

2.4 Aquatic Transport of Chemicals

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2.4.1 INTRODUCTION

Continental debris, both natural and anthropogenic, is transferred to the oceans by the winds, rivers, coastal runoff, waste outfalls, and dumping from ships. The first three processes can be markedly influenced by climate, affecting both entry to and movements within the marine environment. Two climate-related factors are dominant in affecting the fates of substances: the annual precipitation, which determines the amounts and compositions of river flow and coastal runoff; and primary plant productivity in the hydrosphere. There are well-defined geographical differences in these two factors as a function of present-day climatic regimes. An understanding of these climate-controlled parameters can be used to describe and predict the fates of pollutants introduced to marine systems.

A key role is played by organic substances. The behaviour of anthropogenic chemicals during transport within water systems will be strongly affected by organic compounds, both in the dissolved and particulate states. The solid forms can take up pollutants, such as heavy metals or artificially produced radio-nuclides, and enhance their descent through water columns to the underlying sediments. They can also make pollutants more available to filter-feeding organisms. Similarly, some of the dissolved phases have the abilities to form complexes with inorganic cations and to alter their involvements with solids through sorption processes or their accumulation by marine organisms. Further, the reducing abilities of some of the organics can involve them in redox reactions with pollutants.

2.4.2 PRIMARY PRODUCTIVITY

The primary plant productivity in the surface waters of the oceans initiates most of the chemical reactions within the marine system. The photosynthetic fixation of carbon dioxide and water into organic matter is accompanied not only by

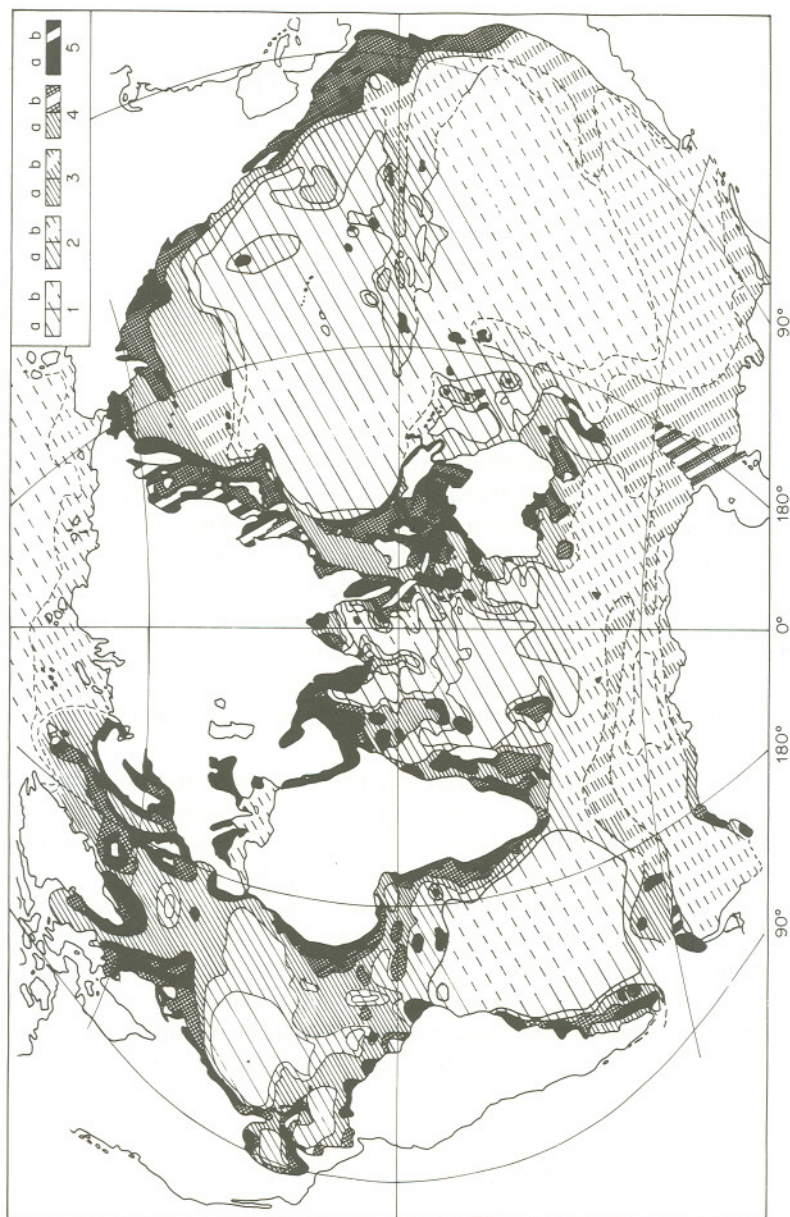


Figure 2.4.1 Distribution of primary production in the World Ocean. Units are in mg C/m²/day. (1) Less than 100; (2) 100-150; (3) 150-250; (4) 250-500; (5) more than 500. a = data from direct ¹⁴C measurements; b = data from phytoplankton biomass, hydrogen, or oxygen saturation. From Koblenz-Mishke *et al.* (1970). Reproduced with permission

the uptake of plant nutrients, such as nitrate and phosphate, but also by the incorporation of many inorganic elements, such as manganese, copper, and iron. The plants provide the food base for higher organisms. As a consequence there is an overall transfer of particulate organic phases from the upper layers of the oceans where photosynthesis occurs to depths; this occurs through gravitational settling, through uptake of materials by higher trophic levels, and through the discharge of metabolic waste products. Also, the organic phases are oxidized by dissolved oxygen with the release of various chemical species back into the dissolved states. Overall, the initial plant productivity results in the transfer of many elements from surface to deeper waters.

As an example, the particulate organic phases have been associated with the transport of naturally occurring thorium isotopes (Bacon and Anderson, 1982) and artificially produced plutonium isotopes (Toggweiler, 1983) downwards in the oceanic water column. Bacon and Anderson developed a simple scavenging model in which dissolved thorium, the principal form of the element in the oceans, is taken up by small particles which subsequently can become attached to larger particles. These larger particles during their fall through the water column can be broken up and re-formed through biological activity. Further, during this sinking, there is simultaneous adsorption/desorption of the metals from the solids.

Plutonium profiles in the Pacific Ocean have a unique character — maxima at depths around 500 m. Toggweiler (1983), utilizing the rate constant of Bacon and Anderson (1982) for the dissolved thorium uptake and loss term for the destruction of larger particles to the smaller particles and to the dissolved state, was able to model the observed plutonium distribution. Utilizing a 50 m/day sinking rate, the destruction of the large particles is found to take place daily. The loss term is related to the average lifetime of faecal pellets produced over all depths by grazing organisms. With particle destruction, the plutonium enters the dissolved state for a period of several years before encountering another sinking particle. The downward motion of plutonium takes place at about 40 m/year as derived from the model. This overall transfer of plutonium from upper to deeper waters is thus clearly dependent upon the production of primary organic materials.

Present-day primary plant productivity in the world ocean has been summarized by Koblentz-Mishke *et al.*, (1970). The distribution of values was divided into five classes: less than 100, 100–150, 150–250, 250–500, and more than 500 mg of carbon fixed per square metre per day (Figure 2.4.1).

Quantitatively, the global picture of primary productivity is described by two main variables: the supply of nutrients and the quantity of light energy available to the algae. The latter factor is of importance, for example, in the polar regions where the presence of sea ice and the brevity of daylight in winter limit the amount of light penetrating the waters. The lowest levels of primary productivity are found in such areas.

The higher levels of primary productivity occur in shallow coastal waters, i.e. within the 180 m depth contour (Ryther, 1969). Herein there is re-use of biostimulants, such as P, N, and Si. Especially productive waters are those of the continental shelf and slope, islands, and the upwelling regions of the oceans. The highest values of primary productivity are found along western continental coasts, especially at subtropical latitudes where there are prevailing offshore winds and eastern boundary currents. Surface waters are diverted offshore and are replaced by nutrient-rich deep waters—the upwelling phenomenon. The upwelling areas constitute about 0.1% of the world ocean (Ryther, 1969).

2.4.3 RIVER FLOW

The world's rivers deliver both natural and anthropogenic substances in the dissolved and particulate states to the coastal ocean. Variations in compositions of the major chemical elements (Al, Fe, Mg, Ca, Na, Si, Ti) can be understood in part through the climatic features of the river system (Martin and Meybeck, 1979). The intensity of weathering, both present and past, appears to be the controlling factor. Al, Fe, and Ti are high in the suspended materials of tropical rivers, while the concentrations of Ca and Na are low. This is a consequence of the intense leaching action of waters upon tropical soils. Over time, the readily soluble materials will have been removed. On the other hand, the temperate and Arctic rivers have higher levels of Ca, Fe, and Ti. Their suspended loads are derived from poorly weathered rock and as a consequence their compositions are quite similar to those of average crustal materials.

In addition to climatic factors, the topography of the river basin and human activities can characterize river composition. With respect to morphology, Richey (1983) indicates there are four patterns: (1) the river load is derived from mountains marginal to the flatlands, like the Amazon and Mississippi; (2) the river is marginal to a fold belt and flows parallel to it (Ganges and Parana); (3) the river flows along the strike of a mountain chain (Mekong and Magdalena); or (4) is superimposed across mountain chains (Columbia and Danube). The combination of precipitation, discharge (rainfall), basin area, and suspended load then influence the natural character of a river. For example, Asian rivers transport relatively large amounts of suspended solids as a consequence of high erosion rates and the steep relief of the continent.

The riverine export of organic materials that can interact with a variety of substances is clearly climate related. The greatest export appears to be in the sediment-rich waters of Asia and the organic-rich rivers of tropical America and tropical Africa. Meybeck (1982) indicates the linkages between the dissolved organic carbon (DOC) levels and climatic features. Taiga rivers have high values, with a median of 10 mg/l, while the wet tropics and temperate zones have 6 and 3 mg/l respectively. Lower concentrations exist in rivers draining tundra, with levels of around 1 mg/l. Maximum natural DOC values, at levels of 25 mg/l,

are found in rivers passing through swamps or poorly drained soils. The lowest values, < 1 mg C/l, are found in mountain rivers of the French Alps and New Zealand.

The concentration of total organic matter is highly variable, ranging from < 1 mg C/l in alpine streams to > 20 mg C/l in some tropical or polluted rivers (Richey, 1983). A substantial portion of this organic matter is in the form of fulvic and humic acids, which constitute the bulk of the organic matter in soils and sediments. These highly polymerized and highly aromatic compounds have molecular weights in the thousands and tens of thousands, with large numbers of functional groups, including phenolic, carboxyl, ketonic, alcoholic, and quinoidal types. As a consequence they have remarkable complexing abilities with metals, especially those characterized as hard acids. The dissolved fulvic and humic acids can significantly complex such metals as Zn(II), Cd(II), and Pb(II) if their concentrations are of the order of 1 mg/l (Raspor *et al.*, 1984). In the open sea, where these acids rarely exceed 0.2 mg/l, their associations with metals will be minimal. At 1 mg/l, around 10% of these three metals will be complexed as humates and fulvates.

The complexing of heavy metals with humic substances and with other organics in marine waters has been presumed to reduce the free metal ion concentrations, such as those of copper, which is toxic to aquatic organisms. Thus, Florence *et al.* (1984) found that many naturally occurring complexing agents, including the fulvic and humic acids, decrease the toxicity of copper. However, with synthetic ligands, lipid-soluble complexes turned out to be more toxic than the inorganic copper. Such complexes include oxine and 1-(2-pyridylazo)-2-naphthol. These investigators indicated that strong chelation with copper was essential for high toxicity. This sense that toxic responses may be a function of type and concentration of organic ligand present was also found for Ni and Cd. For example at $10 \mu\text{M}$ citric acid, about 25% of the Cd is complexed. Yet there is increased toxicity to algae at lower Cd concentrations (Laegreid *et al.*, 1984). Thus, the possibility that the organic molecules are toxic to marine organisms, either alone or in association with metals, seems reasonably high. Further, some pollutant organic chemicals carried to marine systems could in principle behave similarly.

A second important group of organic compounds entering the oceans from the rivers includes the plant building-block lignin and its degradation products, which can be oxidized to cinnamyl, syringyl, and vanillyl acids (Hedges and Mann, 1979).

The river load of particulate organic carbon (POC) is inversely related to the total amount of suspended matter (Meybeck, 1982). This relationship is apparently valid for about 99% of the world's rivers and can be coupled to the well-known increase of total suspended load with water discharge. The river POC, taken to mainly autochthonous, is diluted with increased levels of land-derived mineral matter. This phenomenon explains the relationship.

Table 2.4.1 DOC levels in rivers, range of TOC export rates compared to terrestrial primary production, and TOC budget to the ocean. From Meybeck (1982)

Environment	Total area (10 ⁶ km ²)	DOC (mg/l)	TOC export rate g/m ² /yr	Average total TOC load (10 ¹² g C/yr)	Mean net primary production (g C/m ² /yr)
Tundra	7.55	2	0.6	4.5	65
Taiga	15.85	10	2.5	39.6	360
Temperate	22.0	3	4.0	88	225–585
Tropical	37.3	6	6.5	241	315–900
Semi-arid	13.5	3	0.3	4.6	32
Desert	1.7		0	0	1.5
Total of the exoreic runoff	99.9		3.8	378	480
Tropical rain	15.9		10	159	900

The dissolved organic carbon loads in rivers and the export is given in Table 2.4.1. The relationship between the export of total organic carbon (TOC) and river runoff is evident. Maximum rates are found in the rain forests of temperate and tropical regions. Lowest rates are noted in semi-arid regions (Meybeck, 1982).

Of importance to the fate of some pollutants is the organic carbon entry into the oceans, both in the dissolved state (DOC) and particulate state (POC). For example, high levels of components of the dissolved load, such as the humic and fulvic acids, can chelate metals and reduce their availability to marine organisms and their sorption onto solid phases. The greatest input of organic carbon appears to be in the tropical rivers of South America and Africa (Richey, 1983). Further, there is evidence that a large amount of the organic carbon within rivers is respired or stored. Richey and Salati (cited as an article to be published in Richey, 1983) suggest that only 30% of the exported organic matter from the Amazon river actually enters the ocean.

One of the widespread impacts of human activity upon the oceans is the increased mobilization of nutrients to the coastal zone and the consequential increase in plant productivity. Richey (1983) estimates that the river fluxes of phosphorus and nitrogen have increased from prehistoric times to the present by a factor of two: N from 2–5 to 11 Tg/year and P from 0.5 to 1 Tg/year. He indicates that the current consumption of phosphate fertilizer is greater than the natural river export. Nitrogen is also mobilized by human society as a consequence of the high-temperature fixation of nitrogen to oxides of nitrogen during the burning of fossil fuels and of its use in fertilizers.

Nutrient supplies within riverine systems have been related to increased plant productivity in the lower reaches of the river (Richey, 1983). The entry of these biostimulants has been related to the productivity of the Amazon, the flood

plains of Shatt el Arab, and the Zaire and Nile rivers. Further, high fish populations have been found in the flood plain rivers of southeast Asia, Africa, and South America. The relationship of natural nutrient levels in rivers and climate is not yet clearly defined and is in need of further investigation.

The entry of excessive levels of plant nutrients can lead to the high production of organic matter, which may be capable of consuming all of the dissolved oxygen in the waters and in the sediments. This leads to a state of anoxia, where sulphate becomes the primary oxidizing agent with the production of hydrogen sulphide. When all of the sulphate is utilized in oxidative processes, fermentation and carbon dioxide reduction result, with the production of methane. In addition, the diatoms, which form the base of the marine food chain, are displaced by dinoflagellates, the weeds of the sea. This alteration of normal communities can be felt in higher trophic levels.

The trend towards anoxia may be self-sustaining. The increased flux of organic matter to the sediments may be compensated by an increased flux of nutrients out of the sediments. Following oxidation of the organic matter in the sediments, the nitrate and phosphate ions can return to the water column primarily by molecular diffusion. Coupling this flux with that of the rivers and coastal runoff to the surface waters can result in further enhanced productivity, and the formation of organic matter can thus become self-sustaining.

Biomass increases, anoxia, and alteration of the plant community structure have been observed worldwide in coastal waters and in estuaries. Chesapeake Bay, the New York Bight, the southern and northern California coasts, the Baltic Sea, Kaneohe Bay, Hawaii, the Adriatic Sea, the Oslo Fjord, Omura Bay, Japan, and Tokyo Bay, Japan, are but a few of the zones responding to these anthropogenic stresses of increased inputs of biostimulants.

2.4.4 RIVERS AND PRIMARY PRODUCTIVITY

Changes in climate can exert an influence upon the fate of pollutants through coupling of river flow and the production of organic matter in the coastal ocean. Clearly, the importation via a river of substances that are toxic to photosynthetic activity, such as copper, halogenated hydrocarbon pesticides, etc., is well recognized. However, there are other possible impacts upon nutrient and light availability that may be significant.

The effects of rivers on primary productivity in the oceans may take several forms: (1) an alteration of nutrient concentrations of the coastal waters by dilution, enhancement, or removal on river-borne particulates; (2) changing light penetration through the introduction of particles; and (3) an effect on the stability of the water column. For example, by increasing its stability through low-density surface layers, the possibility of photosynthesizing cells being carried below the photic zone is minimized.

2.4.5 ESTUARIES

Estuaries play an important regulatory role in the transport of river-borne materials to the coastal ocean. Depending upon the morphology and hydrodynamical properties of an estuary, the materials introduced by rivers can be held or delivered to the open ocean (Wollast, 1983). The vertical stratification of estuarine waters and the amounts of mixing in part govern the movement of materials through the estuaries. The waters of rivers entering well-mixed estuaries have longer residence times than those flowing into highly stratified systems. In the latter case, the freshwater flow takes place in well-defined surface layers with little mixing with the underlying more saline waters. Such river waters rapidly reach the sea (Wollast, 1983).

Wollast (1983) points out that the particulate organic matter of terrestrial origin is often partially, if not completely, removed in the estuarine zone and carries with it many inorganic species. Similarly, colloidal species in rivers, usually negatively charged, flocculate in estuarine streams. Positively charged materials are carried down with the flocs through neutralization of the surface colloidal charges. Thus, river-borne pollutants may meet an accommodation in estuarine sediments.

The primary plant production within the estuary and the subsequent respiration of these materials and of river-borne organics determine the outflow of organic phases. In those estuaries where the waters have long residence times, bacterial degradation of the non-refractory organic matter takes place. If primary productivity and the river fluxes are high, anoxia can develop (Wollast, 1983).

The fate of nitrogen and phosphorus entering estuaries has been investigated for the Scheldt Estuary, Belgium (Wollast, 1983). Three biochemical reactions govern the speciation of nitrogen: nitrification, denitrification, and uptake during primary productivity. A mass balance for the nitrogen species has been prepared (Table 2.4.2). The total riverine nitrogen input of 34 tonnes is compensated by a loss of 20 tonnes annually to the coastal ocean, a loss of 3 tonnes to the sediments, and a loss of 11 tonnes of nitrogen gas to the atmosphere through denitrification.

Table 2.4.2 A proposed mass balance for nitrogen species in the Scheldt Estuary. The processes considered include freshwater input, denitrification, nitrification, primary productivity, and sedimentation, as well as output to the North Sea (Wollast, 1983). Units are tonnes of N/year

Species	Input	Denitrification	Nitrification	Primary Productivity	Sedimentation	Output
NH ₄	23	-	- 12	- 6	-	5
NO ₃ + NO ₂	9	- 11	+ 12	-	-	10
N particulate	2	-	-	+ 6	- 3	5
N total	34	- 11	-	-	- 3	20

Table 2.4.3 A proposed mass balance for phosphorus for the Scheldt Estuary in units of kilotonnes per year (Wollast, 1983)

	Input	Chemical precipitation	Plankton uptake	Sediment	Output
Dissolved P	5.6	- 3.3	- 0.8	0	1.5
Particulate P	1.5	+ 3.3	+ 0.8	- 4.9	0.7
Total P	7.1	-	-	- 4.9	2.2

Phosphorus occurs nearly completely in the phosphate form, both dissolved and particulate. The estuarine input of 7000 tonnes per year is compensated by an output of 2200 tonnes and a deposition of 4900 tonnes (Table 2.4.3).

Clearly, the above data are specific for the Scheldt. A greater percentage of the river input can reach the oceans for more highly stratified estuaries.

2.4.6 MONITORING

The monitoring of atmospheric and riverine fluxes of pollutants to the coastal environment takes a variety of forms depending upon the time interval to be averaged. For example, instantaneous measurements of pollutants in the air or water streams can be made by direct sampling. Such measurements usually involve time periods of days or less. At the other extreme, the sedimentary strata, where dating techniques are applicable, provide integrations of fluxes over periods of years or less. The use of sentinel organisms, such as bivalves, has been effective in monitoring pollutants where the integration periods appear to be of the order of months to years, depending upon the nature of the pollutant. Atmospheric fallout collected upon plates or into buckets can also be integrated over periods of days to months.

The sedimentary record of fluxes to the coastal zone depends upon the development of an adequate time base (usually a radioactive geochronology) and upon the absence of disturbance to the sediment, either through bioturbation or physical mixing processes. For example, the anthropogenic fluxes of Pb, Cr, Cd, Zn, Cu, Ag, V, and Mo into the coastal zone off southern California were measured in anoxic sediments (Bruland *et al.*, 1974). The contributions from different transporting agencies—the winds, sewer outfalls, storm runoff, and river runoff—could not be evaluated on the basis of the measurements. The time base was provided both by the counting of the annual varves of the sediments and by ^{210}Pb geochronologies. There was no evidence of mixing of the solid phases of the deposit. The lead fluxes were increased by a factor of four as revealed in the sedimentary record, whereas there was less than a 50% increase in vanadium fluxes over the past century.

The atmospheric fluxes of metals, including the radioactive element plutonium, to the California coastal zone were determined with buckets, which

collected fallout over monthly periods (Hodge *et al.*, 1978). The flow of these aerosols to the oceans appeared to measurably govern some metal concentrations in surface waters but did not account for the overall accumulation of metals in coastal sediments. The metal-containing aerosols were removed from the atmosphere mainly by dry fallout. The lower atmospheric residence times of the metals appear to be of the order of a half day to several days.

Monitoring of sentinel organisms for their pollutant concentrations is most useful to determine measures of environmental levels and of their bioavailability at a given site. However, often the behaviour of pollutants can be understood through monitoring of extended coastal areas (Farrington *et al.*, 1983). For example, elevated Cd and $^{239+240}\text{Pu}$ concentrations in bivalves from the central California coast compared to their counterparts either to the north or south are apparently related to enrichments of these metals in intermediate depth waters of the north Pacific and to the upwelling of this water associated with the California current system. Both metals are transferred from the surface waters to deeper waters through biological activities.

Bivalves, including mussels and oysters, are especially adapted to pollutant monitoring. They are cosmopolitan, often in communities with large populations which can be sampled without fear of destroying a community. Being sedentary as adults they can effectively characterize through their body burdens some pollutants in a given area. The concentration factors of such pollutants as chlorinated hydrocarbon pesticides, heavy metals, and transuranic elements often achieve values of between 100 and 100 000. The bivalves clearly assess the biological availability of the pollutants under study. In addition, there is little evidence that they metabolize many xenobiotics. Thus, a quite accurate evaluation of the environmental levels can be made through measurements of their body contents. Moreover, they survive under pollutant concentrations that reduce or eliminate other species, and they can be transplanted from one area to another. Finally, since some bivalves are commercial seafood resources, the level of their contamination is important from a public health standpoint (Farrington *et al.*, 1983).

Primary productivity measurements over long times and over wide areas in the oceans and rivers may be effectively pursued using satellite imagery. Present measurements from ships give inadequate spatial and temporal coverage to study such problems as a trend towards anoxia which may be occurring at a very slow pace.

The Coastal Zone Color Scanner (CZCS) aboard the Nimbus 7 has been obtaining near-surface phytoplankton pigment concentrations in the world ocean since 1978. The procedure for converting the satellite pigment images into water column primary productivity has been described by Eppley *et al.*, (1985). The spatial resolution is around 1 km². Cloud cover often obscures the pigment image. Still a coverage of 50 images a year for a given area will provide an understanding of the short-term temporal changes in primary productivity and

will allow comparisons to be made with other areas and subsequent years. A trend towards eutrophication of coastal areas will most effectively be assessed with these techniques.

2.4.7 OVERVIEW

The time scales over which climate related parameters can change and hence influence primary productivity and river flow/coastal runoff can extend over periods of days (the episodic event) through years to millenniums. The resultant impacts upon the fate of pollutants introduced to natural waters will have similar time constants.

For instance, tropical storm Agnes in June 1972 caused massive flooding of Chesapeake Bay, Maryland. The movement of suspended solids from the Susquehanna River into the estuary during a one week period exceeded that of the previous several decades (Schubel, 1974). The solids were distributed in the upper reaches of the Bay. The salinities in Bay waters were reduced substantially and remained low over the summer, recovering to normal values in September. Several consequences which would influence the fate of pollutants are evident. The reduced salinities can decrease primary productivity. The increased net seaward flow of waters carried pollutants to the ocean. Pollutants at the sediment/water interface in the upper reaches of the Bay were covered over by the river solids.

On a somewhat longer time scale, alterations in primary productivity as a consequence of the El Nino during February and March 1983 were observed around the Galapagos Islands (Feldman *et al.*, 1984). The El Nino is an oceanic response to atmospheric forcing functions. The satellite measured pigment concentrations indicated a decrease in primary productivity in the region. This may explain the observed reproductive failures of seabirds and marine mammals noted in the area. Clearly, such an event also can be involved in the redistribution of pollutants over periods of years.

There are other climate-controlled parameters that can change water temperatures in the photic zone, concentrations of plant nutrients (such as phosphate and nitrate) through alterations in patterns of water movements, and the flow of continental waters into the oceans. Tsunamis, storms, tidal amplitude changes, and upwelling intensity changes are episodic events affecting pollutant behaviour. Climate-controlled changes in surface water temperature of the photic zone can alter primary productivity and hence the fate of pollutants. The impact of temperature on gaseous oxygen solubility at the surface waters can affect the rate of combustion of organic phases, both natural and anthropogenic.

Overall, the persistence of pollutants and the production of interacting chemicals are climate controlled. Our abilities to predict the course of climate will be reflected in our abilities to predict the fates of pollutants.

2.4.8 REFERENCES

- Bacon, M. P., and Anderson, R. F. (1982). Distribution of thorium isotopes between dissolved and particulate forms in the sea. *J. Geophys. Res.*, **87**, 2045–2056.
- Bruland, K. W., Bertine, K., Koide, M., and Goldberg, E. D. (1974). History of metal pollution in the Southern California Coastal Zone. *Environ. Sci. Technol.*, **8**, 425–432.
- Eppley, R. W., Stewart, E., Abbott, M. R., and Heymann, V. (1985). Estimating ocean primary production from satellite chlorophyll. Introduction to regional differences and statistics for the Southern California Bight. *J. Plankton Res.*, **7**, 57–70.
- Farrington, J. W., Goldberg, E. D., Risebrough, R. W., Martin, J. H., and Bowen, V. T. (1983). U.S. Mussel Watch 1976–1978: an overview of the trace metal, DDE, PCB, hydrocarbon and artificial radionuclide data. *Environ. Sci. Technol.*, **17**, 490–496.
- Feldman, G., Clark, D., and Halpern, D. (1984). Satellite color observations of the phytoplankton distribution in the eastern Equatorial Pacific during the 1982–1983 El Niño. *Science*, **226**, 1069–1071.
- Florence, T. M., Lumsden, B. G., and Fardy, J. J. (1984). Algae as indicators of copper speciation. In: Kramer, C. J. M., and Duinker, J. C. (eds.), *Complexation of Trace Metals in Natural Waters*, pp. 317–327. Martinus Nijhoff/Dr. W. Junk Publishers, The Hague.
- Hedges, J. I., and Mann, D. C. (1979). The characterization of plant tissues by their lignin oxidation products. *Geochim. Cosmochim. Acta*, **43**, 1803–1807.
- Hodge, V., Johnson, S. R., and Goldberg, E. D. (1978). Influence of atmospherically transported aerosols on surface ocean water composition. *Geochim. J.*, **12**, 7–20.
- Koblentz-Mishke, O. J., Volkovinsky, V. V., and Kabunova, J. G. (1970). Plankton primary production in the world ocean. In: Wooster, W. S. (ed.), *Scientific Exploration of the South Pacific*, pp. 183–193. U.S. National Academy of Sciences, Washington, D.C.
- Laegreid, M., Alstad, J., Klaveness, D., and Seip, H. M. (1984). Metal speciation—biological response. In: Kramer, C. J. M., and Duinker, J. C. (eds.), *Complexation of Trace Metals in Natural Waters*, pp. 419–424. Martinus Nijhoff/Dr. W. Junk Publishers, The Hague.
- Martin, J., and Meybeck, M. (1979). Elemental mass balance of material carried by major world rivers. *Marine Chem.*, **7**, 173–206.
- Meybeck, M. (1982). Carbon, nitrogen and phosphorus transport by world rivers. *Am. J. Sci.*, **282**, 401–450.
- Raspor, M., Nurnberg, H. W., Valenta, P., and Branica, M. (1984). Significance of dissolved humic substances for heavy metal speciation in natural waters. In: Kramer, C. J. M., and Duinker, J. C. (eds.), *Complexation of Trace Metals in Natural Waters*, pp. 317–327. Martinus Nijhoff/Dr. W. Junk Publishers, The Hague.
- Richey, J. E. (1983). Interactions of C, N, P, and S in river systems: a biogeochemical model. In: Bolin, B., and Cook, R. B. (eds.), *The Major Biogeochemical Cycles and Their Interactions*, SCOPE 21, pp. 363–383. John Wiley & Sons, Chichester.
- Ryther, J. H. (1969). Photosynthesis and fish productivity in the sea. *Science*, **166**, 72–76.
- Schubel, J. R. (1974). Effects of tropical storm Agnes on the suspended solids of Northern Chesapeake Bay. In: Gibbs, R. J. (ed.), *Suspended Solids in Water*, pp. 113–132. Plenum Press, New York.
- Toggweiler, J. R. (1983). A simple model solution for the bomb-plutonium maximum observed in the Pacific Ocean. *EOS*, **64**, 1089.
- Wollast, R. (1983). Interactions in estuaries and coastal waters. In: Bolin, B., and Cook, R. B. (eds.), *The Major Biogeochemical Cycles and their Interactions*, pp. 385–407. John Wiley & Sons, Chichester.