REPRIN'

NEUTRON ACTIVATION ANALYSIS
TRACE-ELEMENT STUDIES OF
DOVER SOLE LIVER AND MARINE SEDIMENTS

Jeroen J. M. de Goeij Vincent P. Guinn David R. Young Alan J. Mearns

Reprinted from Comparative Studies of Food and Environmental Contamination, pages 189-200. International Atomic Energy Agency, Vienna, 1974.

SOUTHERN CALIFORNIA COASTAI WATER RESEARCH PROJECT 1500 East Imperial Highway El Segundo, California 9024 0.01

NEUTRON ACTIVATION ANALYSIS TRACE-ELEMENT STUDIES OF DOVER SOLE LIVER AND MARINE SEDIMENTS

J.J.M. DE GOEIJ Interuniversity Reactor Institute, Delft, The Netherlands

V.P. GUINN
University of California at Irvine,
Calif., United States of America

D.R. YOUNG, A.J. MEARNS Southern California Coastal Water Research Project, El Segundo, Calif., United States of America

Abstract

NEUTRON ACTIVATION ANALYSIS TRACE-ELEMENT STUDIES OF DOVER SOLE LIVER AND MARINE SEDIMENTS.

This study has been aimed at determining the present levels of trace elements in the liver of Dover sole, collected from polluted as well as unpolluted areas around and down-current of the major Los Angeles area sewage outfalls in the Pacific Ocean. A radiochemical-separation scheme was devised for the analysis of Dover sole liver and some sediment samples. The post-irradiation chemistry includes a destruction with sulphuric acid and hydrogen peroxide, a distillation with hydrobromic acid, and an absorption of quite a few elements of the distillate and residue, each on a Dowex anion exchanger. In the residue resin the elements molybdenum, cadmium, copper, zinc, iron and cobalt, and in the distillate resin the elements mercury, selenium, arsenic and antimony were simultaneously measured using a Ge(Li) detector. The ranges of concentrations found in Dover sole liver (wet-weight basis) are: 0.050 - 0.39 ppm Hg, 0.23 - 1.9 ppm Se, 0.001-0.007 ppm Sb, 0.70-4.3 ppm As, 0.040-0.20 ppm Mo, 0.060-6.9 ppm Cd, 1.1-9.2 ppm Cu, 19 - 39 ppm Zn, 105 - 319 ppm Fe, 0.017 - 0.10 ppm Co. Surprisingly, no significant differences have been observed in these element levels between sole caught in polluted and unpolluted areas, even though sole is a "bottom-feeder" type of fish and the ocean sediments in the polluted areas sometimes contain concentration of these elements 10 to 150 times higher than in the unpolluted areas. The method has also been applied to the analysis of a sediment core taken near an outfall. The results show a strong decrease of the levels of mercury, arsenic, selenium and antimony with increasing depth of the sediment layers.

1. INTRODUCTION

This marine biological trace-element study, conducted at the Universi of California at Irvine with the support of the Southern California Coastal Water Research Project, has been aimed at determining the present levels of quite a number of (metallic) trace elements in fish samples taken at varilocations along the coast of Southern California. A principal objective has been to ascertain whether unusually high concentrations of these elements occur in fish samples taken from areas around and down-current of the major Los Angeles area sewage outfalls in the Pacific Ocean. Furthermor attention has been focused on several of the target elements which previous had not been determined in marine sediments near sewage outfalls.

90 DE GOEIJ et al.

The selected procedure for analysis is an example of how targets and echniques can be set in order to carry out a desired program within a specific period of time.

2. BIOLOGICAL SPECIES AND TRACE ELEMENTS OF INTEREST

Immature Dover sole (Microstomus Pacificus) was selected as the contamination-indicator species for this study because: (i) it is a coastal lish and does not migrate to any great distances at juvenile age; (ii) it is a bottom feeder; (iii) it occupies an intermediate position in the ocean food chain; and (iv) it is known to be affected by waste-water discharges. Liver, rather than flesh tissue, was selected, since more trace-elements can be letected in the liver (due to its well-known ability to concentrate metals); the liver is an important organ in respect of detoxification.

During the autumn of 1971 and the spring of 1972, immature (150-250 mm) specimens of Dover sole were captured in bottom trawls taken at various listances from areas covering a wide range of sediment metal contamination. The locations from which the Dover sole were collected were grouped into four categories on the basis of atomic absorption values for the sediments—already available from Galloway [1]:

- 1) Natural The Santa Catalina Islands area, assumed to have natural trace-metal concentrations in surface sediments;
- 2) Intermediate Coastal areas near waste water discharges that have slightly elevated trace-metal concentrations in the surface sediments;
- 3) High Three areas (directly off the Hyperion 7-mile outfall, and off the northern and southern tips of the Palos Verdes Peninsula) that have significant enrichment of trace elements in surface sediments;
- 4) Very High The area centred approximately 5 km northwest of the Whites Point outfall system that has the highest surface sediment concentrations of metals.

As can be seen from Table I, the ratios of the sediment element levels for the most contaminated ("very high") region and to the levels in the uncontaminated ("natural") region can be quite large.

In the overall Southern California Coastal Water Research Project nvestigation, ten trace elements were selected as being of primary interest: arsenic, cadmium, chromium, copper, lead, mercury, nickel, selenium, silver and zinc. Eleven additional elements were considered of secondary interest: antimony, bismuth, cobalt, iron, manganese, molybdenum, tellurium, tin, titanium, tungsten and vanadium. In this contribution to the total project, the aim has been to characterize, using neutron activation analysis, the liver tissues on the basis of at least ten important trace elements.

In the study of Galloway [1], concentration profiles of various trace elements in polluted sediments have been determined, using atomic absorption spectrometry. The results show a marked decrease of the levels of many elements with increasing depth of the sediment layers. Since it appeared of interest to collect similar information on antimony, arsenic, mercury and selenium, a 34 cm deep "box" sediment core was taken in the most contaminated ("very high") area [2].

TABLE I. TRACE-ELEMENT LEVELS IN SEDIMENTS FROM THE "VERY HIGH" AND "NATURAL" AREAS

Data for the non-volatile elements from Galloway [1,2] and for the volatile elements from this study (sub-section 4.2).

Trace element	Concentra µg element/g o	"very high"	
	"very high"	"natural"	"natural"
Antimony	11	0.84	13
Arsenic	124	8.1	15
Cadmium	59	0.37	160
Cobalt	7.6	6.2	1.2
Copper	360	16	23
Iron	30 000	25 000	1.2
Mercury	3.4	0.04	85
Selenium	4.8	0.34	14
Silver	3.0	1.0	3.0
Zinc	1100	63	17
			i

3. ANALYTICAL PROCEDURE

3.1. Criteria for the development of the procedure

Within the limited amount of time and man-power, and within the limits imposed by the available reactor flux and irradiation times and by the counting equipment, an effort was made to devise an analytical procedure that would produce dependable values for a substantial number of trace elements of interest, for a sizable number of samples.

Earlier studies by Guinn and Kishore [3,4] showed that the levels of mercury, selenium and zinc could be determined in many kinds of fish samples by purely (non-destructive) neutron activation analysis, using the available irradiation and counting conditions. In some samples, one or a few additional important trace elements were also detectable. The results made it clear that, in order to detect and measure as many as ten trace elements of interest consistently and with acceptable precision and accuracy in every fish sample, a radiochemical-separation procedure would have to be used.

The best solution appeared to lie in developing a simple chemical group separation system and counting with a germanium detector. The following standard working conditions for the analysis were adopted: sample weight between 2 and 3 g of wet material; irradiation at a flux of 7×10^{11} n/cm²·s (thermal) for 6 h; counting on a 36 cm³ germanium detector for 4 h. Due to the high radiation level induced by irradiating marine material, a cooling time of at least two days proved to be necessary.

192 DE GOEIJ et al.

In order to obtain the maximum amount of relevant data, only elements leading to gamma-emitting radionuclides with half-lives longer than 12 h were taken into consideration. These radionuclides permit of the simultaneous irradiation and processing of several samples, while all counting fractions can be counted afterwards for a reasonable time. This criterion reduced the number of elements of interest that could be determined from 21 (10 of primary interest and 11 of secondary interest) to 14. On the basis of literature data for fish (liver) and some preliminary experiments, it was to be expected that under the standard working conditions information about the following eleven elements could be obtained: antimony, arsenic, cadmium, cobalt, copper, iron, mercury, molybdenum, selenium, tungsten and zinc. A suitable chemical separation scheme was developed which obeyed the following five criteria:

- (1) The counting fractions should be almost free of interfering radionuclides (especially sodium-24, potassium-42, bromine-82, and phosphorus-32). Even small interfering amounts may give rise to 'noise', and would necessitate inadmissably long counting times. Moreover, corrections might be necessary, e.g. for the contribution of sodium-24 to the 511 keV peak of copper-64.
- (2) The fractions resulting from the chemically-processed samples should occupy small volumes to ensure maximum counting efficiency.
- (3) A compromise between two conflicting requirements must be sought: on the one hand the number of fractions resulting from the chemical processing should be kept to a minimum in order to reduce the counting time, while on the other the mixture of radionuclides should not have too high a density of peaks of variable intensities and energies since this could severely decrease the sensitivity of detection for any shorterlived radionuclides of interest, especially in the low-energy region.
- (4) The chemistry involved should be simple with respect to both time and apparatus, so that a certain minimum number of elements could be determined each week, while leaving sufficient time for calculations, etc. Time-consuming steps, such as the determination of chemical yields, should be avoided.
- (5) The accuracy and precision attained should lie around ±10% to ±15%. The achieving of a smaller error is, in general, for biological samples, not worth the extra time and effort needed, since the biological variation itself is usually considerably larger.

Taking all five criteria into account, a scheme for the eleven target elements was devised and thoroughly tested by processing inactive samples with radiotracers. A scheme being developed at the Interuniversity Reactor Institute at Delft (The Netherlands) [5] was taken as the basis when devising the radiochemical-separation procedure.

3.2. Irradiation

The 2 to 3 g wet weight samples were sealed in polyethylene vials and irradiated in the rotary specimen rack of the University of California at Irvine's 250 kW TRIGA Mark I reactor at a flux of $7\times10^{11}~n_{\rm th}/{\rm cm}^2$'s for 6 h. Normally 6 samples were irradiated simultaneously, with two pieces of metallic zinc used as single comparator. The zinc comparator was periodically calibrated against standards consisting of a $2\underline{\rm N}$ hydrochloric acid solution of arsenic, antimony, cadmium, chromium, cobalt, copper,

iron, mercury, molybdenum, selenium and zinc. This procedure improve the precision of the analysis, and leads to a higher sample output rate [9]. The standard solutions were irradiated in quartz vials, since it was found that substantial amounts of mercury were lost from standard solutions we these were irradiated in polyethylene vials.

3.3. Radiochemical separation scheme for liver samples

The radiochemical-separation scheme devised is shown schematicall in Fig. 1. To each activated sample, 1 ml of 48% hydrobromic acid soluti and 0.5 ml of a 2M hydrochloric acid carrier solution containing 50 μ g of each trace element of interest were added. The mixture was then charre

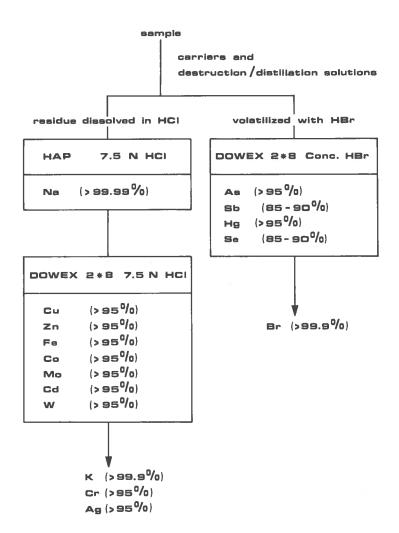


FIG.1. Outline of the radiochemical group separation scheme.

y heating with 2 ml of concentrated sulphuric acid. Complete dissolution vas achieved by five to eight successive 1 ml additions of 30% hydrogen per-xide, followed by heating. The entire wet-ashing operation was carried out n a distillation apparatus under a small air flow, using 20 ml of 48% hydroromic acid as the collector for the volatile species. The elements antimony, rsenic, mercury, selenium and bromine (an interfering element) were istilled over in five repeated boilings following 1 ml additions of 48% ydrobromic acid.

The hydrobromic acid solution containing the volatile elements was nade up to 50 ml with 48% hydrobromic acid, and then passed through a .3 g Dowex 2 × 8 anion-exchanger column in hydrobromic acid form (7 mm lia.). The column was washed twice with 10 ml portions of 48% hydrobromic cid. Under these conditions, the antimony, arsenic, mercury and selenium vere quantitatively retained on the column, while for bromine-82 a decontamination factor of over 1000 was achieved. The small amount of resin was then ransferred to a polyethylene vial for counting.

The distillation residue was diluted with 15 ml of 7.5M hydrochloric cid, passed through a 3 g HAP (hydrated antimony pentoxide) column 7 mm dia.), and washed with 5 ml of 7.5M hydrochloric acid. The HAP olumn retained the large sodium-24 activity almost quantitatively, whereas he elements of interest passed through. The sodium-24 free effluent was hen passed through 2.3 g Dowex anion-exchange column in hydrochloric cid form (7 mm dia.), and the column was washed twice with 5 ml portions f 7.5M hydrochloric acid. The elements cadmium, cobalt, copper, iron, nolybdenum, tungsten and zinc were quantitatively retained, whereas for otassium-42 and phosphorus-32 decontamination factors of over 1000 were chieved. The resin was then transferred to a polyethylene vial for counting.

The elements chromium and silver were present in the effluent. Although hey are of primary interest, it was decided not to focus much attention on hem, since it was estimated that their concentrations in the samples were so low for detection under the standard working conditions. However, hromium-51 and silver-110m may be looked for in the effluent after decay f potassium-42.

Carrier yields were not determined in each analysis, as the earlier adiotracer studies showed that the yields were constant to within a few er cent, and the standards were processed identically to the samples.

.4. Radiochemical-separation scheme for the sediment samples

For the sediment samples the scheme as outlined in sub-section 3.3 ras used, with only a slight modification. The amount of sulphuric acid ras increased to 10 ml, while the amount of irradiated material for processing was lowered to 1 g. This was necessary in order to avoid complete olidification of the cadmium-rich sediment samples during destruction. If the destruction and distillation, only the distillate was further processed a counting fraction.

.5. Counting and calculations

The samples were counted with a 36 cm³ coaxial lithium-drifted geranium detector (2.8 keV resolution, 6% relative cobalt-60 efficiency, 3:1 peak-to-Compton ratio) coupled to a 4096-channel pulse-height analyser.

The analyser was equipped with a PDP-8 computer, a teletypewriter, and an Ampex magnetic-tape system. The counting time normally amounted to four hours. The residue counting fractions were allowed to stand for 24 hc prior to counting in order to re-establish the equilibrium for molybdenum/technetium-99(m) and cadmium/indium-115.

All calculations were made on the University of California at Irvine's PDP-10 computer, using a standard net-peak-area method. In the compute program, provisions were inserted to correct for the zinc-65 contribution to the 511 keV gamma ray of copper-64 and for the contribution of iron-59 to the 140 keV gamma ray of molybdenum/technetium-99(m).

3.6. Testing the overall analytical procedure

The precision and accuracy of the overall procedure was tested by analysing six aliquots of NBS Orchard Leaves SRM No.1571, each of approximately 600 mg. The elements antimony, arsenic, cobalt, copper, iron, molybdenum, mercury, tungsten and zinc were easily detected under the standard working conditions. Cadmium, however, could not be detected and chromium and selenium were only detectable after prolonged counting times. With the exception of the results for mercury, the agreement with the NBS certified values was good (Table II). A small loss of mercury from

TABLE II. TRACE-ELEMENT LEVELS IN NBS ORCHARD LEAVES SRM No. 1571

The results of the present study, shown to a 95% confidence level, are based on six different measurements. All values are in micrograms element/gram dry material.

Element	This study	NBS certified values	Averages calculated from literature values; number of laboratories in parenthesis	Ref.
Antimony	2.7 ± 0.2		3.0 ± 0.3 (4)	[4,6]
Arsenic	11.5 ± 1.5	14 ± 2^a		
Cobalt	0.13 ± 0.01		0.16 ± 0.05 (4)	[4,6]
Chromium	2.9 ± 0.3		2.4 ± 0.3 (4)	[4,6]
Copper	12 ± 1	12 ± 2		
Iron	315 ± 25	300 ± 20		
Mercury	0.12 ± 0.01	0.155 ± 0.015		
Molybdenum	0.30 ± 0.03		0.30(1)	[7]
Selenium	0.06 ± 0.02	0.08 ± 0.01		
Tungsten	$D_{\mathbf{p}}$		< 2.0, < 5.0 (2)	[4,6]
Zinc	27 ± 2	25 ± 3		

This value has recently been questioned as too high [8]; the values mostly found range from 10 to 13 ppm [4-6, 8]. [Ed. note: As can be seen from the presentation of P.D. LaFleur (paper IAEA-SM-175/25; these Proceedings) the certified value for arsenic has been re-set as 11 ± 2 ppm.]
 D = detected, but not measured quantitatively.

196 DE GOEIJ et al.

the polyethylene container during irradiation is thought to be the cause of the 20% lower mercury value obtained. However, no mercury loss has been found to occur during irradiation of wet fish and sediment samples at low temperature and at low neutron flux. For the elements antimony, chromium, cobalt and molybdenum, no certified values are as yet available for comparison, but the present values agree well with literature data.

4. RESULTS AND DISCUSSION

4.1. Dover sole liver

Ten out of the eleven target elements could be detected in the Dover sole samples, each consisting of liver tissue from three or more fish specimens (Table III). Only tungsten was not detectable under the standard working conditions. Apparently, this element is present in the liver at lower levels than was estimated earlier (sub-section 3.1). On the other nand silver, which was originally estimated to be present at too low a concentration to be detected, was almost always detected in the 30 ml effluent of the Dowex residue column, following prolonged counting. In the same effluent, chromium (not shown in Table III) was only found in 25% of the liver samples, at levels of about 0.1 ppm. It can be concluded that silver and, to a lesser extent, chromium also have good prospects for detection under the standard working conditions if the activity is concentrated into a small volume (instead of 30 ml) and if interferences, especially phosphorus-32, are removed.

There were no significant differences in the chromium concentrations n the liver samples from four types of collection sites, and the best estimate for the level of chromium in Dover sole livers is about 0.05 ppm (wet-weight basis). The data, presented in Table III, indicate the quite remarkable fact that the concentrations of 12 trace-elements (chromium included) in the livers of Dover sole do not increase as a result of exposure to and feeding in the contaminated sediments. The fish associated with the sediments that have elevated concentrations of trace elements sometimes even show somewhat ower concentrations in their livers than do fish living on normal sediments far from the discharges and, in most cases, lower than those reported for similar fish in areas far from any direct effect due to mankind [2].

Since the average fish lengths were not exactly the same for the four ampling locations, the degree to which differences in the average fish engths could be held responsible for the differences in trace-element levels was investigated. Correlation studies of trace-element levels versus lengths, lowever, revealed that size effects — if any — do not account for the higher values of arsenic, cadmium, cobalt and selenium in the fish livers from the "natural" area. In the case of molybdenum, the somewhat higher value may partially be attributed to the differences in size. In any event, no marked correlations of trace-element levels with length (=age) were found.

The absence of substantial differences between the liver data from the our areas considered may seem to question the relative non-mobility of the Dover sole, especially of the specimens from the outfall ("very high")

Experience obtained at the Interuniversity Reactor Institute at Delft, and at the University of California t Irvine.

TABLE III. TRACE-ELEMENT CONCENTRATIONS, SHOWN TO A 95% CONFIDENCE LEVEL, IN DOVER SOLE LIVER COLLECTED FROM FOUR LOCATIONS WITH DIFFERENT DEGREES OF POLLUTION

All concentrations are given in microgram element/gram wet material, except for silver which is presented in arbitrary units.

	Degree of sediment pollution, and number of samples used				
Trace element	"natural" 6 samples	"intermediate" 9 samples	"high" 12 samples	"very high" 12 samples	
Antimony	0.0035 ± 0.0016	0.0028 ± 0.0009	0.0022 ± 0.0006	0.0029 ± 0.0009	
Arsenic	3.1 ± 0.7	1.3 ± 0.2	1.5 ± 0.3	1.3 ± 0.2	
Cadmium	0.58 ± 0.29	0.29 ± 0.06	0.33 ± 0.16	0.19 ± 0.06	
Cobalt	0.061 ± 0.016	0.041 ± 0.006	0.043 ± 0.012	0.037 ± 0.008	
Copper	2.2 ± 0.5	2.5 ± 1.0	3.4 ± 1.2	2.0 ± 0.4	
Iron	182 ± 59	194 ± 31	176 ± 35	209 ± 27	
Mercury	0.11 ± 0.04	0.14 ± 0.03	0.19 ± 0.06	0.11 ± 0.02	
Molybdenum	0.13 ± 0.04	0.093 ± 0.018	0.081 ± 0.011	0.081 ± 0.017	
Selenium	1.2 ± 0.3	0.66 ± 0.19	0.97 ± 0.25	0.65 ± 0.15	
Silver	2.2	2.1 ± 0.7	6.3 ± 2.2	1.8 ± 0.5	
Zinc	27 ± 4	29 ± 5	25 ± 4	26 ± 3	

region. The Dover sole is known to settle into the coastal zone during the spring from offshore larval populations. It is also believed that the juveni remain on the coastal shelf and slope for at least a year, possibly two yea before beginning the offshore-onshore migrations related to spawning activities. The fish used in the present study were within this juvenile age range and were apparently feeding, as evidenced by full stomachs containing sediment material. There is considerable evidence that the Dover sole trawled from the outfall ("very high") region had indeed resided in the contaminated sediments for some time. In contrast to the fish collected in the control ("natural") area, these specimens showed signs of fin erosion disease syndrome, known to occur at a high frequency around the outfall system. The disease is believed to originate from contact with chemical or biological agents in the contaminated sediments [2].

Additional evidence of the relative non-mobility of the outfall specimes is provided by the high concentrations of DDT compounds in the flesh. In a "very high" region, the Los Angeles County Sanitation Districts outfall has been the predominant local source of this pesticide to the coastal system in recent years [2]. Along the coast, within a few kilometres of the submarine dischargers, the surface sediment concentrations of total DDT fall by more than a factor of ten, and the sediment values in the control ("naturarea - about 35 kilometres to the southwest - are lower than those around the outfalls by factors of more than one hundred. Corresponding gradients in flesh concentrations of total DDT for Dover sole trawled from these

.98 DE GOEU et al.

sediments, including those individuals analysed for liver trace-element concentrations, confirm that the outfall specimens used in this study had been intimately associated with the contaminated sediments of the "very high" area.

In conclusion, it seems apparent that the concern about metals in benthic marine fish cannot be justified on the basis of contaminated sediment concentrations alone. The data presented in the present study clearly suggest a need for evaluating the biological availability of enhanced concentrations of the sediment-associated metals in the marine environment, and the processes which may make them more or less available for uptake by benthic fish and other benthic organisms.

1.2. Sediments

The concentration profiles for antimony, arsenic, mercury and selenium n the 34 cm sediment core — sectioned into 2 cm portions — are presented n Figure 2. The general shapes of all four curves are in good agreement with those for other elements as determined by Galloway [1]. The upper 20 cm of the sediment layer is due to the outfall deposits, whereas layers below 30 cm indicate near-background concentrations [2].

Since no data were available of representative surface sediment concentrations of antimony, arsenic, mercury and selenium in the "very high" and "natural" trawling areas, these values were estimated from the vertical profiles measured. The approximate outfall ("very high") value for each

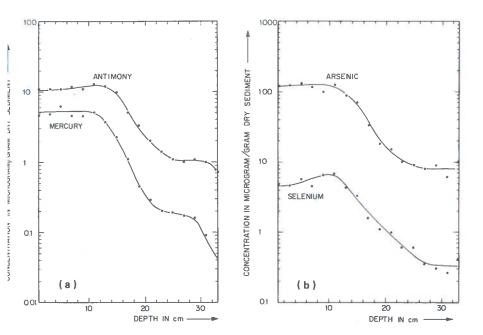


FIG. 2. Vertical profile of the (a) antimony and mercury concentrations and (b) the selenium and arsenic concentrations in sediments collected near the Whites Point outfall ("very high" area).

of these elements was obtained by averaging the concentrations found in the top two layers (0 - 2 cm and 2 - 4 cm) of the core. Corresponding con ("natural") values were obtained by averaging the values for the two deep layers (30 - 32 cm and 32 - 34 cm). From these averages, estimates of "very high": "natural" ratios for surface sediment concentrations of antin arsenic, mercury and selenium were calculated (Table I). The validity o this approach is supported by the analysis results for four surface sedim from the "natural" area. For all four trace elements the average concentrations in the surface sediments of the control ("natural") area were four equal to or lower than the sub-surface sediments of the polluted ("very hi area. These results support the assumption that, relative to the highlycontaminated surface sediments found in the outfall region, the surface sediments in the control area are indeed essentially uncontaminated by pollution trace elements, and that the "very high": "natural" sediment rat listed in Table I represent the striking differences in surface-sediment metal concentrations between the two areas studied.

REFERENCES

- GALLOWAY, J.N., Man's alteration of the natural geochemical cycle of selected trace-elements, Dissertation, University of California at San Diego, San Diego, Calif. (1972).
- [2] The Ecology of the Southern California Bight: Implications for Water Quality Management, Southern California Coastal Water Research Project Rep., El Segundo, Calif. (1973).
- [3] GUINN, V.P., KISHORE, R., "Results from multi-trace-element activation analysis of marine mater paper at Int. Coll. CNRS, Saclay, Oct. 1972, to be published in J. Radioanal. Chem.
- [4] Baseline Studies of Pollutants in the Marine Environment, (GOLDBERG, E.D., Ed.), Background pape for a workshop sponsored by the National Science Foundation's Office for the International Decade of Oceanography, BNL Upton, N.Y., 24-26 May 1972.
- [5] TJIOE, P.S., DE GOEIJ, J.J.M., HOUTMAN, J.P.W., "Automated chemical separations in routine activation analysis", paper at 4th Int. Conf. Modern Trends in Activation Analysis, Saclay, Oct. 19 to be published in J. Radioanal, Chem.
- [6] MORRISON, G.H., POTTER, N.M., Multi-element neutron activation analysis of biological materia using chemical group separations and high resolution gamma spectroscopy, Anal. Chem. 44 (1972) 839-42.
- [7] LaFLEUR, P.D., private communication, Washington, D.C., 1972.
- [8] DAMSGAARD, E., HEYDORN, K., "Arsenic in orchard leaves", paper at 3rd Symp. Recent Develops in Neutron Activation Analysis, Churchill College, Cambridge, UK, July 1973.
- [9] GUINN, V.P., DE GOEIJ, J.J.M., "Environmental/oceanographic neutron activation analysis traceelement studies", Trace Elements in Relation to Cardiovascular Diseases, WHO/IAEA Res. Coördinati Mtg., Vienna, 1973), unpublished Rep. IAEA-157 (1973) 163.

DISCUSSION

E. SOMER: In Denmark, we are successfully using the muscle of flounder (<u>Platichthys flesus</u>) as a mercury monitor in locating marine pollution sources for very much the same reason as your choice of Dover sole.

The lack of correlation noted by you between the mercury concentration the fish and the level of marine contamination is probably due to the fact that you are analysing liver samples; mercury has a short biological half-life in liver, being quickly transferred — mainly to muscle tissue, from where it is excreted slowly.

00

Do muscle tissue measurements confirm your findings that the fish oes not respond to increased mercury contamination levels in sediments?

J.J.M. DE GOEIJ: As a matter of fact, we did not choose Dover sole ver as a contamination monitor, for we knew from sediment data that here was trace-element pollution. We were interested primarily in the xtent to which such pollution affects the trace elements in fish and other harine organisms, and Dover sole liver was chosen for its representativeness.

Nevertheless, you have raised an important point, but as we have not nalysed muscle tissue, I cannot say how far your findings for North Sea ounder are applicable to Pacific Ocean Dover sole.

- K. SAMSAHL: Why did you use a 30% hydrogen peroxide solution istead of a 50% solution for the chemical separations?
- J.J.M. DE GOEIJ: It was just that the 50% solution, which I actually refer, was not readily available at the time of our study.
- K. SAMSAHL: As you were measuring only long-lived isotopes of ilver and chromium in the effluent of your anion-exchange column, why id you remove ²⁴Na as a separate group?
- J.J.M. DE GOEIJ: One can omit the sodium removal step when orking with most biological materials. In the case of marine materials ith a high sodium content, however, we felt that the removal of ²⁴Na was orth the little extra effort involved. Moreover, the HAP column acts as filter for example, for the silica particles remaining after the estruction and distillation of orchard leaves we used when testing our nalytical procedure.
- A. PRESTON: The results for metals reported in this paper are very imilar to those obtained in the United Kingdom for fission-product radiouclides ($^{144}\mathrm{Ce}$, $^{106}\mathrm{Ru}$, $^{95}\mathrm{Zr}$, $^{95}\mathrm{Nb}$), which are not found to any significant xtent in the liver or flesh of flatfish in the vicinity of nuclear installations. Ioreover, other studies by United Kingdom workers have shown that agworms taken from sediments with copper and zinc concentrations iffering by as much as a factor of 1000 have very similar copper and zinc ody burdens.

This suggests that sediments may be a useful final sink for many metals, ne strength of the adsorption of these metals to the surface of sediment articles virtually precluding their uptake by biological systems.

- M.J. FRISSEL: Did you try to obtain an adsorption isotherm for any f the trace elements studied? Although one would not expect it at such ow concentrations, a saturation value might be reached, so that the oncentrations in sediment would be unrelated to the concentrations in ea-water.
- J.J.M. DE GOEIJ: No, we did not. In the polluted areas, the sediment-sociated trace elements may become partially (but slowly) mobilized and nter the sea-water. However, Galloway (see Ref.[1] of our paper) found o significant differences between sea-water from polluted areas and sea-vater from unpolluted areas at least not for the trace elements investiated and within the analytical accuracy. We therefore assumed that the ntake of an extra load of trace elements via the water played, if any, only minor role and focused our attention on a bottom feeder, for which the ngestion of sediments may constitute an additional mode of uptake of trace lements from pollution sources.

