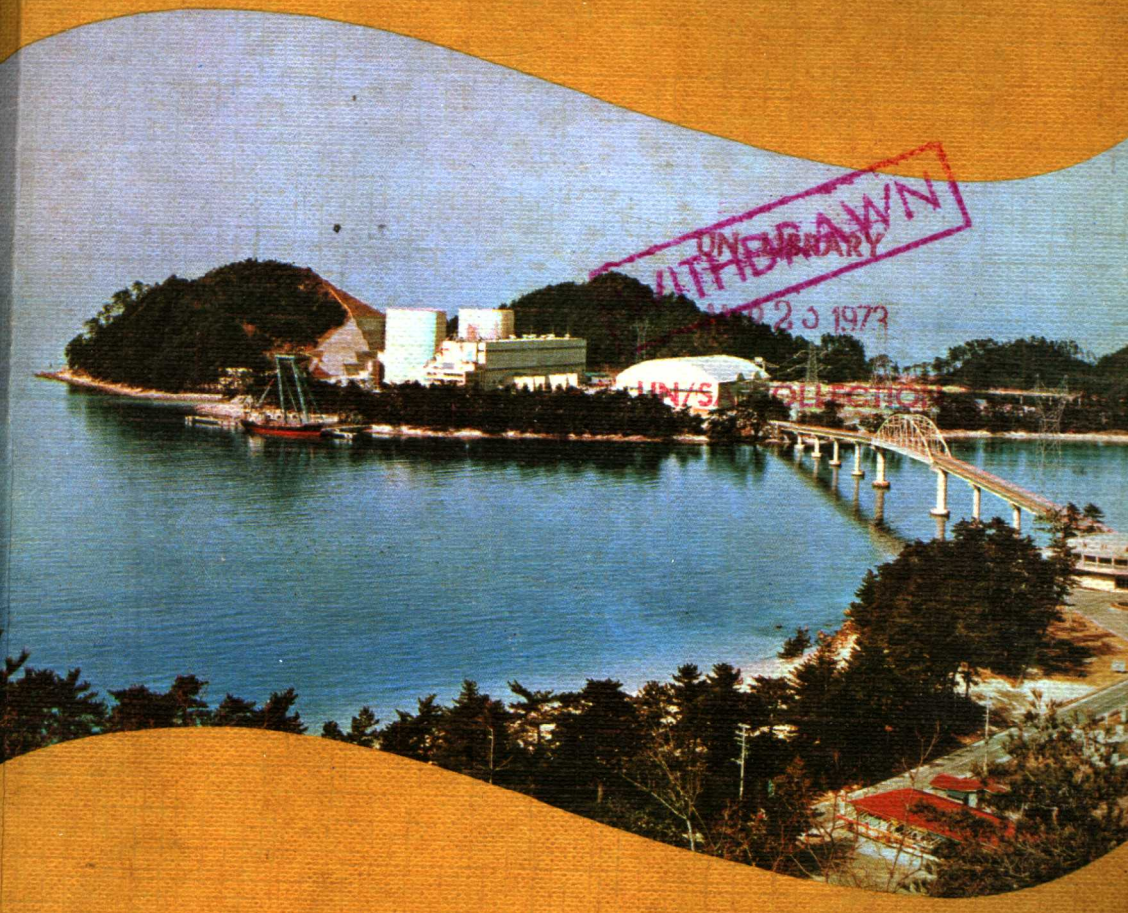
RADIOACTIVE CONTAMINATION OF THE MARINE ENVIRONMENT

Proceedings of a Symposium Seattle 10-14 July 1972



INTERNATIONAL ATOMIC ENERGY AGENCY, VIENNA, 1973

PROCEEDINGS SERIES

RADIOACTIVE CONTAMINATION OF THE MARINE ENVIRONMENT

PROCEEDINGS OF A SYMPOSIUM
ON THE INTERACTION OF RADIOACTIVE CONTAMINANTS
WITH THE CONSTITUENTS OF THE MARINE ENVIRONMENT
HELD BY THE
INTERNATIONAL ATOMIC ENERGY AGENCY
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FOREWORD

The nuclear energy industry has grown during the past several years and a continuing growth is predicted over the next few decades during which time nuclear power is expected to become the main source of energy for fulfilling the needs of many of the more developed nations. Although considerable effort is being made to minimize the release of the increasing amounts of radioactive wastes into the marine environment, it is evident that the potential for radioactive contamination will continue to grow. In addition, nuclear weapons testing in recent years has added to the contamination of the marine environment through fallout which has taken place on a global scale. Although fallout levels are lower than in previous years, the recent resumption of such tests clearly indicates the need for continued surveillance of fallout radionuclides in all constituents of the marine environment so as to be more able to evaluate the potential hazards to man and to the biological components of the marine ecosystem.

A previous IAEA symposium on the Disposal of Radioactive Wastes into Seas, Oceans and Surface Waters, held in Vienna in 1966, covered much of what was then known concerning the disposal of radioactive wastes into aquatic ecosystems. One conclusion drawn from that symposium as well as subsequent IAEA panels on marine radioactivity studies was that a better understanding of the consequences of artificial radionuclide contamination could be gained through knowledge of the interaction of radionuclides and their stable isotopes, particularly as pertains to the different physico-chemical forms and their behaviour in relation to organic substances, sediments, and marine biota. Accordingly, the Agency convened a Symposium on the Interaction of Radioactive Contaminants with Constituents in the Marine Environment in Seattle, Washington, USA, on 10 - 14 July 1972. The meeting covered four main topics: physical and chemical forms of radioactive contaminants in the marine environment; interaction of radionuclides with marine biota; evaluation of hazards to the health and safety of man; and study of radiologically labelled environments. The 48 papers comprising these Proceedings give results of recent research on many aspects of the topics mentioned and should serve as a guide not only for those interested in marine radioactivity studies but also in the whole subject of oceanography.

The Agency would like to express its appreciation to the United States authorities who did so much to make the symposium a success.

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PHYSICAL AND CHEMICAL FORMS OF RADIOACTIVE CONTAMINANTS IN THE MARINE ENVIRONMENT

(Sessions I and II, and Session III, Part 1)

Chairmen

Session I	W.R. SCHELL (United States of America)
Session II	M. BERNHARD (Italy)
Session III	B. PATEL (India)

INTERCALIBRATION OF METHODS FOR MEASURING FISSION PRODUCTS IN SEAWATER SAMPLES

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Abstract

INTERCALIBRATION OF METHODS FOR MEASURING FISSION PRODUCTS IN SEAWATER SAMPLES.

To examine the present-day comparability of fission product measurements on seawater samples with the aim of achieving better comparability in the future, an intercalibration exercise was organized by the Monaco Laboratory in 1970-71; two kinds of homogeneous seawater samples contaminated with various radionuclides under natural conditions at monitoring levels were distributed to laboratories around the world – 46 laboratories reported the results of measurements on fission products in these samples. In this paper a survey made on the reported results is presented together with the results of homogeneity tests of the samples. The "preferred values" for strontium-90, ruthenium-106, caesium-134 and caesium-137 are estimated for these samples by statistical treatments of the obtained results. The scatter of the results is less pronounced for strontium-90 and caesium-137 than for zirconium-niobium-95, ruthenium-106, caesium-134 and cerium-144. For ruthenium-106 in the higher level sample, the results are especially noteworthy, being spread over almost two orders of magnitude. This seems to relate to the incapability of some methods to measure different chemical forms of this radionuclide occurring in seawater. Specific observations made on the results for each radionuclide as well as general remarks on the reported results are also given.

1. INTRODUCTION

In recent years considerable progress has been made in improving techniques for measuring radioactivity in marine organisms and their environment. This has been due in particular to the increasing requirements for monitoring the surroundings of nuclear installations and also to the expansion of research coverage in marine radioactivity. Recent developments of analysis methods for several radionuclides have been reviewed by a group of experts at an IAEA panel, which presented a series of reference methods for measuring radionuclides of strontium, caesium, cerium, cobalt and zinc as well as their stable counterparts occurring in the marine environments [1]. Although these methods have been widely applied to marine radioactivity studies, it was also noted that the results obtained for specific elements by different laboratories were not always comparable owing to the use of different experimental techniques. In some instances, this has even led to conflicting conclusions being drawn (e. g. Ref. [2]). As the results of radionuclide measurements are the basis of any radioecological studies, it is especially important to ensure the comparability of results obtained by different laboratories from various countries in environmental studies of international interest: the sea.

To achieve the comparability of results of measurements by different laboratories several approaches can be made. One is to adopt a unified method for measurements of a specific element and to recommend its use in all laboratories concerned. The effectiveness of this approach has

been demonstrated by the well-known example of chlorinity determination in the oceanographic research; the argentometric titration method established by Knudsen in 1902 [3] had been used everywhere until replaced by conductometric measurements in the 1960s. This standardization of the method had a tremendous impact on the developments of physical oceanography as a whole.

In marine radioactivity studies as in many other research fields, however, it is generally not advisable to recommend one method as the only standard procedure since the speed of development of modern technology is so rapid that widespread acceptance of a single method is unlikely before new and perhaps better techniques appear. In this case the necessary assurance of the comparability of measurement results can only be provided by group intercalibration analyses of aliquots of homogeneous samples or by analyses of standard reference material. In the latter, certified values of compositions concerned must be given and these values should be determined by several independent methods of analysis.

Based on these considerations, an intercalibration exercise of methods for measuring fission product radionuclides[1] in seawater samples was organized by the Monaco Laboratory in 1970-71. The main object of this exercise was to examine present-day comparability of fission product measurements on seawater samples to achieve improved comparability in the future. This paper is a survey of the results reported by laboratories participating in the intercalibration exercise. The results of homogeneity tests of seawater samples distributed are also discussed in detail.

It should be emphasized that the contents of this paper are a result of the joint efforts of a number of participating national institutions as well as the IAEA laboratories, and represent a good example of voluntary international collaboration towards achieving a common scientific goal.

2. COLLECTION AND PREPARATION OF SEAWATER SAMPLES

Since there are still considerable uncertainties about the chemical forms in which radionuclides occur in seawater in situ, the preparation of spiked seawater samples with known amounts of radionuclides for intercalibration was purposely avoided; any practical analytical method should be capable of measuring not only radionuclides in known chemical forms in synthesized samples, but also in samples taken in a monitoring program.

The field collections of two kinds of seawater which were expected to be contaminated in nature with various radionuclides at monitoring levels, were made by the British Fisheries Radiobiological Laboratory, Lowestoft, with IAEA financial support. For each collection 1000 litres of seawater were taken on board and stored in a plastic tank, filtered through membrane filters of 0.45 μm pore size, homogenized thoroughly, acidified to pH 1.5 ~ 2 with hydrochloric acid and sub-sampled into 200 5-litre polyehtylene containers. Since no special precaution was taken against contamination with trace metals, these seawater samples

[1] Although strictly speaking caesium-134 is not a fission product, it was treated similarly to the fission products presented in this paper.

should not be considered as representative of natural levels of stable trace elements. The 5-litre bottles were transported by rail from England to Monaco. The seawater collected in November 1969 and January 1970 was code-numbered as SW-I-1 and SW-I-2, respectively. Each 5-litre bottle was arbitrarily numbered at Monaco.

3. HOMOGENEITY OF THE SAMPLES

To examine the homogeneity of the samples several 5-litre containers were picked at random from the batches and the seawater in each container was independently analysed for several radionuclides at the Monaco Laboratory (Monaco) and Woods Hole Oceanographic Institution (WHOI). The results of these analyses are given in Tables I and II, respectively for SW-I-1 and SW-I-2.

In Table III the results of analyses of Mediterranean water spiked with known amounts of radionuclides, such as strontium-90, ruthenium-106, caesium-134 and caesium-137, are also presented. These analyses were performed at Monaco in order to estimate the variations in the analytical results which are inherent to the methods used. The methods adopted were those described by Bowen [4] for strontium-90, by Yamagata and Iwashima [5] for ruthenium-106, and by Fukai et al. [6] for caesium-134 and caesium-137. On the basis of these analytical data standard deviations for single determination of each radionuclide were computed, as given also in Table III; these values are between ±3 and 4% of the averaged values of the spiked samples for strontium-90 and caesium-137, slightly greater for ruthenium-106 in different chemical forms, and much greater for caesium-134. Since caesium-134 and caesium-137 had been added into the same water sample in a similar chemical form and were analysed simultaneously by chemical separation and γ-spectrometry, the greater standard deviation for caesium-134 analysis should be caused only by the procedure of data processing. The greater variations of the data for ruthenium-106 are probably due to uncertainty involved in the chemical recovery of this isotope in the adopted procedure. These values of standard deviation offer certain measures of aid for the evaluation of the homogeneity data.

For the evaluation of the homogeneity of the water samples information on the stability of radionuclides in solution is also useful. The studies carried out by the British Fisheries Radiobiological Laboratory (Preston and Dutton [7]; unpublished data) using seawater sample SW-I-2, showed that the stability of the fission products concerned, with the exception of cerium-144, was good even after more than 200 days storage. In the case of cerium-144 a considerable fraction was attached to the wall of the polyethylene containers, even when the pH-value of the water samples was kept between 1.5 and 2. On the basis of this information it is quite likely that, if the content of one bottle is inhomogeneous in relation to that in other bottles, the inhomogeneity identified by the analysis of one radionuclide of strontium-90, ruthenium-106, caesium-134 or caesium-137, should reflect, to a similar degree, the inhomogeneity of the other three radionuclides. This implies that inhomogeneity of the contents of the bottles should be detected by examining systematic deviations from averaged values of sets of data on the above-mentioned radionuclides.

TABLE I. RESULTS OF THE HOMOGENEITY TESTS ON SW-I-1 CARRIED OUT BY MONACO LABORATORY (MONACO) AND WOODS HOLE OCEANOGRAPHIC INSTITUTION (WHOI)

Laboratory	Bottle No.	Quantities found (pCi/kg)			
		^{90}Sr	^{106}Ru	^{134}Cs	^{137}Cs
MONACO	1	5.0	-	2.5	12.5
	2	4.8	-	2.3	12.7
	3	5.3	-	2.7	12.4
	4	5.2	-	2.4	12.8
	5	5.1	-	2.5	13.2
	6	5.3	-	2.5	12.9
	7	5.4	-	2.5	12.9
	8	5.3	2.9	2.2	13.4
	9	4.8	3.5	2.9	13.2
	10	5.4	2.8	-	-
	Average	5.2	3.0	2.5	12.9
	σ (single det.)	± 0.2 (3.8%)	± 0.4 (13%)	± 0.2 (8.0%)	± 0.3 (2.3%)
	Chauvenet's range	± 0.4 (7.7%)	± 0.6 (20%)	± 0.4 (16%)	± 0.6 (4.6%)
WHOI	21	4.64	-	0.88	14.1
	22	5.35	-	1.26	13.7
	23	4.59	-	1.59	13.6
	24	4.82	-	1.42	13.6
	Average	4.85	-	1.29	13.8
	σ (single det.)	± 0.35 (7.2%)	-	± 0.30 (23%)	± 0.2 (1.4%)
	Chauvenet's range	± 0.54 (11%)	-	± 0.57 (44%)	± 0.3 (2.2%)

With the foregoing discussions in mind the data in Tables I and II were evaluated. For SW-I-1 (Table I) the standard deviations for a single determination estimated on stronium-90 and caesium-137 data are ±3.8% and ±2.3%, respectively, of the averaged values by Monaco, and ±7.2% and ±1.4%, respectively, by WHOI; standard deviations for the results on ruthenium-106 and caesium-134 are much greater than those for strontium-90 and caesium-137, as may be predicted from the data in Table III. After being tested by Chauvenet's criterion [8, 9], no results

TABLE II. RESULTS OF THE HOMOGENEITY TESTS ON SW-I-2 CARRIED OUT BY MONACO LABORATORY (MONACO) AND WOODS HOLE OCEANOGRAPHIC INSTITUTION (WHOI)

Laboratory	Bottle No.	Quantities found (pCi/kg)			
		^{90}Sr	^{106}Ru	^{134}Cs	^{137}Cs
MONACO	5	54.8	-	-	-
	6	54.0	-	-	-
	7	53.6	34.0	23.1	184
	8	52.6	30.3	26.1	179 [a]
	9	52.4	-	22.8	183
	10	53.8	-	26.8	187
	97	52.7	28.2	24.6	188
	101	53.9	36.0	24.8	190
	102	53.6	32.2	33.4	186
	103	54.8	34.3	30.2	185
	Average	53.6	31.7	29.4	185
	σ (single det.)	±0.8 (1.5%)	±2.8 (8.8%)	±4.8 (16%)	±3 (1.6%)
	Chauvenet's range	±1.6 (3.0%)	±4.8 (15%)	±8.9 (30%)	±6 (3.2%)
WHOI	21	51.8	-	25.1	200
	22	52.2	-	23.7	198
	23	50.9	-	23.4	194
	24	52.2	-	22.5	197
	25	50.0	-	15.8	170*
	26	59.9*	-	28.2	196
	27	52.7	-	30.1	182
	28	53.6	-	20.7	195
	Average	52.9	-	23.7	192
	σ (single det.)	±3.0 (5.7%)	-	±4.4 (19%)	±10 (5.2%)
	Chauvenet's range	±5.6 (11%)	-	±8.2 (35%)	±19 (9.9%)

[a] The values which should be excluded according to Chauvenet's criterion.

TABLE III. RESULTS OF ANALYSES ON MEDITERRANEAN WATER SPIKED WITH RADIONUCLIDES (PERFORMED BY MONACO LABORATORY)

Radionuclide	^{90}Sr	^{106}Ru CL-form [a]	^{106}Ru NN-form [b]	^{134}Cs	^{137}Cs
Source of supply	IAEA	Amersham (UK)	Amersham (UK)	CEA (France)	CEA (France)
Quantity spiked (pCi/l)	46.7	103	103	99	109
Quantity found (pCi/l)	46.7	97	101	95	109
	48.2	103	101	113	112
	47.7	108	98	104	104
	44.3	110	110	105	113
	46.0	104	107	101	111
Average (pCi/l)	46.6	104	103	104	110
σ (single det.)	±1.4 (3.0%)	±5 (4.8%)	±5 (4.9%)	±7 (6.7%)	±4 (3.6%)
Chauvenet's range (pCi/l)	±2.3 (4.9%)	±8 (7.7%)	±8 (7.8%)	±12 (12%)	±7 (6.4%)

[a] Chloride complex forms.
[b] Nitrato-nitrosyl complex forms.

from Table I should be excluded. Considering that the radionuclides in solution other than cerium-144 are similarly stable to each other and that the best reproducibility of series of analytical results obtained for one radionuclide among various radionuclides analysed should thus be a measure of the sample homogeneity, it can be said that in terms of per cent standard deviation of the content of the radionuclide concerned (excluding cerium-144) the homogeneity should be better than ±3% for SW-I-1. This value is based on the caesium-137 data.

For SW-I-2 (Table II) standard deviations estimated for strontium-90 and caesium-137 data are respectively ±1.5% and ±1.6% of the averaged values by Monaco, and ±5.7% and ±5.2% by WHOI; those for ruthenium-106 and caesium-134 are much greater, as is the case of SW-I-1. In the case of SW-I-2, however, the results marked by an asterisk (*) should be discarded according to Chauvenet's criterion. This means that those samples where the results are marked by (*) should be suspected for occurrence of the sample inhomogeneity. The inspection of the sets of data for the various radionuclides in these specific samples excludes the possibility of occurrence of sample inhomogeneity, except for the