}\text{Cr}$ , etc. as identified by gamma-spectroscopy. As the beta-activities from these impurities mask the beta-activities of the activated actinides to be measured, it is impossible to measure these actinides by beta-counting. The feasibility of measuring the beta-decay products of these activated actinides by alpha-spectrometry after radiochemical separation is being investigated.

## 2.5 Gamma-X spectrometry of natural and artificial radionuclides

(E. Holm, N.E. Whitehead and P. Zombori\*)

The installation of a new high purity Germanium Gamma-X detector in 1984 provided an extension of our detection capabilities into the low energy regions. This is specially useful for measuring natural radionuclides such as  $^{210}\text{Pb}$ ,  $^{230}\text{Th}$ ,  $^{234}\text{Th}$ ,  $^{234}\text{U}$ , etc. The method will not however, replace alpha-spectroscopy which is capable of measuring these isotopes at much lower levels, but requiring more elaborate and time-consuming laboratory procedures.

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\*IAEA Fellow from the Central Institute for Physics, Budapest, Hungary.



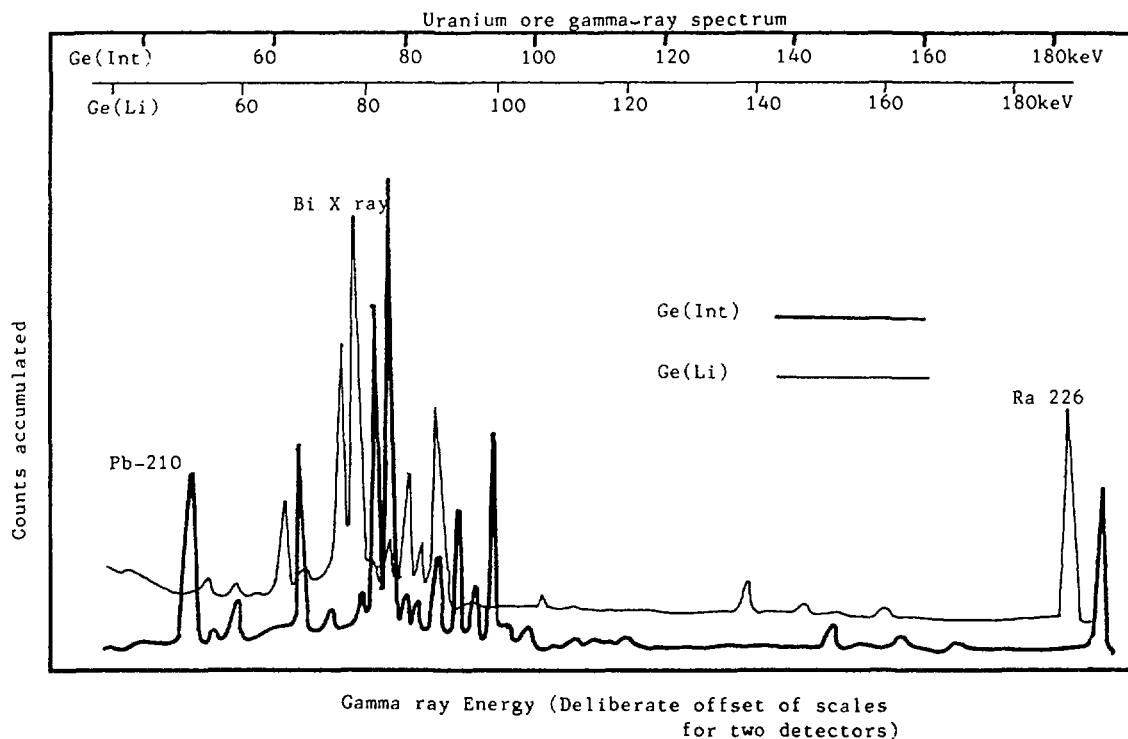


Fig. 2.2 Comparison of Ge(Li) and Ge(Int) spectra of uranium ore S-20.

In Fig. 2.2 a comparison is given of a sample of IAEA uranium ore S-20 counted on both systems under the same conditions and for the same interval of time. The superiority of the new system for the low energy region is apparent especially below about 70 keV. At higher energies, however, the conventional Ge(Li) detector has higher efficiency.

The detector system is also useful for some experiments in which natural radionuclides are used as tracers. For example, the gamma emitting  $^{234}\text{Th}$  which can be milked from natural uranium salts in large amounts has been used successfully as a tracer in improving the radiochemical procedures for thorium separation.

The pure Ge detector is also useful for measuring low energy gamma emitting artificial radionuclides, such as  $^{129}\text{I}$ ,  $^{241}\text{Am}$ , etc.

## 2.6 Analytical Quality Assurance Programme

(R. Bojanowski, E. Holm, S. Ballestra, D. Vas and A. Veglia\*)

As in previous years the Laboratory continued its commitment to the Member States by supplying them with intercomparison and reference samples of marine origin and organising intercalibration exercises on a worldwide basis as well as within the framework of special projects.

\*Scientific Centre of Monaco, Principality of Monaco.

In 1983-1984 two worldwide intercalibration exercises were terminated and they resulted in certification of activity concentrations for  $^{60}\text{Co}$ ,  $^{90}\text{Sr}$ ,  $^{137}\text{Cs}$ ,  $^{238}\text{Pu}$ ,  $^{239+240}\text{Pu}$  and  $^{241}\text{Am}$  in sediment sample SD-N-1/1 and for  $^{90}\text{Sr}$ ,  $^{137}\text{Cs}$ ,  $^{238}\text{Pu}$ ,  $^{239+240}\text{Pu}$  and  $^{241}\text{Am}$  in sea water sample SW-N-2. Six other intercalibration exercises were carried out on a world-wide basis using the following samples: Marine sediment SD-N-1/TM (trace metals), marine sediments SD-N-1/2NR (natural radionuclides), marine sediment SD-N-2 (artificial radionuclides), marine algae AG-B-1 (artificial radionuclides), mussel flesh MA-M-2/TM (trace metals) and MA-M-2/OC (organochlorine compounds). The period for the reception of results was closed at the end of 1984 and data evaluation is in progress. It is hoped that the samples will become available as reference materials during the course of 1985.

In response to the demands of the scientific community of the Member States, we embarked on the development of two new materials for intercalibration and certification purposes. They are shrimp flesh MA-A-3 and fish flesh MA-B-3. The first one will comprise trace metals and organochlorine compounds, while the second will include both artificial and natural radionuclides in addition to those aforementioned. The shrimp sample is being tested for homogeneity. Preparation of the fish sample was somewhat delayed due to difficulties encountered in obtaining a satisfactory degree of homogeneity.

Several quality control tests were organised at the request of scientists participating in Coordinated Research Programmes, as well as other special projects involving international cooperation. Twelve laboratories from eight Baltic countries participated in intercomparison measurements of a number of radionuclides in four different natural matrices, including those of Baltic origin. The Laboratory evaluated the results which were generally found to be satisfactory. An evaluation report summarising four years of activities within the framework of CRP "Radioactive materials in the Baltic Sea" will be published in an IAEA Technical Document.

A small-scale intercomparison exercise was initiated in 1984 on the  $^{99}\text{Tc}$  in marine algae AG-B-1 and will continued during 1985.

### 3. Studies for Evaluating Environmental Impacts of Radionuclide Releases into the Sea

#### 3.1 Studies on Vertical Transport of Radionuclides

##### 3.1.1 Vertical transport of transuranics in the upper columns of the northeast Pacific Ocean (S.W. Fowler, S. Ballestra, J. La Rosa and J. Gastaud)

As part of the U.S. National Science Foundation's VERTEX Programme, the Laboratory participated on two cruises (VERTEX II and III) off the coast of central Mexico during 1980-81, another north of Hawaii in the mid-Pacific Gyre (VERTEX IV, 1983), and a fourth off Monterrey, California (VERTEX V, 1984), the latter consisting of simultaneous sampling by two ships on a transect between Hawaii and California. On all cruises samples of water, suspended particles, sediment trap material and fresh biogenic debris were collected for analyses of plutonium and americium. The aim of the study is to assess the role these particles play in removing transuranics from the surface layers to depth (Fowler et al., 1983).

Samples from VERTEX V are currently being analyzed, however, results from VERTEX II-IV indicate several similar features. Profiles of transuranics in the water column generally show transuranic maxima between 400-600m. In all cases the  $^{239+240}\text{Pu}$  maximum was more pronounced than that of  $^{241}\text{Am}$ . Furthermore, in the surface layers there was little association of transuranics (~1-2%) with the fine, suspended particles. In the more oligotrophic waters north of Hawaii, this fraction changed little with depth. These observations were in contrast to those made earlier in productive waters of the California current where transuranic fractions associated with a phytoplankton bloom were as high as 20-30% (Fowler et al., 1983).

Results of the sediment trap analyses indicate a substantial enrichment in Pu and Am in the particles making up the mass flux. Similar enrichment of these transuranics in freshly-produced zooplankton fecal pellets collected over the traps was also noted. There was a general tendency for increasing transuranic concentration with depth in the large sinking particles. As one example, data from VERTEX IV are shown in Table 3.1. The increase in  $^{239+240}\text{Pu}$  and  $^{241}\text{Am}$  concentration (at least to 1000 m) suggests active scavenging of these radionuclides onto biogenic particles sinking through the transuranic maxima. A concomitant increase in the Am/Pu ratio on large particulates with depth indicated that Am was scavenged to a greater extent than Pu. At some stations below a certain depth (450m for Am at VERTEX II and III; 1000m for Pu at VERTEX IV), a decrease in transuranic concentration

Table 3.1 Results of PIT samples (concentrations, activity ratios and fluxes) from VERTEX IV  
Analyses of surface sediment (top 1 cm) from cores are included

PIT depth (m)	Sample Dry wt. (g)	Concentrations (pCi Kg <sup>-1</sup> dry)					Approx. mass flux (mg dry m <sup>-2</sup> d <sup>-1</sup> )	FLUX	
		<sup>239+240</sup> Pu	<sup>238</sup> Pu	<sup>241</sup> Am	$\frac{^{238}\text{Pu}}{^{239+240}\text{Pu}}$	$\frac{^{241}\text{Am}}{^{239+240}\text{Pu}}$		<sup>239+240</sup> Pu (fCi m <sup>-2</sup> d <sup>-1</sup> )	<sup>241</sup> Am (fCi m <sup>-2</sup> d <sup>-1</sup> )
140	1.035	25.1 <sub>±2.6</sub>	1.3 <sub>±0.5</sub>	5.9 <sub>±1.4</sub>	0.052 <sub>±0.020</sub>	0.24 <sub>±0.06</sub>	175	44.0 <sub>±0.5</sub>	1.0 <sub>±0.2</sub>
250	0.571	58.1 <sub>±14.5</sub>	3.2 <sub>±1.6</sub>	23.5 <sub>±5.9</sub>	0.055 <sub>±0.030</sub>	0.40 <sub>±0.10</sub>	108	6.3 <sub>±1.6</sub>	2.5 <sub>±0.6</sub>
500	0.439	199 <sub>±30</sub>	5.5 <sub>±3.0</sub>	126 <sub>±11</sub>	0.028 <sub>±0.016</sub>	0.63 <sub>±0.09</sub>	75	15 <sub>±2</sub>	9.5 <sub>±0.8</sub>
1000	0.248	405 <sub>±35</sub>	11.9 <sub>±5.4</sub>	271 <sub>±22</sub>	0.029 <sub>±0.014</sub>	0.67 <sub>±0.06</sub>	48	20 <sub>±2</sub>	13 <sub>±1</sub>
1500	0.179	301 <sub>±45</sub>	8.9 <sub>±4.4</sub>	273 <sub>±24</sub>	0.030 <sub>±0.015</sub>	0.91 <sub>±0.14</sub>	34	10 <sub>±2</sub>	9.3 <sub>±0.8</sub>
Bottom Sediment		~ 1		~ 1					

in these particles was noted suggesting that some leaching of the radionuclide had taken place. The finding of very low transuranic concentrations ( $\sim 1 \text{ pCi kg}^{-1}$ ) in the surface layer of deep-sea sediments (5550m) from the same region gives further evidence for an apparent loss of transuranics from sinking particles.

Despite decreasing mass flux with depth at all stations, particulate fluxes of Pu and Am increased up to a certain depth (450m off Mexico, 1000m in the mid-Pacific Gyre) and then began to decrease. It would appear that transuranics scavenged by particles sinking through the maxima were subsequently released at greater depth either as a result of desorptive processes or biodegradation of biogenic material which comprises the majority of the fluxing particulates. In general, Pu and Am fluxes in the oligotrophic waters off Mexico and north of Hawaii were roughly an order of magnitude less than those measured in the highly productive waters of the California current.

In summary, for all regimes studied to date vertical transport of Pu and Am was more rapid out of the euphotic zone where biological activity was greatest. These observations coupled with data on Pu and Am concentrations in biogenic material have led to the following general conclusions:

1. Relatively large, rapidly sinking particles of biogenic origin are primarily responsible for the downward vertical flux of transuranics from the upper mixed layer.
2. Increases in transuranic flux with depth in the upper 1000m appear to be a result of active scavenging of the radionuclides by large particles as they sink through the subsurface maximum of transuranics usually observed in the Pacific between 400-600 meters depth.
3. Fractionation of Pu and Am on particles depends on the nature of the particle and its location in the water column.
4. There is evidence to suggest that as particles sink, particulate-associated transuranics are released back to the water column in deeper water.

#### Reference

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3.1.2 Comparative role of salps and other zooplankton in the cycling and vertical flux of selected elements and natural radionuclides  
(S. Krishnaswami\*, M. Baskaran\*, S.W. Fowler and M. Heyraud)

Much of the driving force in elemental cycling by plankton comes from a steady production of biogenic debris (fecal pellets, molts, phytoplankton hard parts, carcasses, etc.) in the upper water layers. Gelatinous zooplankton such as salps commonly constitute a major part of the plankton in oceanic and coastal waters during various times of the year. Despite their importance in terms of biomass the role of these organisms in the cycling and removal of trace elements and radionuclides from the water column is only poorly understood. To obtain more information on gelatinous species, we collected several samples of salps and a sample of salp feces using techniques reported previously (Fowler, 1977; Higgs *et al.*, 1980) and analyzed them for P, Ca, Sr, Fe, Al, Zn, Cu,  $^{228}\text{Th}$ ,  $^{232}\text{Th}$ ,  $^{234}\text{Th}$ ,  $^{238}\text{U}$ ,  $^{210}\text{Po}$  and  $^{210}\text{Pb}$ .

The results indicate that elemental abundances in the gelatinous salps are of the same order as those in crustacean zooplankton. Geometric mean enrichment factors (metal/Al ratio in organisms divided by metal/Al ratio in crustal rock) computed for salps are  $^{210}\text{Po}$ =810, Sr=164, Zn=140, Ca=114,  $^{210}\text{Pb}$ =55, U=52, Cu=26, Th=5.3, Mn=4.3 and Fe=2.1. Whereas Mn, Fe and Th show little if any enrichment in salps relative to crustal rock, the high enrichment factors for Ca, Sr, Zn, Cu, U,  $^{210}\text{Po}$  and  $^{210}\text{Pb}$  suggest some degree of biological uptake. The geometric mean enrichment factor for  $^{210}\text{Po}$  in salps (810) is lower than the "typical"  $^{210}\text{Po}$  enrichment factors of 4000 reported for crustacean zooplankton by Cherry *et al.* (1983); however, their compilation did not include data for gelatinous species like salps. The low  $^{210}\text{Po}$  enrichment factor in salps compared to those in crustacean zooplankton suggests a richer alumino-silicate content in salps.

Salps produce an abundance of fecal pellets or flakes which are large and settle very rapidly. Elemental and radionuclide concentrations in salps and their fecal pellets are given in Table 3.2. It is evident that for most nuclides there is considerable enrichment in the fecal material of salps. Similar observations have been noted for trace elements and radionuclides in fecal pellets of euphausiid crustaceans (Fowler, 1977; Higgs *et al.*, 1980) and copepods (Fowler *et al.*, 1983). Particularly noteworthy with salp feces is the fact that it contained 2.84% Al, 1.2% Fe,  $4 \mu\text{g g}^{-1}$   $^{232}\text{Th}$  and  $24 \text{ dpm g}^{-1}$   $^{210}\text{Pb}$ , concentrations which indicate a high alumino-silica content.

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\*Physical Research Laboratory, Ahmedabad, India.

Table 3.2 Range and mean elemental and radionuclide concentration in salps (n=5), their feces and the estimated flux contribution due to defecation

Nuclide	Salps		Salp Feces ( $\mu\text{g g}^{-1}$ dry)	Feces/Salps	Flux via defecation ( $\mu\text{g g}^{-1}$ dry salp $\text{d}^{-1}$ )
	range ( $\mu\text{g g}^{-1}$ dry)	geometric mean			
P	1866-10228	5560	3621	0.65	905
Ca	12821-63998	46041	82378	1.8	20595
Sr	30.7-1905	684	415	0.6	104
Fe	269-4078	1190	11818	9.9	2955
Al	205-3052	906	28490	31	7123
Zn	35.6-312	110	196	1.8	49
Cu	7.3-22.4	16.0	34.3	2.1	8.6
Mn	20.9-84.0	45.9	169.0	3.7	42.0
$^{234}\text{Th}$	17-111	47*	750*	16	187.0**
$^{228}\text{Th}$	0.155-0.428	0.238*	2.16*	9.1	0.54**
$^{232}\text{Th}$	0.042-0.186	0.104*	1.01*	9.7	0.25**
$^{238}\text{U}$	0.26-1.33	0.75*	0.97*	1.3	0.24**
$^{210}\text{Po}$	9.9-20.1	15.6*	39.5*	2.5	9.9**
$^{210}\text{Pb}$	0.31-4.37	1.1*	24.0*	22	6.0**

\* In units of  $\text{dpm g}^{-1}$  dry wt.

\*\* In units of  $\text{dpm g}^{-1}$  dry  $\text{d}^{-1}$ .

It is possible to derive first estimates of element and radionuclide cycling rates through salps using measured nuclide concentrations in salp feces and published salp fecal pellet production rates. These fluxes are given in Table 3.2. For certain elements such as Cu and Zn, the estimated fluxes through salps are nearly the same as those that have been computed for euphausiids (Fowler, 1977). However, fluxes of Sr, Fe, Mn,  $^{210}\text{Po}$ ,  $^{210}\text{Pb}$ ,  $^{232}\text{Th}$  and  $^{238}\text{U}$  through salps ranged from 3 to 35 times greater than corresponding fluxes through euphausiids from the same waters in the Mediterranean (Fowler, 1977; Higgs *et al.*, 1980). Since the nuclide concentrations in fecal pellets from both zooplankters are roughly similar, the large observed differences in flux are due primarily to the 5-fold higher computed defecation rate in salps compared to that for euphausiids.

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### 3.1.3 Vertical transport studies in the coastal Mediterranean

(S.W. Fowler, S. Heussner, M. Heyraud, J. La Rosa and R. Bojanowski)

Sediment-trap studies have continued making quantitative assessments of the downward vertical flux of particulate-associated elements in coastal waters of the northwest Mediterranean. Off Monaco earlier results indicated that the majority of the large particulates trapped at depth are of biogenic origin such as zooplankton faecal pellets, molts and detritus. Temporal measurements made in the same area during 1983-84 confirmed earlier trends of maximum particulate flux during winter and minimum flux during the summer. Generally particle flux increased with depth with the exception of July-August 1983 when large numbers of orange faecal pellets appeared in the 50m trap. Through gut analyses of fish, it was determined that the pellets originated from large populations of sardine (Sardinella aurita) and horse mackerel (Trachurus mediterraneus) residing offshore at that time. Organic matter content of these pellets was high (54-67%) and fluxes through 50m due primarily to these pellets were very high ranging from  $2-5 \text{ g m}^{-2} \text{ d}^{-1}$ . The fact that these fast sinking pellets ( $600-1000 \text{ m d}^{-1}$ ) were rarely noted in the 150m and 250m traps suggests rapid utilization and recycling of this organic rich material in the euphotic zone. Selected data on organic matter flux are shown in Table 3.3.

In other experiments the possibility of radionuclide leaching from large sinking particles was examined. Aliquots of trapped particulates and sea water in the collecting cups were analyzed for  $^{210}\text{Po}$ - $^{210}\text{Pb}$ . High concentrations of  $^{210}\text{Po}$  ( $0.37-0.81 \text{ Bq l}^{-1}$ ) were found in the sea water from the containers and budget calculations based on particulate and sea water  $^{210}\text{Po}$  concentrations in the 50m trap indicated that 7-9% of the  $^{210}\text{Po}$  had leached from the particulate matter during the 9-17 day deployment periods despite the fact that the traps were poisoned with 5% formaldehyde. Corresponding losses for  $^{210}\text{Pb}$  were less (1.1-1.6%) perhaps because lead is associated to a lesser degree with organic matter than polonium. It is planned to examine these aspects in more detail in future experiments.

Similar experiments were carried out during September-October 1983 in the Gulf of Lion off Banyuls as part of the newly-created French programme ECOMARGE. Again faecal pellets were found to comprise a large portion of the sedimenting material. Faecal pellet fluxes as high as  $7.4 \times 10^6 \text{ m}^{-2} \text{ d}^{-1}$  were measured at 325m. These pellets were characterized by form (spherical, cylindrical and ellipsoid) and some differences were noted between pellets from this study and those from Monaco. In the Gulf of Lion, very large pellets with an average volume of  $4.7 \times 10^7 \mu\text{m}^3$  were collected only in the deeper traps (200 and 325m). Pellets of this size

Table 3.3 Percent organic matter\* of particles and organic matter flux off Monaco

Date	Depth(m)	Organic matter	
		% dry weight	flux g m <sup>-2</sup> d <sup>-1</sup>
March 1983	50	45.5%	0.160
	150	16.1%	0.087
	250	6.5%	0.248
April 1983	50	31.2%	0.129
	150	8.9%	0.136
	250	7.3%	0.210
May 1983	50	32.6%	0.113
	150	11.4	0.073
	250	9.3	0.161
July 1983	50	67.1%	0.164
	150	14.5%	0.131
	250	7.7%	0.170
August 1983	50	53.7%	1.467
	150	11.3%	0.052
	250	8.5%	0.095
April 1984	50	19.0%	0.518
	150	9.4%	0.381
	250	7.5%	0.460
May 1984	50	60.2%	0.194
	150	10.6%	0.167
	250	16.7%	0.311

\* Organic matter determined by weight loss after combustion at 450°C for 4 hr.

were never seen off Monaco and their origin at present is unknown. Calculations indicated that fecal pellets accounted for 20-56% of the large particle (>40µm) flux but only 3% of the total mass flux during this period. Aliquots of trap material were also analyzed for various natural series radionuclides. The concentrations and ratios of different thorium isotopes indicated the presence of a terrigenous component in the particulate matter. For example <sup>232</sup>Th concentrations in particulates from all three depths (2.95-3.55 Bq g<sup>-1</sup> dry) were typical of those found in suspended clays and sediments. Furthermore low <sup>228</sup>Th/<sup>232</sup>Th ratios (~2) also are characteristic of suspended matter in coastal zones. In sum, the data suggested that most of the particles collected in the traps was terrigenous matter resuspended into a nepheloid layer.

Several improvements and modifications to the sediment trap programme were made during this period. Together with TECHNICAP, INC., an automated sediment trap has been designed which will collect from 1 to 6 samples at desired frequencies up to 46 days. The system is designed to operate down to 5000m and can be manipulated on fairly small oceanographic vessels. Use of the system will greatly facilitate temporal sampling in cases where shiptime is limited.

For rapid and precise sample fractionation of trap material, a system using peristaltic pumps has been devised which subsamples the material in suspension by successive sampling of small volumes (<1 ml) on a cyclic basis. With this system it has been possible to obtain fractions up to 1/1000th in 15 to 20 min with a reproducibility on the order of 1%. This technique has greatly facilitated sample preparation for characterization of the biogenic components and fecal pellet numeration.

Previously C/N analyses were carried out in collaboration with Oregon State University. In late 1984 a C/H/N analyzer was purchased and will be operational in early 1985. This instrument will now allow increasing the number of samples from the sediment trap programme, as well as those from other programmes, that can be characterized for these organic constituents.

#### 3.1.4 Remineralization of radionuclides and trace metals from biogenic particles (S.W. Fowler and J. La Rosa)

Sinking biogenic particles, mainly of zooplankton origin, have been implicated by many studies in the vertical transport and cycling of radionuclides and trace elements in marine waters (for review see Fowler, 1982). One important class of particles, zooplankton fecal pellets, obtain these elements directly from the organisms excretion products and through scavenging from the water column. Earlier studies have indicated that certain elements are not irreversibly bound to these particles but, in fact, are released back to the water column during the process of biodegradation. Thus, a knowledge of elemental release rates is a necessary prerequisite to predict the fate of particulate-bound radionuclides and metals. Since studying these kinetic processes in nature is difficult, if not impossible, to do given current technological constraints, laboratory radiotracer experiments have been initiated to obtain first approximations of release rates from euphausiid fecal pellets under different conditions.

To obtain radio-labelled fecal pellets from typical marine zooplankton, the euphausiid Meganycitiphanes norvegica is allowed to graze brine shrimp (Artemia) which have themselves been previously exposed to radiotracer for several days in sea water containing a rich suspension of mixed phytoplankton species. Following ingestion of the thoroughly labelled Artemia, ejected euphausiid fecal pellets are collected by pipet, counted for radionuclide content by gamma spectrometry, and resuspended in 1 Lit. of clean, filtered sea water maintained at either 4°, 13° or 18°C (typical surface and deep oceanic water temperatures).

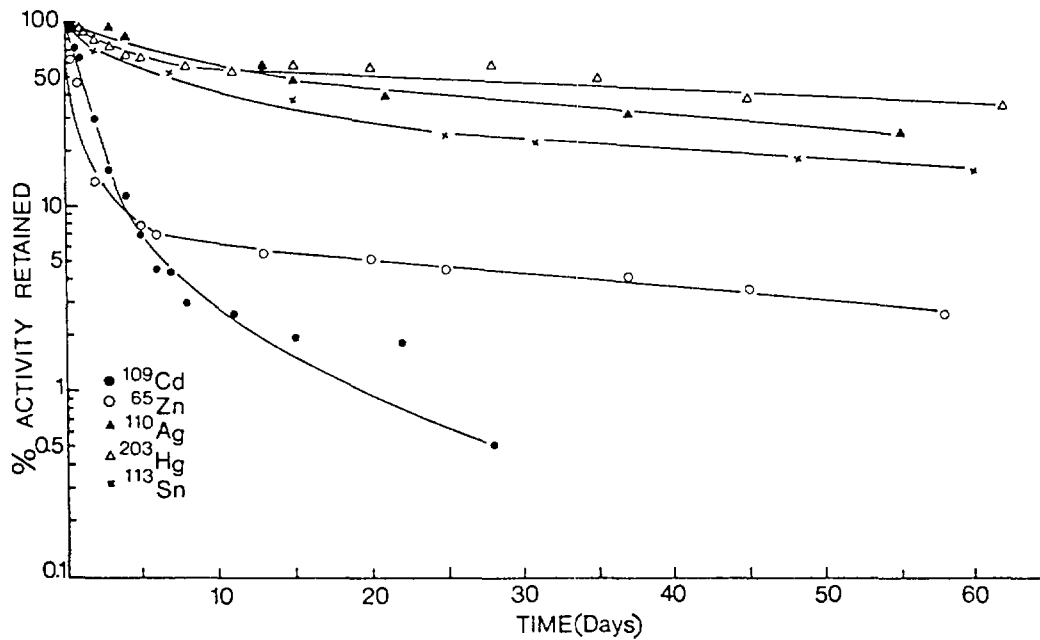


Fig. 3.1 Release of metals from labelled euphausiid fecal pellets.  
Temperature = 13°C.

For the next several weeks pellets are periodically removed, monitored for radioactivity and replaced in clean sea water. Pellets are also examined microscopically to assess any visible biodegradation of the membrane or contents.

Typical results for several metals at 13°C are shown in Fig. 3.1. For zinc and cadmium, roughly 90% of the incorporated metal is rapidly released (about 4 days). In contrast metals such as tin, silver and mercury have a much stronger affinity for these particles as evidenced by retention fractions ranging from 15 to 35% approximately two months after pellet formation. Furthermore, release kinetics appeared to involve loss from more than one radionuclide pool in pellets. For the radionuclide fraction which was released slowly, fitting loss data to an exponential model resulted in release half-times ranging from approximately 6 days for Cd to 60 days for Hg. Temperature had some effect on release rates; for example at 4°C release rates for most elements were slower than at higher temperatures, presumably due to a retardation of pellet decomposition. This effect was far less noticeable between 13°C-18°C.

Future studies will examine kinetics of other trace metals as well as long-lived radionuclides. In addition, loss rates determined from the tracer experiments will be compared with release rates of stable elements and radionuclides in natural fecal pellets produced by field-collected *M. norvegica* (Heyraud et al., 1976) and similar samples from sediment traps. Tracer experiments designed to measure adsorption rates for these types of natural large particles will also be undertaken. Resultant data

in conjunction with information on particle sinking rates will be used to model the vertical transport of these elements under different oceanic conditions.

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#### 3.1.5 Sedimentation of particulate matter in the ocean (B.T. Hargrave\*)

The Nuclear Energy Agency (NEA) sponsors an international group of oceanographers and engineers (the Seabed Working Group) to evaluate the feasibility of using one or more sites in the deep sea (>4500 m) for within sediment burial of high level radioactive waste. One of the current tasks of the Working Group is the development of a box model to describe the distribution of radioactive substances introduced into the deep sea from a source on the seafloor. Assessments of the potential release of long-lived radionuclides from the sediment, and their subsequent distribution throughout the water column are required even though the proposed disposal method is based on the assumption that material buried at depth (30-50 m) in the sediment will remain isolated from the water column for long periods (>10<sup>6</sup> years) of time. Thus oceanographic models of various kinds are needed to predict concentration fields of radioactivity (or other potentially toxic substances) arising from waste deposited in or on the deep-sea floor.

In the event that radioactive substances may be released from waste in the seabed and then become distributed into the water column, it is important to quantify those physical variables, such as horizontal and vertical advection and diffusion, which are known to be important for the dispersion of material in the ocean. However, removal of particle-reactive elements from the water column by scavenging on vertically settling particles or by direct uptake on bottom sediments have been implicated as causes for depletion of substances like <sup>210</sup>Pb from ocean regions adjacent to continents. Recent work in this laboratory (Fowler et al., 1983) has also shown that increased

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\*Government Expert from the Marine Ecological Laboratory,  
Bedford Institute of Oceanography, Dartmouth, Canada.

concentration and vertical flux of plutonium and americium with depth down to 750 m in the Northeast Pacific are probably due to scavenging of these elements by sinking biogenic debris. These observations show that knowledge about downward particle flux, both as quantity and quality (particle size, organic composition, ability of settling material to scavenge reactive substances, for example) must be included in numerical models of advection and diffusion if the flux of material in the ocean is to be adequately described.

One requirement for representing effects of particle scavenging in any oceanic dispersion model is an estimate of the rate of particulate sedimentation. Dr. Hargrave, the Canadian member of the Biology Task Group, was asked to provide this for the Working Group. Recent studies with sediment traps in areas which differ in levels of phytoplankton production have shown that particulate matter sedimentation might be predicted by a relationship between phytoplankton primary production and small particle sedimentation (Betzer *et al.*, 1984). The importance of biological production cycles in the photic zone for controlling the rates and nature of sedimenting material in the ocean is well recognized, and an empirical relationship between organic carbon production by phytoplankton and sedimentation has been described (Suess, 1980). These studies were used to calculate dry matter sedimentation in different ocean regions for which estimates of phytoplankton production are available.

The calculations showed that particulate matter sedimentation at bathy-pelagic depths (>1000 m) in central ocean regions varies within narrow limits ( $5-50 \text{ g m}^{-2} \text{ y}^{-1}$ ). However, sedimentation in upwelling and shelf-slope areas is underestimated by the empirical equation derived from studies of sedimentation away from ocean margins. Rates are high over shelf areas ( $25-250 \text{ g m}^{-2} \text{ y}^{-1}$ ) where terrigenous material and laterally transported particulate matter increase sedimentation. Areas of high phytoplankton production in upwelling regions have rates of dry matter flux an order of magnitude greater than those in the central ocean.

Scavenging of particle reactive elements from the water column by settling particulate matter is thus greatest near the margins of ocean basins. This explains the short residence time (water column inventory/flux) of one to four years estimated for  $^{239+240}\text{Pu}$  in the Santa Barbara Basin (Sholkovitz, 1983) and of one to thirty-six years for  $^{241}\text{Am}$  and  $^{239+240}\text{Pu}$  over 750 m off California (Fowler *et al.*, 1983). Where particle sedimentation rates are lower, as in the equatorial Atlantic and Pacific Ocean, estimates for Pu residence time below 1000 m exceed 400 years (Livingston and Anderson, 1983).

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### 3.2 Studies on Biokinetics and Food-chain Transfer

#### 3.2.1 Accumulation of radionuclides by marine phytoplankton

(N.S. Fisher, J.-L. Teyssié, M. Bohe and S. Krishnaswami\*)

The experimental program to examine radionuclide accumulation by marine phytoplankton was continued, with particular attention being paid toward some of the little studied metals, toward some of the "natural series" radionuclides, and toward the procaryotic picoplankton and their interactions with metals.

In virtually all cases, metals were found to associate with phytoplankton (both eucaryotic and procaryotic forms) by passive adsorption in accordance with Freundlich adsorption isotherms (Fisher et al., 1984; Fisher, in press). Dead and living cells accumulated comparable amounts of metal. Concentration factors were determined, using the lowest metal concentrations tested, and found to range from zero to  $10^6$  (Fig. 3.2). Regression analyses show that, at equilibrium, the log of the concentration factors are exponentially related to

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\*Physical Research Institute, Ahmadabad, India.

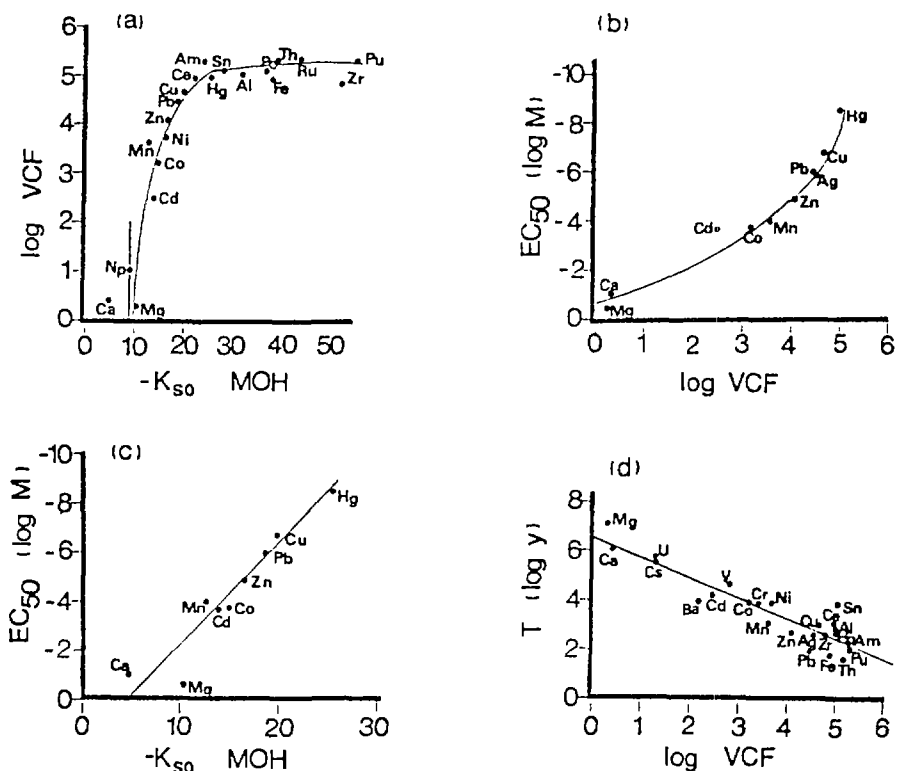


Fig. 3.2 (a) Correlation of VCFs of metals in marine phytoplankton with solubility products ( $-K_{so}$ ) of metal hydroxydes. Error bar around Np indicates that VCF somewhere between zero and 100. Ag not included. Equation for line:  $y = (0.117 e^{17.124/x})^{-1}$ ;  $|r| = 0.847$  ( $P < 0.001$ ),  $n = 21$ .

(b) Correlation of VCF data with sublethal toxicity data ( $EC_{50}$ ) metal concentrations, equal to those molar concentrations necessary to depress growth rate by 50%. Equation for line:  $y = 0.655 e^{-.512x}$ ;  $|r| = 0.978$  ( $P < 0.001$ );  $n = 10$ .

(c) Correlation of sublethal toxicity data ( $EC_{50}$ ) with solubility products ( $-K_{so}$ ) of metal hydroxides. Equation for line:  $y = 1.877 - 0.408x$ ;  $|r| = 0.945$  ( $P < 0.001$ );  $n = 9$ .

(d) Correlation of mean oceanic residence times (T, expressed in log years) of metals with their VCF values in marine phytoplankton. Equation for line:  $y = 6.641 - 0.847x$ ;  $|r| = 0.917$  ( $P < 0.001$ ), SE estimate = 0.568;  $n = 24$ .

solubility products of metal hydroxides and to cytotoxicity, and are linearly related to the log of the mean oceanic residence times (years) of the metals (Fig. 3.2). It would appear that concentration factors and toxicity of metals in marine phytoplankton and oceanic residence times of metals can be predicted to within an order of magnitude from the chemical literature (Fisher, submitted). This suggests that, in the absence of direct data, oceanographic and radioactive waste disposal models can predict the biological accumulation of metals based on their chemical behaviour.



The blue-green picoplankter Synechococcus sp. was found to accumulate metals in the same way as larger phytoplankters, although concentration factors were 1-4 fold greater due to the higher surface to volume ratio of the picoplankters. Given the ambiguity and abundance of the picoplankton ( $\geq 10^7$  cells  $l^{-1}$  in the open ocean) and their high affinity for some metals, it is estimated that picoplankton-based food webs would represent a major route for the movement of particle-reactive metals (e.g. Sn, Hg, Pb, Pu, Am, etc.) in marine ecosystems (Fisher, in press).

The accumulation of natural series radionuclides (U, Ra, Th, Pb) by phytoplankton was studied using radiotracer techniques and cultured phytoplankton. Samples were counted for gamma emissions at our laboratory and for alpha emissions at the Physical Research laboratory, Ahmedabad, India. Uranium and radium were generally found to concentrate  $\approx 10^2$  times in phytoplankton, Pb  $\approx 10^4$  times, and Th  $\approx 10^5$  times. Research in this area is still in progress.

The toxicity of Cd, Zn, Ag, and Hg were examined in four phytoplankton species -- a diatom, a green alga, a coccolithophore, and a filamentous blue-green alga. Metal toxicity, as measured by depression of the cell division rate, could generally be described as an exponential function of the log of the external (or cellular) metal concentrations, consistent with the concept of cell thresholds of safe metal accommodation. Interspecific differences in algal sensitivity were partly attributable to differential metal accumulation but primarily a result of differential ability to tolerate cellular metal loads (Table 3.4). The green alga Dunaliella tertiolecta was generally the most

Table 3.4 Concentration factors (VCF<sub>s</sub>)( $\times 10^3$ ) and sublethal toxicity (EC<sub>50</sub>) of four metals in four marine phytoplankters. Cellular EC<sub>50</sub> values are normalized on a cellular volume basis ( $-\log \text{ mol metal } \mu\text{m}^{-3} \text{ cell}$ )

	Cd		Zn		Ag		Hg	
	VCF	EC <sub>50</sub>	VCF	EC <sub>50</sub>	VCF	EC <sub>50</sub>	VCF	EC <sub>50</sub>
<u>Thalassiosira pseudonana</u> (diatom)	0.3	16.7	12	16.8	34	16.6	93	18.6
<u>Dunaliella tertiolecta</u> (green)	1.0	16.8	10	15.7	13	16.2	32	16.9
<u>Emiliana huxleyi</u> (coccolithophore)	0.4	16.7	4.6	16.7	24	17.8	95	18.8
<u>Oscillatoria woronichinii</u> (blue-green)	1.0	nd	5.2	16.6	66	18.0	76	19.1

metal-resistant species and was capable of tolerating up to 10 (Zn) or 100 (Ag and Hg) times more cellular metal than the other species, indicating safe accommodation of cellular-bound metal.

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#### 3.2.2 Mussel accumulation of transuranic elements (P. Bjerregaard\*, N.S. Fisher and S.W. Fowler)

Research on the accumulation and loss of Pu and Am by mussels has been continued, with emphasis placed on experiments which may assist in interpreting Mussel Watch data. Experiments focused on the kinetics of accumulation and loss of these transuranic elements, their sites of deposition in the animal (Mytilus edulis), and the degree to which transuranic accumulation in the whole animal, or specific tissues, depends upon ambient transuranic concentration in the water. It was shown (Fig. 3.3) that Pu and Am content in whole mussels, soft parts, and especially shell were a direct function of the ambient concentration of the elements, indicating that the Mussel Watch concept of using mussels as bioindicators of ambient transuranic levels is valid.

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\*Institute of Biology, Odense University, Denmark.

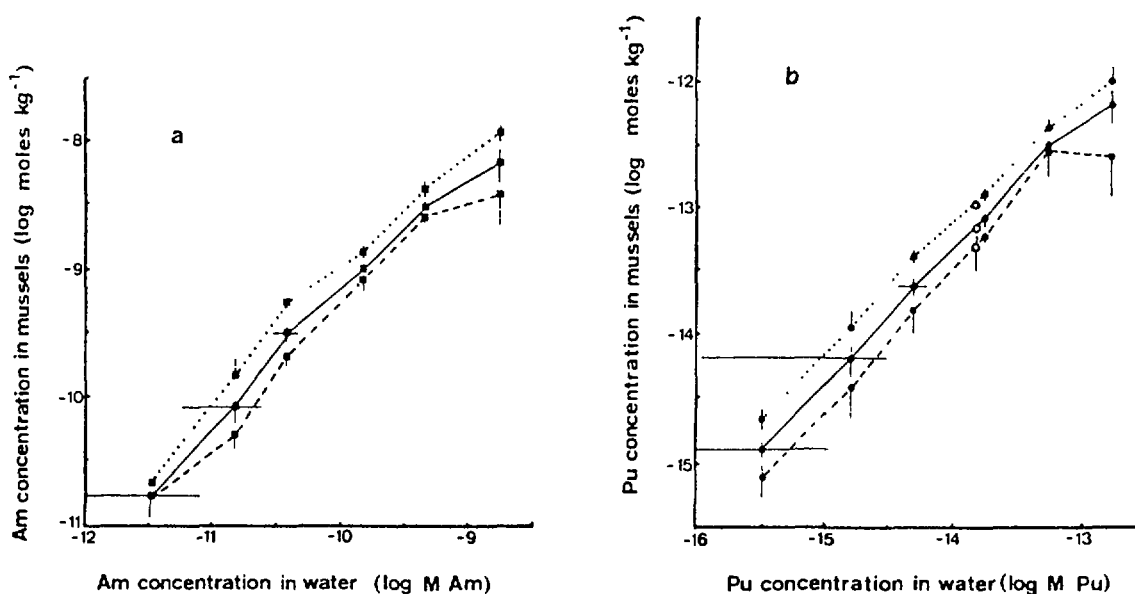


Fig. 3.3 Mytilus edulis. Uptake of  $^{241}\text{Am}$  (a) and  $^{237}\text{Pu}$  (b) in whole individuals (—), soft parts (---), and shells (....) in mussels exposed to a range of  $^{237}\text{Pu}$  and  $^{241}\text{Am}$  concentrations in double-labelled seawater for 24 h. Open symbols in (b) represent a group of mussels exposed to  $^{237}\text{Pu}$  alone. Mean  $\pm$  SEM for 3 mussels in each group. Horizontal bars: counting errors on water samples.

### 3.2.3 Americium particle formation in freshwater (N.S. Fisher)

A laboratory investigation tested various filtration methods to study the particulate-water fractionation of  $^{241}\text{Am}$  added to filtered freshwater (Monaco tap water) adjusted to different pH's. By using a system of washed Nuclepore polycarbonate filters, the particulate association ( $>0.2\ \mu\text{m}$  or  $>1\ \mu\text{m}$ ) was found to increase hyperbolically with pH and with time, so that less than 1% of the Am was filterable (i.e., retained by a filter) at pH 4.2 and about 5% was filterable at pH 8.2 after 1 day (Fig. 3.4); light had no apparent effect on the filterability of the Am (Fisher, 1985). These values are somewhat greater than those for particle association of Am in seawater but substantially lower than previous estimates of Am particulate association in filtered freshwater. Filter adsorption problems and experimental artifacts have been identified for other filtration systems commonly employed to assess metal particulate association. Contrary to previous studies, the results suggest that Am in freshwater is unlikely to form particles to an appreciable extent at pH's  $\leq 8$ .

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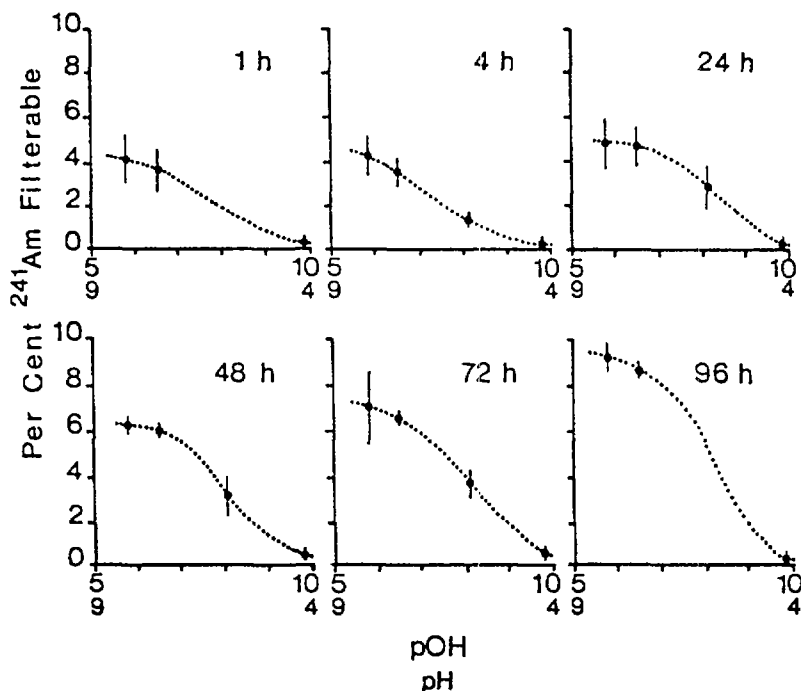


Fig. 3.4 Fraction of water column <sup>241</sup>Am filterable on 1 µm Nuclepore filters at different pOH's. Data points are means ± 1 SD from 3 replicate flasks at each of 6 sample times (1, 4, 24, 48, 72 and 96 h). Samples from replicate flasks, unopened until 96 h, indicated that sampling introduced particles which accumulated 1.3% of the water column Am at pH's 7.5 and 8.2 and 0% at pH 4.2.

### 3.2.4 Accumulation and transfer of transuranic nuclides in benthic organisms (S.W. Fowler and F.P. Carvalho\*)

Work on delineating the bioaccumulation and transfer of transuranic radionuclides through benthic food chains is continuing. At the first trophic level three species of macrophytic algae (a green, *Ulva rigida*; a brown, *Fucus vesiculosus*; a red, *Gigartina stellata*) were exposed to <sup>243</sup>Am for 1-6 h to determine the rates at which Am deposits on the blades (Carvalho and Fowler, 1985). Americium was taken up in direct proportion to its concentration in seawater, with the green alga accumulating 3 to 5 times more tracer than the brown or red species. Results from uptake experiments carried out in the light and dark suggest that Am accumulation is a passive process and that adsorption takes place mainly on the thin outer organic coating of the seaweed. The Am transport coefficients ( $0.9 - 4.1 \times 10^{-5} \text{ Bq cm}^{-2} \text{ s}^{-1} / \text{Bq ml}^{-1} \text{ seawater}$ ) are quite similar to that previously found for the naturally occurring alpha-emitter <sup>210</sup>Po, but are an order of magnitude lower than a plutonium transport coefficient reported in the literature. Because surface

\*IAEA Fellow from National Laboratory of Energy and Industrial Technology, Sacavem, Portugal.

phenomenon are involved in Am uptake, release of labelled extracellular products associated with the algal surface coating is considered to be responsible for the observed rapid loss of Am, from macroalgae.

The scavenging isopod, Cirolana borealis was exposed to  $^{237}\text{Pu}$ ,  $^{241}\text{Am}$  and  $^{252}\text{Cf}$  in seawater for several weeks and then dissected to determine the distribution of these radionuclides in its tissues (Table 3.5). The major fraction of Am and Cf was associated with the calcified exoskeleton of the isopods. Both transuranics were also accumulated by internal tissues but to a far lesser extent. In contrast, Pu(IV) and Pu(VI) were comparatively less adsorbed on the exskeleton

Table 3.5 Cirolana borealis. Average ( $\pm$  1 SD) concentration factors for plutonium, americium, and californium in tissues after 23 days exposure to labelled seawater

Tissues	$^{237}\text{Pu(IV)}$ (n=2)	$^{237}\text{Pu(V)}$ (n=2)	$^{241}\text{Am}$ (n=3)	$^{252}\text{Cf}$ (n=3)
Exoskeleton	39	74	245 $\pm$ 40	280 $\pm$ 88
Gut	190	450	210 $\pm$ 181	610 $\pm$ 229
Digestive gland	243	386	61 $\pm$ 44	766 $\pm$ 618
Muscle	298	283	105 $\pm$ 107	397 $\pm$ 131
Haemolymph	36	14	10 $\pm$ 7	71 $\pm$ 34

than Am and Cf and more absorbed by internal tissues. Taking into account relative weights of different tissues, the contribution of exoskeleton to the whole body radionuclide burden is the largest for all three transuranics even though CFs for Pu and Cf were higher in digestive gland (hepatic caeca) and gut.

Food chain transfer experiments have demonstrated differences in transuranic assimilation and retention that are related to the radionuclide ingested as well as the different feeding-digestion strategies of the organisms. For example, high  $^{241}\text{Am}$  assimilation efficiencies were noted in both the brittlestar Ophiura textura (87%) and the squat lobster Galathea strigosa (58%) following ingestion of labelled mussel (Fowler and Carvalho, 1985). However, subsequent retention of the assimilated fraction in these two species was significantly different as evidenced by a biological half-life of 78 days for the brittlestar and 14 days for the squat lobster. The relatively long half-life in the brittlestar is primarily a result of the slow gut turnover-times for food characteristic of ophiuroids and asteroids. Likewise, brittlestars fed a

single ration of mussel labelled with  $^{252}\text{Cf}$  assimilated a comparable fraction ( $\approx 90\%$ ) of the ingested radionuclide. However, the subsequent half-life for excretion of the assimilated fraction was only 36 days indicating a much more rapid turnover of Cf compared to Am in this echinoderm.

In the future similar studies are planned to examine the comparative behaviour of Np and Cm in these species using appropriate photon-emitting radiotracers, viz.,  $^{235}\text{Np}$  and  $^{242}\text{Cm}$ .

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#### 3.2.5 Accumulation of $^{241}\text{Am}$ by marine bacterioplankton (F. Azam, N.S. Fisher and S.W. Fowler)

The bacterioplankton represents 10-20% of the total planktonic biomass and 50% of the biotic surface area due to the very small size (mostly 0.2-0.6  $\mu\text{m}$ ) of marine bacteria. Radionuclide uptake by the marine phytoplankton and zooplankton is roughly proportional to their surface area. If the same is true for bacterioplankton, then uptake by bacterioplankton may be a significant factor in marine radionuclide dynamics. For this reason a program has been initiated to study these aspects, by initially examining  $^{241}\text{Am}$  uptake by bacterioplankton.

Previous work with radionuclides has employed only cultured bacteria, however, these organisms may not be representative of natural bacterioplankton assemblages. Bacteria in enriched culture media are larger, and their surface properties as well as their uptake physiology may be different from those of bacteria growing naturally in seawater. Therefore we have used either natural bacterioplankton assemblages or "seawater cultures" (natural assemblages grown in particle-free, un-enriched seawater) (Ammerman et al., 1984) for  $^{241}\text{Am}$  uptake studies.

To measure uptake, samples of natural plankton assemblages (collected from 0, 3, and 7 miles offshore from Monaco) were incubated with 86 pM  $^{241}\text{Am}$  and then were size-fractionated (0.2-1  $\mu\text{m}$ , 1-3  $\mu\text{m}$  and >3  $\mu\text{m}$  fractions by Nuclepore filtration) after different time periods. It was therefore possible to determine the uptake by the bacterial size particles (0.2-1  $\mu\text{m}$ ) and compare it with that of the other size particles. When seawater cultures were used, they were also incubated with 86 pM  $^{241}\text{Am}$ , but aliquots were only filtered on 0.2  $\mu\text{m}$  filters since these samples presumably contained only bacteria. Time-course experiments (generally 24 to 72 h incubations) were also run.

In one natural assemblage, the 0.2-1  $\mu\text{m}$  fraction (bacteria) accumulated, at 24h, up to 10-20% of the total  $^{241}\text{Am}$  uptake by the entire plankton assemblage, although in subsequent samples and in other plankton assemblages the  $^{241}\text{Am}$  uptake by bacteria was not detectable. Volume concentration factors (VCFs) of Am in bacteria were calculated to be as high as  $3-5 \times 10^5$  (in the one community at 24 h). About half of the  $^{241}\text{Am}$  accumulation by natural assemblages (45-55%) was associated with the 1-3  $\mu\text{m}$  fraction. Epifluorescence microscopy revealed that this fraction contained  $1-3 \times 10^7$  cells  $\text{l}^{-1}$  of cyanobacteria (1.5  $\mu\text{m}$  diameter), possibly Synechococcus. If we assume that the cyanobacteria were the only particles responsible for the  $^{241}\text{Am}$  uptake in the 1-3  $\mu\text{m}$  fraction, then the VCF for cyanobacteria in the natural assemblages would be  $2-6 \times 10^7$ . Three cultured isolates of Synechococcus were tested for  $^{241}\text{Am}$  uptake and these cultures gave VCF values around  $10^5$ , within the range observed for other planktonic algae. Seawater bacteria cultures took up  $^{241}\text{Am}$  with a VCF ranging between  $10^6$  and  $10^7$ .

These early results indicate that in natural planktonic assemblages, heterotrophic bacterioplankton may, under certain conditions, concentrate Am comparably to the phytoplankton. Further research is needed to explore the influence of environmental conditions in bacterial accumulation of Am and other particle-reactive metals. The additional finding that cyanobacteria are highly effective in accumulating Am has been confirmed in subsequent, detailed experiments (Fisher, in press) and may be of importance particularly in oligotrophic waters where they are thought to be the dominant primary producers.

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3.2.6 Influence of food composition on the assimilation of zinc and americium in mussels (N.S. Fisher and J.-L. Teysseyé)

A series of radiotracer experiments was conducted to investigate the influence of food type on the biokinetics of zinc and americium in the common mussel, *Mytilus edulis*. Four types of food - a diatom, a green alga, glass beads, and egg albumin particles - were labelled with gamma emitting isotopes (either  $^{65}\text{Zn}$  or  $^{241}\text{Am}$ ) and fed to the mussels. The beads and albumin particles, of comparable size to the algal species, were used as representative pure mineral and pure protein particles, respectively, enabling a direct comparison of the assimilation of the two metals from a common source. Wet weight concentration factor of  $^{65}\text{Zn}$  and  $^{241}\text{Am}$  in whole mussels ranged from 12 to 35 after 5 d of feeding. Americium-241 was retained longer than  $^{65}\text{Zn}$  by shells, while  $^{65}\text{Zn}$  was retained much longer than  $^{241}\text{Am}$  in the soft parts (Fig. 3.5). In the soft parts,  $^{241}\text{Am}$  was predominantly found in the

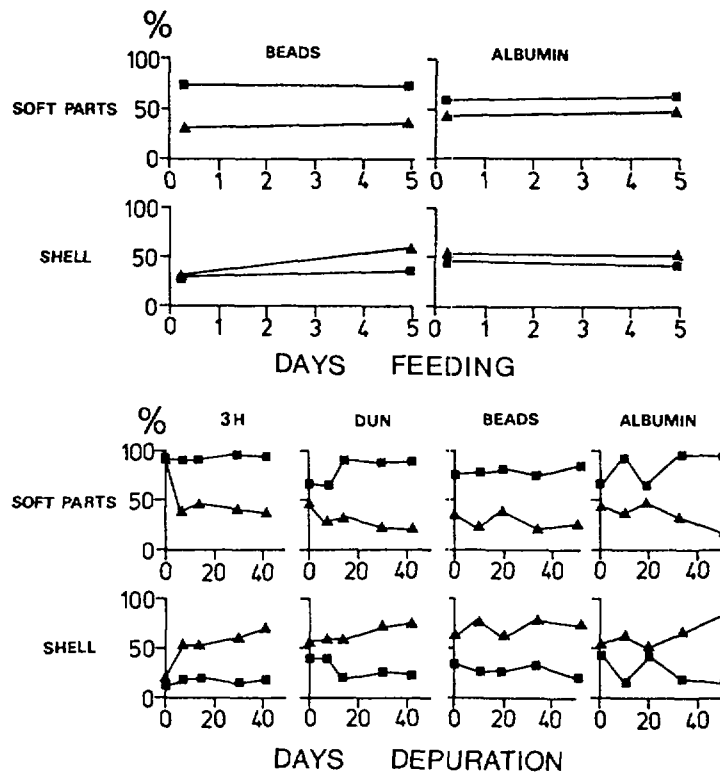


Fig. 3.5 Fractionation of  $^{65}\text{Zn}$  (■) and  $^{241}\text{Am}$  (▲) in shell and soft parts of mussels fed radioactive food. Values are percentages of radioactivity measured in whole mussels found in total soft parts or shells after dissection. Fractionation of radionuclides after 6 h and 5 d feeding on labelled glass beads or albumin particles (from two different experiments) is shown together with fractionation in mussels fed radioactive diatoms (3H), green algae (Dun), glass beads, or albumin particles during 6 - 7 weeks depuration in unlabelled seawater.



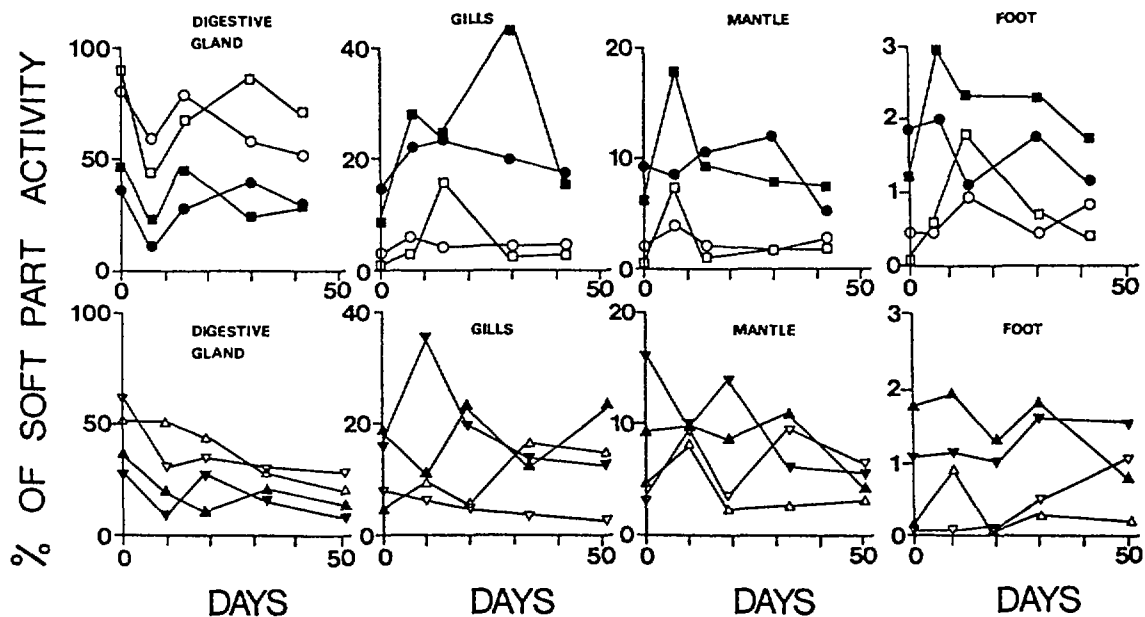


Fig. 3.6 Fraction of total soft parts radioactivity found in digestive gland, gills, foot and mantle after dissection of mussels during 6 - 7 weeks of depuration in unlabelled seawater. Mussels were fed either diatoms --3H-- (■, □), green algae --Dun-- (●, ○), glass bead (▲, △), or albumin particles (▼, ▽) labelled with either  $^{65}\text{Zn}$  (solid symbols) or  $^{241}\text{Am}$  (open symbols).

digestive gland, while  $^{65}\text{Zn}$  crossed the gut lining far more effectively than  $^{241}\text{Am}$  and was distributed to a greater extent in the gills, muscle, mantle and foot (Fig.3.6). There was no appreciable influence of food type on the assimilability of the radiotracers, as the mussels were able to distinguish between the  $^{65}\text{Zn}$  and  $^{241}\text{Am}$ , irrespective of food. This was probably a result of the rapid desorption of these radionuclides from the food particles into the acidic gut of the animals, followed by binding of  $^{65}\text{Zn}$  to specific ligands or molecules which introduce it into specific metabolic pathways.

### 3.2.7 Potential use of $^{210}\text{Po}$ levels (and $^{210}\text{Po}/^{210}\text{Pb}$ ratios) as natural tracers of the diet of marine organisms (R.D. Cherry\* and M. Heyraud)

On several occasions we have suggested that  $^{210}\text{Po}$  measurements have considerable potential as an indicator of the nature of the food consumed by marine organisms (Cherry and Heyraud, 1982; Boyd *et al*; 1984). Interested by this suggestion, P. Domanski of the Institute of Oceanographic Science (UK) offered us some collaborative work on biological samples, mainly shrimp, taken in the water column in the

\*Physics Department, University of Cape Town, Cape Town, South Africa.

region of  $40^{\circ}\text{N}$  close to the Azores on both sides of a pronounced frontal area. The aim of the project was to check whether differences in the shrimp communities across the front, probably due to differences in diet, would be reflected by differences in  $^{210}\text{Po}$  (and possibly  $^{210}\text{Pb}$ ) levels in the same species on either side of the front. Formalin preserved specimens of shrimp caught in Spring 1984 during the Discovery cruise were dissected (when possible) into: hepatopancreas, stomach (and contents), gut (and contents) and the remainder. Although the results obtained to date are still preliminary, it is very likely that these results will not be altered significantly when corrected for  $^{210}\text{Pb}$  supported  $^{210}\text{Po}$ . The  $^{210}\text{Po}$  levels in the same species are definitely different on either side of the front.

On one side, in which bloom and post bloom conditions were experienced at the time of collection, the results show  $^{210}\text{Po}$  levels consistently higher than the already high levels we had found two years ago in comparable shrimp samples. These levels were much higher than in the samples of the same species caught on the other side of the front (pre-bloom conditions), particularly so far penaeid shrimp. Once again the striking difference between penaeids and carids was found, among the penaeids the Gennadas and Bentheogennema genera being the highest. In one sample the natural radiation dose in the hepatopancreas is between a thousand and ten thousand times the natural radiation dose to which man is exposed! These differences in  $^{210}\text{Po}$  levels, more pronounced in the hepatopancreas and digestive tract (and its contents) clearly indicate a difference in the food ingested. The measurements are not only useful in clarifying the feeding regimes, but also they provide some knowledge of the concentrations of  $^{210}\text{Po}$  in the feces of these organisms. Feces are well known to be an important factor in vertical transport of many elements or radionuclides, but due to the difficulty in collecting them, no data exists on feces of deep living organisms. When finalized, these results will be used in a joint publication with P. Domanski of IOS.

In another project in 1984, we obtained samples of freshly caught Mediterranean fish to supplement  $^{210}\text{Po}$  and  $^{210}\text{Pb}$  measurements we had made on anchovies and pilchards from near Cape Town in 1983. All indications are that the Mediterranean data are consistent with those from the South Atlantic specimens. The preliminary results are being studied in terms of seasonal variations, animal size, fish type and the absolute levels of  $^{210}\text{Po}$ .

If one tries to coherently group the considerable body of  $^{210}\text{Po}$  data we have published in recent years, one can see that allometric plots of these data, which cover euphausiids and fish as well as shrimp, showed, on logarithmic scales extending over four orders of magnitude on

both axes, that they grouped into fairly neat bands of  $^{210}\text{Po}$  levels depending on the type of organism involved. We believe that this banding reflects the nature of the feeding regime of the organisms.

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#### 3.2.8 Biokinetics of $^{113}\text{Sn}$ in benthic marine organisms (S.W. Fowler, S. Brown and S. Heussner)

Tin has many industrial uses and consequently its environmental levels have been increasing (Siedel *et al.*, 1980). Radioactive tin ( $^{113}\text{Sn}$ ) is a biproduct of processes in nuclear power stations, particularly boiling water reactors (Coughtrey *et al.*, 1983). Furthermore, the radionuclide  $^{126}\text{Sn}$  present in nuclear reprocessing wastes may be important in deep-sea waste disposal context because of its potential mobility and long physical half-life ( $10^5\text{a}$ ). Inorganic tin may be converted to a more toxic organic species by biomethylation in the aquatic environment. For these reasons, tin is receiving interest as a marine pollutant but, at present, very little information is available on the accumulation of tin by marine organisms (GESAMP, 1984).

Accumulation of inorganic tin and retention times in several benthic species have been examined using the gamma-emitter  $^{113}\text{Sn}$  as a tracer and counting its metastable daughter nuclide  $^{113}\text{In}$ . In some cases the daughter nuclide,  $^{113}\text{In}$  (half-life: 99 min) was taken up preferentially by the test species. This required correction either by letting the excess  $^{113}\text{In}$  decay to equilibrium levels of the radionuclide before radioanalysis of the sample, or application of a computer program based on sequential counting of the sample to automatically correct for a known amount of excess  $^{113}\text{In}$ .

Bioaccumulation from water was followed for approximately 2 weeks in several species of macroalgae and in a single species of clam and polychaete. Brown algae accumulated tin to a greater degree than the two species of green algae (Table 3.6). Concentration factors for the red algae were more varied and were greatest in the highly branched species,

Table 3.6 Estimates of concentration factors (C.F.) and biological half times (Tb $\frac{1}{2}$ )  
For loss of  $^{113}\text{Sn}$  in macroalgae, clams and worms

Species	Mean C.F.	Slow Pool Tb $\frac{1}{2}$ (d)	Rapid Pool Tb $\frac{1}{2}$ (d)
<b>Brown seaweeds (Phaeophyceae):</b>			
<u>Padina pavonia</u>	3.06 X 10 <sup>3</sup>	24	
<u>Cystoseira compressa</u>	2.04 X 10 <sup>3</sup>	42	
<u>Cystoseira</u> sp.	2.91 X 10 <sup>3</sup>	42	
<u>Dictyota dichotoma</u>	6.33 X 10 <sup>3</sup>	47	
<u>Punctaria</u> sp.	3.17 X 10 <sup>3</sup>	18	
<u>Taonia</u> sp.	(a) 9.37 X 10 <sup>3</sup>		
	(b) 6.30 X 10 <sup>3</sup>		
<u>Scytosiphon lomentaria</u>	1.98 X 10 <sup>3</sup>		
<b>Green seaweeds (chlorophyceae):</b>			
<u>Ulva</u> sp.	(a) 7.99 X 10 <sup>2</sup>	31	2.3
	(b) 8.01 X 10 <sup>2</sup>	37	1.6
<u>Bryopsis</u> sp.	4.30 X 10 <sup>2</sup>		
<b>Red seaweeds ( Rhodophyceae):</b>			
<u>Pterocladia capillaceae</u>	1.82 X 10 <sup>3</sup>	29	1.7
<u>Ceramium rubrum</u>	3.10 X 10 <sup>3</sup>	29	2.7
<u>Petroglossum</u> sp.	(a) 8.29 X 10 <sup>3</sup>	51	3.8
	(b) 8.56 X 10 <sup>2</sup>		
<u>Laurentia pinnatifida</u>	3.86 X 10 <sup>2</sup>	24	1.8
<b>Clams:</b>			
<u>Venerupis decussata</u>	1.70 X 10 <sup>2</sup>	40	
<b>Worms:</b>			
<u>Hermione hystrix</u>	9.3 X 10 <sup>2</sup>	40	

Cermium rubrum. No significant difference in uptake by Padina pavonia was observed between samples in the light, dark, or with heat killed individuals (50°C for 4 mins), suggesting that uptake is a passive process in this brown alga. Also, no consistent differences were observed in short term temperature experiments (24 h and 140 h) at 6°C and 16°C. However,  $^{113}\text{Sn}$  uptake by Ulva was greater in heat-killed than live individuals and higher in individuals held in the dark than those in the light. Furthermore uptake was significantly greater at 6°C than at 16°C.

To examine the "light-dark" effect in more detail, similar uptake experiments were carried out in "conditioned" sea water, i.e. labelled seawater that had previously contained Ulva and was held in either the dark or light for several days. These sea waters were filtered (0.8  $\mu$ m Nuclepore), placed in the dark and received fresh Ulva. The conditioned sea water was replaced with fresh aliquots of the media every day when the alga were counted. Concentration factors for Ulva were considerably greater in the "dark-conditioned" water than in the "light-conditioned" water (Fig. 3.7), suggesting that the form of tin added to sea water was altered by a photosynthetic exudate of this algae and that its bioavailability from water was reduced.

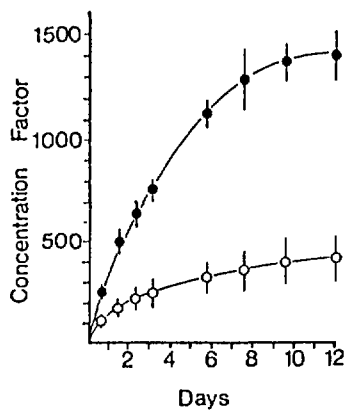


Fig. 3.7

Uptake of  $^{113}\text{Sn}$  by Ulva sp. in the dark using seawater "conditioned" with seaweed in the dark and in the light. See text for explanation. Data points represent the means  $\pm$  95% confidence limits. Experiment conducted at  $16^\circ\text{C} \pm 0.5^\circ\text{C}$ . (o) with "dark conditioned" seawater. (●) with "light conditioned" seawater.

Benthic invertebrates such as clams and worms also took up  $^{113}\text{Sn}$  reaching relatively high whole body concentration factors (Table 3.6). Uptake was considerably greater in the burrowing polychaete than in the filter-feeding bivalve. Tissue dissection at the end of uptake demonstrated that greater than 95% of the incorporated  $^{113}\text{Sn}$  was associated with the worm body wall and shell of the clam, an observation which suggests that adsorption predominates in the uptake process.

Following uptake, several algal species and remaining invertebrates were transferred to clean running seawater to measure depuration. Loss of  $^{113}\text{Sn}$  from the brown algae followed a single exponential model while depuration kinetics in the green and red algae indicated loss from at least two pools. Depuration experiments carried out in the light and dark with Ulva indicated no difference in loss kinetics. Biological half-lives for the slow-loss component varied somewhat between species, ranging from 18 to 51 days. Loss kinetics were similar for the clam and polychaete; the biological half-lives for both invertebrates, 40d, fell within the range of those measured for algae (Table 3.6).

In summary, these preliminary results indicate that inorganic tin is readily accumulated by macroalgae, bivalves and polychaetes probably by passive adsorption processes. Furthermore, brown algae ( $\text{CF}=10^3\text{-}10^4$ ) have

been identified as potentially excellent bioindicators of tin in the environment. Exudates from some algal species can apparently alter the bioavailability of inorganic tin, but the extent of this effect in the natural environment is not known. Further work is needed to examine these aspects in more detail.

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#### 3.2.9 Particle track autoradiography of transuranium nuclides in tissues of marine organisms (P. McDonald\*, S.W. Fowler and M.S. Baxter\*)

The usefulness of thermoset dielectric detectors to determine the localization of transuranium nuclides in the tissues of marine organisms has recently been demonstrated (Hamilton and Clifton, 1980). The advantages of this alpha-track technique are that the tissue distribution of a radionuclide in relative terms can be determined without laborious and time-consuming chemical separation techniques and binding sites within a given tissue can be identified. We have used a plastic dielectric detector medium sensitive to alpha particles to record the distributions of alpha-emitting transuranic radionuclides in mollusc tissues specifically labelled for this study. For this purpose we exposed the common mussel (*Mytilus galloprovincialis*) and the winkle (*Littorina littorea*) to  $^{241}\text{Am}$ ,  $^{239}\text{Pu}$  and  $^{237}\text{Np}$  in seawater at concentrations much higher than those present in the environment. The following trends in transuranic activity were observed in the internal tissues of organisms exposed for 14 days:

##### (1) Mussel

$^{241}\text{Am}$ : Viscera >>Mantle > Gill >> Mantle Edge ~ Foot > Muscle  
 $^{239}\text{Pu}$ : Viscera >>Gill > Mantle Edge > Mantle >>Muscle > Foot  
 $^{237}\text{Np}$ : Viscera >>Gill ~ Mantle >> Mantle Edge > Foot ~ Muscle

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\*Department of Chemistry, University of Glasgow, Glasgow, United Kingdom.

(2) Winkle

<sup>241</sup>Am: Operculum>>>Viscera > Mid-Part > Mantle >> Head > Foot > Muscle  
<sup>239</sup>Pu: Operculum>>>Viscera ~ Mid-Part > Mantle >> Muscle > Foot > Head  
<sup>237</sup>Np: Operculum>>>Viscera ~ Mid-Part > Mantle >> Head ~ Foot = Muscle

Thus, in general, transuranic concentration trends for the mussel and winkle tissues are as follows:

- (1) Mussel: Viscera > Mantle, Gill > Mantle Edge, Foot Muscle
- (2) Winkle: Operculum > Viscera, Mid-Part > Mantle > Head, Foot, Muscle

Similar trends were exhibited by mussels and winkles examined after depuration periods of 14 and 48 days. The above trends are in general agreement with radioanalytical results obtained by Guary and Fowler (1978, 1981) for Np, Pu and Am in mussel tissues. However, in our particle track studies similarities were observed between the distributions of Np and Am in the mussel and winkle, whereas Pu showed some deviation from these trends. Further qualitative studies of the distributions indicated that Pu was taken up to a lesser extent than Am in all tissues. By far the most active tissue in terms of uptake was the winkle's operculum, a calcareous shield which seals the opening of the shell when the foot is retracted. Alpha-activity in the operculum was high for all three nuclides indicating a strong adsorptive capacity similar to that of shell. Further comparison between mussel and winkle distributions showed that on the whole, winkle tissues contained more radioactivity than mussel tissues, particularly the muscle, although the viscera of the mussel was significantly more active than that of the winkle. Hot spots were also commonly observed in the viscera of both organisms and in the mid-part of the winkle, a fact which demonstrates that the radionuclides were not homogeneously distributed in the tissues of these species.

For purposes of comparison with the autoradiographic results, contaminated mussels were collected from the Ravenglass Estuary near the Sellafield (Windscale) Nuclear Fuel Reprocessing Plant in northern England and subsequently analyzed for plutonium. The relative distribution of plutonium in the internal tissues of these environmentally-labelled individuals was similar to that found in experimentally-labelled mussels by autoradiography.

An autoradiographic study is being performed on environmentally-labelled mussels and winkles collected from the vicinity of Windscale. Because these organisms have much lower transuranic activities than those labelled in the laboratory studies, an exposure time of 1-2 years is required; thus, no nuclide distribution information is yet available.

When analyzing environmental samples from Windscale by autoradiography, it has been considered that Pu and Am are the major source of the total alpha-activity (Hamilton and Clifton, 1980). However, preliminary results on the natural  $^{210}\text{Po}$  content of Windscale mussels collected in September 1984 indicate that  $^{210}\text{Po}$  is present in the tissues at levels about a factor of 3 over those of  $^{239+240}\text{Pu}$ . This finding suggests that if autoradiography is used to analyze mussels labelled with currently existing levels of transuranium nuclides in the Windscale environment, the contribution of  $^{210}\text{Po}$  to the alpha tracks in tissue samples can not be overlooked.

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#### 3.2.10 Intracellular localization and binding of technetium-95m in seastars (S.W. Fowler, S. Heussner, J. La Rosa, F. Goudard\*, J. Galey\* and J. Pieri\*)

Interest has focused on the long-lived radionuclide  $^{99}\text{Tc}$  since it is presently released into the coastal zone along with other fuel processing wastes and future projections indicate an increase in the technetium inventory. The Monaco Laboratory has continued its experimental studies on technetium behaviour in selected marine species as part of a Cooperative Research Agreement Programme between IAEA and the College of Oceanography, Oregon State University, U.S.A. All experiments have utilized the gamma-emitter  $^{95\text{m}}\text{Tc}$  as an analogue for  $^{99}\text{Tc}$ . The radiotracer solution was furnished by Oregon State University.

Earlier studies have shown that seastars feeding on technetium-labelled mussels concentrate the radionuclide in their

\*Department of Biochemistry, University of Nantes, Nantes, France.



digestive gland (pyloric caeca) and subsequently excrete it very slowly with a biological half-life of approximately three months. In order to elucidate the nature of the strong association between technetium and seastar tissues, the asteroid Marthasterias glacialis was fed by mussel soft parts labelled with either pertechnetate (VII) or reduced forms of Tc (IV). Ten days after labelling the seastars were dissected. Since the majority (>96%) of the ingested Tc was fixed in the pyloric caeca regardless of oxidation state, this tissue was subjected to a series of fractionation procedures (Goudard et al., in press) to determine the subcellular distribution of the tracer.

Results of the fractionation of the pyloric caeca homogenate by differential centrifugation are given in Table 3.7. Relatively large percentages of Tc, 42% (IV) and 59% (VII), were found in the fraction containing mitochondria and lysosomes, and in the cytosol (52% and 37%, respectively). The enzyme marker data in Table 3.7 indicate that approximately 5% (IV) and 12% (VII) of the lysosomal enzyme acid phosphatase was present in the soluble fraction. The enzyme was most likely released from ruptured organelles during homogenization; thus, the actual proportion of Tc associated with the lysosomes may be greater than that indicated in Table 3.7. To better determine the exact association of Tc in the lysosomal-mitochondrial fraction, these organelles were subjected to density gradient separation using Metrizamide. A good separation of lysosomes and mitochondria was achieved and the results showed that the majority of the  $^{95m}\text{Tc}$  was associated with the lysosomal fraction regardless of the oxidation state ingested.

Chromatography of the cytosol fraction by gel filtration showed that  $^{95m}\text{Tc}$  was distributed between two distinct peaks. Approximately 56% of Tc (IV) and 34% of Tc (VII) were found associated with the first peak which also contained a protein compound of high molecular weight (~150,000). 24% of Tc (IV) and 60% of Tc (VII) were found in the second peak which was characterized by the presence of an anionic protein of low molecular weight (~10,000). These radioactive peaks were associated with only a small amount of protein, indicating a relatively high affinity of Tc for this particular compound, more so for Tc (VII) than for Tc(IV). This anionic protein resembles the metallothioneins or the "low molecular weight metal-binding proteins" which have been reported in the literature and thus may play a role in metal detoxification mechanisms at the cellular level.

Future studies will examine the interaction of Tc and Cd binding at the subcellular level and the possible induction of the Tc-binding low molecular weight protein by heavy elements.

Table 3.7 *Marthasterias glacialis*. Distribution of different oxidation states of  $^{95m}\text{Tc}$  and marker enzymes in subcellular fractions of the pyloric caeca.  $1\sigma$  based on propagated counting errors

	Tc		<sup>a</sup> Specific activity			
	% total cpm	cpm $\text{mg}^{-1}$ protein $\pm 1\sigma$	C O	A P	5'N	G6P
Tc (IV)						
Nuclei	1.9	22 $\pm$ 3	0	85	239	248
Mitochondria + Lysosomes	42.3	36 $\pm$ 4	3277	1886	828	1234
Plasmic membranes	2.0	11 $\pm$ 3	153	1436	622	1169
Microsomes	2.0	12 $\pm$ 3	0	1393	888	1548
Cytosol	51.8	28 $\pm$ 3	0	276	0	0
Tc (VII)						
Nuclei	0.6	18 $\pm$ 3	0	143	0	111
Mitochondria + Lysosomes	58.9	40 $\pm$ 5	2586	1669	398	242
Plasmic membranes	2.2	7 $\pm$ 3	100	698	581	213
Microsomes	1.5	7 $\pm$ 3	55	869	503	393
Cytosol	36.8	15 $\pm$ 3	0	463	0	162

<sup>a</sup> Specific activities of the marker enzymes are expressed as  $\mu\text{mol min}^{-1} \text{mg}^{-1}$  protein. C O = cytochrome oxidase; A P = acid phosphatase; 5'N = 5' nucleotidase; G6P = glucose-6-phosphatase.

## Reference

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3.2.11 Biochemical studies on natural  $^{210}\text{Po}$  binding in the hepatopancreas of the rock lobster Jasus lalandii (M. Heyraud, E.B. Dowdle\* and R.D. Cherry\*\*).

During the period March 1983-March 1984, one of us (M. Heyraud) was granted one year's special leave, which she spent at the University of Cape Town acquiring advanced training in biochemical and biophysical techniques which could be used to study the intracellular binding of elements or radionuclides in biological tissues.

Due to the overwhelming importance of the natural alpha-emitter  $^{210}\text{Po}$  as a source of the internal radiation dose received by marine organisms, our work was focused on natural  $^{210}\text{Po}$  binding in the hepatopancreas of the rock lobster Jasus lalandii.

The hepatopancreas was dissected out from freshly caught animals anaesthetised with carbondioxide and immediately homogenized (in the presence of nitro phenylguanidinobenzoate, a serine protease inhibitor) in TKM buffer (tris-HCl, pH 7.4, KCl,  $\text{MgCl}_2$ ). The homogenate was then centrifuged at 15,000 G to eliminate the cell fractions known to contain a minor proportion of the  $^{210}\text{Po}$  (Cherry et al., 1979) or ultracentrifuged at 220,000 G to concentrate the microsomal fraction.

All these operations were conducted at 4°C. After an aliquot had been taken for  $^{210}\text{Po}$  and protein measurements, either the supernatant (15,000 G) or the resuspended pellet (220,000 G) were used in various experiments (sucrose gradient centrifugation, gel-chromatography, ultra-filtration, hydrophobic interaction chromatography), the aim of these experiments being to concentrate the  $^{210}\text{Po}$ -bearing fraction and to obtain information about its molecular weight and the strength of the  $^{210}\text{Po}$  binding.

Results show that the majority of  $^{210}\text{Po}$  (either in the 15,000 G supernatant or the 220,000 G resuspended pellet) is associated with a very heavy fraction ( $\sim 10^7$  Daltons and more) with a high specific activity

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\*Department of Clinical Science and Immunology, University of Cape Town, Cape Town, South Africa.

\*\* Department of Physics, University of Cape Town, Cape Town, South Africa.

(approaching pCi/mg protein). Attempts to remove the  $^{210}\text{Po}$  from this constituent showed that the  $^{210}\text{Po}$  was tightly bound and it was only with the sulphhydryl reducing agents -  $\beta$ mercapto-ethanol or dithiothreitol, DTT - that  $^{210}\text{Po}$  was dislodged to any significant extent. After incubation with DTT, most of the  $^{210}\text{Po}$  was found in the less than 1500 molecular weight region.

Hydrophobic-interaction chromatography using an aliquot of the 15,000 G supernatant as sample material showed a very strong retention of the  $^{210}\text{Po}$  on the column.

A possible association of  $^{210}\text{Po}$  with negatively-charged, hydrophobic sulphur-containing membrane proteins is suggested.

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### 3.3. Studies on the Behaviour of Radionuclides

#### 3.3.1 Comparative studies of the fate of radionuclides released into different marine environments (E. Holm, R. Bojanowski, S. Ballestra, J. Gastaud, B. Oregioni and J.-J. Lopez)

Transport and fate of selected radionuclides (radiocesium, transuranium elements,  $^{99}\text{Tc}$  and activation products) from different sources (nuclear power plants, weapon incidents, fallout, reprocessing of nuclear fuel, etc.) into different types of the marine environment (the North Sea, the Mediterranean Sea, the Baltic Sea and the Arctic Sea) were studied.

The radionuclides were selected according to their importance for collective dose to population both on long-term and short-term basis. Most of them are also excellent tracers for studying physical and chemical processes in the marine environment.

The studies were made by collaboration with different institutes, particularly with Risoe National Laboratory, Denmark, Lund University, Sweden, German Hydrographic Institute, FRG, the Bedford Institute of Oceanography, Canada and the Institute of Radiation Protection, Finland. Our participation in cruises organized by some of these institutions allowed us to investigate, in more detail, the behaviour of radionuclides carried into the sea by rivers.

The behaviour of caesium-137 and transuranium elements in the Rhone basin was studied, comparing the distribution of these radionuclides with that of natural actinide elements. Results showed that radionuclides in particulate form generally have much lower concentrations and reflect better the influence of river inflow into the sea than their dissolved counterparts. River discharge effects could be traced by particulate radionuclides over distances where conventional indicators such as dilution effect and suspended loads failed. Thorium isotopes were found to be particularly useful in tracing land-derived particulate caesium-137 and transuranic radionuclides as their concentrations exhibit a similar distribution pattern.

The North Atlantic region comprises in this project the waters around Greenland, the North Atlantic Ocean between Norway and Greenland and the North and Baltic Seas. In this region the salinity ranges from ocean water to brackish water, the climate from arctic to temperate. Although fallout nuclides from nuclear weapons testing in the atmosphere are still the main source for man-made radioactivity, the discharges of radionuclides from reprocessing plants in the Western Europe contribute measurably to the radioactive contamination of the North Atlantic. The radio-nuclides  $^{90}\text{Sr}$ ,  $^{99}\text{Tc}$ ,  $^{134}\text{Cs}$  and  $^{137}\text{Cs}$  are at present detectable in the North, Baltic, Norwegian, Barents and Greenland Seas. The purpose of this project is to study this contamination, using these isotopes as tracers for investigating transport of water masses to the North Atlantic.

As part of the project the contamination with transuranics from a nuclear weapon accident in 1968 at Thule in N.W. Greenland was studied. The aim of the project is to study the behaviour of Pu and Am in the Arctic marine environment in order to follow the deposition of these radionuclides to the sediments. The results may be applicable to deep ocean disposal of low-level waste containing transuranic elements. This project is conducted in collaboration with the Risoe National Laboratory, Denmark and sampling expeditions are expected to be performed at 4-5 years interval. On the basis of samples collected at the Thule expedition 1984, we are investigating physical and chemical speciation of Pu and Am in the sediments and also the possible contamination of uranium at the incident.

For the open Mediterranean Sea, delivery and distribution of transuranium elements and radiocesium has been studied early by this laboratory. Compared to the Baltic Sea the amount of plutonium delivered into the Mediterranean is about the same. While water volume of the Mediterranean is 180 times greater, the concentrations of plutonium in surface seawater is 5 times higher in the Mediterranean than in the Baltic. The computed inventories show that 60-80% of the Pu remains still in the Mediterranean water column, while in the Baltic Sea 99% is present in the sediments.

The major delivery of transuranium and radiocesium to the Mediterranean is fallout while delivery from runoff is of minor importance. For other elements such as  $^{99}\text{Tc}$  discharges from rivers might be of greater importance. In studying  $^{99}\text{Tc}$  in the Mediterranean, bioindicators such as macroalgae are important. Sampling of different species is being conducted regularly along the coast of France and Monaco.

### 3.3.2 Measurements of $^{241}\text{Pu}$ in fallout samples collected at Monaco (S. Ballestra, G. Barci, E. Holm and J. Gastaud)

The analysis of the proportion of  $^{241}\text{Pu}$  in environmental plutonium samples is important because of the concern over the radiotoxicity of its daughter  $^{241}\text{Am}$  and also because of the possibility of identifying the origin of plutonium released into the environment on the basis of characteristic  $^{241}\text{Pu}/^{239+240}\text{Pu}$  atomic and activity ratios from various sources.

The delivery by rain of  $^{137}\text{Cs}$ ,  $^{238}\text{Pu}$ ,  $^{239+240}\text{Pu}$  and  $^{241}\text{Am}$  in the course of 1978-1979 has already been measured in our laboratory already (Thein *et al.*, 1980) and we report here the measurements of  $^{241}\text{Pu}$  in rain at Monaco during the period April 1978-December 1979. The determination of  $^{241}\text{Pu}$  is made by measuring the  $^{241}\text{Am}$  built up through the decay of  $^{241}\text{Pu}$  in the isotopic mixture of plutonium electro-deposited originally on stainless steel discs for the measurements of  $^{238}\text{Pu}$  and  $^{239+240}\text{Pu}$ . The results of the  $^{241}\text{Pu}$  determinations in the rain samples collected at Monaco during the period April 1978-December 1979 are presented in Table 3.8 together with those of  $^{239+240}\text{Pu}$  and  $^{241}\text{Am}$ . Based on the data given in Table 3.8, the monthly variations of  $^{241}\text{Pu}$ ,  $^{239+240}\text{Pu}$  and  $^{241}\text{Am}$  are illustrated in Fig. 3.8. The variations of  $^{239+240}\text{Pu}$  concentrations in rain show distinct spring peaks in June 1978 and May 1979, while the same trend is also observed with  $^{241}\text{Pu}$ . Since the amounts of fallout radionuclides delivered by rain are dependent not only on the

Table 3.8 Concentrations and activity ratios of transuranic elements in rain at Monaco

Sample number	Date of rainfall	Precipitation (mm)	Radionuclide concentration <sup>+</sup> ( $\mu\text{Bq}\cdot\text{l}^{-1}$ )			Activity ratio	
			$^{239}\text{Pu}^*$	$^{241}\text{Am}$	$^{241}\text{Pu}(\times 10^{-2})$	$^{241}\text{Am}/^{239}\text{Pu}^*(\times 10^2)$	$^{241}\text{Pu}/^{239}\text{Pu}^*$
1978							
1	April 29	59	960 $\pm$ 40	26 $\pm$ 4	58 $\pm$ 7	2.7 $\pm$ 0.4	6 $\pm$ 1
2	May 26	46	630 $\pm$ 40	26 $\pm$ 4	22 $\pm$ 4	4 $\pm$ 1	3.5 $\pm$ 0.7
3	June 16-17	19	1550 $\pm$ 70	63 $\pm$ 11	140 $\pm$ 23	4 $\pm$ 1	9 $\pm$ 2
4	August 28	53	280 $\pm$ 20	13 $\pm$ 2	38 $\pm$ 8	5 $\pm$ 1	14 $\pm$ 3
5	Sept. 4-5	14	630 $\pm$ 40	44 $\pm$ 7	80 $\pm$ 10	7 $\pm$ 1	13 $\pm$ 2
6	Oct. 2-3	27	310 $\pm$ 20	78 $\pm$ 11	33 $\pm$ 6	25 $\pm$ 4	11 $\pm$ 2
7	Nov. 26-27	17	260 $\pm$ 20	78 $\pm$ 15	34 $\pm$ 4	30 $\pm$ 6	13 $\pm$ 1
8	Dec. 7-16	104	370 $\pm$ 30	30 $\pm$ 4	38 $\pm$ 7	8 $\pm$ 1	11 $\pm$ 2
9	Dec. 20-27	41	100 $\pm$ 20	13 $\pm$ 2	11 $\pm$ 4	13 $\pm$ 3	11 $\pm$ 3
1979							
10	Jan. 4-9	38	190 $\pm$ 10	26 $\pm$ 3	20 $\pm$ 3	14 $\pm$ 2	10 $\pm$ 1
11	Jan. 20	32	180 $\pm$ 10	17 $\pm$ 2	28 $\pm$ 4	9 $\pm$ 1	15 $\pm$ 2
12	Jan. 27-28	58	370 $\pm$ 20	27 $\pm$ 3	44 $\pm$ 5	7 $\pm$ 1	12 $\pm$ 1
13	Feb. 5-7	14	170 $\pm$ 10	37 $\pm$ 7	16 $\pm$ 3	22 $\pm$ 4	10 $\pm$ 2
14	Feb. 10-11	29	240 $\pm$ 10	41 $\pm$ 7	21 $\pm$ 3	17 $\pm$ 3	9 $\pm$ 1
15	Feb. 15-17	22	70 $\pm$ 4	16 $\pm$ 2	7 $\pm$ 1	21 $\pm$ 3	10 $\pm$ 2
16	Feb. 28	31	160 $\pm$ 10	14 $\pm$ 2	9 $\pm$ 2	9 $\pm$ 1	6 $\pm$ 1
17	March 15	21	410 $\pm$ 40	19 $\pm$ 2	43 $\pm$ 6	5 $\pm$ 1	10 $\pm$ 2
18	March 17	74	370 $\pm$ 40	33 $\pm$ 4	28 $\pm$ 4	9 $\pm$ 1	8 $\pm$ 1
19	March 25	29	520 $\pm$ 40	25 $\pm$ 3	46 $\pm$ 6	5 $\pm$ 1	9 $\pm$ 1
20	March 28	18	200 $\pm$ 10	19 $\pm$ 4	23 $\pm$ 3	9 $\pm$ 2	11 $\pm$ 2
21	April 11-17	33	220 $\pm$ 10	26 $\pm$ 7	27 $\pm$ 5	12 $\pm$ 3	13 $\pm$ 2
22	April 23	16	200 $\pm$ 10	19 $\pm$ 4	20 $\pm$ 4	9 $\pm$ 2	10 $\pm$ 2
23	April 25-27	5	44 $\pm$ 15	-	-	-	-
24	May 19-27	7	1480 $\pm$ 220	-	-	-	-
25	June 4-7	3	1370 $\pm$ 110	-	-	-	-
26	June 13-18	23	170 $\pm$ 30	-	-	-	-
27	July 3	13.5	210 $\pm$ 20	11 $\pm$ 2	38 $\pm$ 7	5 $\pm$ 1	18 $\pm$ 4
28	August	41.7	160 $\pm$ 20	25 $\pm$ 4	19 $\pm$ 4	15 $\pm$ 3	12 $\pm$ 2
29	September	42.6	110 $\pm$ 10	20 $\pm$ 2	10 $\pm$ 1	20 $\pm$ 3	9 $\pm$ 1
30	October	282	170 $\pm$ 20	9 $\pm$ 1	11 $\pm$ 4	6 $\pm$ 1	7 $\pm$ 2
31	November	45.7	30 $\pm$ 4	4 $\pm$ 1	5 $\pm$ 3	12 $\pm$ 3	14 $\pm$ 7
32	December	70.8	30 $\pm$ 4	5 $\pm$ 1	2 $\pm$ 1	15 $\pm$ 4	7 $\pm$ 3

+ Uncertainties given are 16 propagated errors.

\*  $^{239}\text{Pu}$  represents  $^{239}+^{240}\text{Pu}$ .

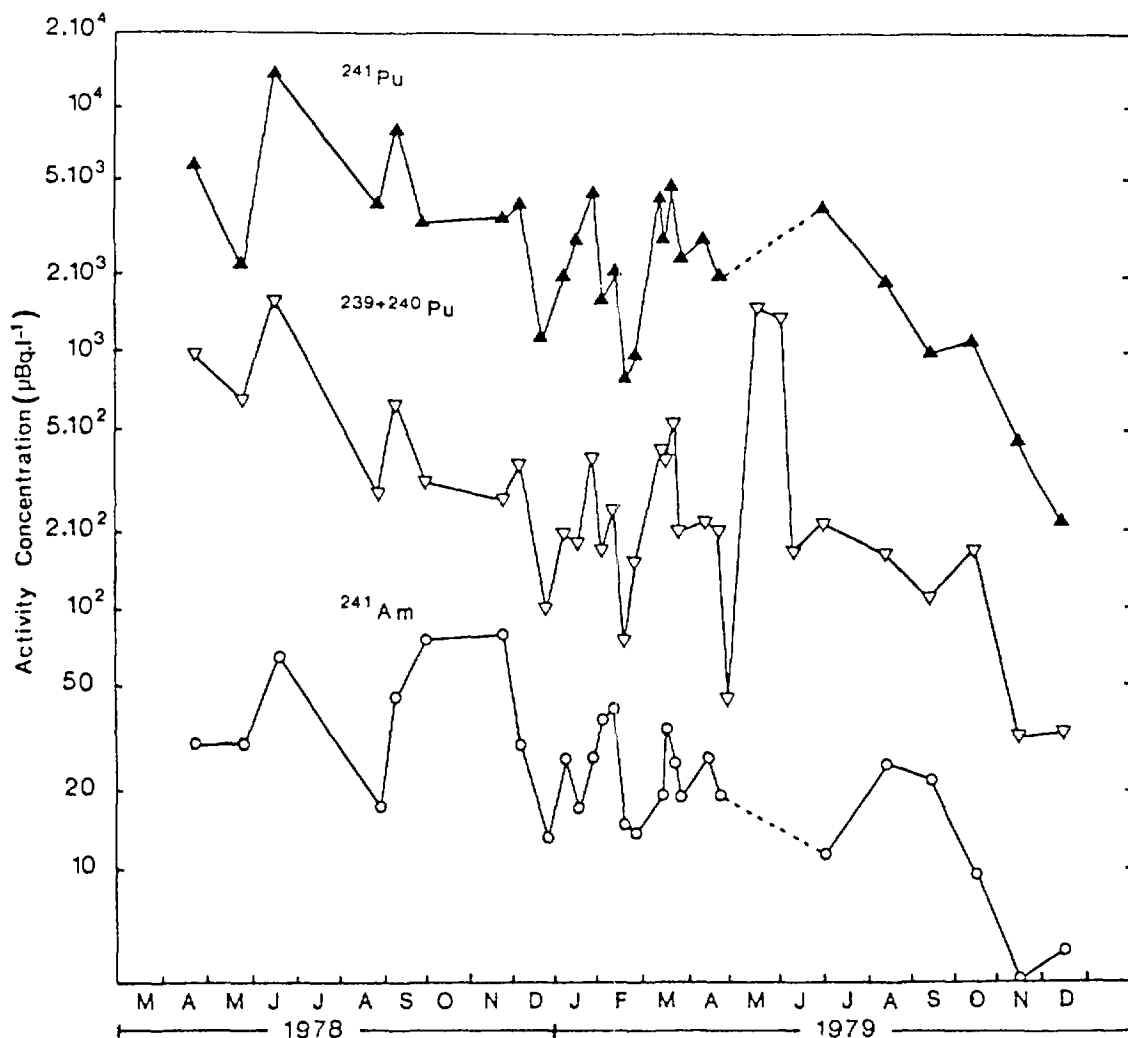


Fig. 3.8 Monthly variation of the  $^{241}\text{Pu}$ ,  $^{239+240}\text{Pu}$  and  $^{241}\text{Am}$  concentrations in rain water at Monaco.

concentration of radionuclides in rain but also on the amount of precipitation, the monthly delivery, of the three isotopes have been calculated. Based on the monthly delivery, the cumulative delivery of  $^{241}\text{Pu}$  by rain at Monaco for the 12 month period (April 1978–April 1979) was calculated to be  $2753 \pm 154 \text{ mBq m}^{-2}$ . By comparison the deliveries of  $^{239+240}\text{Pu}$  and  $^{241}\text{Am}$  for the same period were  $296 \pm 4 \text{ mBq m}^{-2}$  and  $22 \pm 1 \text{ mBq m}^{-2}$  respectively. Based on the annual delivery values, the activity ratio for  $^{241}\text{Pu}/^{239+240}\text{Pu}$  in 1978–1979 is found to be  $9.3 \pm 0.5$ .

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3.3.3 Behaviour of artificial radionuclides in the northwestern Mediterranean basin influenced by river discharge  
 (S. Ballestra, R. Bojanowski, R. Fukai and D. Vas)

While the long-lived artificial isotopes  $^{137}\text{Cs}$ ,  $^{239+240}\text{Pu}$  and  $^{241}\text{Am}$  have long been measured in the Mediterranean waters as well as in other components of the Mediterranean ecosystems, little information is available on the behaviour of these radioelements in the estuarine and seawater bodies adjacent to or influenced by river water discharges.

Samples of seawater, suspended matter and sediments were collected at several stations located between Monaco and the mouth of the Rhone River, during the cruise of R.V. "Suroit" in April 1982 and R.V. "Gauss" in April-May 1982, for radiochemical analysis of Cs, Pu and Am. The position of sampling stations are shown in Fig. 3.9. With the exception of GS-T and GS-1, which are respectively the closest and farthest stations from the coastline, other stations are considered to cover the zone of possible river-sea interaction.

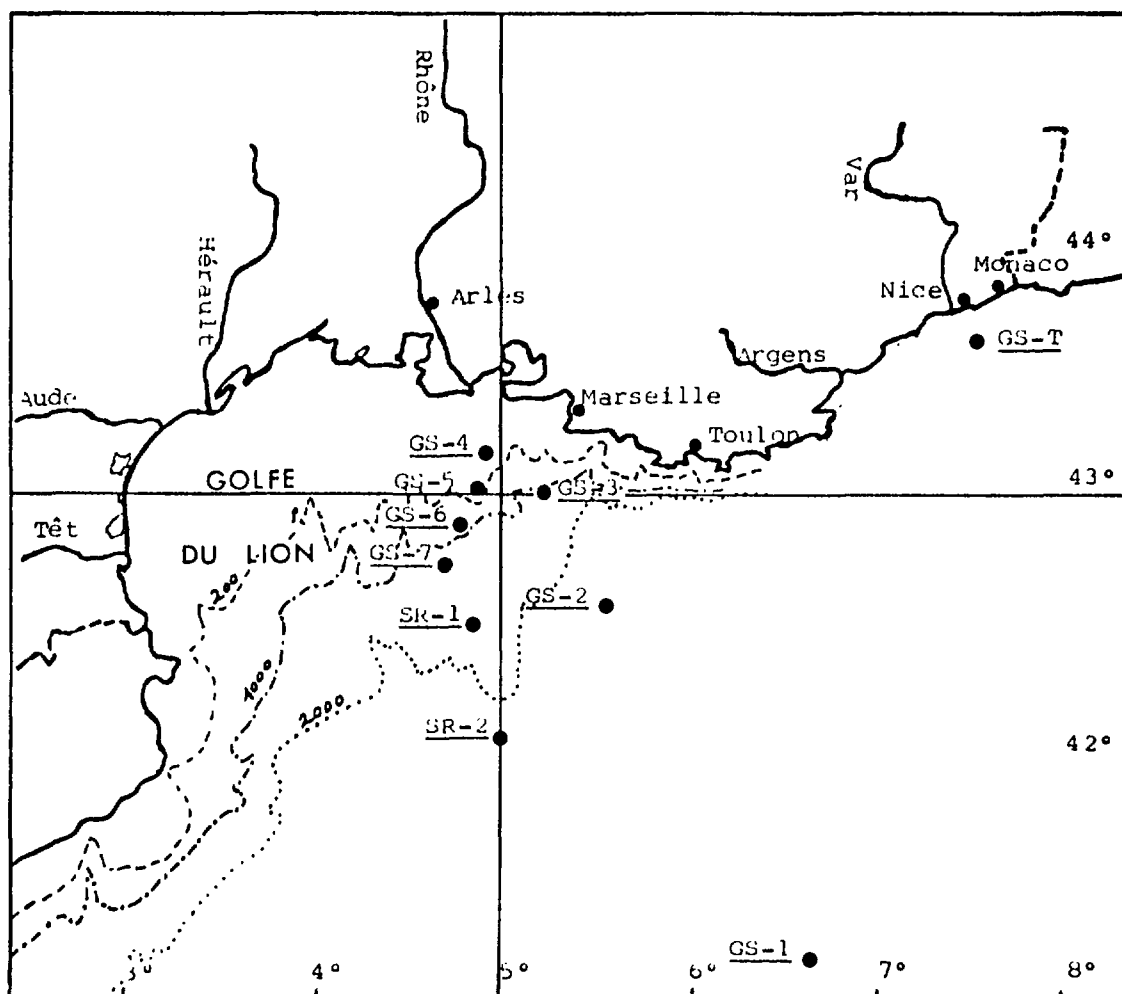


Fig. 3.9 Location of sampling stations during the cruise on board R/V Gauss 27 April - 4 May 1982.

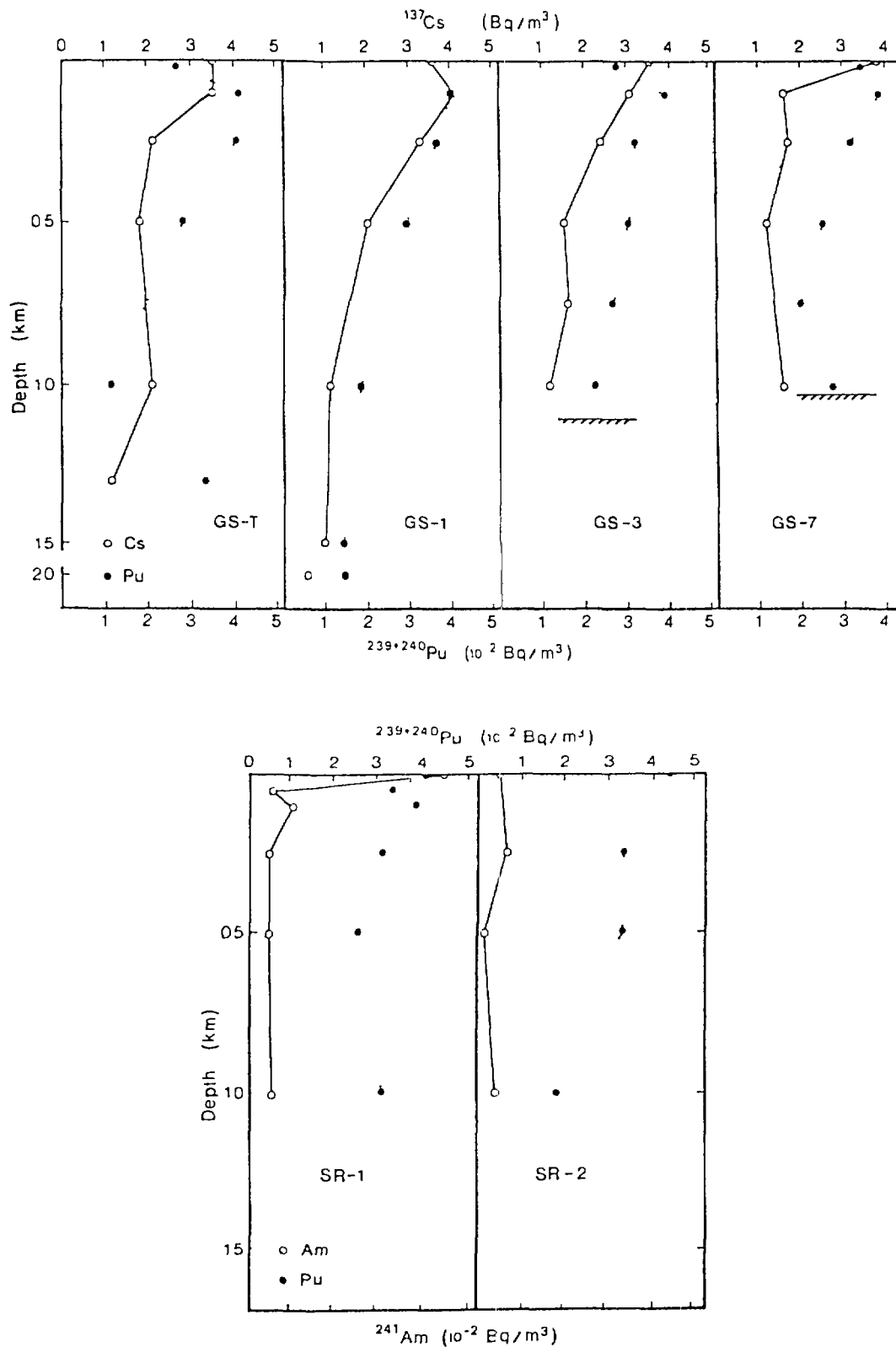


Fig. 3.10 Vertical distribution of  $^{137}\text{Cs}$ ,  $^{239+240}\text{Pu}$  and  $^{241}\text{Am}$  at different stations in the Northwestern Mediterranean.

The vertical distribution of  $^{137}\text{Cs}$ ,  $^{239+240}\text{Pu}$  and  $^{241}\text{Am}$  at different stations are shown in Fig. 3.10. In the distribution pattern of  $^{137}\text{Cs}$  and  $^{239+240}\text{Pu}$  in seawater the same general features can be observed as those described in our earlier work, i.e. the rather uniform activity levels at the surface, more or less pronounced maxima at about 250m and a steady decrease of activity below this depth for  $^{239+240}\text{Pu}$ . The water column inventories show that 30-70% of plutonium and 60-90% of  $^{137}\text{Cs}$  delivered by atmospheric fallout are still present in the water column. The remaining activity was not found to be deposited on the sea floor at the sampling sites. There, the integrated activities were in the range  $1-11 \text{ Bq m}^{-2}$ , i.e. 1-14% of the fallout delivery for Pu and  $2.4 \text{ Bq m}^{-2}$ , i.e. 13-26% for Am. This agrees with the observations regarding the sedimentological structure of the region, which showed that the bottom of the Rhone River discharge area has a fan-like structure with abrupt down valleys and canyons where the sedimentation is being highly perturbed.

Examination of the analytical results for particulate radionuclides revealed a marked relation between the radionuclide concentration and the sampling site. The highest concentrations were recorded in stations closest to the river mouth and the lowest were found in the farthest stations.

The percentage of  $^{239+240}\text{Pu}$  and  $^{241}\text{Am}$  retained on the  $0.45 \mu\text{m}$  filters are generally between 1-3% and 5-10%, respectively. Particulate matter is enriched during its vertical transport from the surface to 250m both with  $^{239+240}\text{Pu}$  and  $^{241}\text{Am}$ .

The results of the study indicate that an isotopic analysis of particulate matter in sea water provides a useful tool in tracing the transport of river discharges. Effects of the River discharge can be detected in the sea at distances, where salinity changes and suspended loads are no longer discernible.

### 3.4 Studies on Marine Sediments

#### 3.4.1 Studies of trace element partitioning in marine sediment

(S. Aston, B. Oregioni and J. Gastaud)

The vexed questions of how trace elements, including radionuclides, are partitioned between the various geochemical components of sediments remain difficult to answer. Various selective chemical leaching

techniques were evaluated in order to compare their relative usefulness in determining these geochemical distributions. Uncontaminated and polluted sediments from several marine environments were employed to obtain some idea of how anthropogenic additions of trace elements are distributed in accumulating sediments.

Table 3.9 The sequential extraction procedure used to determine the geochemical partitioning of radionuclides in the deep-sea sediment

Geochemical Partition Phase	Chemical Extraction Technique
Exchangeable	1 M ammonium acetate
Carbonate	1 M acetic acid
Fe/Mn hydrated oxides	0.1 hydroxylamine hydrochloride + 25% v/v acetic acid
Organic matter	40 vol. hydrogen peroxide + 1 M acetic acid
Resistant	conc. nitric + hydrofluoric and perchloric acids

The geochemical partitioning of technetium and transuranic tracers (Np, Pu, Am and Cf) adsorbed onto marine sediments in laboratory experiments was studied in detail. Some of the results of these studies were already reported (Aston *et al.*, 1984). These studies centred on sediment from the OECD/NEA Northeast Atlantic radioactive dumpsite. In addition to geochemical partitioning studies, the rates of adsorption and equilibrium Kd values were studied. Table 3.9 shows the selective sequential chemical leaching techniques employed, and some example results for the partitioning of transuranic radionuclides are provided in Table. 3.10.

All the transuranic radionuclides studied gave 1% in the exchangeable fraction. Neptunium displayed a marked affinity for the "carbonate" fraction (46%), which supported the observations of Fowler and Aston (1982). The other transuranics showed a strong affinity for the "resistant" fraction, especially Pu (90%), while Np was not enriched in this phase (6%). A surprising result was the paucity of Pu in the "Fe/Mn hydrated oxide" fraction. Field observations on coastal and lake sediments contaminated by nuclear fuel reprocessing wastes and fallout respectively have indicated the importance of this phase for Pu partitioning (Aston and Stanners, 1981). However, the present deep-sea sediment is of a fundamentally different character to those sediments.

Table 3.10 Results of the sequential leaching studies to determine the geochemical partitioning of radionuclides adsorbed onto the NE Atlantic OECD-NEA dumpsite sediment

Partitioning of Radionuclides	Percentage Distributions			
	Np	Pu*	Am	Cf
Exchangeable	2	1	1	1
Carbonate	46	7	18	19
Fe/Mn hydrated oxides	15	1	1	1
Organic matter	32	1	18	18
Resistant	6	90	62	63

\* Mean data for sediment labelled with Pu (III + IV) and (V + VI) oxidation states. No significant differences were observed for the two forms of Pu.

The geochemical partitioning of  $\text{Am}^{3+}$  and  $\text{Cf}^{3+}$  ions adsorbed onto the NE Atlantic sediment are remarkably similar. The proportions of these transuranics in the "exchangeable" and "organic matter" fractions are negligible, while the "resistant" phase is definitely dominant for both nuclides. In general terms, the geochemical partitioning data support the  $K_d$  and rate of adsorption data in as much as Np shows contrasting behaviour to Pu, Am and Cf.

Geochemical partitioning studies on  $^{241}\text{Am}$  adsorbed onto different deep-sea sediments have been used successfully to explain Am bioaccumulation results for benthic fauna (Vangenechten *et al.*, 1983). The sequential leaching techniques used here have now been extended to other deep-sea and coastal sediments for the interpretation of transuranic biogeochemical data.

#### References

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#### 3.4.2 Experimental studies on sediment-animal transfer processes for long-lived radionuclides (S. Aston, S.W. Fowler and P. Parsi)

The transfer of long-lived radionuclides from sediments to benthic organisms is one route by which radioactive wastes may enter the marine food chain if such wastes are disposed of onto the seafloor. Experiments have been carried out to evaluate this process. Attention has centered on the transuranics and other long-lived radionuclides of technetium (Fowler et al, 1983) and has recently been extended to tin.

In the experiments the rates of radionuclide uptake by different benthic species from deep-sea sediments were evaluated. The concentration factors for whole body and individual organs were determined and expressed in relation to both solid sediment and pore water radionuclide concentrations. Parallel uptake experiments from sea water were carried out to enable a comparison to be made with sediment-animal uptake. This combination has allowed some estimates to be made on the relative importance of pore waters in transfer of radionuclides to benthic species. The experiments also involved depuration studies in which labelled animals were placed in uncontaminated sea water or sediment and losses of radionuclides followed as a function of time. In all these experiments, attention has been paid to the oxidation states of the radionuclides involved eg. Tc (IV) and Tc (VII), and Pu (III + IV) and Pu (V + VI).

In order to enable the sediment and sea water transfer of californium to marine organisms, a method for using  $^{252}\text{Cf}$  in radioecological experiments was developed (Aston, 1984). Photon counting was accomplished with a 12 x 12 cm well-type NaI (Tl) scintillation detector connected to a 512 channel pulse height analyser. The detector gain was set to detect only photons in the energy range 2.6 - 5.5 MeV. This restricts the detection to only 3% of the photons coming from spontaneous fission and the decay of short-lived fission products in

equilibrium. However, restricting the detection range to 2.6 MeV provides an extremely low background since natural background gamma rays from the U, Th decay series,  $^{40}\text{K}$ , etc. are eliminated.

The remaining very low background at  $> 2.6$  MeV results from cosmic gamma radiation. Using lead shielding of 15 cm around the NaI (Tl) crystal, the signal-to-background ratios for counting a 10 nCi  $^{252}\text{Cf}$  source in the energy ranges 0-6 MeV and 2.5-6 MeV were 2.6 and 32 respectively. The efficiency of the detection system was calculated to be about 5%. This low efficiency is compensated for by the very low background, and allows good counting statistics to be achieved in experiments where only a few nCi of  $^{252}\text{Cf}$  are used.

The non-destructive technique of counting the prompt photons at energies  $> 2.6$  MeV from spontaneous fission events of  $^{252}\text{Cf}$  is very useful for in vivo and other environmental and ecological experiments. The low efficiency of detection is compensated for by extremely low background counts, and realistic tracer concentrations can be employed for a wide range of studies.

Using similar techniques described previously (Aston and Fowler, 1983; Vangenechten et al., 1983), the bioavailability of  $^{252}\text{Cf}$  from Northeast Atlantic sediments (NEA dumpsite,  $46^{\circ}02'\text{N}$ ,  $16^{\circ}55'\text{W}$ ) was examined in a long-term experiment using the clam Venerupis decussata and the polychaete Hermione hystrix. Mean transfer factors from sediments exposure times ranging from 3 to 4 months were 0.0061 for clams and 0.046 for worms. These values were similar to those measured for  $^{241}\text{Am}$  in the same sediment (Vangenechten et al., 1983), a finding which supports the conclusions of Aston and Fowler (1983) that Cf behaves nearly identical to Am in marine organisms. Furthermore, concentration factors calculated from Cf concentrations in animals and pore water were found to be similar to those achieved following exposure to the radionuclide in sea water, thus, it appears that major pathway for the accumulation of Cf from these contaminated sediments is the interstitial water.

The bioavailability of  $^{237}\text{Pu}$  in the (III + IV) and (V + VI) oxidation states from sea water and a NE Atlantic deep-sea sediment has been studied for clams (Venerupis decussata) and polychaete worms (Hermione hystrix). After 22 days exposure in sea water transfer factors (TF) has not reached equilibrium, and were  $74 \pm 5$  and  $61 \pm 1$  for clams and  $370 \pm 10$  and  $275 \pm 11$  for polychaetes, for Pu (III + IV) and Pu (V + VI) respectively. Depuration rates after sea water exposure followed a single exponential form (half-life: 50 days) for clams, and for polychaetes at least a two component form with half-lives of 1.3 days and

54 days. TF values for  $^{237}\text{Pu}$  bioaccumulation from sediments were very low,  $6 \times 10^{-3}$  and  $5 \times 10^{-2}$  for clams and polychaetes, respectively, after 20 days' exposure.

Plutonium appears to be about 50% more bioavailable to the same species than americium as measured by laboratory experiments using a similar deep-sea sediment. Depuration experiments with clams after 40 days' exposure to labelled sediment indicated loss followed a single exponential form with a half-life of 24 days. Significant differences in the behaviour of Pu introduced into the uptake and loss experiments in different oxidation states were not observed in general.

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#### 3.4.3 Transfer of $^{241}\text{Am}$ and $^{237}\text{Pu}$ between organic biogenic particles and sediments (B.T. Hargrave\*)

Some biogenic material is important for transporting particle-reactive elements to the bottom and the behavior of these elements in sediments should be studied in association with substrates to which they are bound. 'Spiking' experimental water and sediment mixtures

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\*Government Expert from the Marine Ecological Laboratory, Bedford Institute of Oceanography, Dartmouth, Canada.



with nuclides (usually added in acidic solutions) to follow sorption kinetics may not correspond to delivery pathways for these elements when they are added to sediment associated with settling particles. Rates of transfer within sediments may also be controlled by rates of degradation and fragmentation of carrier substrates.

A study was undertaken to quantify the transfer of two particle-reactive actinides ( $^{241}\text{Am}$  and  $^{237}\text{Pu}$ ) between labelled moulted euphausiid exoskeletons and a carbonate-rich (Mediterranean) sediment. The moults were used as an analogue for organic detrital particles which are a predominant pathway of particulate matter flux through the ocean water column. Separation of particle size classes at various times during incubations, which lasted up to 100 days, permitted the transfer of radioactivity to be quantified simultaneously as loss from moults and gain by sediment. Incubations were carried out in oxidized and reduced sediments, with and without  $\text{HgCl}_2$  (which prevented microbial decomposition of moults) and at  $5^\circ\text{C}$  and  $15^\circ\text{C}$  to consider effects of microbial activity on retention rates.

Concentrations of both actinides adsorbed onto moulted exoskeletons over one to seven day exposures decreased exponentially with 50% retention times of three to seven days when moults were incubated in filtered seawater with small amounts of sediment collected off the coast of Monaco. Over 95% of sediment weight was present as  $43\ \mu\text{m}$  silt

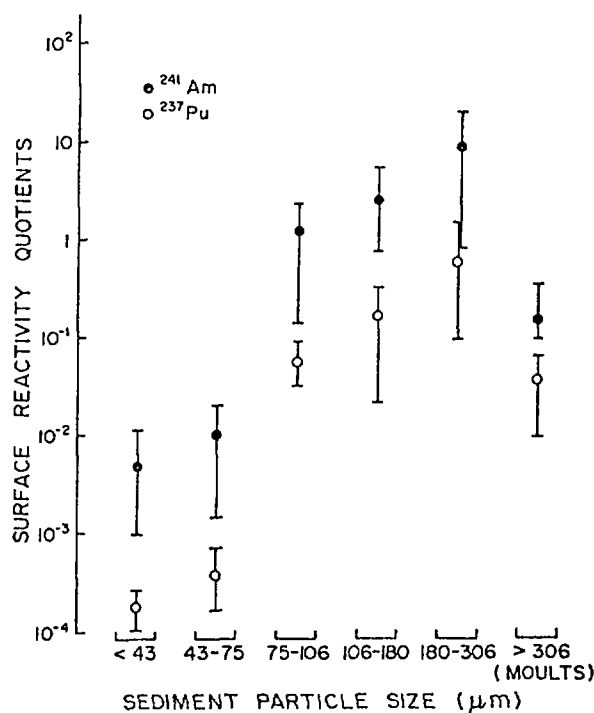


Fig. 3.11 Relationships between the sediment particle sizes and the surface reactivity quotients.

particles and  $91 \pm 4\%$  of radioactivity lost from moults was recovered within this size fraction. Adsorption of both actinides on a particle surface area basis ( $\text{atoms} \cdot \mu\text{m}^{-2}$ ) was greatest in the medium fine sand fraction which had the highest carbonate content (Fig. 3.11). These particles constituted 0.4% of total sediment dry weight, but their reactivity ( $\text{atoms} \cdot \mu\text{m}^{-2} \text{ surface} : \text{atoms m}^{-3} \text{ solution}$ ) was from  $10^3$  to  $10^4$  higher than similar quotients for 43  $\mu\text{m}$  particles. The reactivity quotients also showed the lower affinity for  $^{237}\text{Pu}$  for particle surfaces in comparison to  $^{241}\text{Am}$ . The distribution is consistent with  $K_d$  values ( $10^3$  to  $10^4$ ) of  $^{237}\text{Pu}$  in marine sediments, particularly in the presence of organic complexation, compared with  $^{241}\text{Am}$  ( $K_d = 10^5$  to  $10^6$ ).

The enrichment of the carbonate-rich medium fine sand fraction shows that non-homogeneous distributions of these actinides may arise between particle types. These elements are rapidly desorbed from organic surfaces and transferred to sediment particles. However, animals which sort sediments on the basis of particle size, density or carbonate content, and use these for ingestion or construction of burrow walls will be exposed to different concentrations than bulk analyses of sediments would indicate. Further studies on the small-scale distribution of particle-reactive actinides within sediments are needed to fully assess the importance of the non-homogeneous distribution among sediment particle sizes and types.

#### 3.4.4 Study of distribution of uranium and thorium isotopes in bioturbation (N.E. Whitehead, P. Parsi, M.C. Navarro and J. Vaugelas\*)

The results of the final meeting of the Coordinated Research Programme held in Monaco, emphasised the importance of bioturbation in the redistribution of radionuclides (IAEA TECDOC, to be published).

At the meeting it was reported that the burrow linings of a Calianassa shrimp contained more americium than did the surface sediments in the Irish Sea. Such studies are possible only where the environment contains higher quantities of americium or other waste nuclides of interest than those present in the Mediterranean, where the levels of these radionuclides are very low. However, it is possible to study the natural radionuclides such as  $^{234}\text{U}$  and  $^{230}\text{Th}$  in the Mediterranean.

A new Calianassid has recently been described from the Red Sea (Vaugelas and Saint-Laurent, 1984) called Callichirus laurae. Analyses

\* Laboratory of Marine Ecology, University of Nice, Nice, France

of uranium and thorium in specimens of the mucus on the burrow linings and the surrounding sediments are being carried out in order to detect the differences between these samples, similar to those observed for americium in the Irish Sea.

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#### 3.4.5 Investigation of natural marine high-silica glass

(N.E. Whitehead, J. Veselsky and D. Seward)

To investigate the behaviour of radionuclides in marine sediments, laboratory experiments can be performed, but investigations on materials actually known to have been in such natural environments for known times is likely to give much more realistic information on processes which would take place in situ. Microscopic grains of volcanic glass, which have been separated from marine sediments and already dated by fission-track methods, are available to such investigation. Study of the distribution of various elements within such grains should yield useful information about the fate of the corresponding radionuclides.

In practice, a few milligrams of the grains were irradiated in a reactor with a flux of  $2 \times 10^{13} \text{ n cm}^{-2} \text{ sec}^{-1}$  for two days, then sequentially leached with hydrofluoric acid, and the fractions counted using gamma-spectrometry.

Preliminary results have shown that the distribution of radioactivity generally follows a U-shaped distribution with most on the outside and in the centre fractions, and least in the other fractions.

The results of this type of study are expected to be relevant to subseabed disposal of wastes in vitrified form, especially if the form is high in silica which is thought to be superior in leach resistance over borosilicate glasses (Barkatt et al, 1984).

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#### 4. Contribution to International Marine Pollution Monitoring and Research

##### 4.1 Evaluation of methods for monitoring petroleum hydrocarbons in marine samples (K.A. Burns and J. Cenciarini)

Non-biogenic hydrocarbons enter the marine environment from a variety of sources which include crude oil and petroleum products. In addition, the incomplete combustion of not only petroleum products, but of any material containing carbon and hydrogen generates PAHs which, through a variety of pathways, such as atmospheric deposition, discharge of bilge oil, urban run-off, etc., reach the marine environment. The complexity of the chemical composition of the various contaminant sources and the changes in residue composition due to biological, physical, and chemical processes including photo-oxidation cause additional difficulties to the analytical chemist.

Currently there are not methodologies that can quantify all of the non-biogenic hydrocarbons in an environmental sample. Most environmental chemists define an analytical range of material to be quantified and choose chemical markers within this range that are assumed to provide the needed information on contaminant content.

Relatively inexpensive and general techniques have evolved around the crude measurement of the concentration of aromatic hydrocarbons in a sample as detected by its UV-fluorescence signal compared to that from standards of chrysene or appropriate reference oils. Such methods have proven useful in tracing known pollution events but are not sufficient for precise quantification or for source identification of highly weathered or unknown HC contaminants. At best, the technique serves as a screening technique to be followed up by more precise measurements. That the method requires careful verification was shown by Farrington *et al.* (1984). In this study of a marine worm, Nephtys incisa from the New York sewage sludge dump site, UV-F analysis showed a synchronous excitation emission spectrum which would indicate contamination by hydrocarbons rich in double and triple ring aromatic structures supposedly indicative of contamination by PAHs derived from petroleum or pyrolysis. However, when extracts were analyzed by gas chromatography-mass spectroscopy, the samples did not show the expected pattern of phenanthrenes and other hydrocarbons expected on the basis of the UV-F spectra. One single component, identified as an octahydrochrysene derivative, predominated the GCMS signal and accounted for the UV-F spectra.

These and other findings support the contention that the nonspecific methods chosen for implementing regional or global monitoring

programs must be expanded to include the quantification of markers chosen to address the central questions of: 1) the distinction between biogenic or recently biosynthesized hydrocarbons from contaminant hydrocarbons; 2) the distinction between petroleum products and combustion residues; and 3) the recognition of changes in residue patterns in environmental samples resulting from a variety of biogeochemical processes.

During our studies on the biogeochemical cycling of organic contaminants it has become clear that there must be a distinction between the methodology required to assess ambient water quality on a local scale and to assess the long term distribution and accumulation patterns of organic contaminants on a global or regional scale.

Methodology for regional water quality assessment must be tailored for individual circumstances. Two clear examples of where different approaches are justified is the routine monitoring of petroleum pollution in a region such as the Arabian Gulf which is continually subject to large inputs of crude oils and in monitoring coastal areas adjacent to large urban and industrial complexes and continually exposed to pollution from very mixed sources which require sophisticated analytical techniques for identifications.

Results of monitoring efforts in the coastal waters of Oman confirmed that discharges by crude carriers operating offshore and accidental discharges of oil during loading operations introduce large quantities of crude oil into the coastal ecosystems. Tar levels on beaches were measured to range up to and beyond 2 tonnes per km (Burns et al., 1982). Data from the chemical analysis of oysters were consistent with beach tar observations in showing the overall trend of increasing oil pollution from the country's southern border to the Strait of Hormuz. The lack of exceedingly high levels of hydrocarbons in oyster tissue and very little tar observed in neuston tows confirmed visual observations that not as much oil was present in the water column as would be expected on the basis of the amount of tar seen on the beaches. This and visual observations of the movement of tar on the seabed near to the beaches suggested that tar surveys on beaches were the best indication of the severity of oil pollution in areas adjacent to offshore tanker operations. Basic chromatographic analysis of sediments and oysters provided ancillary but extremely costly information. Petroleum residues in the region consisted of high boiling fractions that would not entirely elute from, and left ruinous deposits on high resolution gas chromatographic columns. Thus it was concluded that UV-F analysis as specified by the methods manuals for the regional monitoring program to be conducted by selected national laboratories would be a feasible method for determining relative water quality; but that chemical cleanup

Table 4.1 Comparison of gas chromatographic and fluorescence analysis of petroleum hydrocarbons in KAP samples April 1984

Sample	µg/g by GC F1	µg/g by UVF F1 + F2	Oil Type GC / UVF
<u>Oysters</u>			
Lima	494	141	crude, bunker fuel / fuel, lt. crude
Al Qurum	79	142	h. crude / fuel. lt. crude
Ras Al Yei	36	25	fuel, lt. crude / fuel, lt. crude
Raysut Head	43	29	fuel / lt. crude. fuel
Ummal Quwain	25	10	lt. crude, bunker fuel / fuel, lt. crude
Abu Dhabi	57	30	lt. crude, bunker fuel / lt. crude
Jebel Ali	29	7	fuel, lt. crude / fuel, lt. crude
Bahrain East	na	84	na / h. fuel, lube oil
Bahrain West	na	18	na / fuel

Freeze-dried oyster tissue was soxhlet extracted with methanol for 8 hours. Extracts were saponified by KOH during a further 2 hours extraction time. Non-saponifiable lipids were partitioned into hexane and dried with Na<sub>2</sub>SO<sub>4</sub>. Hydrocarbons were eluted from extracts in 1 ml hexane charged onto preparative chromatography columns containing 10 ml silica gel under 10 ml alumina (both adsorbants of 5% water content) with 20 ml hexane (F1) followed by 20 ml 10% benzene in hexane plus 20 ml 20% benzene in hexane (F2).

GC estimates of petroleum were made by quantification of total hydrocarbons in the F1 fractions eluting in the C14 - C35 n-alkane range and subtraction of obvious biogenics. Oil patterns were assigned on the basis of maximum elution range of the unresolved complex mixture. Many samples did not return to baseline at C35 indicating the presence of high boiling petroleum residues that could not be quantified on SE-52 columns.

UVF analyses are in units of light Arabian crude oil (ROPME standard oil) from curves generated at 310 nm excitation, 360 nm emission. Oil type assignments are based on the relative predominance of double, triple and higher ring structures seen in a coupled excitation-emission spectrum (23 nm wavelength difference).

procedures for the analysis of biota and sediments must be more clearly defined than manuals currently available in the UN system. Also the UV-F methods must be expanded to cover emission scanning and synchronous excitation/emission scanning to permit the assessment of oil type in samples and the suitability of various quantification standards.

We applied both GC and UV-F analysis to selected samples collected during the regional monitoring programme in the Arabian Gulf. Saturated hydrocarbons eluting in F1 were analyzed by GC and aromatic hydrocarbons eluting predominantly in F2 were estimated by UV-F with reference to the ROPME crude oil standard. In spite of these completely different measurements, the concentrations of total petroleum estimated in these samples which contained highly weathered residues showed fairly reasonable agreement (Table 4.1). Major disparities arose in samples contaminated by fuel or other oils which had very different fluorescence spectra compared to the ROPME standard.

Pollution assessment in areas subject to mixed urban and industrial inputs show much more complicated mixtures of organic contamination and requires the application of specific techniques capable of quantifying important individual contaminants and combination of sophisticated chemical data with biological effects assessment. Malins *et al.* (1984) provide a clear examples of the contamination of coastal ecosystems by an exceedingly diverse assemblage of both HC and halogenated hydrocarbons. These and other studies show the necessity to apply the most advanced techniques available to quantify even a portion of the contaminants present in the environment and to relate environmental chemistry with biological effects.

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#### 4.2 Analysis of individual halogenated hydrocarbon contaminants

(K.A. Burns, J.-P. Villeneuve and C. Cattini)

Analysis of halogenated hydrocarbon contaminants including the chlorinated pesticides has evolved around the quantification of peaks generated on a selective detector such as an electron capture detector of a gas chromatograph. Incomplete resolution of coeluting contaminants makes individual peak quantification extremely inaccurate, especially for mixtures of compounds such as the polychlorinated biphenyls (PCBs). Incomplete resolution of the residues seen in extracts of environmental samples in combination with the largely varying response factors generated on an ECD even by closely related isomers of halogenated hydrocarbons have caused great inaccuracy in the determination of residue levels if quantification is based on average responses (Duinker et al., 1980). Thus great effort has been expended toward increasing the efficiency of preparative chemistry procedures for separating compounds according to classes and in expanding the resolution of the gas chromatographic systems to achieve accurate individual peak quantification. In trying to advance current methodology into regional monitoring programmes we have noted that the availability of reliable analytical standards is a limiting factor for laboratories equipped with only GC capability. Thus, we have undertaken to prepare and distribute standards as our resources permit.

Environmental chemists are often faced with considerable difficulty in identifying even the major components in the complex mixture of contaminants seen in marine samples. For certain classes of compounds the ECD is several orders of magnitude greater than a flame detector thus making it possible to quantify trace halogenated contaminants without interference by other hydrocarbons in the sample extract. However, identification of unknown ECD peaks cannot be made unless a standard is available for matching chromatographic elution patterns and/or a fairly accurate guess of the unknown's structure is made followed by a successful selected ion search using a computerized GCMS system. Even large ECD peaks are usually not visible in a reconstructed total ion chromatogram. Since no relative retention indexing system is currently available for common ECD contaminants under modern temperature programmed capillary GC conditions, we have developed an indexing system similar to the one suggested by Lee et al. (1979) for PAHs. To aid in the search for ECD compounds by GCMS confirmation procedures we chose a set of compounds that are visible by both ECD and FID. Alkylated phthalates are readily available in a series which elutes over the required GC range. We are currently testing the feasibility of developing reproducible relative retention indexes for common ECD contaminants.



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### 4.3 Steps toward developing combined analytical procedures for halogenated and other hydrocarbon contaminants

(K.A. Burns, J.-P. Villeneuve, J. Cenciarini and C. Cattini)

Because of extreme complexity in the patterns of organic contaminants seen in marine samples, the sample preparation techniques as well as detailed analytical methods assume strategic importance in residue identification and quantification. Every type of sample used in marine monitoring programmes has its own particular problems to solve with respect to isolating trace contaminants. Organic contaminants in seawater are generally present in such minute quantities that residues must be concentrated from hundreds to thousands of liters to achieve reasonable signal levels above analytical blanks. Many marine animals concentrate both HCs and HHCs in their body tissues to many times that present in ambient seawater and are thus used as biological monitors. Sediments can provide a record of the longer term accumulation and distribution patterns of contaminants in the marine environment.

Several groups engaged in marine monitoring activities have been successful in developing combined methods for the analysis of the relatively non-polar fractions of HCs and HHCs. Tests of extraction efficiencies of several solvents have shown that hexane is sufficient to recover PCBs and the saturated HCs from freeze-dried sediments and biological materials. But extraction with more polar solvent may be necessary to recover residues such as the polynuclear aromatics (PAHs), toxaphenes (PCCs) and the reaction products of hydrocarbon contaminants. This is especially true for sediments in which these more polar residues are often tightly bound to the sample matrix and often are the majority of residual HCs present. Thus sediment analysis may require stronger extraction conditions than seawater or most biological materials.

We gave special consideration to the improvement of methods for the quantitative analysis of trace organics in seawater. We constructed a

set of stainless steel reservoirs which we used in a totally enclosed sampling system. Deep profile samples were taken with a stainless steel Bodman bottle. Seawater was then forced from sampling bottles into the reservoirs, and then through glass fiber filters to isolate particulates and finally through adsorption columns to isolate dissolved components. The system appears to have potential for the determination of residue levels in the Mediterranean. However, many questions remain on the relative efficiency of various adsorbants, the reduction in analytical blanks, breakthrough volumes for specific contaminants, etc. Since the analysis of trace organics in seawater is still in the research and development stage, it is not feasible to recommend reference methods for use in the Regional Seas Monitoring Programmes at this time.

Attempting to develop combined methods for the extraction of HCHs and HCs we tested the following procedure. Samples of sediments or biological materials were freeze-dried and extracted in a Soxhlet apparatus for 8 hours with hexane. This permitted the recovery of the non-volatile saturated and light aromatic hydrocarbons and the relatively non-polar HCHs such as the PCBs and DDTs, directly into hexane solution and negated the need to change solvents for further preparative work by adsorption chromatography. Samples were then extracted a second time with methylene chloride to recover more of the relatively polar HC residues. The second extract can then be reduced and the solvent replaced with hexane and combined with the first hexane extraction. Extraction is followed by appropriate clean-up steps to remove sulphur and interfering lipids and to fractionate the HCs into polarity classes for analysis by FID and ECD gas chromatography. This combined procedure worked reasonably well for low fat samples such as sediments and seawater extracts. With such samples, a single adsorption chromatography step is sufficient to remove most interfering lipids and to fractionate contaminants into classes. Several published procedures for class separation including those by Risebrough et al. (1983) and by Zell and Ballschmiter (1980) were tested. These methods which are based on column chromatography with Florisil provide a reasonable compromise for combined HC and HHC analysis. Fraction 1 eluted with hexane was calibrated to recover DDE, PCBs, saturated and light aromatic hydrocarbons; F2 was eluted with 30% MeCl<sub>2</sub> in hexane or 10% ether in hexane to recover PCCs, DDT and many of the PAHs. The scheme was tested for the recovery of a variety of halogenated hydrocarbons and the PHCs and could of course be expanded to elute more polar contaminants. However, even with low fat samples there was always difficulty in separating the more polar contaminants from the biogenic fats. High lipid samples increased this problem.

Table 4.2 Elution of CHCs from Florisil and stability of standards to common clean-up procedures (FAO, 1983)

Compound	A. FLORISIL ELUTION <sup>1</sup>			B. STABILITY TO TREATMENT	
	HEXANE	30% MeCl <sub>2</sub>	ETHER	H <sub>2</sub> SO <sub>4</sub> <sup>2</sup>	KOH <sup>3</sup>
<b>Industrial Products</b>					
PCBs	+			+	+
HCB	+			+	-
Phthalate esters			+	-	-
<b>Pesticides</b>					
Aldrin	+			+	+
Dieldrin			+	-	
DDT		+		+	-
DDE	+			+	+
DDD		+		+	-
2β,γHCH		+		+	-
Toxaphene		+		+	-
<b>Herbicides</b>					
Ramrod			+	-	-
2,4 Dimethyl ester			+	-	-
C 1 PC			+	-	-
2,4,5 T methyl ester			+	-	+
2,4 DB methyl ester			+	-	-
DEF			+	-	-
Silvex PBEE			+	-	-
2,4 Di octyl ester			+	-	-
1,2,3,4 tetrachlorodibenzo β-dioxin		+		+	+
2,4,5, T iso octyl ester			+	-	-

1. Florisil was preextracted, dried, activated at 250°C for 8 hours, deactivated with 0.5% water, shaken for 15 hours and used immediately.
2. To standards in 4 ml hexane, 1 ml H<sub>2</sub>SO<sub>4</sub> was added; the glass tube was stoppered, shaken, and allowed to settle. The hexane was drawn off and dried with Na<sub>2</sub>SO<sub>4</sub>.
3. To standards in 4 ml hexane in a glass concentrator tube, 4 ml MeOH and 1 pellet KOH were added. The tube was fitted with Kuderna-Danish apparatus and refluxed for 30 min. The solution was then diluted with water and extracted twice with hexane. Hexane extracts were dried with Na<sub>2</sub>SO<sub>4</sub>.

Several preparative column procedures were tested and all were found to show serious interference from biogenic lipids in the fractions containing the PCCs and the PAHs. Even when column reactivities were carefully controlled and lipid loadings kept to a minimum ratio of 100 to 1, adsorbant to sample weight and breakthrough of fats into the aromatic HC fractions seriously affected GC analysis. Thus further clean-up procedures are necessary for the polar contaminants and for high fat samples.

The common clean-up procedures applied to the routine analysis of samples for HCs and HHCs are saponification and acid digestion of lipids (e.g. FAO, 1983; UNESCO/IOC, 1982; UNEP/FAO, 1984). Saponification destroys several of the common contaminants quantified by ECD and acid treatment destroys a significant portion of the HCs detected by both GC and fluorescence procedures. Table 4.2 is an expansion of that from FAO (1983) and is based on tests of the stability of various standards to acid and base treatment. Obviously the use of these treatments would not be feasible for a combined preparative procedure for HCs and HHCs.

We have expanded our capacity to analyze some of the more polar contaminants and isolate these from the lipid matrix of high fat samples by developing a high performance liquid chromatography step using a commercially available gel permeation column. We intend to continue these efforts in methods development as time and resources permit.

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#### 4.4 Development, testing and intercalibration of reference methods for marine pollution studies (S. Aston)

In 1984 a co-operative project with UNEP was started to develop, test and intercalibrate Reference Methods for marine pollution studies in the framework of UNEP's Regional Seas Programme.

Methods for the analysis of marine environmental materials are now many and various. Much effort has been expended by marine scientists to measure those substances and micro-organisms which are of interest as potential pollutants of the ocean, e.g. heavy metals, chlorinated hydrocarbons and pathogenic bacteria. There is a requirement to choose, test and intercalibrate specific methods which can be adopted as Reference Methods for UNEP's Regional Seas Programme. A quotation from the preface which accompanies each published UNEP Reference Method helps to set the scene:

"One of the basic components of the action plans sponsored by UNEP in the framework of the Regional Seas Programme is the assessment of the state of the marine environment and of its resources, and of the sources and trends of the pollution, and the impact of pollution on human health, marine ecosystems and amenities. In order to assist those participating in this activity and to ensure that the data obtained through this assessment can be compared on a world-wide basis and thus contribute to the Global Environment Monitoring System (GEMS) of UNEP, a set of Reference Methods and Guidelines for marine pollution studies are being developed and are recommended to be adopted by Governments participating in the Regional Seas Programme."

At a glance the obvious answer to the selection of a Reference Method is to choose the latest and best technique available. The problem begins with the question - what does "best" mean for the purposes to which Reference Methods will be used by participants in Regional Seas Programmes. The "best" method in this context is not necessarily that in the sense of being the most sophisticated, accurate and precise technique. In the real world several other factors have to be taken into account if the Reference Methods for marine pollution studies are to be of genuine practical use.

The four marine pollution monitoring studies in Regional Seas action plans may be summarised as:

- a. Monitoring of sources of pollution to provide information on the type and amount of pollutants reaching the marine environment from coastal sources.

- b. Monitoring of the coastal waters, including estuaries, within the limits defined by the relevant action plan and convention, under the direct influence of pollutants from identifiable primary (e.g. outfalls, discharge or coastal dumping points) or secondary (rivers and other water courses) sources.
- c. Monitoring of reference areas which are not under direct influence of pollutants from identifiable primary or secondary sources.
- d. Monitoring of the transport of pollutants to the marine and coastal areas defined by the action plan and convention through the atmosphere.

The Reference Methods being developed cover a wide range of pollutants, e.g. trace metals, chlorinated hydrocarbons, petroleum hydrocarbons, tar, bacteria, etc. as well as providing guidelines for sampling strategies, preparation of samples, toxicity tests, data handling and evaluation. In addition, they include information on how basic oceanographic parameters are to be assessed and used to supplement the data on marine pollution.

The Reference Methods are being formulated in such a way to meet some substantial requirements. These requirements include:

- a. Analytical methods must be applicable throughout the world, including many developing countries. Thus, they must make use of easily available and serviceable equipment, reagents and facilities.
- b. They must be reliable and procure data which are both reasonably accurate, precise and reproducible. When stating "reasonably" this means of sufficient accuracy and precision to allow meaningful interpretation for the purposes and objectives of regional marine pollution studies. They should be adequate for intra-regional and inter-regional comparisons for the GEMS of UNEP.
- c. The Methods must be used in conjunction with appropriate mandatory quality control which is achieved through reference materials (standards) available on an international basis.

Furthermore, the Methods cannot ever be regarded as "once only". Rather, as analytical techniques and instrumentation improve and become more generally available, the Reference Methods are revised and re-tested. One of the most important constraints is that the availability of instrumentation and other facilities does, of course, vary throughout the world. This is perhaps the most important factor in determining the "best" Method for a given pollutant.

With the above in mind, the actual formulation of the Reference Methods is as follows:

They are developed and tested through inter-agency co-operation (e.g. UNEP, WHO, FAO, WMO, IOC, UNESCO, IAEA, ICES), with the assistance of consultant experts, marine research institutes and individual scientists. The Methods are also reviewed by the IOC/UNEP co-sponsored Group of Experts on Methods, Standards and Intercalibration (GEMSI).

The first draft of the Method is usually prepared by an expert in the relevant field. The draft is widely distributed to selected experts, usually though not exclusively to those participating in the Regional Seas Programme, with an invitation to test the Method. The results of the tests are then reviewed by expert group meetings and the draft is afterwards turned into a regular issue which is recommended to be used by all participants in the Programme. After further experience is gained with the application of the method it may be revised, again as a result of recommendation from an expert group meeting. Reference Methods which have been thoroughly tested and found to satisfy the legal requirements of the countries participating in the Regional Seas Programme are submitted to the governments (at intergovernmental meetings) for formal adoption as mandatory Methods in the context of specific Regional Seas Action Plans and Conventions. The technical co-ordination of the development and testing of Reference Methods is carried out by the International Laboratory for Marine Radioactivity of the IAEA in Monaco on behalf of UNEP.

This multi-lateral and comprehensive approach to the development, drafting, revision and testing of the Reference Methods is conceived as an indispensable approach to satisfy the requirements of the marine pollution studies in the framework of the Regional Seas Programme. This procedure ensures that, inter alia, methodologies are effectively optimised and updated with respect to the specific requirements of the Programme. Furthermore, it provides a viable mechanism for continued and wide-ranging co-operation on the improvement of Reference Methods in the light of the development and availability of analytical technology on a global basis.

Finally, an important factor in the growth and strength of the Methods is the use of intercalibration/intercomparison exercises. This depends on the availability of suitable samples of marine environmental materials, e.g. homogenates of fish flesh, molluscs, marine sediments, sea water, etc. These materials provide a sound basis for the development of Reference Methods.

#### 4.5 Fluxes and residence times of hydrocarbons in the coastal Mediterranean (K.A. Burns and J.-P. Villeneuve)

Many recent studies have demonstrated the importance of large rapidly sinking particles in transporting organic and other contaminants entering the sea surface to ocean depths. Collection of surface plankton and freshly defecated fecal material has shown that the biota are important vectors in packaging diffuse organic contaminants into fast sinking feces and are thus an important link between surface inputs and redistribution to depth.

Building upon samples analysed during the long term sediment trap experiment at the station 2 Km off the Monaco coast we expanded our efforts to calculate fluxes from several independent data bases. Particle transport is highly variable and is dependent on seasonal productivity cycles. We measured the flux of petroleum and selected chlorinated hydrocarbons from PIT samples collected in a time series covering three years. We analysed surface plankton, freshly collected feces, surface waters and sediments over a seasonal time frame. From these independent data bases we computed fluxes at several points in the system (Table 4.3), estimated residence times of organic contaminants in surface waters (Table 4.4), and provided evidence on the long term trend of PCB concentrations in surface waters of the Mediterranean (Table 4.5).

By evaluating the discrepancies in fluxes calculated from independent data bases and looking at the changes in composition of organic residues between ecosystem compartments, we concluded that the biota are effective in transporting both particulate and dissolved organic contaminants to ocean sediments. Stable residues such as the PCBs and DDE show reasonably good quantitative agreement when fluxes are calculated from settling particles or sediments. But processes of dissolution and degradation are clearly illustrated by the large differences in estimated fluxes for the semisoluble pesticides and the more labile petroleum residues. Residence times of compounds such as Lindane clearly cannot be accurately estimated from settling particles and calculations must rely on physical-chemical partition models. A residence time in the surface waters of one to five years appears a reasonable estimate for most hydrocarbon residues. Thus for monitoring purposes it should be possible to detect major changes in contaminant inputs within this time scale. Comparison of PCB levels in coastal Mediterranean samples show that there has been a reduction in levels in all ecosystem compartments analysed. Thus, although PCBs appear to be declining in the northwestern Mediterranean, they still remain an important class of pollutants in the mixture of halogenated contaminant seen in Mediterranean samples. We have also noted the increasing importance of other contaminants such as Lindane, HCB and Toxaphene.



Table 4.3 Fluxes of selected hydrocarbons predicted from biomass estimates and observed concentrations of hydrocarbons in animal feces; average flux of hydrocarbons through the water column based on analysis of sediment trap material; and average flux of hydrocarbons into the sediment based on surface sediment concentrations and calculated sedimentation rate (Burns & Villeneuve, 1983)

	PCB <sub>2</sub> (ng cm <sup>-2</sup> yr <sup>-1</sup> )	Petroleum (μg cm <sup>-2</sup> yr <sup>-1</sup> )	DDE (ng cm <sup>-2</sup> yr <sup>-1</sup> )	Lindane (ng cm <sup>-2</sup> yr <sup>-1</sup> )
Estimated flux on feces <sup>a</sup>	2.2 <sub>-1.7</sub> (10)	8.2 <sub>-10.1</sub> (5)	0.03 <sub>-0.002</sub> (2)	0.002 <sub>-0.001</sub> (2)
Measured flux	3.7 <sub>-3.2</sub> (44)	9.0 <sub>-6.6</sub> (27)	0.13 <sub>-0.09</sub> (25)	0.09 <sub>-0.06</sub> (30)
Flux into sediments	2.8 <sub>-2.6</sub> (3)	0.9 <sub>-0.9</sub> (3)	0.08 <sub>-0.06</sub> (3)	0.005 <sub>-0.001</sub> (3)
Log (mg l <sup>-1</sup> ) solubility <sup>b</sup>	< -1	1 to < -2	-1	+1

(a) Calculations are based on the following:

1. Average zooplankton biomass in the top 100 m in this region of the N.W. Mediterranean was estimated at approximately 0.01 g dry wt m<sup>-3</sup> (Razouls & Thiriot, 1973, Franqueville, 1975; Nival et al., 1975).
2. An average fecal pellet production rate for zooplankton is about 0.05 g dry feces per g dry zooplankton per day (Small et al., 1973, 1983; Heyraud, 1979).
3. Mean concentrations of residues in plankton fecal pellets were 1222+953(10) ng g<sup>-1</sup> PCB; 4.5+5.6(5) mg g<sup>-1</sup> petroleum; 0.85+0.36(2) ng g<sup>-1</sup> lindane; 14.2+8.4(2) ng g<sup>-1</sup> DDE.

(b) Solubility estimates from Chiou et al. (1977, 1979); Karickhoff et al. (1970); Means et al. (1980).

Table 4.4 Estimated residence times, R, of hydrocarbon residues in the top 100 m of the Mediterranean water column

Data base	PCB	Petroleum	Lindane
Surface particles and seawater concentrations <sup>a</sup>	0.5 yr	0.6 yr	5.8 yr
Sediment trap material <sup>b</sup>	2.6 yr	1.0 yr	55 yr
Seawater and sediment concentrations <sup>c</sup>	4.0 yr	10.5 yr	940 yr

- (a) Calculated using the assumption of Tanabe & Tatsukawa (1983) and  $R=N_{100}/(3.86 CH_{ss} C_{prod})$ ; where  $N_{100}$  is the amount of hydrocarbons present in the water column  $1 m^2$  by 100 m depth,  $CH_{ss}$  is the average concentration of hydrocarbons on suspended matter in the surface waters and  $C_{prod}$  is the rate of primary production of carbon at the surface.
- (b) Calculated from sediment trap data;  $R=N_{100}/(\text{flux at 100 m})$ .
- (c) Calculated from sediment data given in the Burns & Villeneuve (1983) and water concentrations integrated over 100 m of the water column;  $R=N_{100}/(\text{flux into sediments})$  from Burns *et al.*, in press.

Table 4.5 Concentrations of PCB (quantified as Aroclor 1254 or Phenoclor DP-5 equivalents) in the Mediterranean ecosystem and factors of change in approximately 5 years time

	Concentrations (ng g <sup>-1</sup> )		Factors of change in approximately 5 years
	1974-1978	1978-1982	
Seawater	3.2 <sub>±</sub> 2.2(x10 <sup>-3</sup> )(9) <sup>a</sup>	1.0 <sub>±</sub> 0.4(x10 <sup>-3</sup> )(6) <sup>b</sup>	- 3.2x
Plankton	1.5 <sub>±</sub> 1.8(x10 <sup>3</sup> )(6) <sup>c</sup>	2.3 <sub>±</sub> 1.5(x10 <sup>2</sup> )(14) <sup>b</sup>	- 6.5x
Plankton Feces	1.7 <sub>±</sub> 1.4(x10 <sup>4</sup> )(4) <sup>c</sup>	1.2 <sub>±</sub> 0.9(x10 <sup>3</sup> )(10) <sup>b</sup>	- 14x
Sediment trap material	4.6 <sub>±</sub> 2.5(x10 <sup>2</sup> )(4) <sup>d</sup>	1.3 <sub>±</sub> 1.2(x10 <sup>2</sup> )(44) <sup>b</sup>	- 3.5x

(a) Elder & Villeneuve (1977).

(b) Burns et al. (in press).

(c) Elder & Fowler (1977); Fowler & Elder (1978).

(d) Fowler et al. (1979).

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#### 4.6 Evidence for rapid in situ oxidation rate of pollutant hydrocarbons in the open Mediterranean (K.A. Burns and J.-P. Villeneuve)

Analysis of material collected over three years in the sediment trap experiment near Monaco and comparison with sediment data showed that approximately ten times more petroleum hydrocarbons (PH) fell through the water column than were eventually incorporated into subsurface sediments. This quantitative data as well as observed changes in the gas chromatographic patterns of PH residues between surface and depth samples implied a rapid oxidation rate of PH at the sea/sediment interface. We applied a recent diagenesis model and computed that the rate of oxidation of petroleum hydrocarbons at the sea/sediment interface approximated  $83 \text{ mg/m}^2 \text{ yr}$  under the Monaco trap station with the remaining input utilized in diagenetic processes within the sediment or accumulated there (Fig. 4.1).

These calculations combined with our observations of the rapid vertical transport of hydrocarbons through the water column predict that

HYDROCARBON UTILIZATION AT THE SEA/SEDIMENT INTERFACE

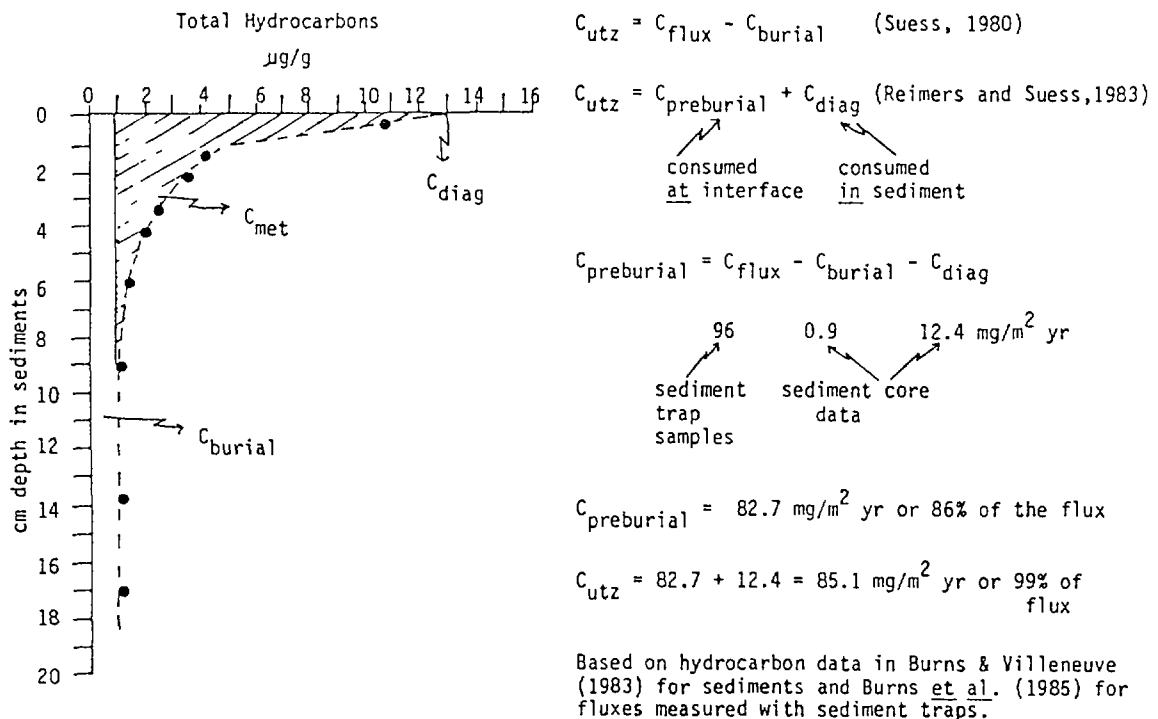


Fig. 4.1 Application of recent diagenesis model to data on the fluxes, and profile of sediment concentrations of petroleum hydrocarbons at the sediment trap station two kilometers off the coast of Monaco in the Western Mediterranean.

high concentrations of organic pollutants should be present at the sea/sediment interface. But the majority of labile residues are degraded before compaction. This rate of in situ oxidation is clearly important with respect to mass balance calculations and to implications for both short- and long-term ecosystem effects.

We took sediments cores from deep stations in the western Basin during expeditions aboard the German research vessel "Gauss" in April 1982 and the French research vessel "Suroit" in September 1983 (PHYCEMED III). We were fortunate in recovering intact cores including overlying water and fine resuspended particulates which we siphoned off and analysed separately from the sediment core. Results are shown in Table 4.6. The concentration and type of PHs and the likely flocculent particles had recently been delivered to the sediment interface from zooplankton feces and in sediment trap material collected at the Monaco station. The sediments, in contrast, contained a higher boiling, exceedingly degraded petroleum residue. This qualitative and quantitative data for hydrocarbons corroborated our previous conclusion on the importance of biota in effecting a rapid settling of organic contaminants by packaging both dissolved and particulate residues into

fast sinking fecal pellets. And the data confirmed our prediction of high levels of contaminants at the sea/sediment interface.

We used the PCB data as a semi-quantitative model to derive further evidence for the rapid in situ degradation rate of petroleum residues in the open Mediterranean. Degradation of PCB residues can be assumed to be comparatively slow based on the agreement in fluxes estimated by independent data bases at the Monaco trap station. The sediment core slices analysed for the data in Table 4.6 were centimeters thick. Thus the recently delivered particles containing the organic contaminants would be diluted by more ancient unpolluted sediments. We assumed the difference in PCB concentration between flocculent particles and the sediments was a measure of this dilution effect. Table 4.6 shows this to be two orders of magnitude for the PCBs but three orders of magnitude for total hydrocarbons. This is further evidence that the balance in recent inputs of hydrocarbons and transport processes results in ten times more hydrocarbons being delivered to the sediments and oxidized at the interface than are eventually incorporated into deep sediments. Of course, areas receiving larger inputs of hydrocarbons or subject to faster sedimentation rates would show significant accumulation of hydrocarbons in the sediment core. This situation is seen in the sediments of some estuaries and coasts.

The relatively rapid rate of oxidation of PHs in the open Mediterranean ecosystem is probably a result of the warm bottom water temperatures which can exceed 12°C even in winter.

The results of these process-oriented studies have specific relevance in terms of calculating mass balances, in developing monitoring strategies and in predicting the effects of organic contaminants in the ecosystem. From the field data it appears likely that in spite of the large petroleum input into the Mediterranean, there is little buildup of the majority of petroleum derived hydrocarbons in deep sediments. However, extremely high levels of organic contaminants exist at the sediment interface. Thus, in terms of toxicity the most important ecosystem components to measure are the interfaces: both the air/sea and sea/sediment. This is where concentrations are highest even though degradation processes are intense. The levels of PHs measured in flocculent particles in the western Basin were as high as those in coastal sediments subjected to oil spill and shown to be toxic to benthic animals (Krebs and Burns, 1977). If only the residues in sediments had been measured, as is usually done in monitoring programmes, this important observation would have been missed. Of course the interfaces are extremely difficult to accurately sample and environmental assessment must depend on extensive integration of data from independent

Table 4.6 Comparison of hydrocarbon residues in sediment material compared to resuspended particles

		Hydrocarbons µg/g	PCBs ng/g dry
GS 3 Flocculent Particles 1982		3 143	105.4
1,060 m Sediments water depth	0-5 cm	1.6	0.8
	5-10 cm	0.9	0.3
	10-15 cm	-	0.5
	15-20 cm	-	0.2
Log Δ		3.5	2.0
GWY Flocculent Particles 1983		1 243	98
2,900 m Sediments	0-1 cm	8.2	1.9
	1-2 cm	1.5	0.5
	2-3 cm	1.5	0.6
	etc.		
Log Δ		3.1	2.0

measurements including estimates of vertical flux, sediment accumulation and in situ oxidation rates. Our results show that in terms of the long-term accumulation of organic contaminants the important classes of pollutant hydrocarbons to measure in the Mediterranean are the polynuclear aromatic hydrocarbons derived from combustion processes, other highly residual compounds including many of the halogenated hydrocarbons and the reaction products of hydrocarbons which are not routinely analysed in monitoring programmes. This requires continued advancement in both sampling and analytical methodology and an emphasis on the analysis of specific marker compounds.

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#### 4.7 Hydrocarbons in the open Mediterranean water column (K.A. Burns, J.-P. Villeneuve and C. Cattini)

In focusing our attention on processes controlling the distribution of organic contaminants in the Mediterranean, several classes of hydrocarbons were identified as relatively stable geochemical markers of



anthropogenic influences. Among these were the polynuclear aromatic hydrocarbons (PAHs) deriving primarily from the combustion of fossil fuels and the polychlorinated biphenyls (PCBs) released from a variety of industrial applications. The distribution of PAHs in undisturbed sediment cores reflect increased emissions beginning with the industrial revolution, thus providing markers which correlate with independent measures of recent sedimentation rate such as  $^{210}\text{Pb}$  (eg. Burns and Villeneuve, 1983).

To complement our understanding of the geochemical cycling of organic contaminants based on settling particles and to construct mass balances we need accurate measurements on the levels of residues suspended in deep ocean water columns. Such measurements are extremely difficult to make due to low levels and contamination of samples during handling. We have experimented with high volume sampling methods to improve our signal to noise ratios and have developed procedures for separating "dissolved" and "particulate" residues.

We participated in interdisciplinary cruises in the western Basin concentrating on the Gulf of Lion aboard the German ship "Gauss" and the French ship "Suroit" during which we collected water, sediment and biota samples for organic analysis.

Total concentrations of petroleum hydrocarbons in surface waters ranged from  $0.4$  to  $1.3 \mu\text{g l}^{-1}$  and from  $1.5$  to  $5.1 \text{ ng l}^{-1}$  for PCBs. These values are within the range for the western Basin reported by other workers using GC quantification methods. The relative distribution of PCBs was consistent with the general locations of shore based industrial sources. But long-range atmospheric transport distributes these contaminants across the entire Mediterranean ecosystem. Percent particles association of PCBs decreased with distance from the coast and with depth in water column. Profile samples taken in April 1982 showed a significant subsurface maximum in the concentrations of both petroleum and chlorinated hydrocarbons contaminants. We ruled out sampling artefact because two profiles although separated by 60 km gave similar results. Profiles taken September 1983 showed a maximum in particulate PCB concentration at 35 m but no other significant definition in hydrocarbon distribution with depth. We can only speculate on the cause of observed profiles. There is of course the possibility of advective transport of coastal waters moving at discrete depths. But ancillary hydrographic and radionuclide data could not demonstrate any coastal influences in the 1982 samples.

Sorption models predict the downward flux of contaminants depends on particle reactivity and the relative solubilities of various

components. Subsurface distributions would thus depend on the processes of dissolution and degradation occurring on the particles as they sink.

The importance of small particle transport in explaining the distributions of Pu and Am in oceanic water columns was summarized by Sholkovich (1983). Thus although sediment trap studies indicate that the majority of the flux of contaminants out of surface waters is carried on large rapidly sinking particles such as animal fecal pellets and molts, slower sinking particles may be responsible for distributions at intermediate depths. If subsurface maxima in organic contaminants exist, they appear to be transient and/or localized phenomenon and may be dependent on factors such as primary productivity cycles. The question can only be answered by further improvement in the sampling techniques for deep waters including simultaneous read-out of ancillary data on particle loading and other hydrographic features which would permit directed sampling.

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#### 4.8 Anthropogenic and natural volatile hydrocarbons in open ocean surface waters (J.B. Derenbach\*)

In order to study biogeochemical cycling of volatile combustion products water samples had been analyzed from various Atlantic and near Atlantic regions since 1980. Putting some of the data together, it was observed that a uniform pattern of alkylated benzenes was encountered in almost any of the samples taken. This pattern resembled findings of others at a coastal sampling site. The distribution of these alkylated benzenes seems to be dominated by large scale transport in the atmosphere and in water masses (Derenbach, in press).

A minor fraction of the samples also contained traces of alicyclic polyenes. Some of them were found to be identical and/or similar to

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\* Government Expert from University of Kiel, Kiel Federal Republic of Germany.

pheromones from brown algae; they could be phytoplankton pheromones (Derenbach, in press).

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#### 4.9 Baseline studies of toxic metals in Mediterranean rivers (N.E. Whitehead, L. Huynh-Ngoc and S. Aston)

The objective of this programme is to study mass balances and sedimentation rates of various particle-attached metals. Samples from the Var and Roya were analysed by differential pulse anodic stripping voltammetry (ASV) using the sampling precautions to avoid contamination needed previously in sea water samples. A representative set of results is given in Table 4.7. The results found are fairly typical of world rivers for cadmium, but for the other elements they are considerably lower, in some cases (especially lead) the lowest we can find in the literature. It is quite possible that application of clean sampling techniques may necessitate a downwards revision of values reported for many rivers.

By means of prolonged acid digestion (1 hour boiling in 1M HCl) it was shown that considerable amounts of cadmium, zinc, lead and copper are released and that the major mode of transport for these metals, even in non-polluted rivers, is by attachment to particles.

Table 4.7 Trace element concentrations in the Var River  
(all results are measured at pH 2 and expressed in ng l<sup>-1</sup>)

Cd Soluble	Cu Soluble	Cu Suspended	Pb Soluble	Pb Suspended	Locality
30 ± 2	350 ± 60	850 ± 100	222 ± 18	580 ± 10	Cap 3000
34 ± 2	240 ± 10	910 ± 150	112 ± 10	380 ± 30	Pont Lamanda
37 ± 4	370 ± 20	2600 ± 340	365 ± 16	1000 ± 250	Pont Charles Albert
4 ± 2	390 ± 10	350 ± 20	48 ± 4	270 ± 50	Near Vesubie R.
35 ± 9	600 ± 60	3300 ± 240	65 ± 6	930 ± 140	Touët sur Var
29 ± 2	280 ± 60	90 ± 30	129 ± 2	150 ± 10	Vesubie mouth
23 ± 1	80 ± 10	200 ± 50	34 ± 8	200 ± 10	Tinée River
27 ± 1	190 ± 10	0 ± 20	168 ± 7	120 ± 30	Cian River

During the study period a new ASV method was applied for the measurement of zinc at pH8 which has the advantage of far better linearity of the calibration curve and is thus an improvement on existing techniques.

#### 4.10 Instrument maintenance service for Mediterranean pollution monitoring (T. Barisic)

During 1983-1984 new laboratories joined the UNEP Joint Pollution Monitoring and Research Programme in the Mediterranean Sea (MEDPOL PHASE II). Service visits were made for the first time in Pula, Rijeka and Split, Yugoslavia as well as three laboratories in Rabat, Morocco.

Fifteen service visits to the following research centers were also carried out during 1983-1984: Nicosia (Cyprus), Erdemli-Icel (Turkey), Istanbul (Turkey), Izmir (Turkey), Zagreb (Yugoslavia), Piran (Yugoslavia), Rovinj (Yugoslavia), Split (Yugoslavia), Msida (Malta), Casablanca (Morocco), La Goulette (Tunis) and Alger (Algeria).

These service visits revealed that after 8 years of intensive use some of the AAS and GC instruments distributed at the beginning of the MEDPOL PHASE I Programme have become obsolete.

It was observed that most of the laboratories having joined the Programme during the last two years have been equipped with various analytical instruments from different manufacturers. Instruments manufactured by Varian were distributed to the research centers by UNEP/FAO during the pilot phase. This permitted instrument maintenance service using only one set of spare parts. The variety of instruments from various manufacturers would create problems in servicing as it is impossible to keep spare parts for all types of instruments. Therefore, this problem was discussed with the national coordinators of relevant countries and with program coordinators in the laboratories. It was agreed that the Instrument Maintenance Service should collaborate with earlier established local services and support them in emergency cases by providing the required parts, since acquisition of such parts is generally the major problem.

## 5. Special Missions

### 5.1. Selection of analytical equipment for the Kuwait Action Plan Projects (T. Barisic and S.W. Fowler)

During late 1982 to early 1983 the Laboratory established criteria for the selection of analytical and sampling equipment for national institutions participating in the pollution and oceanography programme. The first part of this effort involved contacting prospective manufacturers of pertinent analytical and sampling equipment for the measurements of trace metal and hydrocarbon contaminants as well as various oceanographic parameters. Once identified, manufacturers were requested to provide the Laboratory with technical specifications and bids for various alternatives and configurations of the instruments. Bids for all major items were completed near the end of February 1983. Since the major items for the pollution monitoring programme were the GC, AAS and fluorescence spectrophotometers, high priority was given to the examination of bids and selection of these instruments. A full report describing their relative merits and recommendations for purchase was submitted to ROPME in March 1983.

Since the KAP oceanography programme was delayed in starting, selection of sampling and analytical equipment for oceanographic measurements was considered as second priority. As with the analytical instruments, bids were sought from acceptable manufacturers and selection recommended on the basis of price, adequacy, robustness in the field and personal experience in their use. A final report containing criteria for selection and recommendations for purchase was forwarded to ROPME in May 1983.

Based on the contents of these reports and the results of an ad hoc equipment selection meeting sponsored by ROPME, the items necessary for the KAP programme were selected. This activity was completed in July 1983.

### 5.2. Assistance in pollution studies in Oman, UAE and Bahrain (S.W.Fowler, L. Huynh-Ngoc, B. Oregioni, K.A. Burns, J.-P. Villeneuve, J. Cenciarini and C. Cattini)

As part of IAEA's assistance to the Regional Organization for the Protection of the Marine Environment (ROPME) in the implementation of the Kuwait Action Plan (KAP), the Monaco Laboratory has completed three pollutant sampling missions to Bahrain, UAE and Oman. The aim of the

missions is to assist each country in fulfilling its obligations to the 18-month KAP monitoring programme which began in 1983. This includes surveying beaches for tar, collecting various marine matrices for pollutant analyses at KAP reference stations and rendering training in the field on various sampling techniques to national counterparts.

Three missions took place in the three Gulf countries (3-16 January 1983, 18-29 October 1983 and 23 April-4 May 1984) during which a series of predetermined stations in each country were sampled. Counterparts from each country assisted the Laboratory staff in all aspects of the sampling programme. During the second mission a separate set of biota samples were collected from the KAP ecology study site in southern Oman. These samples were also analysed for a series of metal and hydrocarbon pollutants as part of a joint project with IUCN. During the third mission samples of selected edible fish were also collected for mercury analysis since information on mercury levels in fish from the Gulf are generally lacking. Most all analyses were completed by end 1984.

Tar on the beaches of these countries continues to be a major problem. A 1980 survey found tar levels along the coast of Oman to be among some of the highest values recorded to date. While the 1983-84 surveys indicated that tar levels varied with season and that loads on Omani beaches tended to be somewhat lower, high loads were still present, particularly at Masira and at many stations in northern Oman. It appears that the majority of the beach tar originates from tanker deballasting and local oil spills, two events which have led to chronic oil pollution in the region.

Concentrations of dissolved petroleum hydrocarbons in water and levels in oysters and sediments do not appear to be exceptional and spatial variations and local hot spots are related to inputs in the vicinity of oil terminals and harbours. The concentrations of PCB and DDT residues, or lack of them, in oysters and sediment samples confirm the very low level of contamination by those compounds in this region of the Gulf. However, some peaks of unidentified organochlorine compounds were significantly higher in concentration than either the DDTs or PCBs examined and thus could be important. An effort is presently underway to identify these compounds. Likewise heavy metal concentrations (Cd, Cu, Pb, V, Hg) in oysters and sediments were quite low and probably reflect present background levels in the region.

In summary, the data indicate that aside from some concentration hot spots related to local inputs, Bahrain, UAE and Oman are not at present impacted by PCBs, DDT or the heavy metals examined. On the other

hand oil, in the form of tar on beaches, does appear to be problem compared to other areas of the world, particularly in Bahrain, on Masira Island and at some stations in northern Oman. However, levels on beaches fluctuate widely with the season and further sampling will be necessary to better establish trends.

Detailed reports on results of the sampling were prepared and distributed to ROPME and IUCN in 1984.

### 5.3. Assistance in the creation and establishment of a national marine pollution monitoring network in Algeria (S.W. Fowler)

Algeria is presently experiencing a rapid surge of urban and industrial growth with much of the industrial development taking place along the coastal zone. This fact coupled with the proximity of growing population centers along the coast, greatly increases the potential for pollution in Algeria. Despite an apparent concern over coastal contamination by a myriad of pollutants, at present a coordination marine pollution monitoring network does not exist in Algeria. With this in mind, upon request by the Algerian Government, a mission was organized by UNEP.

During November 1983 a multi-disciplinary team of five scientists was sent to Algeria to make a preliminary assessment of the state of pollution in the air, soil and waters of the country. The task of the IAEA marine expert was to evaluate the degree of pollution in the coastal zone through visual observation of pollutant input sources and by analyses of a limited number of environmental samples, and to advise on the establishment of a national monitoring network taking into account available national resources of expertise, equipment and existing facilities. In this regard, sites along the eastern coast and around Algeria were visited in order to observe firsthand the levels of tar on beaches and when possible to obtain samples of sediments, sea water and marine organisms for analyses of selected pollutants such as heavy metals, organochlorine compounds and petroleum hydrocarbons. The Secretariat d'Etat aux Forets and the Centre de Recherches Oceanographique et des Peches (C.R.O.P.) were instrumental in helping to obtain the necessary samples for analyses.

Pollutant analyses of a limit number of marine samples identified the usual hot spots near industrial complexes and urban agglomerations, however, levels were not unduly high and fell within the range reported for similar samples throughout the Mediterranean. The mission recognized

that while concern about marine pollution was evident among the industrial sector through the application of limited controls of emissions and effluents, there was at present no monitoring or control of the extent or effects of these wastes once they reach the sea. It became clear that the creation of a fully-operational national environmental pollution laboratory would take some time and, in the meantime, Algeria could achieve early results through the organization of a modest monitoring programme built around the analytical infrastructure already existing at C.R.O.P. It was suggested that a national body such as the Secretariat d'Etat aux Forets, which was presently charged with overseeing environmental pollution problems, should take the first steps towards organizing the necessary resources for a national marine monitoring network.

#### 5.4. Identification of technical needs for pollution monitoring at institutes in the West and Central African Region (T. Barisic)

The UNEP Action Plan for West and Central Africa was approved at the Conference of Plenipotentiaries on Cooperation in the Protection and Development of the Marine and Coastal Environment of the West and Central Africa Region (Abidjan, March 1981). The international agencies such as UNEP, FAO, IAEA, WHO, IOC, etc. are requested to be involved in the implementation of the project. In cooperation with FAO, IAEA is responsible for the intercalibration of sampling and analytical techniques.

FAO contacted institutions in countries of the region, and 8 institutions were selected from Gambia, Ghana, Ivory Coast, Nigeria, Senegal and Sierra Leone. In January-February 1984 a mission was sent to these selected institutions, to identify specific needs of the participating laboratories in equipment and training. I participated in this mission. It was observed that the nature of problems encountered in the institutions vary from one country to the other. However, there are the following common difficulties:

- (a) faulty equipment and lack of spare parts;
- (b) frequent power failures;
- (c) shortage of chemicals and glassware;
- (d) lack of trained manpower; and
- (e) lack of experience in pollution monitoring.

Based on these observations the following recommendations were made:

- (1) FAO should send to all participating institutions the following material:



- (i) literature on recommended methods for the sampling;
- (ii) a general inventory of chemical, glassware and small items of equipment; and
- (iii) a list of mandatory biota species.

(2) Where manpower training is needed, FAO should endeavour to arrange the training of staff.

(3) FAO should organize regular maintenance of all analytical apparatus to be used for the project.

#### 5.5. Instrument maintenance mission in Cuba (T. Barisic)

Within the framework of the project "Research and Control of Marine Pollution in Cuba", the project authorities requested UNEP to organise a maintenance service visit for analytical instruments used within the project. I was asked to visit these institutes in Cuba to fulfill their requirements.

In February-March 1984, I visited Instituto Investigaciones del Transporte and Institute of Chemical Research, both in Havana, and serviced several types of instruments to be used for pollution monitoring.

During my stay in Havana, I discussed service problems with the service engineer at the Instituto Investigaciones del Transporte and gave him instruction and service hints.

#### 5.6 Consultation and technical assistance at institutes in Australia and Thailand (E. Holm)

Some years ago a laboratory for environmental radioecological survey and research was established at Jabiru, Australia, a uranium mining and milling site by the Office of Supervising Scientist, Australia. I visited the laboratory in April 1984 and took part in its research programme. Especially, consultation and assistance in radioanalytical techniques and alpha-spectrometry were given to the laboratory staff in order to familiarize them with new techniques developed in the Monaco Laboratory. Special equipment for the electro-deposition was also supplied.

One scientist from Khon Kaen University, Thailand was trained through an IAEA fellowship at the Department of Radiation Physics, Lund University, Sweden. This fellowship was also supported by SAREC (the Swedish Agency for Research Cooperation with Developing Countries). In

order to follow up the results of his training, I visited his home institute, the Department of Physics, Khon Kaen University for a week in April 1984. Special instrumentation and isotopes for alpha-spectrometry were brought to the institute for the determination of polonium, uranium and thorium in environmental samples and advice was given on the application of radiochemical techniques.

5.7. Training mission for hydrocarbon analysis in the Sultanate of Oman  
(J.B. Derenbach)

In response to a request from the Regional Organization for the Protection of the Marine Environment in the Kuwait Region a training programme for organic pollutant measurements was provided at a government laboratory belonging to the Council of Conservation of Environment and Prevention of Pollution in the Sultanate of Oman. While working on actual samples with the local staff, the advice and consultation were given in sample handling and preparation, fluorimetric techniques of oil measurements and application of a capillary gas chromatograph.

## APPENDIX 1

STAFF LIST OF THE MONACO LABORATORY  
(1983-1984)Professional Staff

Aston, S.	UK	Leader of Geochemistry Group (until September 1983) Coordinator for UNEP Projects
Azam, F.	USA	Biology (until December 1983)
Ballestra, S.	France	Chemistry
Barisic, T.	Yugoslavia	UNEP - Engineering Services
Blessington, M.	UK	Administration
Bojanowski, R.	Poland	Chemistry
Burns, K.	USA	Chemistry
Derenbach, J.	FRG	Chemistry - Government Expert
Fisher, N.	USA	Biology
Fowler, S.	USA	Leader of Biology Group
Fukai, R.	Japan	Director
Heyraud, M.	France	Biology
Hargrave, B.	Canada	Biology - Government Expert (until July 1984)
Holm, E.	Sweden	Leader of Chemistry Group
Huynh-Ngoc, L.	France	Geochemistry
Whitehead, N.	New Zealand	Leader of Geochemistry Group

General Service Staff

Avaullee, F.	France	Engineering Services
Bousquet, M.	USA	Secretariat (temporary)
Brown, S.	UK	Biology (temporary, until July 1984)
Cattini, C.	France	Chemistry (temporary)
Clark, J.	UK	Secretariat (temporary, until July 1983)
Cenciarini, J.	France	Chemistry (temporary)
Fonseca, D.	Spain	Secretariat
Galliot, J.	France	Engineering Services
Gastaud, J.	France	Geochemistry
Guerrin, C.	France	Chemistry (temporary, until September 1983)
Harvey, M.	Australia	Secretariat (temporary)
Henry, S.	USA	Secretariat (temporary, until November 1984)
Heussner, S.	France	Biology
Ho, R.	France	Chemistry (temporary, until December 1983)
La Rosa, J.	France	Biology
Lopez, J.-J.	France	Chemistry (temporary)
McManus, S.	UK	Secretariat
Navarro, M.-C.	France	Geochemistry (temporary)
Oregioni, B.	Italy	Geochemistry
Parsi, P.	France	Geochemistry
Sanna, P.	UK	Secretariat (temporary)
Searle, C.	Canada	Chemistry (temporary, until August 1984)
Taylor-Jones, B.	UK	Secretariat (temporary)

Teyssie, J.-L.	France	Biology (temporary)
Vas, D.	France	Chemistry
Villeneuve, J.-P.	France	Chemistry

#### Consultant/Experts

Aston, S.	UK	Geochemistry (1983)
Baxter, M.	UK	Geochemistry (1984)
Bilinski, H.	Yugoslavia	Chemistry (1984)
Bjurman, B.	Sweden	Chemistry (1984)
Blaylock, G.	USA	Biology (1984)
Bjerregaard, P.	Denmark	Biology (1983)
Cherry, R.	South Africa	Biology (1983)
Dunic, S.	Sweden	Chemistry (1983)
Edgington, D.	UK	Geochemistry (1983)
Golik, A.	Israel	UNEP Projects (1984)
Gabrielides, G.	Greece	UNEP Projects (1983)
Hagstrom, A.	Sweden	Biology (1983)
Holm, E.	Sweden	Chemistry (1983)
Krishnaswami, S.	India	Biology (1984)
Luoma, S.	USA	Biology (1984)
Okamoto, K.	Japan	Biology (1984)
Olsson, O.	Sweden	Chemistry (1984)
Rioseco, J.	Chile	Chemistry (1984)
Skwarzec, B.	Poland	Chemistry (1984)
Tronczyski, J.	Poland	Chemistry (1984)

#### Fellowships

Barci, G.	France	Chemistry (1984)
Cerrolaza-Gili, M.	Spain	Chemistry (1983-1984)
McDonald, P.	UK	Biology (1983)
Portakal, S.	Turkey	Chemistry (1983)
Romero-Gonzales, L.	Spain	Chemistry (1983-1984)
Zombori, P.	Hungary	Chemistry (1984)

#### UNEP Trainees

Abaychi, J.	Iraq	Trace Metal Chemistry (1983)
Abdilly, A.	Kuwait	Organic Chemistry (1983)
Ali, M.	Kuwait	Organic Chemistry (1983)
Biney, C.	Ghana	Trace Metal Chemistry (1984)
Douabul, A.	Iraq	Organic Chemistry (1984)
Najjar, E.	Lebanon	Organic Chemistry (1984)
N'dene, J.	Gambia	Organic Chemistry (1984)
Planinc, R.	Yugoslavia	Organic Chemistry (1984)
Tilbian, M.	Lebanon	Trace Metal Chemistry (1984)
Tusnik, P.	Yugoslavia	Organic Chemistry (1984)

#### Interns

Andreani, M.	France	Chemistry (1984)
Bohe, M.	France	Biology (1983)
Fukai, E.	Japan	Biology (1984)
Germain, C.	France	Chemistry (1983)
Gras, J.-M.	France	Chemistry (1983)
Kelleher, M.	UK	Biology (1983)
Lopez, J.-J.	France	Chemistry (1983)

## APPENDIX 2

### LIST OF PUBLICATIONS (1983-1984)

#### 1983

- BALLESTRA, S., FUKAI, R., An improved radiochemical procedure for low-level measurements of americium in environmental matrices, *Talanta*, 30 (1983) pp. 45-48.
- FOWLER, S.W., ASTON, S.R., BENAYOUN, G., PARSI, P., Bioavailability of technetium from artificially labelled North-East Atlantic deep-sea sediments, *Mar. Environm. Res.*, 8 (1983) pp. 87-100.
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- FISHER, N.S., BURNS, K.A., CHERRY, R.D., HEYRAUD, M., Accumulation and cellular distribution of  $^{241}\text{Am}$ ,  $^{210}\text{Po}$ , and  $^{210}\text{Pb}$  in two marine algae, *Mar. Ecol. Prog. Ser.*, 11 (1983) pp. 233-237.
- ASTON, S.R., FOWLER, S.W., Preliminary observations on californium-252 behaviour in sea water, sediments and zooplankton, *Health Phys.*, 44 (1983) pp. 359-365.
- BURNS, K.A., VILLENEUVE, J.P., Biogeochemical processes affecting the distribution and vertical transport of hydrocarbon residues in the coastal Mediterranean, *Geochim. Cosmochim. Acta*, 47 (1983) pp. 995-1006.
- FISHER, N.S., BJERREGAARD, P., FOWLER, S.W., Interactions of marine plankton with transuranic elements. 1. Biokinetics of neptunium, plutonium, americium, and californium in phytoplankton, *Limnol. Oceanogr.*, 28 (1983) pp. 432-447.
- FISHER, N.S., BJERREGAARD, P., HUYNH-NGOC, L., G.R. HARVEY, Interactions of marine plankton with transuranic elements. II. Influence of dissolved organic compounds on americium and plutonium accumulation in a diatom, *Mar. Chem.*, 13 (1983) pp. 45-56.
- BURNS, K.A., Comments on 'the search for standardized methods in analysis of environmental samples for hydrocarbons', *Mar. Chem.*, 13 (1983) pp. 75-76.
- BAXTER, M.S., ASTON, S.R., Deep-ocean radioactive waste disposal: An evaluation of the seaweed critical pathway, *Health Phys.*, 45 (1983) pp.139-144.
- GALEY, J., GOUDARD, F., PIERI, J., FOWLER, S.W., CARVALHO, F.P., Tissue and subcellular distribution of  $^{252}\text{Cf}$  and  $^{241}\text{Am}$  in the seastar *Marthasterias glacialis*, *Mar. Biol.*, 75 (1983) pp.253-259.
- FISHER, N.S., BJERREGAARD, P., S.W. FOWLER, Interactions of marine plankton with transuranic elements. 3. Biokinetics of americium in euphausiids, *Mar. Biol.*, 75 (1983) pp. 261-268.

- VANGENECHTEN, J.H.D., ASTON, S.R., FOWLER, S.W., Uptake of americium-241 from two experimentally labelled deep-sea sediments by three benthic species: A bivalve mollusc, a polychaete and an isopod, Mar. Ecol. Prog. Ser., 13 (1983) pp. 219-228.
- CHERRY, R.D., HEYRAUD, M., HIGGO, J.J.W., Polonium-210: Its relative enrichment in the hepatopancreas of marine invertebrates, Mar. Ecol. Prog. Ser., 13 (1983) pp. 229-236.
- FUKAI, R. Scientific publications of the International Laboratory of Marine Radioactivity (1962-1982), RITS No. 73, IAEA, Vienna (1983) 24 p.
- BOJANOWSKI, R., FUKAI, R., BALLESTRA, S., ASARI, H., Determination of natural radioactive elements in marine environmental materials by ion-exchange and alpha- spectrometry, "Proc. 4th Symp. on the Determination of Radionuclides in Environmental and Biological Materials", Paper No. 9, Lab. of Government Chemists, London (1983) 15 p.; RITS No. 74.
- FOWLER, S.W., FISHER, N.S., Viability of marine phytoplankton in zooplankton fecal pellets, Deep-Sea Res., 30 (1983) pp. 963-969.
- CARVALHO, P.P., FOWLER, S.W., LA ROSA, J., Assimilation, inter-organ transfer and excretion of americium in two teleost fish, Mar. Biol., 77 (1983) pp. 59-66.
- SMALL, L.F., FOWLER, S.W., MOORE, S.A., LA ROSA, J., Dissolved and fecal pellet carbon and nitrogen release by zooplankton in tropical waters, Deep-Sea Res., 30 (1983) pp. 1199-1220.
- FOWLER, S.W., BALLESTRA, S., LA ROSA, J., FUKAI, R., Vertical transport of particulate-associated plutonium and americium in the upper water column of the Northeast Pacific, Deep-Sea Res., 30 (1983) pp. 1221-1233.
- WALTON, A., Concluding remarks (Oceans Pollution 1981), Can. Jour. Fish. Aqua. Sci. (1983) pp. 354-356.
- BALLESTRA, S., THEIN, M., FUKAI, R., Distribution of transuranic nuclides in the coastal ecosystems of the northwestern Mediterranean, VI<sup>es</sup> Journees Etud. Pollutions, Cannes, C.I.E.S.M. (1983) pp. 47-52.
- BURNS, K.A., VILLENEUVE, J.P., Vertical flux of petroleum and chlorinated hydrocarbons in the coastal Mediterranean, VI<sup>es</sup> Journees Etud. Pollutions, Cannes, C.I.E.S.M. (1983) pp. 89-93.
- FUKAI, R., BALLESTRA, S., VAS, D., Characteristics of the vertical transuranic elements through the Mediterranean water column, VI<sup>es</sup> Journees Etud. Pollutions, Cannes, C.I.E.S.M. (1983) pp. 95-101.
- BURNS, K.A., Review Paper: Petroleum, VI<sup>es</sup> Journees Etud. Pollutions, Cannes, C.I.E.S.M. (1983) p. 175.
- VILLENEUVE, J.P., BURNS, K.A., Transport of lindane in the Mediterranean Sea, V<sup>es</sup> Journees Etud. Pollutions, Cannes, C.I.E.S.M. (1983) pp. 455-460.

- BURNS, K.A., Review Paper: Other pollutants, VI<sup>es</sup> Journées Etud. Pollutions, Cannes, C.I.E.S.M. (1983) p. 489.
- POLIKARPOV, G.G., PARSI, P., FOWLER, S.W., Chronic effects of a PCB (DP5) upon Nereis diversicolor in spiked Mediterranean sediments, Rapp. Comm. int. Mer Médit., 28 7 (1983) pp. 167-168.
- FISHER, N.S., FOWLER, S.W., Radioecological Research Activities (Particularly Marine-Related) in the Mediterranean Region and Nearby Countries, Rapp. Comm. int. Mer Médit., 28 7 (1983) pp. 189-203.
- BOJANOWSKI, R., BALLESTRA, S., FUKAI, R., Natural radionuclides in the North-western Mediterranean Sea, Rapp. Comm. int. Mer Médit., 28 7 (1983), pp. 205-207.
- FOWLER, S.W., Report on the activities of the Marine Radioactivity Committee, Rapp. Comm. int. Mer Médit., 28 7 (1983) pp.227-228.
- FISHER, N.S., BJERREGAARD, P., FOWLER, S.W., Biokinetics of americium in marine plankton, Rapp. Comm. int. Mer Médit., 28 7 (1983) pp.247-251.
- CARVALHO, F.P., FOWLER, S.W., LA ROSA, J., Am-241 assimilation and excretion in marine fish - An experimental approach, Rapp. Comm. int. Mer Médit., 28 7 (1983) pp. 253-256.
- TOPCUOGLU, S., FOWLER, S.W., Biokinetics of technetium (<sup>95m</sup>Tc) in marine macroalgae, Rapp. Comm. int. Mer Médit., 28 7 (1983) pp. 257-260.
- FOWLER, S.W., Bibliography of related activities of the members of the Marine Radioactivity Committee (1981-1982), Rapp. Comm. int. Mer. Médit., 28 7 (1983) pp.267-278.
- FOWLER, S.W., Radioecological aspects of deep-sea radioactive waste disposal. "Atti del 3<sup>o</sup> Convegno Nazionale di Radioecologia", A.I.R.P., Bologna (1983) pp. 236-258.

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- GORSKY, G., FISHER, N.S., FOWLER, S.W., Biogenic debris from the pelagic tunicate, Oikopleura dioica, and its role in the vertical transport of a transuranium element, Estuar. Coast. Shelf Sci., 18 (1984) pp. 13-23.
- ASTON, S.R., Use of <sup>252</sup>Cf in environmental and radioecological laboratory experiments, Int. J. Appl. Radiat. Isot., 35 (1984) p. 549.
- ASTON, S.R., FOWLER, S.W., Experimental studies on behaviour of long-lived radionuclides in relation to deep-ocean disposal of nuclear waste, "Radioactive Waste Management, Vol. 5", IAEA, Vienna (1984) pp. 339-354.
- TOPCUOGLU, S., FOWLER, S.W., Factors affecting the biokinetics of technetium (<sup>95m</sup>Tc) in marine macroalgae, Mar. Environm. Res., 12 (1984) pp. 25-43.

- ANDREWS, C.C., KARL, D.M., SMALL, L.F., FOWLER, S.W., Metabolic activity and bioluminescence of oceanic faecal pellets and sediment trap particles, *Nature*, 307 (1984) pp. 539-541.
- ASTON, S.R., FOWLER, S.W., Experimental studies on the bioaccumulation of plutonium from sea water and a deep-sea sediment by clams and polychaetes, *J. Environ. Radioactivity* 1 (1984) pp. 67-78.
- FUKAI, R., BALLESTRA, S., BOJANOWSKI, R., VAS, D., Experience gained through the intercalibration programme for low-level alpha-spectrometric measurements, *Nuc. Inst. Meth. Phys. Res.*, 223 (1984) pp. 472-476.
- SMITH, J.D., PLUES, L., HEYRAUD, M., CHERRY, R.D., Concentrations of the elements Ag, Al, Ca, Cd, Cu, Fe, Mg, Mn, Pb and Zn, and the radionuclides  $^{210}\text{Pb}$  and  $^{210}\text{Po}$  in the digestive gland of the squid *Nototodar* gouldi, *Mar. Environm. Res.*, 13 (1984) pp. 55-68.
- FOWLER, S.W., HUYNH-NGOC, L., FUKAI, R., Dissolved and particulate trace metals in coastal waters of the Gulf and western Arabian Sea, *Deep-Sea Res.*, 31 (1984) pp. 719-729.
- JUMARS, P.A., NEWELL, R.C., ANGEL, M.V., FOWLER, S.W., POULET, S.A., ROWE, G.T., SMETACEK, V., Detritivory, "Flows of Energy and Materials in Marine Ecosystems: Theory and Practice" (M.J.R. Fasham, ed.), Plenum Press, New York (1984) pp. 685-693.
- FISHER, N.S., BOHE, M., TEYSSIE, J.-L., Accumulation and toxicity of Cd, Zn, Ag, and Hg in four marine phytoplankters, *Mar. Ecol. Prog. Ser.*, 18 (1984) pp. 201-213.
- FISHER, N.S., Concentration of radionuclides by marine phytoplankton, "Role of Microorganisms on the Behaviour of Radionuclides in Aquatic and Terrestrial Systems and their Transfer to Man" (E. Bonnyns-Van Gelder, R. Kirchmann, eds.), International Union of Radioecologists, Brussels (1984) pp. 8-19.
- BOYD, C.M., HEYRAUD, M., BOYD, C.N., Feeding of the Antarctic krill *Euphausia superba*. *Crust. Biol.*, 4 (Spec. No. 1) (1984) pp. 123-141.
- ASTON, S.R., GASTAUD, J., OREGIONI, B., PARSI, P., Observations on the adsorption and geochemical associations of technetium, neptunium, plutonium, americium and californium with a deep-sea sediment, "International Symposium on the Behaviour of Long-Lived Radionuclides in the Marine Environment" (A. Cigna, C. Myttenaere, eds.), CEC, Luxembourg (1984) pp. 179-187.
- BALLESTRA, S., BOJANOWSKI, R., FUKAI, R., VAS, D., Behaviour of selected radionuclides in the northwestern Mediterranean basin influenced by river discharge, "International Symposium on the Behaviour of Long-Lived Radionuclides in the Marine Environment" (A. Cigna, C. Myttenaere, eds.), CEC, Luxembourg (1984) pp. 215-232.
- CARVALHO, F.P., FOWLER, S.W., Experimental studies on biokinetics of americium in benthic marine organisms, "International Symposium on the Behaviour of Long-lived Radionuclides in the Marine Environment" (A. Cigna, C. Myttenaere, eds.), CEC, Luxembourg (1984) pp. 297-315.



VILLENEUVE, J.-P., HOLM, E., Atmospheric background of chlorinated hydrocarbons studied in Swedish lichens, *Chemosphere.*, 13 (1984) pp. 1133-1138.

SCHULTE, E.H., SCOPPA, P., SECONDINI, A., FOWLER, S.W., HEUSSNER, S., WOJCIK, A., Experimental studies on the behaviour of technetium in the marine environment, "Radiation-Risk-Protection, Proc. 6th Intern. Cong. of IRPA" (A. Kaul, R. Neider, J. Pensko, F.-E. Stieve, H. Brunner, Eds.), Vol.I, Fachverband fur Strahlenschutz e.V., Julich (1984) pp. 172-175.

### APPENDIX 3

#### MEETINGS AND CONFERENCES ATTENDED AND REPORTS AND PAPERS PRESENTED (1983-1984)

##### 1983

Meeting on transuranic speciation in natural waters, January 1983, Mol, Belgium (N. Fisher). Paper presented: "On recent research in ILMR's biology section" by N. Fisher.

CEA Working Group No. 5 Meeting on Methods for Radionuclide Measurements, 18-19 January 1983, Paris (S. Ballestra).

ROPME Workshop on Oil and Non-oil Pollutant Sampling, Analysis and Data Handling, 12-23 February 1983, Kuwait (S. Fowler).

Thirteenth Session of GESAMP, 28 February - 4 March 1983, Geneva (R. Fukai).

NEA/OECD Second Task Groups Joint Meeting for Co-ordinated Research and Environmental Surveillance Programme (CRESP), 22-24 March 1983, La Spezia, Italy (S. Aston).

Fourth International Ocean Disposal Symposium, 11-15 April 1983, Plymouth, England (S. Aston, N. Fisher). Papers presented: "The role of biogenic debris in the vertical transport of transuranic wastes in the sea" by N. Fisher; "Bioavailability of technetium, plutonium and americium from deep-sea sediments to the clam Tapes decussatus L." by S. Aston, S. Fowler.

Fifteenth Session of the Inter-Agency Advisory Committee for MED POL Projects, 12-14 April 1983, Athens (R. Fukai).

Fourth Symposium on the Determination of Radionuclides in Environmental and Biological Materials, 18-19 April 1983, London (S. Aston, R. Bojanowski). Paper presented: "On the determination of natural radionuclides in marine environmental samples" by R. Bojanowski.

Seminar on Alpha Spectrometry and Low-Level Measurements, 10-13 May 1983, Harwell, UK (S. Ballestra). Paper presented: "Results of several intercalibration exercises on low-level alpha spectrometric measurements" by S. Ballestra.

IAEA International Conference on Radioactive Waste Management, 16-20 May 1983, Seattle, Washington, USA (S. Aston). Paper presented: "On the behaviour of long-lived radionuclides in relation to the deep-ocean disposal of nuclear wastes" by S. Aston, S. Fowler.

First Interagency Task Team Meeting for KAP, 7-8 June 1983, Kuwait (S. Fowler).

Fifth Session of Group of Experts on Methods, Standards and Intercalibration (GEMSI-V), 13-17 June 1983, Paris (K. Burns).

Meeting on the Selection of Analytical Instruments and Oceanographic Equipment at Regional Organization for the Protection of the Marine Environment (ROPME), 15-16 June 1983, Kuwait (S. Fowler).

Third National Symposium on Radioecology, 22-23 June 1983, Bologna, Italy (S. Fowler). Paper presented: "Radioecological aspects of deep-sea radioactive waste disposal" by S. Fowler.

IAEA Research Co-ordination Meeting on Radioactive materials in the Baltic Sea, 22-26 August 1983, Stockholm (R. Bojanowski).

International Symposium on Marine Science of the North-west Indian Ocean and Adjacent Waters, 3-7 September 1983, Alexandria, Egypt (S. Fowler). Paper presented: "Trace Metals in waters of the Gulf and western Arabian Sea" by S. Fowler, L. Huynh-Ngoc, R. Fukai.

NEA/OECD Executive Group Meeting on Research and Surveillance for Sea Disposal of Radioactive Wastes, 13-16 September 1983, Paris (S. Aston).

CEC International Symposium on the Behaviour of long-lived radionuclides in the marine environment, 28-30 September 1983, La Spezia, Italy (R. Fukai, R. Bojanowski). Papers presented: "Observations on the adsorption and geochemical associations of technetium, neptunium, plutonium, americium and californium with a deep-sea sediment" by S. Aston, J. Gastaud, B. Oregioni, P. Parsi; "Behaviour of selected radionuclides in the northwestern Mediterranean basin influenced by river discharge" by S. Ballestra, R. Bojanowski, R. Fukai, D. Vas; "Experimental studies on biokinetics of americium in benthic marine organisms" by F.P. Carvalho, S.W. Fowler.

GEMSI Intersessional Subgroup Meeting on Intercalibration Exercise for Sampling Sea Surface Microlayer, 3-7 October 1983, Paris (K. Burns).

UNEP/IOC First International Symposium on Integrated Global Ocean Monitoring, 3-8 October 1983, Tallinn, USSR (S. Fowler). Paper presented: "Monitoring trace elements in open Mediterranean organisms" by S. Fowler.

Inter-agency Meeting on UNEP's West and Central African Projects, 24 October 1983, Rome (R. Fukai).

Inter-agency Meeting on a Data Base for a Review of the Scientific and Technical Considerations related to the Dumping at Sea of Radioactive Waste, 19-23 September 1983, Vienna (R. Fukai).

Second Mussel Watch Symposium: Chemical Changes in the Coastal Zone, 6-11 November 1983, Honolulu (S. Fowler, K. Burns) Papers presented: "Current ILMR work on the behaviour of transuranics in mussels" by S. Fowler; "Fluxes and residence times of hydrocarbons in the coastal Mediterranean: How important are the biota?" by K. Burns.

Second Meeting of the Working Group for Scientific and Technical Co-operation for MED POL Projects, 21-26 November 1983, Athens (R. Fukai).

Fifth Session of GESAMP Working Group on Interchange of Pollutants between the Atmosphere and the Oceans, 28 November - 2 December 1983, Athens (N. Fisher).

PIROCEAN Meetings for ECOMARGE Programme, 1-13 December 1983, Paris (S. Fowler, S. Ballestra).

CEA Journees de Spectrometrie Alpha, 12-16 December 1983, Sacley, France (S. Ballestra). Paper presented: "Use of isotopic dilution and determination of low level concentration of transuranic elements in the marine environment" by S. Ballestra.

#### 1984

VERTEX Workshop and Cruise Planning Meeting, 16-20 January, 1984, Moss Landing, California, USA (S. Fowler). Paper presented: "Results of ILMR transuranic measurements from the first three Vertex cruises" by S. Fowler.

Seminar on Polarography Techniques, 30 January - 3 February 1984, Lyon (L. Huynh Ngoc). Paper presented: "Sampling and storage of sea water for trace metal determinations" by L. Huynh Ngoc.

IAEA Consultant Meeting on Key Parameters for Calculations required for Definitions of High-level Waste, 6-10 February 1984, IAEA, Vienna (N. Fisher).

Scandinavian Board meeting on Investigation of Long-lived Radionuclides released into the Aquatic Environment, 23-23 February 1984, (E. Holm).

CEA Working Group Meeting 'CETAMA Spectrometrie Alpha', 20 March 1984, Paris (S. Ballestra).

Fourteenth Session of GESAMP, 26-30 March 1984, Vienna (S. Fowler).

International Conference on Nuclear Method in Environmental and Energy Research, 1-27 April 1984, Puerto Rico (E. Holm).

NEA/OECD Geochemistry Task Group Meeting for Co-ordinated Research and Environmental Surveillance Programme (CREPS), 2-6 April 1984, Hamburg (N. Whitehead).

Seventeenth Session of the Inter-agency Advisory Committee for MED POL Projects, 9-13 April 1984, Athens (R. Fukai).

Third KAP Task Team Meeting, 18-19 April 1984, Kuwait (S. Fowler).

Meeting of International Union of Radioecologists, 25-27 April 1984, Belgium (N. Fisher). Paper presented: "On the accumulation of radionuclides by marine phytoplankton" by N. Fisher.

ICES/IOC/NOAA Symposium on Contaminant Fluxes through the Coastal Zone, 14-16 May 1984, Nantes (K. Burns). Paper presented: "Evidence for the rapid in situ oxidation rate of pollutant hydrocarbons in the open Mediterranean" by K. Burns.

Thirteenth International Symposium on "Chemistry of the Mediterranean", 16-24 May 1984, Primosten, Yugoslavia (N. Fisher, S. Fowler). Papers presented: "Concentration of metals in marine phytoplankton: implications for toxicity, vertical transport and oceanic residence times" by N. Fisher; "Biological control of transuranic residence time in the upper water column" by S. Fowler.

- IAEA Research Co-ordination Meeting on the Role of Sediments in the Transport and Accumulation of Radioactive Pollutants in Waterways, 28 May-2 June 1984, Budapest (N. Whitehead).
- UNEP Workshop on Environmental Monitoring, 28 May - 8 June 1984, Manila, Philippines (B. Oregioni).
- International Conference: The Baltic Sea - Environment Worth Protecting, 4-6 June 1984, Karlskrona, Sweden (E. Holm).
- UNEP Workshop on Reference Method Testing, 4-9 June 1984, Rome (S. Aston, K. Burns, N. Whitehead)
- Gordon Research Conference on "Environmental Sciences", 24-29 June 1984, New Hampshire, USA (N. Fisher).  
Paper presented: "Radionuclide accumulation in marine phytoplankton" by N. Fisher.
- Fourth National Symposium on Radioecology, 25 June 1984, Padua, Italy (S. Ballestra). Paper presented: "Measurements of  $^{241}\text{Pu}$  in rain water fallout samples collected at Monaco during 1978-1979" by S. Ballestra.
- UNEP Meeting on Biogeochemical Cycle of Mercury in the Mediterranean, 27-31 August 1984, Sienna, Italy (S. Aston).  
Paper presented: "Mercury biogeochemistry in the Mediterranean marine environment: "An overview of contamination" by S. Aston, S. Fowler, N. Whitehead.
- First Meeting of SCOR Working Group 71, 28-31 August 1984, Brussels (S. Fowler).
- International Symposium on Heavy Metals in Aquatic Organisms, 3-7 September 1984, Balatonfured, Hungary (S. Fowler).  
Paper presented: "Heavy Metals in Water Organisms" by S. Fowler.
- NEA/OECD Executive Group Meeting on Research and Surveillance for Sea Disposal of Radioactive Wastes, 10-12 September 1984, Paris (N. Whitehead)
- Conference on "Strategies and Advanced Techniques for Marine Pollution studies - Mediterranean Sea", 4-14 October 1984, Beaulieu, France (K. Burns, J. Derenbach).
- IAEA Research Co-ordination Meeting on Radioactive Materials in the Baltic Sea, 24-28 September 1984, Helsinki (R. Bojanowski, E. Holm).  
Papers presented: "Report on intercalibration organized for the laboratories participating in the IAEA's Coordinated Research Programme on the Study of Radioactive Materials in the Baltic Sea" by R. Bojanowski, R. Fukai, S. Ballestra, D. Vas; "Releases, distribution and pathways for radionuclides in the Baltic Sea" by E. Holm.
- Fourteenth Conference of the Baltic Oceanographers, 1-2 October 1984, Gdynia, Poland (R. Bojanowski). Paper presented: "On the distribution of  $^{210}\text{Po}$  in marine biota" by R. Bojanowski.
- Senior Advisory Group Meeting on the IAEA's Waste Management Programme, 8-12 October 1984, Vienna (R. Fukai).

Seventh Workshop on Pollution of the Mediterranean (ICSEM/UNEP/IOC), 11-13 October 1984, Lucerne, Switzerland (N. Whitehead, J.-P. Villeneuve). Paper presented: "Sediment samples and their analysis for trace metals" by N.E. Whitehead, B. Oregioni, R. Fukai.

Twenty-ninth Congress and Plenary Assembly of I.C.S.E.M., 15-19 October 1984, Lucerne, Switzerland (S. Fowler, N. Fisher). Papers presented: "Report on the activities of the Marine Radioactivity Committee during the XXIXth Congress and Plenary Assembly of I.C.S.E.M. held in Lucerne, Switzerland, 11-19 October 1984" by S.W. Fowler; "Bibliography of related activities of the Members of the Marine Radioactivity Committee (1983-1984)" by S.W. Fowler; "Biological control of transuranic flux through the upper water column of the Northeast Pacific Ocean" by S.W. Fowler, S. Ballestra, J. La Rosa, J. Gastaud; "Variations in algal sensitivity to metals" by N.S. Fisher, M. Bohe, J.-L. Teyssie; "Americium adsorption on macroalgal surfaces" by F.P. Carvalho, S.W. Fowler; "Observation on americium biokinetics in benthic invertebrates and its relation to feeding mode" by S.W. Fowler, F.P. Carvalho; "Accumulation and retention of  $^{241}\text{Am}$  and  $^{237}\text{Pu}$  in the mussel Mytilus edulis" by N.S. Fisher, S.W. Fowler, P. Bjerregaard, S. Topcuoglu.

CEC Seminar on the Behaviour of Technetium in the Environment, 23-26 October 1984, Cadarache, France (E. Holm, R. Bojanowski, S. Ballestra). Papers presented: "Technetium-99 in the Baltic Sea" by E. Holm; "Time trend of technetium-99 in seaweed from Greenland" by E. Holm; "Technetium-99 in algae from temperate and Arctic waters of the North Atlantic" by E. Holm.

Sixth Session of Group of Experts on Methods, Standards and Intercalibration (GEMSI-VI), 26-30 November 1984, Woods Hole, USA (S. Aston, K. Burns). Papers presented: "ILMR's role in IAEA/UNEP Project on development, testing and intercalibration of reference methods for marine pollution" by S. Aston.

Third International Congress on Analytical Techniques in Environmental Chemistry, November 19-22 1984, Barcelona (K. Burns). Paper presented: "On use of high performance gel permeation" by K. Burns.

AGU/ASLO Fall Meeting, 3-7 December 1984, San Francisco, (S. Fowler). Paper presented: "On results from ILMR's contribution to VERTEX" by S. Fowler.

#### APPENDIX 4

##### OCEANOGRAPHIC CRUISES (1983-1984)

On board R.V. "Gauss" (German Hydrographic Institute, Hamburg, Federal Republic of Germany), 31 May -21 June 1983, the Baltic Sea (R. Bojanowski).

On board R.V. "Wecoma" (Oregon State University, New Port, Oregon, USA) (VERTEX IV Cruise), 8-24 August 1983, the North-eastern Pacific (off Hawaii and California) (S.W. Fowler, S. Ballestra, J. La Rosa).

On board R.V. "Suroit" (Centre Nationale pour l'Exploration des Oceans, Brest, France) (PHYCEMED II Cruise), 19-29 October 1983, the Western Mediterranean Sea (Malta - Toulon) (J.-P. Villeneuve).

On board R.V. "Wecoma" (Oregon State University, New Port, Oregon, USA) (VERTEX V Cruise), 18-22 June 1984, The North-eastern Pacific (off Mexico) (S.W. Fowler, J. La Rosa).

On board C.S.S. "Baffin" (Bedford Institute of Oceanography, Dartmouth, Canada), 27 July - 18 August 1984, the Laborator Sea and the Western coast of Greenland (E. Holm).

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