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- GESAMP -

REPORTS AND STUDIES

No. 32

Land/Sea Boundary Flux of Contaminants: Contributions from Rivers

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Reports and Studies No. 32

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Unesco, 1987

NOTES

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Definition of Marine Pollution by GESAMP

"POLLUTION MEANS THE INTRODUCTION BY MAN, DIRECTLY OR INDIRECTLY, OF SUBSTANCES OR ENERGY INTO THE MARINE ENVIRONMENT (INCLUDING ESTUARIES) RESULTING IN SUCH DELETERIOUS EFFECTS AS HARM TO LIVING RESOURCES, HAZARDS TO HUMAN HEALTH, HINDRANCE TO MARINE ACTIVITES INCLUDING FISHING, IMPAIRMENT OF QUALITY FOR USE OF SEA WATER AND REDUCTION OF AMENITIES".

* * *

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PREFACE

Contaminants are transported from the land to the sea as a result of natural processes and/or as a result of man's activities such as dredging, direct discharges of wastes and ocean dumping. Natural processes which may control the flux of contaminants to the sea from land based sources include atmospheric and riverine transport, direct runoff from land, and transport by glaciers. To assess the marine environmental impact of the flux of contaminants from land and to develop strategies for monitoring, and ultimately, minimizing, these fluxes the importance of the various transport pathways (both natural and unnatural) must be determined.

Recognizing the importance of this subject GESAMP, at its thirteenth session, agreed to establish a Working Group on the Land/Sea Boundary Flux of Pollutants with the following terms of reference:

(i) to review the scientific literature and assess the sources, pathways and fate of selected substances across the land/sea boundary to allow for a quantitative description of the flux of material to and through the marine environment;

(ii) to describe the processes which control the fate of material being introduced into the estuarine and marine environment, with initial emphasis being given to the nearshore and exchanges with the open ocean;

(iii) to consider and/or stimulate limited case studies to demonstrate the applicability and accuracy of the models generated;

(iv) to develop a report that can be used as input to total mass balance models and the next Review of the Health of the Oceans.

Because of the broad nature of the subject it was agreed that the Working Group should focus primarily on the land/sea flux of contaminants contributed by rivers.

UNESCO, as lead agency, provided administrative and technical support for the Working group, which also received support from UNEP and IAEA. The Working Group met in April 1984 in Mazatlan, Mexico, in July 1985 in Roscoff, France and in December 1986 in Savannah, Georgia, U.S.A.

EXECUTIVE SUMMARY

The aim of this report is to review the state of knowledge on the land/sea flux of three categories of contaminants (i.e. nutrients, trace metals and synthetic organic compounds) resulting from river transport. The report provides a critical review of the scientific literature on riverine and estuarine processes that influence the fate of these contaminants as they are transported from land based sources to the sea.

The terms "gross" and "net" flux are used to define the amount of contaminant transported to the marine environment and the amount transported through the estuarine-nearshore region to the open ocean, respectively. The concept of gross and net land/sea flux implies a boundary zone through which contaminants pass. For the purpose of this report this zone is assumed to be the estuarine-nearshore region. The choice of locations of the boundaries which define this zone are discussed in the report.

The gross flux of contaminants is dominantly influenced by biogeochemical characteristics of the given watershed and its hydrology. In the case of nutrients and trace metals, there are natural contributions to their gross fluxes in addition to anthropogenic contributions. These natural contributions will depend on watershed geology, land use, climatology and weathering regime. There are no natural sources of synthetic organic contaminants, however, the characteristics of the watershed will determine phase association of these materials and thus influence their fate. Hydrology of the watershed has a major control on the rate of transport of contaminants by rivers. Storm events that occur infrequently may be responsible for the major portion of the gross flux of contaminants from rivers. A major position taken in this report is that hydrological considerations have not been taken into account sufficiently in past studies of gross river transport. Techniques and approaches to assess the influence of hydrology on material transport are discussed.

The processes that control net fluxes are primarily those that affect distributions of contaminants between phases during transport through the estuarine-nearshore (or continental shelf) environment. These regions are sedimentary traps thus contaminants associated with particles accumulate nearshore. Important processes include adsorption-desorption and precipitation-dissolution reactions, biological uptake and microbial degradation of organic matter that results in remobilization of some contaminants.

In the report an attempt is made to estimate gross and net land/sea fluxes of contaminants due to rivers. For synthetic organic compounds it is concluded that there are insufficient data available to make global gross river flux estimates. An attempt is made, however, to describe to what extent the available data may be used to estimate net fluxes of these compounds. A specific example is given using data for the export of five PCB congeners to the central North Sea from the Rhine River.

By comparing gross fluxes of dissolved nutrients in unpolluted and polluted rivers it is apparent that the global anthropogenic flux is at least comparable to and probably significantly larger than the natural flux. It is estimated that only a small portion of the gross river flux reaches the oceans.

Trace metal data are available for a number of world rivers and are used to estimate gross river fluxes on a global basis. The value of such estimates is limited because of the insufficient diversity of rivers which have been studied. In addition, because of the insufficient ancillary information accompanying the results of these studies, it is not possible to estimate the anthropogenic component of estimated fluxes.

Net trace metal fluxes to the oceans are calculated by two different approaches. The first uses a generic coastal zone model and the second is based on the zero salinity intercept of dissolved trace metal-salinity regressions for ocean margins. These fluxes are compared to removal rates based on accumulation of pelagic sediments. For the trace metals, considered, with the exception of cadmium, there appears to be a reasonable balance between net fluxes and ocean sediment removal.

Strategies for assessing gross river transport of contaminants should be developed to satisfy national needs but, at the same time, should be designed so as to also provide data suitable for scaling to regional or global river fluxes. The strategies should allow for assessing watershed characteristics of different systems on contaminant transport and should take into account the importance of different hydrologic regimes. National and international cooperation will be required to establish suitable strategies. This would incude agreement on approaches used in river transport studies and support of regional workshops and intercalibration exercises designed to ensure the quality and comparability of data generated.

Programs designed to address contaminant transport in rivers, established using appropriate strategies and cooperation as outlined above, provide an important component of temporal trend monitoring of coastal regions. Without such programs cause and effect relationships in relation to coastal marine environmental degradation are difficult to assess.

Several examples of approaches to estimating net land/sea fluxes of contaminants resulting from river transport are given in the report using the limited amount of existing data. These approaches need further testing, using case studies in different types of coastal areas. Such tests could evaluate different approaches with regard to limitations of existing data, comparability, cost effectiveness, and the influence of different coastal characteristics on net fluxes.

Reports and Studies GESAMP

The following reports and studies have been published so far. They are available from any of the organizations sponsoring GESAMP.

1. Report of the seventh session, London, 24-30 April 1975. (1975). Rep.Stud. GESAMP, (1):pag.var. Available also in French, Spanish and Russian

2. Review of harmful substances. (1976). Rep.Stud.GESAMP, (2):80 p.

3. Scientific criteria for the selection of sites for dumping of wastes into the sea. (1975). Rep.Stud.GESAMP, (3):21 p. Available also in French, Spanish and Russian

4. Report of the eighth session, Rome, 21-27 April 1976. (1976). Rep.Stud.GESAMP, (4): pag.var. Available also in French and Russian

5. Principles for developing coastal water quality criteria. (1976). Rep.Stud. GESAMP, (5):23 p.

6. Impact of oil on the marine environment. (1977). Rep.Stud.GESAMP, (6):250 p.

7. Scientific aspects of pollution arising from the exploration and exploitation of the sea-bed. (1977). Rep.Stud.GESAMP, (7):37 p.

8. Report of the ninth session, New York, 7-11 March 1977. (1977). Rep.Stud. GESAMP, (8):33 p. Available also in French and Russian

9. Report of the tenth session, Paris, 29 May - 2 June 1978. (1978). Rep.Stud. GESAMP, (9):pag.var. Available also in French, Spanish and Russian

10. Report of the eleventh session, Dubrovnik, 25-29 February 1980. (1980). Rep.Stud.GESAMP, (10):pag.var. Available also in French and Spanish

11. Marine Pollution implications of coastal area development. (1980). Rep.Stud. GESAMP, (11):114 p.

12. Monitoring biological variables related to marine pollution. (1980). Rep.Stud. GESAMP, (12):22 p. Available also in Russian

13. Interchange of pollutants between the atmosphere and the oceans. (1980). Rep.Stud.GESAMP, (13):55 p.

14. Report of the twelfth session, Geneva, 22-29 October 1981. (1981). Rep.Stud. GESAMP, (14):pag.var. Available also in French and Russian

15. The review of the health of the oceans. (1982). Rep.Stud.GESAMP, (15):108 p.

16. Scientific criteria for the selection of waste disposal sites at sea. (1982). Rep.Stud.GESAMP, (16):60 p.

17. The evaluation of the hazards of harmful substances carried by ships. (1982). Rep.Stud. GESAMP, (17):pag.var.

18. Report of the thirteenth session, Geneva, 28 February - 4 March 1983. (1983). Rep.Stud. GESAMP, (18):50 p. Available also in French and Spanish

19. An oceanographic model for the dispersion of wastes disposed of in the deep sea. (1983). Rep.Stud.GESAMP, (19):182 p.

20. Marine pollution implications of ocean energy development (1984). Rep.Stud. GESAMP, (20):44 p.

21. Report of the fourteenth session, Vienna, 26-30 March 1984. (1984). Rep.Stud. GESAMP, (21):42 p. Available also in French, Spanish and Russian

22. Review of potentially harmful substances. Cadmium, lead and tin. (1985). Rep.Stud. GESAMP, (22):114 p.

23. Interchange of pollutants between the atmosphere and the oceans (part II). (1985). Rep.Stud. GESAMP, (23):55 p.

24. Thermal discharges in the marine environment. (1984). Rep.Stud.GESAMP, (24):44 p.

25. Report of the fifteenth session, New York, 25-29 March 1985. (1985). Rep.Stud. GESAMP, (25):49 p. Available also in French, Spanish and Russian

26. Atmospheric transport of contaminants into the Mediterranean region. (1985). Rep.Stud.GESAMP, (26):53 p.

27. Report of the sixteenth session, London, 17-21 March 1986. (1986). Rep.Stud. GESAMP, (27):72 p. Available also in French, Spanish and Russian

28. Review of potentially harmful substances. Arsenic, mercury and selenium. (in press). Rep.Stud.GESAMP, (28)

29 Review of potentially harmful substances. Organosilicon compounds (Silanes and Siloxanes). (1986). Printed in limited number only by IMO, but published also as UNEP Reg.Seas Rep.Stud., (78):24 p.

30. Environmental Capacity. An approach to marine pollution prevention. (1986). Rep.Stud.GESAMP, (30):49 p.

31. Report of the seventeenth session, Rome, 30 March - 3 April 1987. (1987). Rep. Stud.GESAMP, (31):36 p. Available also in French, Spanish and Russian

32. Land-sea boundary flux of contaminants: contributions from rivers. (in press). Rep.Stud.GESAMP, (32)

CONTENTS

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1. INTRODUCTION

This report discusses the land/sea flux of pollutants resulting from river transport. Three categories of substances are considered; nutrients, trace metals and synthetic organic compounds. Discussions in the report refer to gross and net river fluxes. The gross river flux is defined as the amount of the substance transported to the land/sea boundary and the net flux is the amount of the substance transported across the boundary. The report reviews the present knowledge on processes controlling gross fluxes and the estuarine and nearshore processes that influence the fate of substances as they are transported through land/sea boundary.

Because of the numerous points (i.e. river systems) of input, accurate estimates of gross and net river transport to the ocean are difficult to make. Nevertheless the report demonstrates approaches that might be useful, given the proper data, and attempts at crude estimates on a global scale are presented. This is followed by recommendations for improving the existing state of knowledge.

In the initial phase of this study an attempt was made to assess, on a global scale, recent research efforts that might have bearing on the subject of this report. It was realized that this could not be accomplished in any detailed way, given the time and resources available. Nonetheless, it was felt that some effort should be made to broaden the perspective of this report. To this end a questionaire was circulated through the UN agency network to assess ongoing riverine studies. The responses to this questionaire are summarized in Appendix I and were used to prepare the "Register of Present and Ongoing Riverine/Estuarine Research" presented there. Clearly the list of respondents in this register represents only a small, but hopefully representative, portion of the individuals involved in river studies world wide.

In preparing this report on the land/sea boundary flux of pollutants and in reviewing the global coverage of investigations in various river systems of the world, due acknowledgment should be given to the related activities of the SCOPE/UNEP Project "Transport of Carbon and Minerals in Major World Rivers" (Degens, 1982, Degens et al., 1983). These coordinated international research efforts produce valuable data on the flux of organic carbon and on the biogeochemical processes in the riverine environment. The reports from this effort are relevant complimentary study materials providing a wealth of information on the discharge characteristics of important rivers of the world. The focus of attention of the present report is in describing the factors that influence the flux of materials (or model substances) considered to be pollutants under the definition of GESAMP and how these fluxes might be quantified.

2. GROSS RIVER FLUXES

2.1 General

Critical to any assessment of the impact of river transport of pollutants on the marine environment are estimates of gross river fluxes. This information is essential whether comparing rivers with other modes of pollutant inputs to coastal systems or when estimates of net pollutant transfer through the system are the objectives. Many of the models for assessing the net land/sea flux of pollutants discussed in this report depend on the accuracy of gross river flux estimates. For the purpose of this report, therefore, the factors influencing gross river fluxes are of particular interest and are discussed in some detail in this section.

2.2 Definition of Boundary for Estimating Gross River Fluxes

It is possible to define the riverine boundary in two different ways depending on the questions being addressed. For the purpose of developing these definitions, consider the diagrams presented in Figure 1 which depict schematically cross-sections of the lower reaches of a river system as it interacts with tidal saline waters.

The top diagram (I) depicts the river cross-section during periods of maximum discharge when the point at which a detectable rise in the concentration of chloride is observed furtherest down the channel at point C. Diagram II depicts the riverine cross-section during the times of minimum flow when the point at which a detectable rise in the chloride concentration is observed at its maximum up-channel location, B. During these extremes in conditions, the flow of water at point A is down channel at all depths. Any location further down-channel from A experiences up-channel flow at some time during the period between the extremes depicted in I and II.

For the purpose of evaluating processes that influence the transport and fate of materials, the riverine boundary can be chosen at point B. Above this point, bottom sediment is always in equilibrium with fresh riverine water, or is continually re-equilibrating with the changing river chemistry and, therefore, water passing at this point at all times can be considered to have characteristics influenced dominantly by riverine processes. Sediments below point B could have equilibrated with saline waters but at some point in time these sediments could be resuspended and moved back upstream to locations above point B. During this up-channel excursion, however, they would re-equilibrate with fresh water assuming all changes that they experienced while in the saline environment were completely reversible. Although this cannot be assumed from a strictly rigorous scientific view, alterations in this material would probably have insignificant impact on observed estuarine chemical characteristic as the sediment is subsequently transported back down the estuary.

For the purpose of estimating absolute riverine fluxes of materials to estuaries, the river boundary must be chosen at A. This is clearly evident by considering diagram III which indicates that material, especially particles, could be transported through a channel cross-section more than once at any location below point A.

To be scientifically rigorous, the riverine boundary should always be chosen at point A, the down river-most position where downstream unidirectional flow occurs from top to bottom. The location of this point is best determined by current direction surveys conducted at times of low river discharge and rising spring tide.

2.3 Biogeochemical Influences on Riverine Transport

A variety of natural watershed characteristics of river systems may influence the transport of nutrients, trace metals and synthetic organics. These include the drainage basin geology, climatology, physiography (i.e. drainage slope) and vegetation (i.e. production of organic matter). These characteristics determine

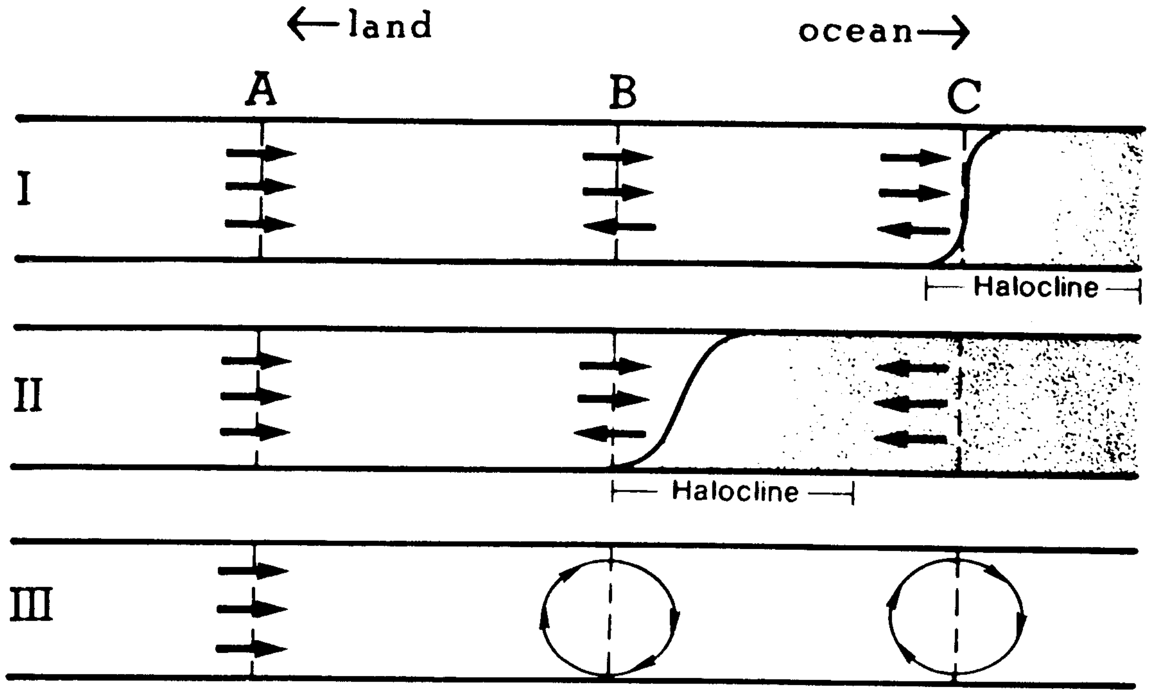

Figure 1. Schematic diagrams of the river-estuarine boundary.

the weathering regime and regulate the production and composition of particles which influences greatly the transport characteristics of the river system. The watershed characteristics are also responsible for the dominant complexing organic ligands and anions that enhance mobilization of many of these substances. The importance of understanding the influences of these characteristics on material transport and a number of important considerations of the biogeochemical behavior of these substances in river systems are discussed in detail in Appendices II, III and IV. Processes that are most important in influencing gross river fluxes of the three classes of contaminants considered in this report are briefly discussed below.

2.3.1 Nutrients

The speciation of the major nutrients N, P and Si and more specifically the transfer of the dissolved inorganic forms to the particulate fraction and vice-verse is almost entirely biological. In surface waters the balance between production of organic matter and respiration in river systems is of primary importance in controlling river fluxes of nutrients. In the case of nitrogen, the speciation of this element is further complicated by bacterial redox processes (nitrification and denitrification).

2.3.2 Trace Metals

The partitioning of trace metals in river water between particles and solution is a major factor governing gross and net river fluxes and will be controlled by:

1. the concentration and chemical nature of suspended sediments.

2. the concentration and composition of dissolved organic matter.

3. the concentration and composition of inorganic anion.

4. pH

All of these are related to varying degrees and interact to determine the transporting efficiency of the river system for trace metals in addition to their particle-solution distribution.

It is important that an understanding of relationships between these controlling parameters and trace metal concentrations be obtained. Without such an understanding it will be difficult to conclude that observed differences in metal concentrations in rivers is natural or the result of anthropogenic increases.

2.2.3 Synthetic Organics

Most of these contaminants, the products and byproducts of industrial synthesis, have no natural source and hence unlike the counterpart studies on the distribution and flux of trace metals, the geology of and the release of weathered products from the drainage basin should be viewed as a potential local or temporary sink rather than a source of these materials. Industrial activities and agricultural practices together with planned or indiscriminate municipal discharges provide the bulk of these materials to the aquatic environment. Drainage basin characteristics exert an influence on the transport of such materials exhibiting strong phase associations with inorganic and organic particulate matter.

Synthetic organics have widely varying and often appreciable vapour pressures (for examples see Fig. 2) and hence even though the concentrations in the aqueous environment may be low to negligible, their concentration in the atmosphere may be significant. Long-range atmospheric transport and wet and dry deposition of such compounds ensures their ubiquitous distribution throughout the global aquatic environment. (Harvey and Steinhauer, 1974, North Atlantic; Murphy and Rzeszutko, 1977, Great Lakes.) In remote areas atmospheric transport may be the dominant source of anthropogenic materials and the inputs to those areas will be influenced to a lesser extent by the river runoff component of the land/sea boundary flux.

For coastal regions and adjacent offshore areas the relative contributions of the aeolian versus the river-input should be evaluated based on such criteria as:

1. production and use patterns and distributions
2. the mode of introduction/dissipation (e.g., spraying, incineration, direct aqueous discharge, etc.)
3. the hydrodynamics and prevailing meterological conditions
4. the physico-chemical properties of the contaminant.

2.3.3.1 Analytical Limitations

Synthetic organic contaminants occur as trace components in complex assemblages with other contaminants and natural products. Any attempt to unravel the complexity of these mixtures is of necessity limited to a small suite of identifiable candidate compounds for which adequate analytical techniques are perceived to exist.

A popular approach has been to analyze for groups or classes of related compounds displaying similar chemical properties or to analyze "bulk" properties (e.g., DOC, POC, fluorescence, total PCB or hydrocarbons) in terms of undefined mixtures. These approaches often do not provide sufficient information on the individual components of these mixtures in order to interpret their physico-chemical behaviour. For example the degree of chlorination and the stereochemistry of individual congeners of chlorinated biphenyls has a marked effect on properties such as vapour pressure, water-particulate partitioning and abiotic and biotic degradation.

Many of the data available can only be used for comparisons (or trend analyses) in the broadest sense provided that the composition of an undefined mixture remains unchanged. In cases where these compositions are different, for instance between dissolved and particulates, the information content of the class analysis approach is greatly reduced.

The analysis of specific, well-defined organic moeities allows for a more detailed evaluation of the sources, processes, sinks, transport

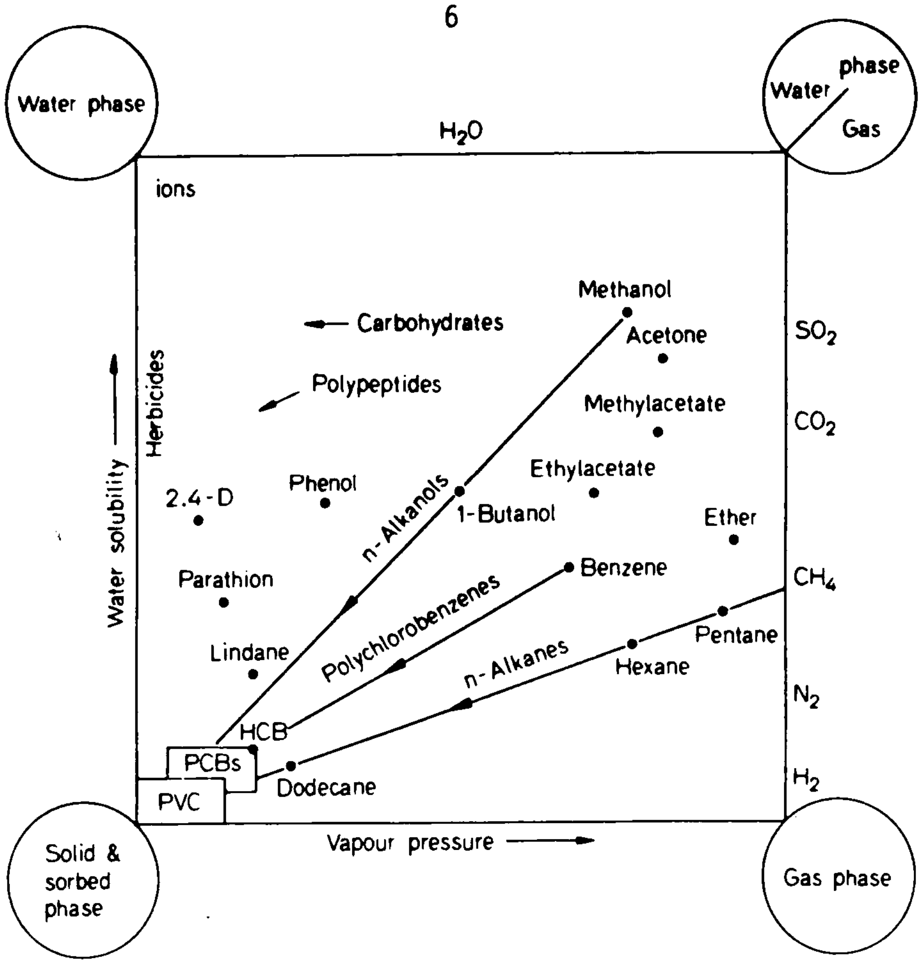

Figure 2. Water solubility and vapour pressure of organic chemicals (from Bruggeman, 1982).

pathways and kinetics. The available data base on the riverine flux of synthetic organics is at present limited to a few studies which have employed high resolution techniques capable of accurately quantifying components in complex mixtures. The following considerations of the riverine transport of synthetic organics will be based for the most part on examples of the behaviours of well-defined compounds and their biogeochemical interactions in the aquatic environment. Discussions presented in Appendix IV attempt to evaluate to what extent the measurements of "bulk parameters" may assist in the understanding of river transport and the limitations of such measurements for quantitative interpretations. The focus of these discussions will be placed on the neutral hydrophobic organics since many of their physical chemical properties have been extensively documented and from this group many model contaminants may be selected for which adequate high resolution techniques exist to quantify individual components with related chemical structures but with widely ranging physical properties affecting their partitioning between the dissolved and particulate phases.

2.3.3.2 Phase Distribution of Synthetic Organics

In addition to an appreciation of the organic composition of river water and the likely association (or the activity) an introduced synthetic organic compound may have in the presence of natural materials, fundamental to an evaluation of the contaminant's transport and fate is an understanding of the chemical setting amongst the constituents of the natural dissolved and particulate fractions of river water and the distribution (both equilibrium and non-equilibrium) of the contaminant between the particulate and dissolved forms (Appendix IV). Consideration of the physico-chemical properties of the contaminant is important in modelling the behaviour of such materials. These aspects are treated in more detail in Appendix IV for the case of neutral hydrophobic contaminants which exhibit a wide range of affinities towards particles.

2.4 Influence of River Hydrology on Riverine Transport

Estimation of the transport of chemical constituents by rivers is a task of considerably greater complexity than it first appears. Although the discharge, or flux, of constituents can be represented by

$$\text{Flux} = \sum C_n \cdot V_n = \int_0^t C_n \, V_n dt$$

where C and V are the instantaneous values of concentration and volume of river flow across a channel section respectively, the determinations of C needed in combination with measurements of flow for all discharge regimes requires considerable effort. C is a complex and varying function of V as well as a variety of other factors. There have therefore been attempts, described in Appendix V, to parameterize C in adequate detail to permit the estimation of chemical fluxes from a river hydrograph which essentially represents V as a function of time. In seeking appropriate parameterizations of C, the manner in which C responds to, or varies with, various features of the hydrology of single rivers has been examined