منظمة الأغذية والزراعة للأمم المتحدة
联合国粮食及农业组织
FOOD AND AGRICULTURE ORGANIZATION OF THE UNITED NATIONS
ORGANISATION DES NATIONS UNIES POUR L'ALIMENTATION ET L'AGRICULTURE
ORGANIZACION DE LAS NACIONES UNIDAS PARA LA AGRICULTURA Y LA ALIMENTACION

FIR/MEDPOL/LBS/3

6 MAY 1991

REPORT OF THE FAO/UNEP/IAEA CONSULTATION MEETING ON THE ASSESSMENT OF POLLUTION BY 14 CHEMICAL ELEMENTS LISTED IN ITEM 1 OF ANNEX II OF THE LBS PROTOCOL

Athens, 13-15 February 1991

Organized in the framework of the Long-term Programme
for Pollution Monitoring and Research in the
Mediterranean (MED POL - Phase II)

In cooperation with

UNEP IAEA

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ADMINISTRATIVE REPORT

1. The 5th Meeting of the Contracting Parties to the Barcelona Convention (Athens, September 1987) approved the calendar for the progressive technical implementation of the Land-based Sources Protocol. Since then, a number of assessment documents have been prepared and recommendations were submitted to the Contracting Parties concerning the groups of substances listed in Annex I to the Protocol.

2. The present Consultation Meeting concerns the following 14 elements which are listed in item 1 of Annex II to the LBS Protocol: antimony, molybdenum, titanium, tin, barium, beryllium, boron, uranium, vanadium, cobalt, thallium, tellurium, silver and selenium. The meeting took place at the premises of the Co-ordinating Unit for the Mediterranean Action Plan in Athens, from 13 to 15 February 1991, and was attended by three Mediterranean experts and representatives of FAO, UNEP and IAEA. The list of participants appears as Annex I to this report.

3. The meeting was opened by Mr. A. Manos, Co-ordinator of the Mediterranean Action Plan, on behalf of the United Nations Environment Programme and by Mr. G.P. Gabrielides, Senior Fishery Officer (Marine Pollution), on behalf of the Food and Agriculture Organization of the United Nations. Mr. A. Manos, after welcoming the participants, stressed the importance of the technical implementation of the LBS protocol and wished the meeting every success. Mr. L. Jeftic, Senior Marine Scientist at the Co-ordinating Unit, explained the guidelines and the approach followed for the technical implementation of the protocol and the preparation of the recommendations which are submitted to the Contracting Parties.

4. Mr. G. P. Gabrielides in explaining the background and scope of the meeting, mentioned that item 1 of Annex II to the LBS protocol includes 20 elements. For 6 of them it was considered that sufficient information is available for the preparation of the assessment documents and therefore relevant consultants were commissioned to proceed with the work. The present meeting is expected to review the available information on the other 14 elements and recommend the steps to be taken towards the preparation of the final assessment documents and the measures to be proposed to the Contracting Parties. In doing so, the meeting may propose the initiation of specific research and monitoring work.

5. The meeting unanimously elected Mr. P. Stegnar, Head of the Department of Nuclear Chemistry of the "Jozef Stefan" Institute and Professor at the University of Ljubljana, as Chairperson, and Mr. A. P. Grimanis, Head of the Radioanalytical Laboratory of the National Research Centre "Democritos", Athens, as Rapporteur. Mr. Gabrielides acted as Technical Secretary. The agenda of the meeting appears in Annex II as adopted. It was also agreed that no rigid timetable would be followed and that discussion and

writing sessions would be decided by the Chairperson as necessary.

6. The meeting reviewed existing information on the following topics relevant to the 14 elements and their compounds in question:

   a) Sources and inputs in the Mediterranean
   b) Biogeochemical cycle
   c) Analytical methods
   d) Levels in the marine environment
   e) Ecotoxicological properties
   f) Existing control measures
   g) Other

7. Any additional information provided by the participants during the discussion, was incorporated into document FIR/MEDPOL/LBS/2 the updated version of which appears as Annex III.

8. During the discussions it was pointed out that for some of these elements (eg. tellurium) very little information is available as regards the marine environment and in fact in certain cases very essential information necessary for the evaluation of the elements was missing. In addition, eventhough analytical techniques are available for their determination in the marine environment, some of these require specialized equipment and present difficulties for certain matrices at the concentration levels found in the marine environment. In view of the above, the meeting decided to divide the elements into three groups:

   Group I : includes those elements for which sufficient information is available for their evaluation and preparation of the relevant assessment document.

   Group II : includes those elements of concern and for which additional information should be generated in the near future to allow a proper evaluation and preparation of the relevant assessment document.

   Group III: includes those elements for which the limited information available indicates low concern and for which no action is necessary at the present.

9. On the basis of the above criteria, the meeting agreed on a provisional grouping as follows:

   Group I : boron and selenium.

   Group II : titanium, beryllium, cobalt, thallium and silver.

   Group III: antimony, molybdenum, tin, barium, uranium, vanadium and tellurium.

   Radioactive properties and effects of the elements were not considered in this evaluation since these are covered in item 9 of Annex I to the Protocol. It is also noted that the assessment document on organotins (Document UNEP(OCA)/MED WG.1/7) includes inorganic tin to a certain extent.

10. The meeting recommended that for the 5 elements of Group II, further monitoring work was necessary especially in hot-spot areas. The dumping sites for titanium oxide were considered as hot-spot areas for titanium while fly-ash dumping grounds were considered as hot-spot areas for beryllium, cobalt, thallium and silver as well as for antimony, molybdenum, uranium and vanadium which belong to Group III. It was therefore decided that any monitoring of fly-ash dumping sites could also include the above-mentioned elements from Group III.

As far as research is concerned, the meeting recommended further studies on the speciation and toxicity of those elements which exist in multiple oxidation states and/or form organometallic compounds.

11. The meeting did not feel that at the present stage it would be appropriate to propose any management measures. As far as the outline of the assessment documents is concerned, it agreed that the one followed for mercury and cadmium is quite suitable.

12. This report was adopted by the participants of the meeting on Friday, 15 February 1991.

13. In his closing remarks, the Technical Secretary expressed satisfaction for the results of the meeting and thanked the participants for their active participation. After the customary exchange of courtesies, the Chairperson closed the meeting.

ANNEX I

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ANNEX II

AGENDA OF THE MEETING

1. Opening of the meeting
2. Background and scope
3. Election of officers
4. Adoption of the agenda
5. Organization of work
6. Review of available information on the elements and compounds in question *
    - 6.1 Sources and inputs in the Mediterranean
    - 6.2 Biogeochemical cycle
    - 6.3 Analytical methods
    - 6.4 Levels in the marine environment
    - 6.5 Ecotoxicological properties
    - 6.6 Existing control measures
    - 6.7 Other
7. Conclusions on item 6 and recommendations for further action
    - 7.1 Monitoring
    - 7.2 Research
    - 7.3 Management/assessment
8. Adoption of the report
9. Closure of the meeting

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* The elements in question are: antimony, molybdenum, titanium, tin, barium, beryllium, boron, uranium, vanadium, cobalt, thallium, tellurium, silver and selenium

ANNEX III

PRELIMINARY ASSESSMENT OF THE STATE OF POLLUTION OF THE MEDITERRANEAN SEA BY ANTIMONY, MOLYBDENUM, TITANIUM, TIN, BARIUM, BERYLLIUM, BORON, URANIUM, VANADIUM, COBALT, THALLIUM, TELLURIUM, SILVER AND SELENIUM

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INTRODUCTION

According to the Protocol for the Protection of the Mediterranean Sea against Pollution from Land-based Sources (LBS protocol) the Contracting Parties shall take all appropriate measures to prevent, abate, combat and control pollution of the Mediterranean Sea Area caused by discharges from rivers, coastal establishments or outfalls, or emanating from any other land-based sources within their territories.

The Meeting of Experts for the Technical Implementation of the LBS protocol (December, 1985) proposed that the measures to be recommended to the Contracting Parties for each group of substances should be based on an "assessment document" which should be prepared by the Secretariat. According to this proposal, which was adopted by the Fifth Ordinary Meeting of the Contracting Parties to the Barcelona Convention (September, 1987), such assessments should include inter alia chapters on:

- sources, point of entries and amounts of pollution for industrial, municipal and other discharges to the Mediterranean Sea;
- levels of pollution;
- effects of pollution;
- present legal, administrative and technical measures at national and international level.

Assessment documents have already been prepared and recommendations adopted for mercury and mercury compounds, cadmium and cadmium compounds, used lubricating oils, organohalogen compounds and organotin compounds. Assessment documents are either ready or under preparation for the remaining groups of substances of Annex I to the Protocol, i.e. organophosphorus compounds, persistent synthetic materials, radioactive substances, and carcinogenic, teratogenic or mutagenic substances.

The following elements and their compounds: zinc, copper, nickel, chromium, lead, arsenic, selenium, antimony, molybdenum, titanium, tin, barium, beryllium, boron, uranium, vanadium, cobalt, thallium, tellurium and silver are included in Item 1 of Annex II to the LBS protocol. For the first six of these elements assessment documents are already under preparation.

The present annex is a preliminary assessment of the remaining 14 elements and was prepared by the participants at the Consultation Meeting on the basis of a document drafted, under contract, by the Department of Nuclear Chemistry of the "Jozef Stefan" Institute, University of Ljubljana, Yugoslavia. It assembles some useful information and could undoubtedly be used as a basis for a more comprehensive assessment.

1. ANTIMONY

1.1 General facts on the element

1.1.1 Properties

Antimony is an element of the Group V of the periodic table. Elemental antimony can be found in a grey metallic form and as yellow, non-metallic antimony; atomic weight, 121.75; specific gravity, 6.69; melting point, 630.5°C; boiling point, 1635°C. In its metallic form, antimony is a good electrical conductor.

In its chemical compounds antimony is normally tri- or pentavalent. Only in $SbCl_4$ and its salts it is tetravalent.

1.1.2 Biogeochemical cycle

Although there are some data available regarding total antimony concentrations in sea water and sediments, its chemical forms and compounds in sea water are not very well known. From an inorganic point of view, the existence of antimony complexes like M_2SbCl_6 are known. The data of Meites and Schlossel (1963) indicated that antimony, under conditions similar to sea water, may exist as monomeric $Sb(OH)_4$- or dimeric $Sb_2O(OH)_4$, with no evidence for polynuclear anion species. As reported by Strohal et al. (1975) the analysis of humic acids isolated from North Adriatic sediments indicate that antimony could be accumulated by organic matter. Stable antimony is reported to be a local marine pollutant and pollution with antimony is usually limited to coastal waters, bays, estuaries or single dumpings (ibid).

A certain tendency for the concentration of antimony to increase towards the bottom of the sea was evidenced by Grancini et al. (1976). Antimony can be concentrated by marine sediments and as predicted, diffusion is the most probable process in this particular case. From this point of view, the concentration of antimony in suspended matter in rivers which flow into the sea can play an important role.

1.1.3 Analytical methods

Instrumental and radiochemical neutron activation analysis (INAA and RNAA), atomic absorption spectrometry (AAS) and inductive coupled plasma combined with atomic emission spectrometry and/or mass spectrometry are common analytical techniques for the determination of antimony in the marine environment.

1.2 Sources and inputs into the Mediterranean

1.2.1 Natural occurrence

Antimony occurs in nature mainly in the form of sulphide, metallic antimonide or as oxide. It is present in the earth's crust at a level of 0.65 mg kg^{-1}; in magmatic rocks its mean concentration is 0.3 mg kg^{-1}, and in sedimentary rocks its concentration ranges up to 3 mg kg^{-1} (Hawkes and Webb, 1968). Antimony concentrations in clean ocean water lie between 0.2 and 0.5 µg l^{-1} (Davey and Phelps, 1977).

1.2.2 Anthropogenic sources

The main uses of antimony are in the production of alloys, paints and in the rubber, textile, ceramic and glass industries; in all these processes antimony trichloride or oxide are the most important antimony compounds. The mobility of antimony in nature is rather low. Higher concentrations of antimony near coastal areas and in estuaries than in open sea areas are reported by Grancini et al. (1976), who predicted a strong influence of polluted continental waters. As far as its radioisotopes are concerned, ^{124}Sb is one of the activation products released from nuclear power stations, while ^{125}Sb is known to be a fission product and its origin in the marine environment is either from nuclear explosions or nuclear fuel reprocessing plants (see Strohal et al., 1975).

1.3 Levels in the marine environment

1.3.1 Sea water

For the Northern Adriatic sea Strohal et al. (1975) reported concentration levels of antimony in sea water to be between 0.17 and 0.53 µg l^{-1}. The samples were filtered through a 0.45 µm Millipore filter. The concentration of antimony in non-filtered water are one to two orders of magnitude higher and vary between 27 and 91 µg l^{-1}, indicating a strong interaction between antimony and suspended matter.

Grancini et al. (1976) reported concentrations of antimony in Northern Adriatic waters to be between 0.86 and 5.6 µg l^{-1}, with an average of 1.6 µg l^{-1}. These values appear to be rather high in comparison with oceanic values (0.22 to 0.5 µg l^{-1}). The indication that Northern Adriatic sea water is under the strong influence of the North Italian industrial region should be taken into account.

Buat-Menard et al. (1981) reported concentrations of antimony at three different locations of the North-western Mediterranean to be between 0.073 and 0.17 ng l^{-1}.

Grimanis and co-workers (1988) reported higher concentrations of antimony in sea water from Saronikos Gulf in the vicinity of the pollution sources (Athens sewage outfall and fertilizer plant). The values were in the range of 0.6 - 1.4 µg l^{-1} for total antimony, 0.5 - 1.0 µg l^{-1} for dissolved antimony and 0.11 - 0.4 µg l^{-1} for antimony bound to particulate.

Typical antimony concentrations for open waters of the Saronikos Gulf ranged from 0.16 to 0.55 µg l^{-1} for total antimony, 0.15 to 0.48 µg l^{-1} for dissolved antimony and 0.01 to 0.08 µg l^{-1} for particulate antimony. Concentration profiles of dissolved antimony across the interface between hypersaline anoxic brines and overlying seawater have been reported for the Tyro and Bannock basins of the Eastern Mediterranean (Van der Weijden et al., 1990).

For non-Mediterranean areas, Buat-Menard et al. (1981) reported a value of 0.15 ng l^{-1} for North Atlantic water. Schultz and Turekian (1965) reported values in the range of 0.12 - 1.1 ng l^{-1} in seawater from a large number of stations in the World Ocean.

1.3.2 Biota

Antimony concentrations in marine organisms as reported by Strohal *et al.* (1975) and expressed in mg kg^{-1} WW are as follows: *Fucus virsoides*, 0.14 mg kg^{-1}; *Cystoseria abrotonifolia*, 0.22 mg kg^{-1}; *Ulva lactuca*, 0.067 mg kg^{-1}; *Zostera marina*, 0.093 mg kg^{-1}; *Octopus vulgaris*, 0.92 mg kg^{-1}; *Loligo vulgaris*, 0.84 mg kg^{-1}; *Mytilus galloprovincialis*, 0.51 mg kg^{-1} (soft part only); planktonic copepod, 0.4 mg kg^{-1}; *Leander serratus*, 0.53 mg kg^{-1}; *Diplodus annularis*, 0.23 mg kg^{-1}; *Boops boops*, 0.16 mg kg^{-1}; *Engraulis encrasicholus*, 0.51 mg kg^{-1}; *Trachurus trachurus*, 0.05 mg kg^{-1}; *Pagellus erythrinus*, 0.24 mg kg^{-1}; *Solea solea*, 0.49 mg kg^{-1}; *Scomber scomber*, 0.52 mg kg^{-1}, and *Clupea pilchardus*, 0.61 mg kg^{-1}.

As reported by Stegnar *et al.* (1979) the concentrations of antimony in mesopelagic fish from the Adriatic were found to range between 2.5 and 16.1 µg kg^{-1} FW, which are much lower than the above values of Strohal *et al.* (1975), which appear to be extraordinarily high.

Concentrations of antimony in four marine organisms reported by Vukadin *et al.* (1985) are as follows: *Mullus barbatus*, 1.8-3.2; *Sardina pilchardus*, 4.2 and *Pagellus erythrinus*, 0.8 µg kg^{-1} FW for the samples collected in the Bay of Mali Ston; and for *Mullus barbatus* collected in the open sea, 1.1 µg kg^{-1} FW.

Grimanis *et al.* (1979) reported values of 5.9 to 28 µg kg^{-1} for antimony in the whole body of *Mytilus galloprovincialis* and values ranging from 1.9-4.3 µg l^{-1} in *Mullus barbatus* from Saronikos Gulf.

Andreotis and Papadopoulou (1983) studied the distribution of antimony in the edible mollusc *Meretric chionae* from the Aegean Sea. Its concentration was found to be 0.074 ± 0.014 in the digestive tract; 0.026 ± 0.005 in the mantle and gills; 0.015 ± 0.002 in the adductor muscle; 0.016 ± 0.002 in the foot; 0.043 ± 0.003 in the muscle and 0.024 ± 0.004 µg kg^{-1} DW in the rest of the body. Most of the median values of antimony concentrations in higher animal tissues fell between 0.05 and 0.15 mg kg^{-1} DW (ibid), which is lower than those found in marine organisms by Strohal *et al.* (1975).

1.3.3 Sediments and particulate matter

The natural concentrations of antimony in North Adriatic sediment analysed by Strohal *et al.* (1975) were found to be around 20 mg kg^{-1} DW. The fact that sediments as carriers of heavy metals play an important role in the transfer of and water pollution with heavy metals, led to some sorption studies of antimony on some particulate materials (ibid). The adsorption rate of antimony on various inorganic particles is rather small and it is indicated that antimony could not be adsorbed significantly by suspended particles of limestone, dolomite and quartz in a sea water medium. Therefore, solid organic matter - detritus, fulvic acids, humic acids etc. - where concentrations between 20 - 30 mg kg^{-1} were found, could have an important role in the adsorption of antimony.

Vukadin et al. (1985) reported antimony values in sediments from the Bay of Mali Ston in the Adriatic Sea. In the upper sediment layer (0-5 cm) the concentrations of antimony varied between 0.20 and 0.68 mg kg^{-1} DW whereas in the subsurface sediment layer (15-20 cm) values varied between 0.19 and 0.56 mg kg^{-1} DW.

Grimanis et al. (1988) reported higher concentrations of antimony found in the silt-clay fraction (particle diameter below 55 µm) of surface sediments from polluted areas of Saronikos Gulf near the fertilizer plant (14-102 mg kg^{-1}), and in the vicinity of the Athens sewage outfall (6.6-32 mg kg^{-1}), as compared with the antimony concentrations found in unpolluted areas (0.3-0.6 mg kg^{-1}) of the Saronikos Gulf.

1.4 Effects on marine organisms and ecosystems

Antimony is known to be moderately toxic to all organisms in all of its chemical forms. Generally, trivalent antimony is more toxic than pentavalent antimony; at the same time antimony has no known function in living organisms (Nielsen, 1977). According to the U.S. Environmental Protection Agency (U.S. EPA, 1972) a hazard in the marine environment is present at levels above 200 µg l^{-1}. See also Table I at the end of the report.

2. MOLYBDENUM

2.1 General facts on the element

2.1.1 Properties

Molybdenum (Mo) is a transition element with atomic weight 95.94, specific gravity 10.2, melting point 2610°C and boiling point 5560°C. In its compounds and complexes molybdenum exists in mono-, di-, tri-, tetra-, penta-, and hexavalent states. The most important and most stable forms are those of hexavalent molybdenum.

2.1.2 Biogeochemical cycle

The average abundance of molybdenum in the earth's crust is estimated to be 10^{-4} % (Fleischer, 1972; Krauskopf, 1972). Its major concentrations (200 mg kg^{-1} and more) are found in ores such as molybdenite (MoS_2) and wulfenite ($PbMoO_4$), while the total molybdenum concentration in soils usually lies between 0.6 and 3.5 mg kg^{-1}.

The natural release of molybdenum into the environment is generally attributed to weathering. In fact, the oxidation velocity of molybdenum is sufficient to cause noticeable molybdenum enrichment in natural waters. Besides, ferrimolybdite ($Fe_2(MoO_4)_3.nH_2O$), an oxidation product of molybdenum and iron, has often been observed near molybdenite deposits.

Hexavalent molybdenum can appear in different forms such as, for example, molybdate (MoO_4^{2-}), paramolybdate ($Mo_7O_{24}^{6-}$), metamolybdate ($Mo_8O_{26}^{4-}$) etc.. Polymolybdates are stable only at pH $\leq$ 6.5 and transform to molybdate in neutral and alkaline solution. Molybdate is, therefore, the principal form of molybdenum in the sea water (Riley, 1975) and in the marine environment in general. In fact, the pH of sea water is too high (7.6 - 8) for the absorption of molybdenum oxo-anions on the colloidal particles of iron hydroxides, which occur in some surface waters as reported by Fleischer (1972) and Krauskopf (1972).

The stability constants of molybdenum complexes with organic ligands are not high enough to cause significant accumulation of the element in marine biota. Diatomaceous phytoplankton contain an average concentration of 0.4 ppm DW molybdenum whereas values of up to 80 ppm have been reported in the organs of some sea stars (Evans et al., 1978; Emelyanov and Shimkus, 1986). Also, concentration factors up to 39 were reported for benthic algae (Yang, 1989), while in fish and oysters the concentration factor for molybdenum is 100 (WHO/UNEP, 1979). According to Lowman et al. (1971), the average concentration factors for molybdenum in molluscs, crustacea muscle and in zooplankton are 60, 10 and 26, respectively.

2.1.3 Analytical methods

ICP-MS and RNAA are the main analytical techniques used for the determination of molybdenum in marine sediments and biota. For the analysis of molybdenum in sea water, preconcentration of molybdenum prior to the analysis is usually a necessary step.

2.2 Sources and inputs into the Mediterranean

2.2.1 Nature occurrence

The Rhône and Po rivers of the Mediterranean have been reported to contain an average dissolved molybdenum concentration of 5 µg l^{-1} and 1.8 µg l^{-1}, respectively (Bertine, 1970; Evans et al., 1978).

2.2.2 Anthropogenic sources

Solubilization of molybdenum is enhanced by mining and milling. Other important pathways of molybdenum release into the environment are related to its industrial uses or its compounds (steel plants, molybdenum oxide production, molybdenum refining) and burning of fossil fuels in power plants (airborne particles, coal ash). The transport of molybdenum away from these sources is primarily atmospheric but can also occur through aqueous pathways. Unfortunately, no reliable information concerning the concentration of molybdenum in various wastes is available.

2.3 Levels in the marine environment

2.3.1 Sea water

Darras et al. (1976) reported a molybdenum concentration of 4.8 µg l^{-1} (NAA) in French coastal waters (Menton). This value is somewhat lower than the concentration of molybdenum in the oceans, which is generally considered to lie in the range of 10-12 µg l^{-1} (Riley, 1975; Volkov, 1973; Whitfield and Turner, 1987).

Higher values are reported by Van der Weijden et al. (1990) and Pilipchuck and Volkov (1974) in the range of 13.8-15.1 µg l^{-1}, for oxic surface water at the Mediterranean but it is not clear whether this discrepancy is caused by regional influences. It is also possible that molybdenum is removed from water by co-precipitation with sulphides (Bertine, 1972; Jacobs et al., 1987).

2.3.2 Sediments and biota

According to Emelyanov and Shimkus (1986) the concentration of molybdenum is the upper sediment layer ranges from 3 - 53 ppm.

Papadopoulou et al. (1981a) reported molybdenum concentrations in the flesh of Trachurus mediterraneus and Japonicus colias ranging from 0.03-0.11 and 0.03-0.12 mg kg^{-1} D.W. respectively, both samples collected from the island of Karystos, Greece. Molybdenum values in the flesh of the same species but collected from the area of the island of Andros were lower (0.03-0.04 mg kg^{-1} F.W.), while higher concentrations were found in the liver of both fish species (0.44-1.0 mg kg^{-1} D.W.) as compared to flesh. Increased concentrations of molybdenum (0.55-1.5 µg g^{-1} D.W.) were also found in plankton samples as compared to those in the two fish species.

Concentration factors of molybdenum were 14 to 31 for plankton, 30 for the liver and 2 for the flesh for both fish species as reported by the same authors.

2.4 Effects on marine organisms and ecosystems

The role of molybdenum in nature is very much like that of selenium. At low levels both elements are essential to plant and animal life and at high levels both are toxic to animals and plants (Chappell, 1975). On freshwater organisms the toxicity of Uranium is low. Parkhurst et al. (1984), in chronic early life stage tests on trout, obtained a NOEL (No Observed Effect Level) higher than 9 mg l^{-1}. Moreover, high hardness greatly reduced uranium toxicity. Bioconcentration factors for uranium are low, ranging from 1.9 and 4.3 (Parkhurst et al., 1984). According to the U.S. Environmental Protection Agency (U.S. EPA, 1972) a hazard in the marine environment is present at levels above 100 $\mu g\ l^{-1}$. Concerning toxicity, no symptoms of molybdenum deficiency in the marine environment were reported. As far as toxicity is concerned, an LC_{50} of 54 mg l^{-1} for algae was reported by WHO/UNEP (1979). No such values are known for marine fauna but an idea of the relative toxicity of molybdenum may be obtained from the results on the effects of some metals on the fathead minnow Pimephales promelas in hard fresh water (WHO/UNEP, 1979). The following order was found:

Cu > Cd > Be > Sb > Ni > V > Pb > Ti > U > Zr > Mo

For marine mammals a similar estimate can be based on the reproductive effects of molybdenum in mice which were studied by Schroeder (1973). He classified molybdenum as less toxic than mercury, cadmium, lead and selenium and more toxic than titanium, nickel and arsenic.

According to WHO/UNEP (1979), there is no hazard for human health from molybdenum in sea food or sea water (Table I).

It has to be pointed out that it is difficult to study the toxicity of molybdenum due to a number of factors which influence its uptake and absorption. The copper - molybdenum - sulphate interaction, and the interchangeability of tungsten with molybdenum are two factors which are currently recognized (Chappell, 1975).

3. TITANIUM

3.1 General facts on the element

3.1.1 Properties

Titanium is a dark grey metal; atomic weight, 47.9; specific gravity, 4.51; melting point, 1820°C. It is non-magnetic and highly resistant to corrosion by many agents.

In its compounds and complexes it is mono-, di-, tri- and tetravalent; the most stable forms are those of tetravalent titanium.

3.1.2 Biogeochemical cycle

There is considerable uncertainty regarding the concentration and speciation of titanium in the sea. Earlier literature data gave different values for typical concentrations of titanium in sea water; Bowen (1966) reported 0.001 µg l^{-1}, while Bernhard and Zattera (1975) reported 2 µg l^{-1}. Riley (1971) estimated the titanium concentration in natural waters to be of the order of a few ng l^{-1}. Titanium is easily hydrolysed and its lifetime, under these conditions, is short; it remains in a colloidal state, generally adsorbed on particulate matter. The different concentrations of titanium reported above, probably reflect the different forms of titanium which were analysed. The general distribution of titanium in sediments and suspended marine particulates has been previously reviewed by Emelyanov and Shimkus (1986).

Concentration factors of 290 and 500 were reported for pilipchvakphyto- and zooplankton, respectively (WHO/UNEP, 1979).

3.1.3 Analytical methods

The most suitable methods for the measurement of titanium in the marine environment include ICP-MS, ICP-AES, AAS and XRF.

3.2 Sources and inputs into the Mediterranean

3.2.1 Natural occurrence

Titanium is widely distributed in the earth's crust. In most soils titanium is present in amounts from 0.5 - 10 %. It occurs in the ores ilmenite ($FeTiO_3$), rutile (TiO_2), and sphene, a silicate and titanate of calcium. Many vegetables and cereals contain high levels of titanium. In plants it is present chiefly in the leaves, where, like iron, it follows the concentration of chlorophyll.

The occurrence of titanium in the Istrian coal basin was reported by Limic and Valkovic (1986).

3.2.2 Anthropogenic sources

Ti is used in the paint and dyeing industries; in the steel industry as a constituent of many alloys and in the manufacture of glass and ceramics. It is also used in cosmetics and in pharmaceuticals; in surgical appliances and in food as a colouring agent.

Titanium pollution as an environmental problem in the Mediterranean sea arose in 1972. Viale (1978) reported that 11 tons of Ti/day were discharged into the sea by the titanium dioxide plant (Montedison) at Scarlino, Italy. For another plant, manufacturing titanium white for paints at Porto-Torres in Sardinia, no production figures were available. The main European producers of TiO_2 were listed in 1974 (Anon., 1976). Since then, the EEC has issued a number of directives concerning the dumping of wastes from the titanium dioxide industry. The latest one (89/428/EEC) of 21 June 1989 is entitled "Directive on procedures for harmonizing the programmes for the reduction and eventual elimination of pollution caused by waste from the titanium dioxide industry."

Atmospheric pathways of trace metals, including titanium, from industrial and urban areas of Italy and France to the Mediterranean sea have been investigated by Doichinov et al. (1985) and Gomes et al. (1985).

3.3 Levels in the marine environment

3.3.1 Sea water

Capitan-Vallvey et al. (1989), using ion-exchange spectrophotometry, determined Ti(IV) in sea water from the Mediterranean coast of Spain (Almeria and Malaga provinces). They found average titanium values to range between 1.9 and 2.9 µg l^{-1}.

Ti, in suspended matter from the North Adriatic, was determined by Toussaint et al. (1985) in order to study the geochemical composition of suspended matter.

3.3.2 Biota

The relationship between elevated titanium contents in Cetacea (and in various elements of their food chains) and pollution inputs by the titanium dioxide plant at Scarlino, Italy, was studied by Viale (1978). For numerous pelagic and benthic fish he found concentrations of 0.13-4.60 and 0.11-1.78 mg Ti kg^{-1} WW, respectively.

3.3.3 Sediments

Shaw and Bush (1978) investigated the mineralogy and geochemistry of surface sediments from the North-eastern Mediterranean; they estimated the content of titanium on the basis of carbonate-free data (4100 mg kg^{-1}) and, in the same way, presented other published data on titanium in the Mediterranean sediments, which showed a range of 4000 - 6000 mg kg^{-1}.

An Fe-Ti-Cr-Ni deposit (covering 28 km^2 and including 64 436 tons of titanium) has been found in the Gulf of Corinth; it is formed in a low-energy sedimentation environment by the discharge of a bauxitic red-mud slurry from an Al_2O_3 processing plant (Varnavas and Papatheodorou, 1987).

3.4 Effects on marine organisms and ecosystems

No essential metabolic role has yet been ascribed to titanium. Titanium salts are insoluble and are thus classified as "suspended, biologically inert material". However, the possibility of direct macrophagic absorption could be assumed. In various organs of Cetacea, Viale (1978) found 0.1-7.3 mg kg^{-1} WW; blubber and lungs were the most enriched organs. In addition, he found that a foetus of Ziphius cavirostris, almost at term, contained 3.5 mg kg^{-1} Ti, while the level in the mother was only 2.3 mg kg^{-1}.

According to WHO/UNEP (1979), titanium, from an environmental pollution standpoint, is classified as "toxic but very insoluble" element; however, the data are insufficient for real evaluation (see also Table I).

4. TIN

Organotin compounds are covered in item 3 of Annex I to the LBS protocol for which the relevant assessment document has already been prepared (Document UNEP(OCA)/MED WG.1/7); consequently, this section deals only with inorganic tin.

4.1 General facts on the element

4.1.1 Properties

Tin is a soft white lustrous metal which, depending on temperature, is found in different forms:

$$\alpha Sn \xrightarrow{13.6°C} \beta Sn \xrightarrow{161°C} Sn$$

At room temperature, it is very resistant to air, weak acids and alkalis. In its compounds it can be in the di- or tetravalent state (Browning, 1969).

Owing to their corrosion resistance, tin coatings are widely used as containers for food and liquids and for equipment in the dairy industry.

With some exceptions, inorganic tin compounds are of low toxicity. The most toxic compounds of tin are its organic compounds which serve as antifouling paints, stabilizers in polyvinyl plastics as well as fungicides, insecticides and authelmintics for poultry (Barnes and Stoner, 1958; UNEP/FAO/WHO/IAEA, 1989).

4.1.2 Analytical methods

Several analytical methods are used for the determination of total tin (ICP/AES, ICP/MS, RNAA, AAS) and organotin compounds in environmental matrices. For the determination of inorganic tin an indirect method (subtraction of organotin from the total tin concentrations) should be applied.

Some data about available methods for tin and organotin compounds in fresh water and marine samples are published in a recent book by Crompton (1989).

4.2 Sources and inputs into the Mediterranean

The increasing worldwide use of organotin compounds and the known toxic potential of some of them has given rise to increasing concern in recent years about the ecotoxicology of these chemicals. The production of organotin compounds, the use of these compounds, the routes of entry into the marine environment, the sources and inputs into the Mediterranean, their distribution in water, sediment and biota, the problems connected with analytical methodology, etc are condensely reviewed in the publication: Assessment of organotin compounds as marine pollutants in the Mediterranean (UNEP/FAO/WHO/IAEA, 1989).

4.3 Levels in the marine environment

Concentration levels of tin in sediments and algae were published by Margaillan et al. (1985). Sediment pollution by tin along the French Mediterranean coast decreased away from the mouth of the Rhône river, but was still 8-9 mg kg^{-1} at a distance of 5 km. The river appears to be a main vector of tin pollution and tin levels 5 and 7 km upstream were 9 and 11 ppm respectively. The highest levels (45-70 mg Sn kg^{-1} sediment) were found at Cortiou but the relatively regular diffusion of metallic pollution in this zone reduced the tin concentrations to 6 ppm at 5 km from the mouth of the Cortiou. The values of tin in the ports of Morillon and Carqueiranne showed evidence of tin input from antifouling paints based on organotin biocides for hull protection.

Comparison of the results for tin in sediments from some marinas and harbours on the Atlantic coast and Mediterranean sea showed that contamination is higher in harbours around the Mediterranean, which is tideless, than on the Atlantic coast (Robbe, 1987).

The concentrations of various forms of tin (which can be naturally methylated), was determinated in sea water, sediments and organisms collected from the north-eastern Mediterranean. Methyltin and tin were converted to their hydrides which were detected with an AAS method. The inorganic tin content of sea water samples was 1.1 - 236 ng l^{-1} but the dominant methylated tin species was dimethyltin. Sediment samples were analysed for their acid-extractable tin content, and the concentrations were 0.17 - 2.3 mg kg^{-1} DW. The methyltin concentration was 0.1 - 9.7 µg kg^{-1} DW. Organisms (limpets) were analysed for their total tin and methyltin contents. The total tin was 7.2 - 564 µg kg^{-1} DW and the methyltin concentrations were 0.5 - 13.9 µg kg^{-1} DW (Yemenicioglu et al., 1987; Salihoglu et al., 1986). For an extensive review see UNEP/FAO/WHO/IAEA (1989).

4.4 Effects on marine organisms and ecosystems

Information about the effects of inorganic tin on marine biota is scarce. Nevertheless the few data available on organisms belonging to different levels of the food chain (algae, crustaceans, fish) indicate that saturated solutions of inorganic tin may be toxic only after prolonged exposition (GESAMP, 1985).

There is no evidence of significant bioaccumulation in marine organisms due to inorganic tin. The high values of bioconcentration factor reported in the literature refer to total tin and the contribution of organic compounds is probably the most relevant (GESAMP, 1985).

It can be assumed that the major source of concern about inorganic tin is the possibility of natural methylation.

5. BARIUM

5.1 General facts on the element

5.1.1 Properties

Barium (Ba) belongs to the group of alkaline-earth elements and is a silver white metal with atomic weight 137.34 and specific gravity 3.5. Its melting and boiling points are 726.2°C and 1696°C respectively. The most important barium compounds are $BaSO_4$, $BaCO_3$, $Ba(NO_3)_2$, $BaCl_2$, BaO and $Ba(OH)_2$; it is exclusively divalent.

5.1.2 Biogeochemical cycle

In aqueous solutions barium exists as Ba^{2+} which is readily precipitated with carbonate and sulphate ions. $BaSO_4$ is chemically very resistant. Accordingly, barium in marine sediments exists as $BaSO_4$ rather than $BaCO_3$ (Riley, 1975; Bowen, 1966).

The concentration of barium in the oceans ranges from 3 to 50 µg l^{-1} (Riley, 1975) and might also vary with time. The latter is due to adsorption of Ba^{2+} on colloidal particles (Bowen, 1966). Turekian and Schultz (1965) found that barium in the ocean is closely related with biological productivity. There is about 60 ppm barium in marine organisms, with 10-30 ppm in foraminiferal shells (Chester and Aston, 1976). Barium can be highly concentrated in some marine species. For example, concentration factors as high as 17000 were reported for phytoplankton (Lowman <u>et al.</u>, 1971).

The residence time of barium in the oceans is 8.4×10^4 years (Goldberg, 1963).

5.1.3 Analytical methods

The most suitable methods for the determination of barium in the marine environment include flame AAS, ICP/AES, ICP/MS, arc OES (arc discharge optical emission spectrometry) and SSMS (spark source mass spectrometry).

5.2 Sources and inputs into the Mediterranean

5.2.1 Natural occurrence

Baryte ($BaSO_4$) and witherite ($BaCO_3$) are the most frequently encountered compounds of barium in nature. Its abundance in the earth's crust ranges from 50 mg kg^{-1} in sandstones to 580 mg kg^{-1} in shales. The average barium concentration in soils is about 500 mg kg^{-1} DW and might be higher in some mining areas (range: 100-3000 mg kg^{-1} DW) (Bowen, 1966).

5.2.2 Anthropogenic sources

Barium and its compounds are mostly used in the paint and paper industries, as well as in metallurgy, production of glass and ceramics and for rubber vulcanization. Waste from these industries represents the major release of barium into the environment.

Another source of barium for the marine environment is represented by drilling fluids that may be used in relatively large quantities in small areas.

Barium concentrations averaging 23 µg l^{-1} with a range of 5 - 43 µg l^{-1} were found in the Alcantara river in Sicily, which transports dissolved materials originating mostly from volcanic activities and anthropogenic pollution to the Mediterranean sea. Analyses were performed by ICP emission spectrometry with a detection limit of 4 µg l^{-1} for barium (Pappalardo <u>et al.</u>, 1983). The authors estimated that 3.3 metric tons of barium are transported annually to the sea via the Alcantara river.

5.3 <u>Levels in the marine environment</u>

5.3.1 Sediments

Roelands and Monty (1987) used NAA to analyse sediments from the northwestern Mediterranean sea (Gulf of Calvi, Corsica, 45 - 55 m deep). In both samples the barium content was under the detection limit for barium (25 mg kg^{-1}).

5.3.2 Biota

Concentration ranges for barium in Mediterranean biota can be estimated on the basis of concentration factors reported by Lowman <u>et al.</u> (1971) and WHO/UNEP (1979). These vary from 62 to 17000 for phytoplankton and from 100 to 900 for zooplankton. For fish muscle a concentration factor of 8 was reported (Lowman <u>et al.</u>, 1971).

5.4 <u>Effects on marine organisms and ecosystems</u>

According to WHO/UNEP (1979), barium can be classified as a toxic element whose toxicity is reduced by its low solubility.

According to the U.S. EPA Water Quality Criteria (1977), soluble barium concentration in fresh and marine water would have to exceed 50 mg l^{-1} before toxicity to aquatic life would be expected. Recognizing that the physico-chemical properties of barium will preclude the existence of the toxic soluble form under marine conditions, a restrictive criterion for aquatic life appeared to the EPA unnecessary.

WHO/UNEP (1979) reported an LC_{50} of 34 mg l^{-1} for algae (Table I). This concentration can be assumed as near the saturation level for barium. No recent data about the effect of barium on marine organisms and ecosystems were found.

6. BERYLLIUM

6.1 General facts on the element

6.1.1 Properties

Beryllium is one of the alkaline-earths. It occurs chiefly as the mineral ore beryl ($3BeO.Al_2O_3.6SiO_2$). Smaragd is another beryllium ore, which is beryl with chromium.

Beryllium is a silver-grey metal ; its atomic weight is 9.02; melting point 1285°C; boiling point 2970°C; density 1.86. In powder form beryllium readily oxidises in moist air and burns when ignited.

There are also two naturally occurring beryllium isotopes. ^7Be (half-life= 53.3 d) is produced by the spallation of nitrogen and oxygen by cosmic rays. The long lived radioactive isotope of beryllium ^{10}Be (half-life= 2.7 x 10^6 years) is also produced by spallation of atmospheric nitrogen and oxygen.

6.1.2 Biogeochemical cycle

Dissolved beryllium occurs in sea water probably as hydroxy species such as $Be(OH)^+$ at a concentration of about 10 ng l^{-1} (Riley, 1975).

The nuclides ^7Be and ^{10}Be enter the ocean via precipitation and they can be detected in pelagic sediments.

Most of the ^7Be in sea water appears to be in a dissolved form and it may therefore be a useful tracer for mixing processes in surface waters on the time-scale of several months (Riley, 1975).

In contrast, Tanaka and Tsunagai (1983) found that ^7Be in the ocean is mostly bound to particulate matter mainly due to surface adsorption rather than to active biological uptake.

6.1.3 Analytical methods

Flame AAS and ICP/AES are suitable analytical methods for the determination of beryllium in the marine environment.

6.2 Sources and inputs into the Mediterranean

6.2.1 Natural occurrence

Low concentrations of beryllium are widely distributed in nature and the element is estimated to have an average abundance of 2 mg kg^{-1} in the earth's crust. Beryllium concentrations in the soil range from 0.1 to 40 mg kg^{-1}. Its concentrations in fresh water and in air are below 0.001 mg kg^{-1} and 0.0001 ng m^{-3} respectively (Bowen, 1966).

6.2.2 Anthropogenic sources

Since beryllium is predominantly associated with the organic constituents of coal, it is probable that most of the element would be contained in small particulates and discharged to the atmosphere.

Beryllium may find its way into the environment in the course of a variety of industrial operations. It is used in alloys with copper, which are strong and have favourable hardness, corrosion resistance and heat transfer properties. It is used also in inertial guidance and optical devices, aerospace components and precision instruments. It is transparent to X-rays and consequently finds use in windows of X-ray tubes. With a low thermal neutron cross-section, beryllium is an efficient neutron moderator. The oxide can be found in ceramic chip substrates. Beryllium is also dispersed into the biosphere with the effluents from coal-burning power stations. The industrial application of beryllium and its compounds is limited by their cost and toxicity.

6.3 Levels in the marine environment

There is a lack of information on the beryllium levels in the Mediterranean. There are only some data about the levels of ^{7}Be in zooplankton from the North Adriatic Sea (2.8-8.9 pCi g^{-1}) (Tassi Pelati and Albertazzi, 1983).

6.4 Effects on marine organisms and ecosystems

Although there have been many studies on the metabolism of beryllium and the pathology of beryllium disease in man, information about the effects on marine ecosystems is scarce.

Toxicity data available for beryllium on freshwater organisms indicate that the effects are relatively low in hard water (US EPA, 1977, 1980). The few data available for marine organisms are not enough for a reliable quality criterion but indicate that harmful effects are unlike at the levels occurring in the marine environment (US EPA, 1980). However, its high bioaccumulation potential seems confirmed. This fact, coupled with its effects on human health (various acute and chronic effects, carcinogenic effects etc.) (US EPA, 1980; Newland, 1982), prompts one to consider beryllium as an element of some concern.

7. BORON

7.1 General facts on the element

7.1.1 Properties

Boron is an element of the third group of the periodic table and in its elemental form it has properties that place it on the borderline between metals and non-metals; atomic weight, 10.811; specific gravity, 2.34; melting point, 2350°C; boiling point, 2550°C. Boron is a semiconductor (with higher conductivity at higher temperatures).

Boron in elemental form practically does not exist in nature, and preparation of pure boron in crystalline form is a matter of considerable complexity and difficulty. Crystalline boron can be found in three different allotropic forms, and also as amorphous dark powder.

Crystalline boron is extremely inert chemically. Amorphous boron reacts above 700°C with oxygen, producing B_2O_3. In its compounds and complexes boron is normally trivalent (see Cotton and Wilkinson (1972) for a review).

7.1.2 Biogeochemical cycle

Details of the distribution of boron in sea water are not well known. As reported by Pappalardo et al. (1983) boron concentrations in fresh and river water range from 0.016 to 0.48 mg l^{-1}. Boron occurs in sea water as free boric acid and as borate ion $B(OH)_4^-$. The latter, which at the pH of sea water amounts to ca. 10 % of the total boron, is probably partly associated with calcium and magnesium as the ion pairs, $CaB(OH)_4^+$ and $MgB(OH)_4^+$, and also as $NaB(OH)_4$. The existence of polynuclear species of boric acid is also predicted, but in less than 0.001% of the total boron present in sea water. Boron concentrations in sea water are near 4.6 mg l^{-1} as reported by Bowen (1966). Increased levels of boron in the oceans are often connected with volcanic emanations (Emelyanov and Shimkus, 1986).

Marine plants contain 60 mg kg^{-1} boron; higher levels are found in plankton and calcareous red algae (Bowen, 1966); in marine animals 10-50 mg kg^{-1} boron was found, with higher levels in siliceous sponges.

The data of Bohn and coauthors (1985) consider marine sediments to contain higher concentrations of boron than terrestrial sediments. But this view is no longer widely accepted. Boron released to solution by weathering interacts primarily with iron and aluminum hydroxyoxides, with adsorption maxima at pH 7 to 9. Experiments of Hernando et al. (1989), where a standard extraction procedure for soils was used for determining the release of boron from municipal solid wastes to water and other solvents, showed that between 12 to 24 % of boron was released from the solid to the water phase.

7.1.3 Analytical methods

The most suitable analytical methods for determining boron in the marine environment include ICP/AES and ICP/MS.

7.2 Sources and inputs into the Mediterranean

7.2.1 Natural occurrence

The most abundant boron mineral is tourmaline, a complex aluminosilicate containing about 10 % boron. The other principal boron ores are borates, such as borax, $Na_2B_4O_5(OH)_4.8H_2O$, which occur in large beds in arid areas. Another important source of boron in nature could be volcanic soil. Natural boron concentrations are as follows: igneous rocks, 10 mg kg^{-1}; shales 100 mg kg^{-1}; sandstone, 35 mg kg^{-1}; limestones, 20 mg kg^{-1}. Soils contain 2 to 100 mg kg^{-1} of boron - the highest values being in saline and alkaline soils (Bowen, 1966).

7.2.2 Anthropogenic sources

The main chemical forms of boron for domestic, industrial or agricultural purposes are boric acid and borates, e.g. perborates. Boron is used for the following industrial purposes: in nuclear power plants as a neutron absorber and shielding material; in the deoxidation of copper-brass bronze in the form of calcium borate; as a constituent of steel alloys to increase the hardening ability; in the manufacture of glass and porcelain enamels, as borax; in the textile industry for dyeing and laudering; as a fire-proofing agent; as pharmaceutical products (boric acid and borax); as an abrasive, boron carbide; as high energy fuels, boron hydrides, etc.

Boron contamination is not well studied; only a few results are found in the literature. Pappalardo <u>et al.</u> (1983) reported boron concentrations in the river Alcantara in Italy to be between 0.016 and 0.48 mg l^{-1} depending on the season and the position of the sampling station. The concentrations were higher in the summer than in winter and increased downstream. It was proposed that the leaching of boron from volcanic soil by water run-off, magnified by irrigation of agricultural plots, was the reason for increased concentrations.

The natural (background) levels of boron in seawater (more than 4 mg l^{-1}) are so high that it is unlikely that anthropogenic sources can produce any significant modifications.

7.3 Levels in the marine environment

The waters of the Mediterranean Sea contain 200 to 9800 µg l^{-1} boron (Vinogradov, 1967). The concentration of boron in a range of different Mediterranean sediments has been reported by Sukhorukov and Emelyanov (1969). The boron concentration ranged from 25 to 300 µg g^{-1} and shows a clear inverse correlation with $CaCO_3$ content.

7.4 Effects on marine organisms and ecosystems

The findings of experiments with boron on higher plants and animals support the hypothesis that boron has an essential function that regulates parahormone action, and, therefore, indirectly influences the metabolism of calcium, phosphorus, magnesium, and cholecalciferol.

Those data are based on the assumption that boron may have a regulatory role in the metabolism of such plant hormones as auxin, gibberellic acid and cytokinin, perhaps through control of the production of a second messenger, such as cyclic AMP, at the cell membrane level. Further indications of a relationship between boron and calcium are that boron compounds can influence calcium metabolism and that tissue boron levels change in animals with abnormal calcium metabolism (See Mertz 1986, for a review).

From the WHO/UNEP (1979) report it is evident that there are no relevant data on the bioaccumulation of boron in marine organisms (Table I).

A recent review on the environmental hazard of boron (Eisler, 1990) indicates that adverse effects on marine algae, invertebrates and fish have been observed at very high concentrations, not lower than many tens of mg l^{-1}.

8. URANIUM

8.1 General facts on the element

8.1.1 Properties

Uranium is a member of the actinide group of elements. It is a heavy, silvery-white metal: atomic weight, 238.03; specific gravity, 18.95; melting point, 1132.3°C; boiling point, 3818°C. Uranium occurs in the +III, +IV, +V and +VI oxidation states, compounds of uranium (IV) and (VI) being of major importance. Acids dissolve the metal, but it is unaffected by alkalis. Uranium has three natural isotopes with long half-lives ($t_{1/2}$) that permit transport into potable water supplies. These isotopes are ^{238}U (99.27 % natural abundance) $t_{1/2}$ = 4.7×10^{9} yr, ^{235}U (0.72 % natural abundance), $t_{1/2}$ = 7.04×10^{8} yr, and ^{234}U (0.006 % natural abundance), $t_{1/2}$ = 2.54×10^{5} yr. All of these isotopes emit alpha particles and produce a long decay series of progeny (Durrance, 1986). These nuclides have been found useful in following certain oceanographic and sedimentary processes.

8.1.2 Biogeochemical cycle

Details of the distribution of uranium in sea water are not very well known. The uranium concentration of sea water is approximately 3 µg l^{-1}. In seawater, dissolved uranium is present as $(UO_2(CO)_3)_3^{4-}$ (Bowen, 1966).

There is relatively little information on the amounts of uranium in the marine biosphere, other than that relating to skeletal material. The average concentration for fish muscle is 0.02 mg kg^{-1} WW. For samples of plankton, including phyto- and zooplankton, the concentrations found are from 0.17 - 0.78 mg kg^{-1} DW, and algae contain 0.04 - 2.35 mg kg^{-1} (Riley, 1975). Concentrations in marine animals are 0.004 - 3.2 mg kg^{-1} in calcareous tissues and it is accumulated by corals; the concentration in fish is < 0.06 mg kg^{-1} (Bowen, 1966).

Measurements of concentrations of uranium in deep-sea sediments indicated a wide variety of deposits containing from 0.6 - 6 mg kg^{-1}, with an average concentration of 2 - 3 mg kg^{-1}; higher values of up to 31 mg kg^{-1} were recorded in some core sections (Riley, 1975).

8.1.3 Analytical methods

There are several suitable analytical methods for the determination of the uranium concentrations in the marine environment including ICP/MS, SSMS, XRF (X-ray fluorescence), INAA (instrumental neutron activation analysis), RNAA, gamma spectrometry and DN (delayed neutron counting).

8.2 Sources and inputs into the Mediterranean

8.2.1 Natural occurrence

Uranium is a naturally radioactive element and is found in the earth's crust at a concentration of 4 mg kg^{-1} (Hursh and Spoor, 1973). Higher values are found in rocks and minerals such as granite, metamorphic rocks, lignites, monazite sand and phosphate deposits, as well as in uranium minerals such as uraninite, carnotite and pitchblende. It is a trace element in coal, peat and asphalt and is present in some phosphate fertilizers at a level of about 100 mg kg^{-1} (Durrance, 1986).

The uranium concentration in ground water depends on factors such as the uranium concentration in the host aquifer rock, the presence of oxygen and complexing agents, chemicals in the aquifer, chemical reactions with ions in solutions and the nature of the contact between the uranium minerals and the water. These factors vary with region and climate and local geology.

8.2.2 Anthropogenic sources

Uranium naturally appears in phosphate rock and therefore in phosphate fertilizers. North African phosphate rock contains on average between 100 and 150 mg kg^{-1} of uranium. Although uranium may reach the marine environment through washout and runoff of agricultural drainage areas, flood water, leachates and runoffs from phosphate mining operations, the main point source is phosphate bulk loading and unloading in major port terminals. Phosphate powder and dust which is wind blown, spilled or washed to the sea near major harbours is the single largest contributor to the marine environment (WHO/UNEP, 1979). Uranium is also released into the environment from industrial wastes and from coal power plants.

8.3 Levels in the marine environment

8.3.1 Sea water

Sea water near the island of Krk in the Northern Adriatic sea was reported to have a concentration of uranium of 3 µg l^{-1} (Marjanovic et al., 1983). Grancini et al. (1976) reported that concentrations of uranium in the Adriatic sea vary from 1.38 - 4.33 µg l^{-1}. The concentration of uranium in seawater in coastal waters of the Tajoura Sea, Libya, is reported to average 3.9 µg l^{-1} (Saleh et al., 1989). The uranium concentration in Arabian coastal waters is 2.8 µg l^{-1} and the range of uranium concentrations in the Black Sea for near bottom waters and coastal and shelf waters are 3-4 and 2-3 µg l^{-1}, respectively (Riley, 1975). These concentrations of uranium represent natural uranium in the sea and does not stem from pollution sources.

8.3.2 Biota and sediments

Data for biota and sediments are very scarce. Kosta et al. (1978) determined the concentration of uranium in the reference samples prepared by the IAEA Marine Laboratory, Monaco, for Copepod MA-A-1 and

Sea plant SP-M-1. The concentration in the first sample was 0.72 ± 0.02 mg kg^{-1} DW and in the second sample 1.55 ± 0.09 mg kg^{-1} DW.

8.4 Effects on marine organisms and ecosystems

In man, the oral toxicity of uranium compounds is rather low; its nephrotoxicity becomes a hazard before levels of radiological concern are reached. Chassard-Bouchaud (1986) investigated the toxicity of cadmium and uranium together in *Mytilus sp.* sampled from different regions of the Mediterranean. The toxicity of these elements caused changes in metabolic pathways.

9. VANADIUM

9.1 General facts on the element

9.1.1 Properties

Vanadium is a transition metal belonging to Group V of the periodic table, with atomic weight 50.94, specific gravity 6.1, melting point 1890°C, and boiling point 3380°C. In its compounds vanadium exists as di-, tri-, tetra- and pentavalent states, the most important and stable being V(IV) and V(V).

9.1.2 Biogeochemical cycle

A considerable amount of new data on vanadium concentrations in sea water, its depth profiles, association with particulate matter, and concentrations in marine biota have become available in recent years. It should be appreciated that because of analytical difficulties at the nanogram level, much of the older data (before the seventies), especially on concentrations in biological samples, is much too high (WHO, 1988; Byrne and Kosta, 1978). Because of the high concentrations of vanadium in dusts and crustal material (several hundred mg kg^{-1}), great care must be taken to prevent sample contamination.

Vanadium is present in sea water at concentrations ranging from 1 to 3 µg l^{-1}; however, recent work suggests that its concentration in oceanic waters is rather constant at about 1.8 µg l^{-1} or 35 nmole l^{-1} (Jeandel _et al._, 1987; Sherrell and Boyle 1988; Collier, 1984). According to Riley (1975) it is probable that the principal dissolved form of vanadium is H_2VO_4-; reduced V(IV) forms are feasible, especially at greater depths, but there seems to be no information on such speciation. The amount of vanadium entering the oceans in suspended (major fraction) and dissolved (minor fraction) forms through riverine inputs and via aerosols is relatively large; vanadium finally accumulates in sediments. Soluble vanadium is slowly removed from the water by particulate matter and biogenic processes. Vanadium concentrations in particulate matter were given by Buat-Menard _et al._ (1981) to vary from 0.3 to 0.8 ng l^{-1} in the Pacific and Atlantic Oceans. For the Pacific, Collier (1984) found the vanadium concentrations in particulates (>53 µm) to fall from about 0.4 at the surface to a steady value of about 0.05 ng l^{-1} (1 pmol kg^{-1}) below a depth of 100 m. He also calculated vertical fluxes and a residence time of dissolved vanadium of about 5x10^4 years.

9.1.3 Analytical methods

Suitable analytical methods for the determination of vanadium in the marine environment include flame AAS, ICP/AES, ICP/MS, arc OES, XRF, RNAA (radiochemical neutron activation analysis) and INAA.

9.2 Sources and inputs into the Mediterranean

9.2.1 Natural occurrence

The crustal abundance of vanadium is around 150 mg kg^{-1} (WHO, 1988) and in soils varies from 5 to 300 mg kg^{-1} being higher in clays and shales. All coals contain vanadium, the average content being about 30 mg kg^{-1} (Waldron, 1980). It is found in high concentrations in some petroleums, where it occurs as vanadium porphoryin complexes. These are concentrated in the low-volatile heavy fractions used for heating.

9.2.2 Anthropogenic sources

The contribution of anthropogenic activities to atmospheric vanadium concentrations is significant, especially from coal and heating oil combustion (Zoller _et al._, 1973). The data of Bertine and Goldberg (1971) suggesting that man's mobilization rate of vanadium is less than natural fluxes are, according to Zoller _et al._ (1973), possibly correct but the relative injection rates into the atmosphere are probably quite similar. The smaller particle size of man-made debris means that the anthropogenic fraction is more important at remote sites (oceanic, polar regions). Industries such as ferrous and non-ferrous metallurgy and those producing or using vanadium contribute because of the relatively low melting point of vanadium pentoxide (690°C). However, virtually no quantitative data are available on inputs either by atmospheric transfer or by riverine or other discharges into the Mediterranean. Since data on these are not available, mass balances and budgets cannot be calculated (Buat-Menard _et al._, 1981).

9.3 _Levels in the marine environment_

9.3.1 Sea water

In agreement with the data of Collier (1984) for the Pacific, Huizenga and Kester (1982) for the N.W. Atlantic, and of Zhou _et al._ (1982), concentrations of vanadium in the Mediterranean exhibit a rather constant concentration profile with depth (Van der Weijden _et al._, 1990; Sherrell and Boyle, 1988; Jeandel _et al._, 1987). Concentrations of dissolved vanadium in oxic waters vary around 2 µg l^{-1}. Slightly lower concentrations observed in surface water can probably be attributed to biogenic scavenging (Collier, 1984; Middelburg _et al._, 1988). The amount associated with particulate matter of 1.9 - 3.9 ng l^{-1} (Buat-Menard _et al._, 1981) is relatively small, though of course of great importance in the long term and to the state of equilibrium. (In the Pacific, the particulate fraction of vanadium was shown (Collier, 1984) to decrease rapidly with depth, from about 0.4 ng l^{-1} to 0.05 ng l^{-1} at depths below 100 m). The highest particulate vanadium concentrations (91-254 µg l^{-1}) were observed in the vicinity of the Athens sewage outfall. Vanadium values near the fertilizer plant ranged form 12-53 ng l^{-1}. Vanadium concentrations decrease with distance from Piraeus coast reaching values that ranged from 3-17 ng l^{-1} in surface waters at stations located 7-20 km offshore. These values are elevated in comparison with the 1.9-3.9 ng l^{-1} reported by Buat-Menard _et al._ (1981) for particulate vanadium concentrations.

9.3.2 Biota and sediments

As far as levels in sediments are concerned, Prohic and Kniewald (1987) showed that there was no anthropogenic influence on vanadium levels in sediments from the Krka river estuary on the Eastern Adriatic coast, while Guerzoni et al. (1984), found little influence even of the River Po on sediments from the N. Adriatic between Ancona and Chioggia.

Studies reported by Kalogeropoulos et al. (1989) show that close to the Athens sewage outfall (ASO) and to the Fertilizer Plant (FP) near the entrance of Piraeus harbour, the combined domestic and industrial wastes have resulted in a considerable increase in the concentrations of vanadium in sediments and suspended solids of the northern Saronikos Gulf.

Atmospheric inputs from the Piraeus industrial site and frequent crude oil spillages from ships and land-based sources seem to contribute significantly to the observed vanadium distribution, which is clearly affected by the prevailing circulation of surface waters and winds.

The high percentage of the 0.5N HCl-leachable vanadium fraction in the most polluted sediments, together with positive correlation with organic carbon and certain other trace metals (e.g. Ag, Co, Cr, Fe, Zn) and negative correlation coefficients with Al and Sc, indicate that a considerable portion of the vanadium is of "anthropogenic" origin not related to lithogenous particles. It enters the system in association with relatively large organic aggregates, either authigenic or derived from sewage.

Considerably high vanadium concentrations were found in the silt-clay fraction of cores taken close to the ASO (45-60 µg g^{-1}, average 50 µg g^{-1}) and the FP-PH area (30-62 µg g^{-1}, average 48 µg g^{-1}). Samples taken from sites 5 km offshore had values ranging between 24 and 35 µg g^{-1} (average 30 µg g^{-1}). These concentrations represent the "background" levels of vanadium in the area studied of the Northern Saronikos Gulf.

Fowler (1986) and Fowler et al. (1979) as well as Elder and coworkers (1986) have studied the levels of vanadium in Mediterranean marine biota. In microplankton, the levels averaged about 1 mg kg^{-1} DW (range 0.3 - 0.8) and in euphausiids about 0.5 mg kg^{-1} (range < 0.06 - 1.2). In a well defined pelagic food chain (microplankton ---> euphausiids ---> amphipods ---> decapods, fish), vanadium levels declined from 1 mg kg^{-1} to < 0.1 mg kg^{-1} DW. This effect is well documented and most fish contain only µg kg^{-1} levels of vanadium.

Papadopoulou (1986), Papadopoulou and Zafiropoulos (1980), Papadopoulou et al. (1979; 1981b), Grimanis et al. (1983) and Andreotis and Papadopoulou (1981) have reported levels for fish, shellfish and pelagic organisms, mainly from Greek waters. Papadopoulou (1986) found a magnification of 10^{-2} from plankton to two fish species, where levels of 0.01 to 0.1 mg kg^{-1} DW were determined in the muscle tissue. Lafaurie et al. (1981) showed that levels of vanadium in Mullus barbatus were constant over the sexual cycle (in contrast to the gonads and liver where large variations were displayed). Papadopoulou et al. (1981b) showed that concentrations of vanadium in the fish Mullus barbatus and the shrimp Papapenaeus longirostris were unaffected by pollution, even near the central Athens sewage outfall. On the other hand, Grimanis et al. (1983) found evidence for the influence of pollution (vessel activity, oil pollution) in terms of increased vanadium concentrations in the soft parts of Mytilus edulis from three Greek gulfs.

Vanadium was determined in the flesh and liver of Gobius niger from Varna bay, Bulgaria and Saronikos and Petalion Gulfs, Greece (Apostolov et al., 1985). Concentrations of vanadium in the flesh of Gobius niger (45.6-54.3 μg kg^{-1} WW) from Varna bay were higher than those found from stations in Saronikos and Petalion Gulfs (10.4-14.5 μg kg^{-1} WW). These increased values of vanadium are comparable to those reported for fish species from the Aegean Sea (Papadopoulou et al., 1979). In the liver of Gobius niger specimens from Varna bay and Saronikos and Petalion Gulfs the vanadium concentrations found were similar (47.9-59.5 ng kg^{-1} WW). Papadopoulou and Zafiropoulos (1980) also reported on vanadium concentrations in organisms from the Aegean Sea. The highest amounts of vanadium were determined in the intestine and stomach of Ciona intestinalis (280 mg kg^{-1} DW), vanadium concentrations in plankton ranged from 4.6 to 13 mg kg^{-1} DW), while fish and molluscs contained lower amounts of vanadium as compared to plankton and tunicates.

A number of tank experiments have been performed on vanadium uptake and excretion in various organisms, using either ^{48}V radiotracer or stable vanadium. Miramand et al. (1979) studied the uptake and rate of excretion in four invertebrates (mussels, worms, shrimps and crabs) as a function of vanadium concentration, salinity and temperature. In crustaceans, the major part of vanadium was concentrated in the shells and moults; excretion was complex and species specific. Papadopoulou et al. (1985a) studied the uptake and partitioning of vanadium in hard and soft tissues of different mollusc species collected from Greek waters. Over 90% of the vanadium was found in the shell and was not easily removed by acid leaching. Similarly Elder et al. (1986) investigated vanadium uptake and elimination in shrimps, crabs and mussels from sea water. The highest accumulation was found in mussels, but mostly in the shell, as was also the case for shrimps (>90%). The byssal thread takes up vanadium remarkably, and it was suggested that it could be used as a monitor to measure changes in vanadium levels in the marine environment. Ballester and Castellvi (1986) studied the transfer of vanadium from seawater to bacteria (pseudomonas), to phytoplankton, to mussels, to crustacea, to fish. Concentration factors were generally low, especially for transfers at the secondary and tertiary trophic levels. Mussels, however, could accumulate vanadium directly from contaminated sea water. To interpret some of their findings, they also measured the actual levels in two species of fish, Mullus barbatus and Pagellus erythrinus and in sediments. The vanadium content of dorsal muscle of Mullus, a demersal fish feeding in high vanadium containing sediments (30 mg kg^{-1}) was lower at 0.02 mg kg^{-1} than in Pagellus erythrinus. High accumulation of vanadium was reported in the hepatopancreas and branchial hearts (25 mg kg^{-1} DW) of the Mediterranean octopus (Miramand and Guary, 1980).

9.4 Effects on marine organisms and ecosystems

Vanadium is considered essential for some green algae and possibly for rats and chickens (WHO, 1988).

Many marine plants and invertebrates (tunicates, echinoderms) contain very high levels of vanadium which appear to be involved in some metabolic processes (Newland, 1982). WHO/UNEP (1979) gives bioaccumulation concentration factors for vanadium from sea water as 10 for fish, 200 for oysters, 100 for phyto- and 200 for zooplankton (Table I).

In vertebrates, vanadium is not readily absorbed by the intestine and is rapidly excreted. This tends to make vanadium less toxic than other metals.

Ballester and Castellvi (1986) found that pseudomonas bacteria were not inhibited in sea water containing high levels of vanadium (50 mg l^{-1}), whereas inhibitory effects were detected for the phytoplankton Dunaliella at this level. According to WHO/UNEP (1979), the LC_{50} for algae is 10-20 mg l^{-1}. Hamilton and Buhl (1990) indicate a 96g LC_{50} to Chinook salmon (Oncorhynchus tshawytscha) of 16.5 mg l^{-1} in brackish water. However, these concentrations are 10^4 times higher than real sea water concentrations, so the probability of their occurrence in the environment seems remote in the extreme.

10. COBALT

10.1 General facts on the element

10.1.1 Properties

Cobalt is a silvery bluish-white metal, its atomic number is 27, lying between iron and nickel and with somewhat similar properties. Its atomic weight is 58.94; specific gravity, 8.9; melting point, 1495°C, and boiling point, 2900°C. It is not corroded by air or water, it is resistant to alkalis but soluble in acids. Its most important properties are its magnetic characteristics, its capacity to form alloys, its role as an essential trace element in the formation of vitamin B_{12} and as a radioactive source (^{60}Co). It is normally bivalent, but trivalent compounds also occur.

10.1.2 Biogeochemical cycle

The normal concentration of cobalt in oceanic waters does not exceed 0.1 $\mu g\ l^{-1}$. The principal dissolved cobalt species is probably hydrated Co^{2+}. The concentration of cobalt in marine particulate matter lies in the range from 1 to 25 $\mu g\ g^{-1}$ (Stoner, 1974). In general, marine organisms concentrate cobalt, since this element is important for the cellular metabolism. The concentration factor of cobalt from sea water for fish is 500, for phytoplankton 190, for zooplankton 365, for molluscs 1000-5000, and for crustaceans 1000-5000 (WHO/UNEP, 1979). Bioaccumulation also depends on many other factors such as salinity, cobalt levels in sea water, and its chemical form: inorganic or organic (for example cyanocobalamin; vitamin B_{12}). Apart from laboratory experiments with radioactive ^{60}Co tracer compounds, there are almost no data on the chemical forms of cobalt present in the natural marine environment. Therefore, it would be more useful to determine the chemical forms of cobalt than just the total amount of cobalt in sea water and sediment. This would be very valuable in explaining its high bioaccumulation by some organisms in certain marine environments.

10.1.3 Analytical methods

Analytical methods for the determination of cobalt in the marine environment include flame AAS, ICP/AES, ICP/MS, XRF arc OES and INAA (instrumental neutron activation analysis).

10.2 Sources and inputs into the Mediterranean

10.2.1 Natural occurrence

Cobalt is a metal widely distributed in combination with other metallic ores, particularly copper, generally as sulphide, oxide or arsenide.

It is an essential trace element for man and animals, but has not been found necessary for plants, though it is present in traces in all except those growing on cobalt deficient soil. A large number of studies have been published on the concentration of cobalt in soils due to its great economic importance in the raising of sheep and cattle. In general, cobalt tends to be deficient in areas where there is granite, sand or limestone, or in volcanic and peaty soils.

10.2.2 Anthropogenic sources

In general cobalt does not occur in the environment to the extent of presenting a health risk, except in connection with the industry of hard metal manufacture. It is important for the manufacture of alloys, magnets, pigments, and paints.

Its concentration in wastes is quite small and the effluent characteristics as well as treatment are almost similar to nickel containing wastes. Manufacturing of cobalt produces liquid wastes as well. Cobalt is also found in wastes of certain plastic, metallurgical and alloy industries, and in radioactive wastes. Concentrations of cobalt vary from industry to industry and reliable data is scarce. Cobalt has also been used in agriculture as a potential growth additive in food for pigs, chickens and freshwater fish.

In order to estimate the input of pollutants from two rivers discharging into the Mediterranean, Var and Rhône, seasonal variation of trace elements including cobalt in water and suspended matter has been studied (Oregioni _et al._, 1979). The mineralogical characteristics of both rivers are similar, and therefore differences in the concentrations of the metal studied are due to anthropogenic inputs. Ranges of concentrations of cobalt in suspended matter (leachable with 1M HCl) in the Var vary between 3.0 - 6.6 $\mu g\ g^{-1}$ and in the Rhône 8.7 - 27 $\mu g\ g^{-1}$. Much greater differences were found for other trace elements (Pb, Cr, Zn, Cu), so it can be concluded that the levels of cobalt in suspended matter are much less affected by anthropogenic inputs than those of the other trace elements.

There are only a few data regarding the effect of industrialization on cobalt pollution around the Mediterranean. One factor which possibly influences the situation in the Mediterranean is the precipitation of considerable wind-blown material from the Sahara, by winds such as the Sirocco. Dust storm air pollution is common to city and to desert areas and represents the "background" in air pollution measurements in the Mediterranean. Global emission inventories show that anthropogenic cobalt is emitted from coal combustion and industrial, commercial and residential combustion of fuels. Emissions of cobalt (t/yr) in some Mediterranean countries were estimated in 1979 to be for Albania 3, France 103, Greece 17, Italy 150, Spain 61, Turkey 30, and for Yugoslavia 40 (Pacyna, 1986). Airborne concentrations from 0.0006 to 1.0 ng m^{-3} and crustal enrichment factors from 0.6 to 13 were reported for various non-Mediterranean areas.

In order to estimate the transport of atmospheric particulates directly to open-ocean areas, the elemental composition of particulates from the lower marine troposphere over the world oceans has been studied (Chester and Stoner, 1974). Cobalt concentrations in soil-sized particulates from the lower marine troposphere range from 3 to 36 $\mu g\ g^{-1}$, with an average of 10 $\mu g\ g^{-1}$, and are of the same order of magnitude as those in average crustal material. Even in "coastal" particulates, cobalt is depleted relative to average crustal material. Atmospheric emissions of some trace elements from the Fos-Berre-l'Etang area, France (Gomes et al., 1985) and Italian remote and urban areas (Doichinov et al., 1985) have shown little contributions to cobalt air pollution. In general, it can be concluded that cobalt appears to exist at levels compatible to crustal origin.

10.3 Levels in the marine environment

10.3.1 Sea water

The first figures published for the concentration of dissolved cobalt in sea water are apparently too high due to analytical error, since in most analytical procedures cobalt was concentrated before final measurement, which risked contaminating the sample, and at best involved many extra analytical checks. A review of various analytical methods for the determination of cobalt in sea water is given by Crompton (1989). Differential pulse cathodic stripping voltametry, a method without preconcentration of cobalt, was used in order to establish cobalt levels in surface water and its vertical profiles in the Northwestern Mediterranean Sea (Huynh-Ngoc and Whitehead, 1986). Cobalt levels of 0.006±0.003 µg l^{-1} were found. Kalogeropoulos et al. (1990) reported on the cobalt levels in sea water from polluted and non-polluted areas of the Saronikos gulf. The concentrations of cobalt ranged from 0.03-0.18 µg l^{-1} in non-polluted areas and from 0.12-0.60 µg l^{-1} in polluted areas of the gulf. Reported seasonal variations of dissolved cobalt in coastal surface waters range from around 2 to 10 ng l^{-1} (Huynh-Ngoc et al., 1989). They claim that this indicates that there is no obvious or gross pollution of the near-shore environment. Huynh-Ngoc and Whitehead (1986) found that the cobalt levels in surface waters were about 0.015 µg l^{-1} decreasing to about half at 700 m and continued to decrease slightly to about 0.003 µg l^{-1} at 2000m. The profile observed shows a reasonable steady decrease towards the bottom, which is in accordance with studies in other oceans (Knauer et al., 1982). Some authors (Bruland, 1980; Kremling and Petersen, 1981) have tried to find a correlation between cobalt and nutrient levels, but they came to opposite conclusions, so in general it is not clear how far the nutrient/metal relationships derived apply to the Mediterranean, since individual ratios of metal to nutrient are noticeably different in the Pacific and Atlantic Oceans.

10.3.2 Biota

Background levels of selected trace elements in pelagic species from the open Mediterranean were reported by Fowler (1986). Average cobalt levels for Euphausiids (omnivorous macroplankton) are 200±70 mg kg^{-1} DW. No differences of cobalt concentrations were observed in these crustaceans sampled from various parts of the Mediterranean. In contrast to this, cobalt levels were consistently higher in mesopelagic fish from the eastern basin compared to other regions. For example, cobalt levels in the myctophid fish, *Myctophum glaciale*, from the eastern Mediterranean sea vary between 120-240 µg kg^{-1} DW, from the Ionian Sea 60-100 µg kg^{-1} DW, from the Tyrrhenian Sea 35-54 µg kg^{-1} DW and from the Northwestern sea 60 µg kg^{-1} DW. Cobalt levels in some edible fish from three Greek Gulfs, the Korinthiakos Gulf, the Kissamos Gulf off the island of Crete, and the Gera Gulf off the island of Lesvos, polluted from agricultural and industrial activities, vary from 5 to 30 µg kg^{-1} FW with insignificant differences between the gulfs (Taliadouri-Voutsinou, 1981; Voutsinou-Taliadouri, 1983a). Higher concentrations (35-80 µg kg^{-1} FW) were found in the northern section of the Saronikos Gulf, which is polluted from the main Athens sewage outfall and industrial activity. Cobalt was determined in the flesh and liver of two edible fishes Sargus annularis and Gobius niger from polluted areas of the Aegean Sea (Grimanis et al., 1978). No significant differences for cobalt in the flesh and liver between polluted and unpolluted areas were found. Cobalt levels in the flesh and liver of Sargus annularis were between 30-40 and 250-630 µg kg^{-1} DW, respectively, while cobalt levels in flesh and liver of Gobius niger were 20 and 50 µg kg^{-1} DW, respectively. Higher cobalt levels in the liver of the two edible fish are not indicative of pollution, since this increase is of the same magnitude in specimens from polluted and unpolluted areas.

No significant differences of cobalt values were found in the flesh of Mullus barbatus from polluted and non-polluted areas of Saronikos Gulf. Concentrations of cobalt ranged form 1 to 23 µg kg^{-1} W.W. (Grimanis and Papadopoulou, 1986); Cobalt was determined in the scales and otoliths of 12 edible fish species collected from 3 sampling areas of Saronikos Gulf. The concentrations of cobalt in the scales ranged from 0.05 to 6.4 mg kg^{-1} DW while those in otoliths ranged from 0.05 to 1.3 mg kg^{-1} DW (Papadopoulou and Moraitopoulou-Kassimati, 1977).

Cobalt levels in the dark muscle of the pelagic fish Auxis rochei from the Aegean sea were higher than in the white muscle (Andreotis and Papadopoulou, 1981). The mean value for dark muscle was 527 µg kg^{-1} and for white muscle 48 µg kg^{-1} DW.

Much higher cobalt concentrations in fish from the eastern Aegean Sea coast were reported (Uysal1978, 1979, 1981; Uysal and Tuncer, 1983). Cobalt levels vary according to species, season and area. Average concentrations of cobalt in 8 fish species sampled from the open Aegean Sea and along the coast of Izmir vary between 57 and 2940 µg kg^{-1} FW with a summer maximum and a winter minimum. In general, concentrations were smaller in pelagic than those found in benthic fish.

Cobalt levels in mussels from polluted and unpolluted areas of Izmir Bay were reported by Tuncer and Uysal (1983). Mussels with different feeding regimes were analysed. Higher values of cobalt were found in spring than in summer time. Cobalt levels in the more polluted area vary from 1.13 to 7.69 mg kg^{-1} FW, while in the less polluted area concentrations varied from 0.65 to 2.14 mg kg^{-1} FW. Among various species, the highest values of cobalt were found in A. amygdalum (deposit filter) and V. verrucosa (filter feeder). Additional studies are needed to explain the high bioaccumulation of cobalt in these two species.

Mytilus galloprovincialis has been selected as a biological indicator in many UNEP pollution monitoring programmes. Cobalt levels in this mussel were reported in many studies showing high variations according to sampling areas. Concentration levels of cobalt in Mytilus galloprovincialis from the eastern coast of the Aegean Sea varied between 0.65 and 1.13 mg kg^{-1} FW (Tuncer and Uysal, 1983), from the Saronikos Gulf between 0.05 and 0.11 mg kg^{-1} FW (Grimanis et al., 1979; Taliadouri-Voutsinou, 1981; Voutsinou-Taliadouri, 1983a), from the Pagassitikos Gulf 0.11 and 0.28 mg kg^{-1} FW, and from the Patraikos Gulf between 0.14 and 0.15 mg kg^{-1} FW (Grimanis et al., 1983). It was concluded that higher cobalt levels in the Pagassitikos and Patraikos gulfs are due to local pollution.

Cobalt distribution in the edible mollusc Meretrix chionae from unpolluted and polluted areas of the Aegean Sea was studied by Andreotis and Papadopoulou (1983). Molluscs from unpolluted waters showed higher concentrations of cobalt in the foot, muscles and rest of the body, while in polluted areas higher concentrations were found in the digestive tract, mantle and gill, and adductor muscle. These findings show that further investigations on the metabolic pathways of cobalt ingested from various pollution areas are needed since it was shown that bioaccumulation and metabolism is dependent on the chemical form of cobalt ingested (Ueda et al., 1982a; 1982b; 1982c; Suzuki et al., 1982).

10.3.3 Sediments

It is difficult to compare results for cobalt in sediments in various parts of the Mediterranean due to different sampling strategies and the particle fraction analysed. Therefore, it is also difficult to establish the background levels. The average cobalt levels in the northern Adriatic Sea are 10 mg kg^{-1} DW, and in the central Adriatic Sea between 14 - 21 mg kg^{-1} DW (Kosta et al., 1978). No differences of cobalt concentration in the sediment profile (0 - 30 cm) were found, indicating a relatively stable sedimentation. Comparison of the cobalt content in surface sediment from different sampling points in the Gulf of Trieste showed that higher concentrations of cobalt were found near the urban and industrial effluents of the Bay of Muggia (18 mg kg^{-1} DW) than in the less polluted area of Grado and Marano Lagoon (4 mg kg^{-1} DW) (Majori et al., 1979). In contrast, cobalt levels in sediment do not correlate with heavily polluted zones in the Gulf of Venice, as is the case for some other trace elements (Angela et al., 1981). Concentration levels of cobalt in surface sediments were between 1.2 and 13.8 mg kg^{-1} DW.

Cobalt levels in the bottom sediment (0-5 cm) of the Patraikos Gulf vary between 16-33 mg kg^{-1} DW (Varnavas and Ferentinos, 1983). Higher concentrations were found towards the central and deeper areas of the bay, while lower concentrations were found along the coast, including the area near Patras.

Cobalt levels in sediments from the Gulfs of Thermaikos and Pagassitikos, Greece, were between 15-35 mg kg^{-1} DW, and 10-50 mg kg^{-1} DW, respectively. (Voutsinou-Taliadouri, 1983b). It was shown that various areas in these two gulfs, which receive industrial effluents and domestic wastes, do not differ significantly from one another in the case of cobalt. Lower concentrations (10-25 mg kg^{-1}) were found in the Eastern Aegean sea. Kalogeropoulos et al. (1990) reported on the cobalt levels in sediments from non-polluted and polluted areas of the Saronikos Gulf. The concentrations ranged from 8 to 10 mg kg^{-1} DW and from 13-87 mg kg^{-1} DW in non-polluted and polluted areas, respectively.

The cobalt level in near-shore surface sediments of the East Alexandria Coast is 14 mg kg^{-1} (Elsokkary, 1979).

In some studies it was shown that extraction with 0.5M HCl, which is in general proposed as a standard method for the investigation of anthropogenic trace element accumulation in the sediment, does not release all the "anthropogenic" fraction (Angelidis et al., 1983). Therefore, it was proposed that this method should also be further investigated for other trace elements. These authors investigated solid wastes in the Saronikos Gulf originating from a fertilizer plant containing non-extractable concentrations of cobalt, which mask the effect of the main sewage outfall. Apart from this finding, concentration levels of extractable cobalt in polluted and unpolluted Greek gulfs are reported in several studies. These are as follows: Saronikos Gulf, 5-16mg kg^{-1} DW; Evoikos Gulf, 15-30 mg kg^{-1} DW (Angelidis et al., 1981); Thermaikos Gulf, 7-20 mg kg^{-1} DW; and Pagassitikos Gulf, 7-14 mg kg^{-1} DW (Chester and Voutsinou, 1981). The partitioning of cobalt into three fractures (reducible with acidified hydroxylomine hydrochloride, oxidizable by acidified hydrogen peroxide and the residual after the previous extractions) of Saronikos Gulf surface sediments was determined by using a sequential extraction technique combined with INAA.

The cobalt content in the reducible and oxidizable fractions increases in the polluted sediments near the Athens sewage outfall and a fertilizer plant. In the non-polluted sediments, the residual fraction is the most important carrier for cobalt. The reducible fraction (mainly Fe/Mn hydroxides) is the most important sink for cobalt in polluted sediments near the Athens Sewage Outfall (Angelidis and Grimanis, 1989).

It was shown that cobalt in the continental shelf sediments along the Côte d'Azur, Golf d'Ajjacio and Pro-delta of the Rhône is linked with organic matter (or sulphides) in the contaminated areas, and with the residue (silicates, etc.) in the zone with little or no contamination (Added et al., 1983). In the sediments of Northern Euvoikos bay, Greece, where enormous amounts of metals are discharged from an Fe-Ni alloy smelting plant, cobalt is mainly associated with the coarser fraction of the sediments, having its highest concentration in the centre of the deposit and lower values at its periphery (Voutsinou-Taliadouri and Varnavas, 1987).

10.4 Effects on marine organisms and ecosystems

Cobalt is oceanographically interesting because of its interactions with biota. An LC_{50} of 0.5 mg kg^{-1} for algae is reported by WHO/UNEP (1979) (Table I). The most sensitive level for copepods was found by Davey and Phelps (1977) to be 0.01 mg kg^{-1} (72hr LC_{50}). Cobalt is an essential trace element, but no data on cobalt deficiency in the marine environment were reported.

Bioaccumulation of cobalt in algae depends on the species, the biotope, the season, the age of the algae, the pH of the sea water, the concentration of cobalt in the aquatic system and the salinity. The uptake of cobalt by two seasonal benthic algae <u>Scytosiphon lomentaria</u> and <u>Enteromorpha intestinalis</u> at various salinities in the northern Adriatic was studied by Munda (1984). Accumulation of cobalt was low; at the highest applied concentration of cobalt a peak in accumulation was observed at medium salinity (19.2%), whereas at lower cobalt concentration, accumulation was negligible.

Seasonal bioaccumulation was studied in green (<u>Ulva lactuca</u>) and red (<u>Gracilaria verrucosa</u>) algae from the Thermaikos Gulf of the northern Aegean sea (Sawidis and Voulgaropoulos, 1986). Larger cobalt concentrations were found in both algae in the most polluted areas, while maxima in metal concentrations coincided with the maximum seasonal growth of each species. Of the two species, green algae accumulates higher cobalt concentrations throughout the whole year.

Bioaccumulation of ^{60}Co in an experimental food chain was studied by Kirchmann <u>et al.</u> (1977). They found that ^{60}Co is mostly concentrated (at least 100 times) at the level of primary producers (unicellular algae <u>Dunaliella bioculata</u> and <u>Acetabularia mediterranea</u> were used). Under laboratory conditions, the primary consumer (<u>Mytilus edulis</u>) concentrates ^{60}Co 20 times, when this radionuclide is bound to <u>Dunaliella</u> cells or <u>Acetabularia</u> chloroplast. However, 50-70% of the ^{60}Co is rapidly (48 h) lost when the mussels are transferred to normal sea water. After a single meal, the secondary consumer crab (<u>Carcinus maenas</u>) ingested an important part (about 30%) of the radioactive food, but by transfer to normal sea water, the radioactivity in the crabs progressively decreases. In a continuous study it was shown by Bonotto <u>et al.</u> (1978) that marine organisms, in general, concentrate ^{60}Co since this element is important for their cellular metabolism. The highest accumulation was observed for the marine algae (C.F. = 200-300).

The accumulation of cobalt by some species of marine organisms is dependent on the chemical forms of cobalt in sea water. Ueda <u>et al.</u> (1982a,b,c) studied the effect of inorganic cobalt and organic cobalt (vitamin B_{12}) in sea water on the metabolism in marine organisms. Differences in the gel filtration profile due to the chemical forms of cobalt in sea water was observed. The same results were observed for some other species of bivalves (ibid). Thus, it was stated that the chemical forms of cobalt in sea water affected the metabolism of cobalt in some species of marine organisms. The uptake and excretion of cobalt by the sea cucumber and a prawn (Suzuki <u>et al.</u>, 1982) showed different biological half-lives (75 and 24 days respectively). Still very little is known about the molecular structure and biological function of cobalt binding proteins in various marine organisms.

A radionuclide addition experiment was conducted to study the behaviour and fate of trace metals in a coastal marine environment (Frithsen, 1984). Radionuclides were added and their concentration in benthic organisms and sediment was measured during the period of nine months. The ability of benthic organisms to concentrate radionuclides was related to the vertical distribution and feeding behaviour of the organisms. The highest activity of ^{60}Co within meiofauna was found to be in harpacticoids and within macrofauna in polychaetes (Mediomastus) but the highest among all organisms was found in bivalves. Compared to biota, low activity was found in sediment and sediment pore water. Surface living fauna incorporated more radionuclides than deeper fauna. Calculations of total annual radionuclide incorporation by benthic fauna indicated that meiofauna incorporated a similar amount of the labelled metals as macrofauna, even though the latter have a larger standing stock biomass. This calculation suggest that benthic metazoan fauna can annually cycle 23% of the amount of added ^{60}Co measured in sediments.

No concentrations of cobalt at levels approaching toxic effects for marine organisms in the Mediterranean were reported. In general, cobalt is an essential trace element for marine life. Its bioaccumulation depends on many factors, one of the most important being its chemical form.

11. THALLIUM

11.1 General facts on the element

11.1.1 Properties

Thallium (Tl) is a grey-white, soft, ductile metal similar to lead. The atomic weight of thallium is 204.37 and its specific gravity 11.65. Pure thallium melts at 302.4°C and boils at 1453°C. Thallium forms compounds in monovalent and trivalent states. In ionic radius and chemical behaviour Tl^+ resembles the alkali metal cations and forms sparingly soluble compounds like sulfides, iodides, chlorides, chromates, etc. Tl^{3+} is assumed to be less stable and can be obtained only through oxidation by very powerful oxidizing agents in very acidic media. An exception is, however, the formation of Tl(III) chloride complexes in high chloride media where trivalent thallium is favoured. More stable are organic Tl(III) compounds of the form R_2TlX, $RTlX_2$ and R_3Tl, where R stands for a hydrocarbon radical and X is a halogen.

11.1.2 Biogeochemical cycle

The Tl^+ ion is more stable in aqueous solution than Tl^{3+}. For illustration, even in 1 M hydrochloric acid the standard electrode potential for the half reaction $Tl^{3+} + 2e^- \Rightarrow Tl^+$ is +0.77 V. However, Batley and Florence (1975) presented thermodynamic arguments and experimental evidence that thallium in sea water (pH 8.1), in equilibrium with atmospheric oxygen, predominates in the trivalent state. They conclude that the Tl(I) species in sea water is TlCl, while Tl(III) exists as $Tl(OH)_2^+$ rather than $Tl(OH)^{2+}$. On the other hand, Lee (1971) states that $TlCl_2^+$ and $TlCl_4^-$ are formed upon the addition of Cl^- to an aqueous solution of Tl^{3+}. However, the arguments for Tl(III) species predomination in sea water at natural pH are not entirely convincing.

The low concentration of thallium in the oceans (0.01-0.02 $\mu g\ l^{-1}$) is primarily due to the coprecipitation of Tl^{3+} with manganese and/or iron in strongly oxidizing conditions and to ionic absorption of Tl^+ on clay sediments in strongly reducing environments.

Thayer (1974) mentioned the possibility of environmental biomethylation of thallium. This is not nearly as important an issue as it is for mercury, because the difference in toxicities between the organic and inorganic forms is so much smaller for thallium.

11.1.3 Analytical methods

RNAA and SMSS can be used as analytical methods for the determination of thallium in the marine environment.

11.2 Sources and inputs into the Mediterranean

11.2.1 Natural occurrence

The average concentration of thallium in the lithosphere is 0.1-1.0 mg kg^{-1} (Lange and Forker, 1967; Hampel, 1968) but thallium ores such as lorandite ($TlAsS_2$), picotpaulite ($TlFe_2S_3$), chalkohallite (Cu_3TlS_2), etc., are very rare. Thallium is, therefore, recovered mostly during processing of sulphide ores of lead, copper and zinc containing thallium in levels up to 10 g kg^{-1}. Relatively high levels of thallium are also present in deep-sea manganese nodules.

During rock weathering thallium is largely retained and enriched in the silt and loam.

11.2.2 Anthropogenic sources

In the past thallium was extensively used in rodenticides but the high toxicity of these compounds resulted in their diminishing use.

At present there are very few uses for thallium; these include metal alloys, electronic devices, special glass and thallium-containing catalysts for industrial organic reactions. Thus, its direct production and use are minor sources of environmental contamination. On the other hand, many common thallium compounds are volatile at smelting and coal burning temperatures. Combustion of fossil fuels probably represents the largest source of thallium losses to the environment. Besides, copper, zinc, lead and manganese mining also represents an important source of thallium release into the environment. Information on particular waste streams is, however, so incomplete, that no detailed estimation of the amounts released is possible.

11.3 Levels in the marine environment

11.3.1 Sea water

Matthews and Riley (1970) measured thallium by neutron activation analysis in the waters of the Bay of Biscay collected from a depth of 2 to 2500 m. Values between 0.0094 and 0.0166 µg l^{-1} were found. The maximum value at 500 m was attributed to the decomposition of planktonic material that had fallen from the surface.

11.3.2 Sediments and biota

No values for thallium concentrations in Mediterranean sediments were reported in the literature. Since concentrations of thallium in the ocean and Mediterranean sea water are very similar, the concentrations in sediments are expected to be similar too. For marine sediments from different oceans, values from 0.08 to 5.7 mg kg^{-1} were reported; however, concentrations of thallium in calcareous sediments were only in the range 0.08 to 0.35 mg kg^{-1} and were inversely proportional to the carbonate content.

In general, concentration factors for thallium in marine plants can be as high as a few hundred, depending on the level of water contamination with thallium. Unfortunately, no information for Mediterranean algae is available. The only available data on

Mediterranean biota concern the analysis of <u>Mytilus galloprovincialis</u> from eastern Sicilian waters. In this work (Castagna and Sarro, 1975) thallium concentrations were determined with atomic absorption spectrometry and varied between 1.6 and 2.09 mg kg^{-1} ash.

11.4 Effects on marine organisms and ecosystems

Thallium and its compounds are toxic to humans, animals and plants with an LD_{50} for different mammal species ranging between 5 and 70 mg kg^{-1} of body weight (Schoer, 1984). Its toxicity results from the physiological similarity of Tl^+ to K^+. Consequently, thallium effects K^+ activated ATPase which uncouples mitochondrial oxidative phosphorylation. Toxic doses adversely affect protein synthesis and cause disaggregation of ribosomes. In addition thallium salts inhibit several enzymes which play an important role in bone formation.

The organothallium(III) compounds are believed to be more toxic than their inorganic counterparts (Il'in, 1938), yet little is known about their effects on marine organisms.

The 96h LC_{50} for thallium to various species of freshwater fish lies between 10 and 60 mg l^{-1} (Nehring, 1962) but, for longer exposure, relatively low concentrations can produce mortality. For juvenile Atlantic salmon, Zitko <u>et al.</u> (1975) reported mortality at a concentration of 30 µg l^{-1} after several months of exposure. Thallium toxicity is proved relatively independent from water hardness (Schoer, 1984).. Hypertension is one of the symptoms of thallium poisoning in fish (Nehring, 1962).

Water levels as low as 2-3 mg l^{-1} reduce the photosynthetic activity of algae (Overnell, 1975), but direct toxicity to most aquatic plants from thallium pollution alone appears to be a remote possibility. However, where algae serve as an animal's primary food source, bioaccumulation is possible. The U.S. Environmental Protection Agency indicates as acute toxicity level for marine life a concentration as low as 2.1 mg l^{-1} (Bodek <u>et al.</u>, 1988).

12. TELLURIUM

The literature search conducted did not reveal any information on tellurium in the marine environment. In older publications and books tellirium is scarcely mentioned.

13. SILVER

13.1 General facts on the element

13.1.1 Properties

Silver is a noble, white lustrous metal; atomic weight, 107.88; specific gravity, 10.5; melting point, 960.8°C; boiling point, 1950°C. Of all the metals, silver has the highest electrical and thermal conductivities and optical reflectivity. Its ductility and malleability are second only to those of gold.

In its compounds and complexes it is mono-, di- and trivalent; the most stable forms are those of monovalent silver, being the only one possible in natural aquatic environments.

13.1.2 Biogeochemical cycle

Details of the distribution of silver in the marine environment are not very well known. In sea water it exists as dissolved and particulate silver. The concentration of dissolved silver in ocean water probably lies in the range 0.01 - 0.08 µg l^{-1}, and the principal chemical species appears to be $AgCl_2^-$ and $AgCl_3^{2-}$ (Riley, 1975). A small quantity of the soluble silver is in the form of complexes with dissolved organic matter according to Stumm and Bilinski (1973). Soluble species may be precipitated by the presence of appropriate anions, by coagulation of colloids, and by adsorption on carbonaceous material, metal hydroxides, clay, etc. Under strongly reducing conditions, silver may precipitate as humate or sulphide (Smith and Carson, 1977).

Marine biota concentrate silver from environmental sources; enrichment factors of 98, 117, 100 and 250 were reported for phyto- and zooplankton, fish and molluscs, respectively (WHO/UNEP, 1979).

13.1.3 Analytical methods

Arc OES and INAA are suitable methods for the determination of silver in the marine environment.

13.2 Sources and inputs into the Mediterranean

13.2.1 Natural occurrence

Silver occurs in nature as native silver as well as in many ores, the most important being argentite (Ag_2S). It is present in the earth's crust in amounts of 0.1 g per ton. Soil contains only small amounts, but there are larger concentrations in the humus from plant remains - up to 5 mg kg^{-1}. It also occurs in coal (<0.1 to 300 mg kg^{-1}) and petroleum (up to 100 mg kg^{-1} in crude oils).

Most silver in natural waters comes from silver in rocks, deposits, and their weathered products; smaller amounts comes from anthropogenic sources. The average dissolved silver content in natural fresh waters is about 0.2 µg l^{-1} (Smith and Carson, 1977).

13.2.2 Anthropogenic sources

Silver is released into the environment as a pollutant from domestic, agricultural and industrial wastes. The main uses of silver are in the photographic and electrochemical industries, pharmacy, metallurgy, and in the manufacture of silverware and jewellery.

Information on the characteristics and composition of the wastes discharged into the Mediterranean from the various industries using silver are given in WHO/UNEP (1979).

The anthropogenic origin of some metals may have some bearing on the variations of the leachability of metals from suspended matter. In this context Oregioni et al. (1979) investigated the relationship between the origin and leachability of silver in suspended matter in two Mediterranean rivers, the Var and the Rhône ; they found no difference in the leachable fractions of silver between the two rivers (concentrations for both rivers ranged from 1.0 - 3.5 mg kg^{-1} DW).

Atmospheric transport of silver was studied by Arnold et al. (1983). From the anomalous enrichment of silver, the authors concluded that anthropogenic aerosols, chiefly from the industrial areas of Western Europe, constitute the main atmospheric flux of silver to the Western Mediterranean.

13.3 Levels in the marine environment

13.3.1 Sea water

Grancini et al. (1976) reported that silver concentrations in the Northern Adriatic sea (determined by NAA) increase from 0.30 µg l^{-1} in the upper layer to 1.2 µg l^{-1} in the bottom layer. They explained this to be probably due to the interaction with the sea sediment as well as to anthropogenic input by rivers.

Ryabinin and Lazareva (1980) reported that the average silver concentration in the whole water column of the open Aegean sea was 0.176 µg l^{-1}. Enhanced concentrations of silver were found in the surface and deep waters in comparison to the intermediate water column; this could reflect anthropogenic impact and natural exchange with sediment, respectively. The distributions of silver in open waters of the Ionian, Tyrrhenian, and Ligurian sea were also investigated (Ryabinin and Saltykova, 1986).

In the waters of the Saronikos Gulf, 90 % of the total silver was found to be in the dissolved form; the concentrations of total, dissolved and particulate silver in the water column ranged from 0.1-1.4, 0.10-1.3 and 0.006-0.10 µg l^{-1} respectively (Grimanis et al., 1986).

13.3.2 Biota

Silver contents in euphausiids (Euphausia sp.), collected from the open waters of different regions of the Mediterranean sea, ranged from 0.92 - 2.7 mg kg^{-1} DW (Fowler, 1986). Plankton sampled from the Aegean sea contained 0.083 mg Ag kg^{-1} DW (Papadopoulou et al., 1985a).

For three different species of pelagic fish caught in the Aegean sea, their mean muscle concentration ranged from 0.015 - 0.045 mg kg^{-1} DW (Papadopoulou et al., 1985b; Andreotis and Papadopoulou, 1981).

Silver concentrations in the flesh of Mullus barbatus from Saronikos Gulf ranged from 3.5 to 9.0 mg kg^{-1} WW (Grimanis and Papadopoulou, 1986).

Silver concentration in Mytilus sp. sampled from different regions of the Mediterranean ranged from 0.009 - 18.9 mg kg^{-1} DW (UNEP 1989; Obiols et al., 1981)

13.3.3 Sediment

The natural concentration of silver in marine sediments (collected from the Western Mediterranean and Saronikos Gulf) was approximately 0.2 mg kg^{-1} DW, as estimated by Rapin and Fernex (1981) and Grimanis et al. (1986). In surface sediments from the same areas, the authors found significantly higher silver concentrations, due to increasing pollution.

13.4 Effects on marine organisms and ecosystems

Silver is a normal trace constituent of many organisms, but there is no evidence about its essential metabolic role.

Silver is highly toxic to marine organisms. The 48 h LC_{50} for clam and oyster larvae lies in the range of 6-21 µg l^{-1}. Other tests on juvenile molluscs showed a 10 d LC_{50} of 34 µg l^{-1} (Calabrese and Nelson, 1974; Calabrese et al., 1977). Effects on the development of sea urchin have been observed at 0.5 µg l^{-1} (Wilber, 1969).

There is a wide variation in the toxicity of silver compounds to aquatic life and the degree of dissociation of these compounds affects toxicity. Since little information is available on the chemical stability of these compounds in the aquatic environment, an evaluation of silver danger must be based on the total silver concentration (U.S. EPA, 1977).

The U.S. EPA proposed a criterion for silver in the marine environment at a level of 0.01 of the 96 h LC_{50} for a sensitive species. This means, in any case, that a safe level should be below 1 µg l^{-1}.

According to WHO/UNEP (1979), the hazard for human health of consuming sea-food, in respect to some of the most prominent metals in sea water, can be ranked as follows:

Hg > Cd > Ag > Ni > Pb > As > Sn > Zn

Accumulation of silver through water and sediment has been investigated by Ho (1989) who found for the deposit-feeding clam Macoma balthica, that sediment-bound silver was a more important source of the metal than aqueous silver.

Coleman and Clearly (1974) demonstrated high silver accumulation in freshwater fish (see also Table I).

14. SELENIUM

14.1 General facts on the element

14.1.1 Properties

Selenium belongs to Group VI of the periodic table, between sulphur and tellurium. It exists naturally in many oxidation states (-2, 0 +2, +4, +6) and some of its chemical forms are volatile. Elemental selenium, like elemental sulphur, exists in several allotropic forms. All oxidation states are found in nature except the +2 state. Selenium in the +6 or selenate state is stable under both alkaline and oxidizing conditions.

14.1.2 Biogeochemical cycle

Most of the selenium found in air is in aerosols while large particulate forms result from windblown dust, volcanic action and from various human activities. However, air can also contain low levels of volatile Se compounds, which are produced by biological systems. The predominant volatile Se compound is dimethylselenide, produced by soil microorganisms as well as by plants (Combs and Combs, 1986).

Selenium enters water as soluble selenites and selenates and as suspended particles of insoluble and organic forms of the element. The chemical speciation of selenium in natural waters was discussed by Robberecht and Van Grieken (1982).

In sea water, selenium can occur in the dissolved state as Se(IV) and Se(VI) oxy-anions, the selenate content being at least fifteen times as high as that of selenite (Robberecht and Van Grieken, 1982). Concentrations of the total dissolved forms of selenium in open ocean waters are approximately 0.1 $\mu g\ l^{-1}$ (Cutter, 1978). The concentrations of Se(IV) in uncontaminated seawaters are quite low (<0.005-0.7 $\mu g\ l^{-1}$) (Sturgeon et al., 1985). A variety of metal hydroxides (Fe, Mn) are capable of co-precipitating selenium thus enriching marine sediments and forming seleniferous sedimentary iron ores (Rosenfeld and Beath, 1964).

14.1.3 Analytical methods

AAS and NAA are suitable analytical methods for the determination of selenium in the marine environment.

Critical reviews of the determination of trace levels of selenium in environmental waters (Robberecht and Van Grieken, 1982) and other environmental samples (Raptis et al., 1983) were published in order to provide overviews of appropriate analytical methods for the determination of selenium.

14.2 Sources and inputs into the Mediterranean

14.2.1 Natural occurrence

Selenium occurs in many natural materials. Its concentration in igneous rocks is low, usually much less than 1 mg kg^{-1}, and similar levels probably occur in metamorphic rocks. Sedimentary rocks, such as sandstone, limestone, phosphorite, and shales may contain from <1 to >100 mg kg^{-1}.

Selenium is mainly found in metal sulphide deposits, mostly of the metals Cu, Zn, Ag, Hg and Pb. In the environment it is widely distributed but in low concentrations. The average crustal abundance is found to be 0.09 mg kg^{-1}. In seleniferous soils it can amount up to 80 mg kg^{-1}. Certain native plants growing on seleniferous soils accumulate high concentrations of selenium, causing selenosis in livestock. An inter-relation between their growth and the geological origin of rock was recognized and thus Se indicator plants may be used to locate seleniferous as well as uraniferous areas (Rosenfeld and Beath, 1964). In some areas, however, very low selenium content in the soil was observed, which can be reflected in the low Se-status of human and animal populations. As was observed by Woittiez and Iyengar (1988), selenium levels in human blood reflect geographical differences and age.

Maksimović et al. (1990) investigated the selenium status of soils, grain and the human population in Serbia, Yugoslavia; they reported selenium concentrations for the soil to be in the range of 0.14-0.21 mg kg^{-1}.

14.2.2 Anthropogenic sources

The main industrial sources emitting selenium into the environment include the mining, milling, smelting, and refining of copper, lead, zinc, phosphate and uranium, the recovery and purification of selenium itself, the use of selenium in the manufacture of various products, and the burning of fossil fuels.

14.3 Levels in the marine environment

14.3.1 Sea water

In the available literature, no data on Se concentrations in Mediterranean sea water were found. For the surface waters of two Italian rivers, selenium speciation and total dissolved Se (25.5 and 76 µg l^{-1}) were reported by Orvini et al. (1981).

14.3.2 Biota

Selenium concentrations in M. galloprovincialis from three Greek Gulfs ranged between 0.29 and 0.55 mg kg^{-1} FW (Grimanis et al., 1983); from the Yugoslav coast of the Adriatic sea they ranged from 0.5-2 mg

kg^{-1} FW (Tušek-Žnidaric et al. , 1983), and from the Barcelona coast they ranged between 0.03 and 0.66 mg kg^{-1} FW (Obiols and Peiro, 1981).

Kosta et al. (1978) reported Se contents in some edible animals from the Gulf of Rijeka, Yugoslavia, to be from 0.3 to 2.6 mg kg^{-1} FW and for plankton collected from different areas of the Adriatic basin, to vary from 1.9-6.4 mg kg-1 DW. Stegnar et al. (1979) reported the concentration range for selenium in some mesopelagic fish caught from different parts of the Adriatic sea to be from 0.7-2.3 mg kg^{-1} FW.

Trace elements, including Se, were determined in the flesh and liver of the two edible fishes Sargus annularis and Gobius niger caught in polluted and unpolluted areas of the Aegean sea. Selenium levels were of the same magnitude in specimens from both areas, but higher mean concentrations in the liver (1.6-6.6 mg kg^{-1} DW) than in the flesh (0.75-1.4) were found for both fish species (Grimanis et al., 1979). In the flesh of different fish species from three Greek Gulfs, selenium concentrations were in the range of 0.18 to 1.03 mg kg^{-1} FW (Grimanis et al. , 1981). Levels of selenium in the flesh of Gobius niger from Varna Bay were found to be higher than those in the same species from Saronikos Gulf (Apostolov et al., 1985).

Selenium contents of 6 tissues of fish-eating birds, sampled in a polluted lagoon near Cagliari, were reported by Cottiglia et al. (1983). The authors also reported an Hg/Se molar ratio of about 1 for the liver of cormorants. Similar findings was reported for the dolphin Stenella coeruleoalba (Thibaud, 1979), but no correlation between Hg and Se was found in the pelagic fish Auxis rochei from the Aegean sea (Andreotis and Papadopoulou, 1981) nor for some fish species (Boops, Merluccius, Scomber) and shrimps (N. norvegicus) from the Ligurian sea (Capelli and Minganti, 1986).

14.3.3 Sediment

No information in the literature was found for selenium in marine sediments from the Mediterranean area.

Selenium concentrations in 13 samples of sediment obtained at different points of the Delta del Ebro, one of the main Spanish rivers flowing into the Mediterranean sea, ranged from 0.01 to 0.04 mg kg^{-1} DW (Obiols and Peiro, 1981).

Selenium concentrations in sediments of the Slovenian rivers Soča (flowing into the Adriatic sea) and Trboveljščica were found to be 0.76 and 1.5 mg kg^{-1} DW, respectively (Polkowska-Motorenko et al., 1982). The high level of selenium can be attributed to mining activities.

14.4 Effects on marine organisms and ecosystems

Selenium is an essential trace element for humans and animals; however, at levels slightly higher than nutritional requirements, it is extremely toxic.

Selenium can be bioaccumulated by fish and other marine organisms through the food chain (Bodek et al., 1988). These animals can accumulate relatively high levels of selenium which are strongly correlated with the mercury content in several organs (Ganther and Sunde, 1974; Koeman et al. , 1973).

Selenium has a protective effect against mercury and methylmercury toxicity in different animal species (Lucu and Škreblin, 1981; Ganther and Sunde, 1974).

Acute toxicity of Selenium on aquatic life lies, in general, at the level of mg l^{-1}. In chronic tests on Daphnia magna a NOEL of 1.5 mg l^{-1} was found (Dunbar et al., 1983). Some larvae of marine crustaceans appear to be very sensitive to silver with a 48 and 96 h LC_{50} of 2.5 and 0.5 mg Se l^{-1} respectively. Marine mollusc larvae are unaffected after 48 h exposure by as much as 10 mg Se l^{-1} (Cardwell et al., 1978). Available data on fish refers to freshwater species and are in the range of 2.1 to 28.5 mg l^{-1} for 96 h LC_{50} (Cardwell et al., 1976).

As for silver, the U.S. EPA proposed for marine aquatic life a criterion of 0.01 of the 96 h LC_{50} on sensitive species (U.S. EPA, 1977). Thus a safe level should be at the concentration of some ppb's (mg l^{-1}).

According to WHO (1987) selenium can be harmful for man and a level of 5 ppm in food can be considered potentially dangerous (Newland, 1982).

Table I

Toxicity and bioaccumulation of the 14 elements
(from WHO/UNEP, 1979)

Element	Toxicity LC_{50} D minimal risk (mg l^{-1})	Bioaccumulation Concentration Factor	Remarks
Antimony		Oyster 300 Fish 100	No hazards for human health from sea food or seawater.
Molybdenum	Algae 54	Fish 100 Oyster 100 Phyto 10 Zoo 20	No hazards for human health from sea food or seawater.
Titanium	Algae 2	Phyto 290 Zoo 500	The residues of titanium bioxide are noxious for acidity and iron content.
Tin	Algae 2	Fish 10000 Oyster 10000	The organotin compounds are included in Table 1. No hazard for human health from sea food or seawater.
Barium	Algae 54	Phyto 62 Zoo 100	Ba is highly toxic; the fatal dose of Ba C12 for man reported to be about 0.8 to 0.9 g. Ba was irreversibility deposited in the Skeleton.
Beryllium	Fish 31		Soluble forms of Be are highly toxic by all routes of administration. Be exerts a strong inhibitory action on enzymatic activity.
Boron			
Uranium			Oral toxicity of U compounds is rather low. The pharmacology and toxicology of U compounds of industrial interest are presented in four volumes comprising about 2300 pages.

Table I (continued)

Element	Toxicity LC_{50} D minimal risk (mg l^{-1})	Bioaccumulation Concentration Factor	Remarks
Vanadium	Algae 10-20	Fish 10 Oyster 200 Phyto 100 Zoo 200 High concentrations are found in ascidian tunicates	The fatal dose for man has been given variously as to 120 mg. It is apparent that amounts of from 24 mg of V in daily divided doses are tolerated by man.
Cobalt	Algae 0.5	Fish 500 Phyto 19 Zoo 365 Mollusc 1000-5000 Crustaceans 1000-5000	The lethal oral dose for rabbits is 700 mg/kg.
Thallium			Thallium is one of the more toxic elements both acutely and chronically, in animals and man, regardless of the route of intake.
Tellurium			The actions of tellurium are similar to those of organic arsenic, specially the injurious effect on the capillaries
Silver	Algae 0.05 Fish 0.01-0.04 Mollusc 0.0006 D 1	Phyto 98 Zoo 117 Fish 100 Mollusc 250	
Selenium	Polichaete 100	Fish 500	Selenium compounds are methylated by micro-organisms and probably these compounds have antagonistic behaviour with mercury, (83).

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