# NON-RADIOACTIVE OCEAN POLLUTION

# **Chen-Tung Arthur Chen**

Institute of Marine Geology and Chemistry, National Sun Yat-sen University, Kaohsiung 804, Taiwan, Republic of China.

**Keywords:** ASEAN, dumping, emulsification, heavy metals, marine pollution, organic compounds, pesticides, pollution, resins, SEAPOL sewage, sludge, trace metals, United Nations Convention on the Law of the sea, UNDP, UNEP.

# Contents

- 1. Introduction
- 2. Trace Metals
- 3. Pesticides and Organic Compounds
- 4. Sewage

5. Temporal Trend Glossary Bibliography Biographical Sketch

# Summary

The pollution of the marine environment has been a major focus of concern in the international community. To illustrate the seriousness of the problem, of the 320 articles of the United Nations Convention on the Law of the Sea, the very first addresses the issue of marine pollution.

The most important sources of pollution and, thus, the major threat to the marine environment come from the land and this includes the continuous discharges through rivers, runoff, ocean outfalls and groundwater discharges. The marine environment in some areas, notably the enclosed and semi-enclosed seas surrounded by very dense populations, has large run-offs from rivers and sewers that contain fertilizers, detergents, pesticides and industrial wastes. Untreated sewage pouring into coastal waters directly, or via rivers or ocean outfalls, can carry hepatitis, cholera, typhoid and a wide range of other diseases and infections. Simply said, in many coastal areas pollution has reached intolerable aesthetic, ecological and social levels. In the deep seas, tar balls on the surface, mercury in the tuna and the dumping of noxious wastes present problems although, surprisingly, usually less important or critical than pollution from certain nutrients. Marine accidents bring concentrated oil pollution to coastal zones with consequent damage to marine life, sea birds, fragile habitats and the loss of recreational rewards from our beaches.

Such disruption of the coastal environment due to pollution from untreated and improperly treated sewage, livestock waste and agricultural fertilizer leakage containing organic substances, nitrate and phosphate, pathogens and persistent toxic metals and organic compounds poses a growing threat to food security and the health of billions of people. Clean-ups are often difficult, if not impossible, and slowly degrading contaminants can leach from sediments back to coastal waters for thousands of years, if not longer. As the total emissions of developing countries begin to exceed those of the developed world, the health of the global oceans is now a major concern, and a number of international conventions have taken aim at solving the problem.

Table 1 summarizes the sources of marine pollution around the world. Pollution from sewage, petroleum hydrocarbons, organic chemicals, mining, food processing, metal industries, chemical industries, pulp manufacturers, agriculture, siltation, sea-salt extraction, thermal effluents and dumping in various parts of the oceans are listed.

# **1. Introduction**

All life on Earth came from the oceans, and until this day they directly supply half of the world's population with a vital source of food. Unfortunately, despite their importance, these vast bodies of seawater have long been regarded as too large to ever be harmed or threatened by human activities. Yet the marine environment is delicate and, especially now, highly fragile because of the wide variety of foreign objects sent into it. Even seemingly innocuous, thoughtlessly discarded objects can harm marine animals and sea birds. Mighty as the celebrated Moby-Dick in 19th century art and literature, even the sperm whale cannot escape environmental hazards. Biologists who performed an autopsy on a skinny male sperm whale beached at Sea Side Heights, New Jersey, in the summer of 1985 found a rubber party balloon blocking the animal's digestive tract. Similarly, scores of pelicans and other animals were starved to death because they played with the ring from a six-pack of canned drinks and choked.

The marine environment in some areas is now a receptacle for the unwanted, like untreated sewage, dredged material, fertilizers, pesticides, detergents, oil, thermal effluents as well as domestic, agricultural and industrial wastes. For instance, the sewage from about ten per cent of Britain's population is discharged untreated into the sea, as is 30 per cent of their sewage sludge. It is obvious from this short list that the major threats to the marine environment come from the land. Suffering the most are the coastlines and the nearby continental shelves.

To cite a few examples, sediments, often contaminated and lying on the bottom of a harbour or channel, sometimes need to be dredged. The resulting disturbance of the already stable condition may then make it possible for pollutants to re-enter the water column or otherwise spread. Even when the sediments dredged are pristine in terms of quality, loosening, lifting and transporting them can result in significant amounts of extraneous material entering the water column. Because they reduce light and are suspended before subsequent settling, particles can have an adverse impact on marine life and tourism. The smothering effect of fine sediments on corals is perhaps the most obvious example.

The indefinite disposal of dredged material has traditionally been achieved by using the sea as a dump yard despite the detrimental effects on marine life. Fortunately, there is a growing awareness that dredged material can be regarded as a resource rather than a waste. Notable benefits include its use for land reclamation projects and for nourishment of our beaches by replacing sand that is washed away.

Water discharge or other process or activity potentially causing contamination	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
Sewage	Х	X	Х	х	Х	Х	Х	Х	Х	х	Х	х	x	Х		Х
Petroleum hydrocarbons (maritime transport)	х	X	Х	x	х	Х	X	X	Х	X	Х	х				Х
Petroleum hydrocarbons (exploration and exploitation)		x		x	х			x		x	X	x	x	х		
Food and beverage processing	х	x	х			Х				X	Χ	х	х	Х	Х	Х
Metal industries		X	х		х				X	x		x			Х	Х
Petrochemical industries		X		х	Х				$\mathbf{\nabla}$	х	Х	х				Х
Mining			X					X		х			x	х		
Chemical industries	х	x	X		X				X	х						х
Pulp and paper manufacturing	X				X					х			X	Х	Х	Х
Agricultural runoff (pesticides and fertilizers)			X		x		X	Х		х					х	Х
Thermal effluents					C	х	X		X	х	X	х				Х
Siltation from agriculture and coastal development						x	x	х			х					x
Dumping of sewage sludge and dredge spoils		X							X	X						X
Sea-salt extraction		5			r		X				X					

1 Baltic Sea, 2 North Sea, 3 Mediterranean Sea, 4 Persian Gulf, 5 West African areas, 6 South African areas, 7 Indian Ocean region, 8 South-East Asian region, 9 Japanese coastal waters, 10 North American areas, 11 Caribbean Sea, 12 South-West Atlantic region, 13 South-East Pacific region, 14 Australian areas, 15 New Zealand costal waters, 16 Taiwan Strait

Table 1. Sources of Marine Pollution Around the World (modified from Kumar and Hader, 1999).

Table 1 lists a number of marine pollution types in terms of their areal coverage in various parts of the world. The sewage problem occurs almost everywhere, followed by petroleum hydrocarbons, due to exploration, exploitation and maritime transportation. Although usually not toxic, food and beverage processing produces widespread pollution, mainly concerning biological oxygen demand. The metal and petrochemical industries, mining, chemical industries, pulp and paper manufacturers, pesticides and fertilizers from aquicultural runoff also contribute to the problem. Thermal effluents, siltation from agriculture and coastal development, the dumping of sewage and dredge spoils, and the influences from desalination complete the list, which is, however, by no means all-inclusive.

Because of its wide scope, it is not possible to discuss all aspects of marine pollution. This article concentrates on trace metals, organic compounds and sewage. Past trends and international collaborations are also discussed.

### 2. Trace Metals

Trace metals in the oceans have two major natural external sources: the riverine and atmospheric transport of weathering products of continental rocks, and the introduction of material by the interaction of seawater with newly formed oceanic crustal basalt at mid-ocean spreading centers via both high temperature hydrothermal activity and low temperature interaction with the newly formed crust. Most of those trace metals are ultimately transported from seawater reservoirs to marine sediments after undergoing varying degrees of internal recycling, which is linked to the production, sinking and decomposition of particulate matter, often organic. Heavy metals may be accumulated by and have severe physiological effects on filter-feeding animals and reef fish. Additionally, they may be accumulated in higher predators which are subsequently consumed by humans.

Although they often carry negative connotations, trace metals are not in fact all bad. Whether or not a trace metal can interact with the biota is dependent upon the exact chemical form of the element in the marine environment as well as its abundance. For example,  $Hg^{2+}$  is acutely toxic, but HgS is not. The overall pattern of the degree of acuteness of the toxicity of trace metals to marine organisms is, in descending order:

$$Hg^{2+} > Ag^{+} > Cu^{2+} > Zn^{2+} > Ni^{2+} > Pb^{2+}$$
 and  
 $Cd^{2+} > As^{3+} > Sn^{2+} > Fe^{3+} > Mn^{2+} > Al^{3+} > Be^{2+} > Li^{+}.$ 

Mercury is generally considered to be the most serious metallic pollutant of the oceans. Human activities have released about five times as much mercury as is derived from natural sources. Mercury has a particularly high affinity for organic species and is almost invariably associated with organic compounds in either soluble or particulate form in freshwater, albeit to a somewhat lesser extent in seawater. Mercury is therefore readily transmitted to the biota, especially when contaminated particles, such as nearshore sediments are ingested. The high affinity of mercury and organic material leads to a high degree of bioaccumulation of the metal in marine plants and animals, including tuna fish and shellfish (see Table 4, *Natural and Anthropogenic*).

# Radionuclides).

The best known incidence of mercury pollution was witnessed by over two thousand people who were poisoned, and at least 730 who died, because of mercury released into the ocean from a factory at Minamata, Japan. These people had eaten shellfish taken from Minamata Bay and they suffered from kidney failure. Others developed neuromuscular deterioration, had birth defects, went insane, and some eventually died miserably. The source of the mercury was a plastic plant that was dumping waste mercuric chloride into the bay through a small creek. Bacterial action changed this chemical into a form that could be taken up and concentrated by benthic organisms such as clams and oysters which were subsequently consumed by the local people.

Copper, another hazard, is so effective at killing marine organisms that it has long been used to clean aquariums. A freighter, Pac Baroness, carrying  $2.1 \times 10^4$  tons of finely powdered copper sank off the coast of central California after a collision in 1987.

A plume of copper-tainted water was detected 40km downstream from the wreck, and marine life was significantly disrupted in the area, which is a major fishing ground for Dover sole and rock cod. A similar incident occurred off Holland in 1965 when 20 tons of accidentally dumped copper sulfate caused the death of some  $10^5$  fish and affected some mussel populations as well. Fortunately, except for the highly localized effects of copper in ships' antifouling paints, incidents resulting from acute copper toxicity are very rare.

Lead has been used by humans for thousands of years and is among the most widely dispersed of the environmental contaminants. In fact, human activities have released some 17 times as much lead as is derived from natural sources. The incidence of lead poisoning in humans goes back to as early as the Roman times. However, compared to levels of lead in non-marine foods and drinking water, the marine environment represents a negligible source of lead to humans.

This is mainly because the natural lead concentration in the oceans is extremely low (see *General Chemistry of Seawater*, Table 2). Aeolian input of the anti-knock compound in gasoline, tetra-alkyl lead, has been a major source of lead in the oceans. Incidents involving freighters carrying tetra-alkyl lead have not resulted in damage to the marine biota although alkyl lead compounds were implicated in an incident in the River Mersey estuary in 1979 when some 2400 seabirds were found dead or dying. The banning of the sale and use of leaded fuel has resulted in decreased lead concentrations in recent years.

The quantities of tin, as a replacement for copper, that have been introduced to the oceans as a result of human activities have also increased steadily, reflecting the great usefulness of the metal in many industrial processes. Of particular concern, however, is the highly toxic organotin derived from two principal sources: through the bacterial methylation of inorganic tin compounds and through the leaching of alkyl and aryl tins from some types of antifouling paints used on the hulls of ships.

The use of tin, rather than copper, in antifouling paints has provoked still other

concerns. To be effective, the organotin must be present in the paint/seawater interface so as to deter fouling organisms. The leaching action of seawater, however, releases tin into seawater where it no longer influences fouling organisms, but instead, produces unwanted effects on non-target species over a wide area.

The adverse effects of tributyl tin oxide in antifouling paints were first detected in France where it was observed that there was a correlation between boat density and shell abnormality in a Pacific oyster which is grown commercially. Similar findings have popped up elsewhere and many harbors, marinas and estuaries have now been affected. Tributyl tin-containing paints have been banned in several countries and copper-based antifouling paints are increasingly used again.

Like mercury, cadmium has been shown to pose a real threat to any human population which receives a high level of exposure. Again in Japan, the itai-itai (ouch-ouch) cadmium-poisoning disease was first observed in the inhabitants of the Jinzu River basin where the Kanoucoka mine had first contaminated the river, and then the rice paddies with zinc, lead and cadmium. Fortunately, high concentrations of cadmium in fish or shellfish have rarely been linked to human illness.

Zinc, nickel, arsenic  $(As^{3+}, rather than As^{5+})$ , chromium  $(Cr^{6+}, rather than Cr^{3+})$ , vanadium and selenium have all been found to be toxic to at least some marine organisms. Fortunately, their concentrations in the marine environment are lower than the water quality criteria for trace elements, as set by the US Environmental Protection Administration (Table 2).

	Fresh water	conc. (ppb)	Salt-water conc. (ppb)				
Element	Max. 24h average	Max. permissible	Max. 24h average	Max. permissible			
As(III)	-	440	-	-			
Cd	0.01-0.05*	1.5-6.3*	4.5	59			
Cr(VI)	0.29	21	18	1260			
Cr		2000-10000*	-	-			
Cu	5.6	10-43*	4.0	23			
Pb	0.75-20	74-400*	-	-			
Hg	0.00057	0.00017	0.025	3.7			
Ni	56-160*	1000-3100*	7.1	140			
Se	35	260	54	410			
Ag	-	1-13*	-	2.3			
Zn	47	180-570*	58	170			

• The exact value depends on the water hardness.

Table 2. US EPA Water Quality Criteria for Trace Elements.

- -
- -
- -

# TO ACCESS ALL THE **23 PAGES** OF THIS CHAPTER, Visit: <u>http://www.eolss.net/Eolss-sampleAllChapter.aspx</u>

#### Bibliography

Ahrland S. (1988). Trace metal complexation by inorganic ligands in sea water, in "*The determination of trace metals in natural waters*" eds. T.S. West and H.W. Nurnberg, Blackwell, Oxford, 233-253. [This article presents many trace metal concentrations in the oceans.]

Benchley P. and Gradwohl J. (1995). *Ocean Planet*, Harry N. Abrams, Inc., N.Y., 192 pp. [This book explores the role that the oceans play in all of our lives: as a source of inspiration and spiritual well-being, as an environment that binds communities and even entire cultures, as a place of natural wonders almost beyond the powers of the imagination to comprehend. The authors introduce these themes in various essays.]

Bregman J. I. (1999). *Environmental Impact Statements*, 2nd ed., Lewis Publishers, N.Y., 248 pp. [This book covers all the requirements for a wide variety of EISs on the U.S. federal, state and local levels.]

Brewer P.G. (1975). Minor elements in sea water, in "*Chemical Oceanography*", V. 1, 2nd ed., eds. J.P. Riley and G. Skirrow, *Academic Press*, London, pp. 415-496. [This chapter discusses different types of distribution, input and recycling of minor elements in the oceans.]

Bruland K.W. (1983). Trace elements in sea-water, in "*Chemical Oceanography*", V. 8, 2nd ed., eds. J.P. Riley and R. Chester, Academic Press, London, 157-220 pp. [This chapter discusses various types of distribution, input and recycling of trace metals in the oceans.]

Chen C.T.A. (1990). Obtaining past trends in marine environmental conditions with contemporary data, in "*Ocean Resources*", eds. D.A. Ardus and M.A. Champ. *Kluwer Acad. Pub.* Vol. 1, 293-305. [This article describes how past trends in marine pollution may be obtained based mainly on corals and sediments.]

Chen, C.T.A., Chang K.H., L.S. Fang L.S., Chen Y.C., Hung T.C., Hou H.S., and Marsh J.B., (1992). Trace metals, radionuclides, and thermal diffusion in Taiwan's coastal waters, in *"Environment and Resources in Asia's Marine Sector"*, ed. J.B. Marsh, Taylor and Francis, N.Y., 361-380. [This article describes how past trends in marine pollution may be obtained based mainly on corals and sediments.]

Garrison T. (1993). *Oceanography*. Wadsworth, Inc. Belmont, Ca. 540pp. [This is an introductory marine science textbook.]

Goldberg E.D. (1963). The oceans as a chemical system, in "*The Sea*", Vol. 2, ed. M.N. Hill, Interscience, New York, pp. 3-25. [This article is one of the earliest to provide a comprehensive covrage of the chemical systems in the ocean.]

Goldberg E.D. (1975). Marine pollution, in "*Chemical Oceanography*" eds. J.P. Riley and G. Skirrow, *Academic Press*, London, pp. 39-89. [This is a chapter on marine pollution-related problems.]

Horne R.A. (1969). "*Marine Chemistry*", Wiley-Interscience, New York, 568pp. [This is a textbook on marine chemistry.]

Kumar H.D. and Hader D.P. (1999). *Global Aquatic and Atmospheric Environment*, Springer-Verlag, Berlin, 393pp. [This is a textbook on aquatic systems, lakes and wetlands, marine environment, ozone changes and solar ultraviolet radiation.]

Preston M.R. (1989). Marine pollution, in *Chemical Oceanography*, V9, ed. J.P. Riley, Academic Press, London, pp 53-196. [This is a chapter on marine pollution-related problems, including petroleum hydrocarbons, sewage and nutrients, persistent organic compounds, trace metals and artificial

radionuclides. Marine contamination monitoring and international laws are also discussed.]

Sverdrop H.U., Johnson M.W., and Fleming R.H. (1942). *The Oceans*. Prentice Hall, Inc. Englewood Cliffs, *N.J.* 1087pp. [This treatise is the first to provide comprehensive coverage of all aspects of the oceans.]

United Nations Convention on the Law of the Sea (1982). [This is the official text of the United Nations Convention on the Law of the Sea with annexes and index. The Convention represents not only the codification of customary norms, but also, and more significantly, the progressive development of international law which establishes a comprehensive framework for the regulation of all ocean space. It is divided into 17 parts and nine annexes and contains provisions governing, inter alia, the limits of national jurisdiction and the preservation of the marine environment, exploitation of living resources and conservation, scientific research, sea-bed mining and other exploitation of non-living resources as well as the settlement of disputes. In addition, it establishes new international bodies to carry out functions for the realization of specific objectives.]

### **Biographical Sketch**

Born in Changhwa, Taiwan, on 22 April 1949, **Prof. Chen-Tung Arthur Chen**, his wife and two daughters are currently residing in Kaohsiung, where he has been Professor at the Institute of Marine Geology and Chemistry since 1986. After receiving his B.Sc. degree in Chemical Engineering from National Taiwan University in 1970, Prof. Chen was awarded his Ph.D. degree in Chemical Oceanography from the University of Miami in 1977. In the same year, he was appointed Assistant

Professor in the College of Marine Sciences of Oregon State University, where he was later promoted Assistant (NSYSU) in Kaohsiung, Taiwan, and as Chargé de Recherche (CNRS), Université Pierre et Marie Curie in Paris during 1984-1985. During this period, he founded the Institute of Marine Geology at NSYSU, and served as its director until 1989 when he was made Dean of the College of Marine Sciences, a position he held until 1992.

Prof. Chen has sat on numerous international committees, including the Scientific Committee on Oceanic Research and the World Ocean Circulation Experiment. He also served as one of the executives of the Scientific Steering Committee of the Joint Global Ocean Flux Study (JGOFS) between 1992-1995. Just prior to that, he had helped to form the Joint JGOFS / LOICZ Marginal Seas Task Team in 1991, and served as its chairman until 1995. Prof. Chen is at present one of the editors of *Oceanography Journal* and associate editor of *Marine Chemistry*. Besides having more than 150 of his own scientific papers published, Professor Chen was awarded the highly-coveted Biowako Prize for Ecology from Japan in 1997.