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- GESAMP -

REPORTS AND STUDIES

No. 32

Land/Sea Boundary Flux of Contaminants: Contributions from Rivers

United Nations Educational, Scientific and Cultural Organization

Reports and Studies No. 32

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Land/Sea Boundary Flux of Contaminants: Contributions from Rivers

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.

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APPENDICES

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

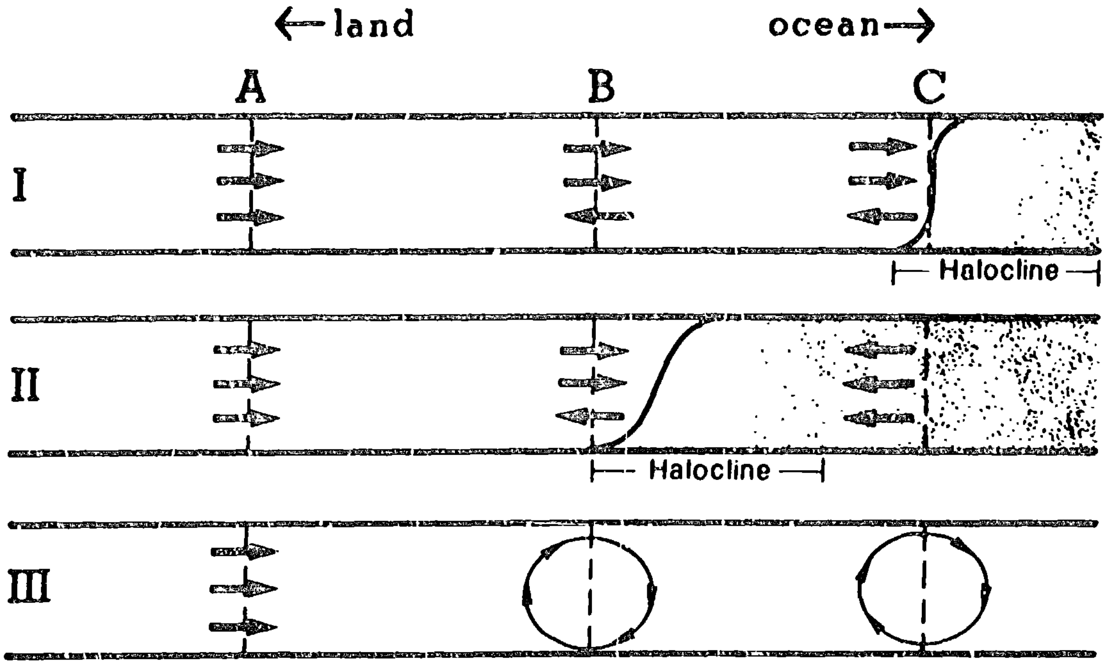

Figure 1 Schematic diagrams of the river-estuarine boundary.

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

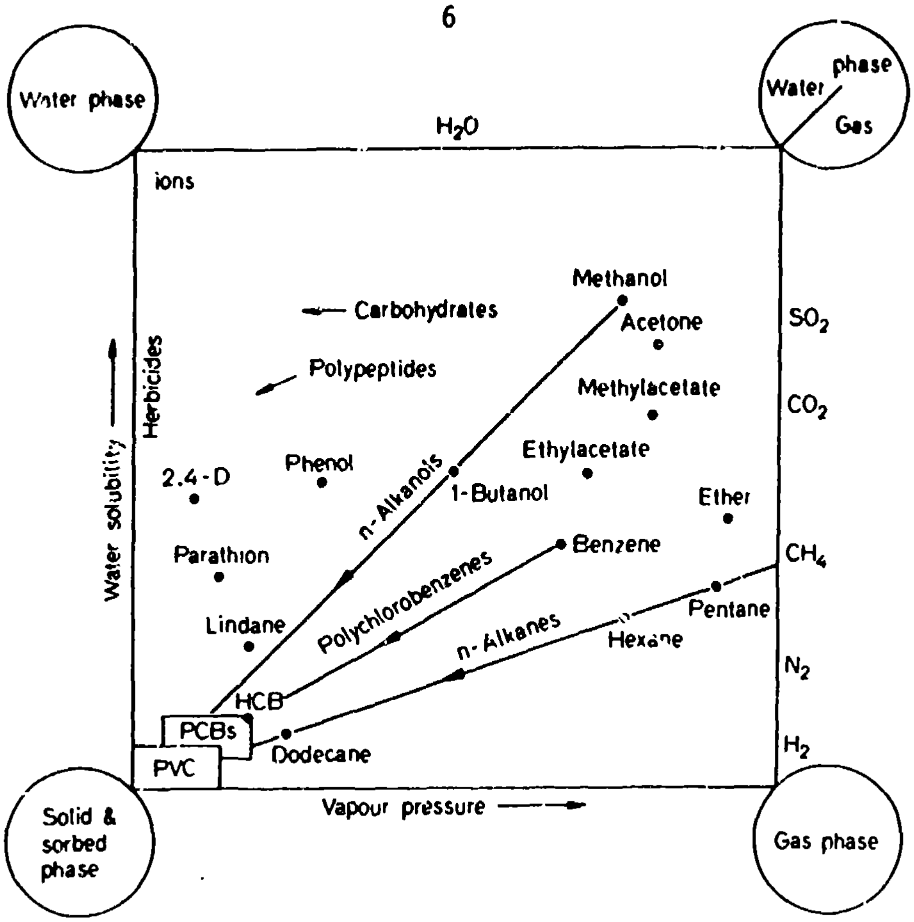

Figure 2. Water solubility and vapour pressure of organic chemicals (from Bruggeman, 1982).

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 and this is also discussed in Appendix V. It is common for dissolved species to have a chemograph (i.e., the plot of chemical constituent with time during an annual cycle) that is a simple inverse of the river hydrograph. In such situations, there tends to be less contrast in the seasonal chemical discharge than in the flow hydrograph. Some dissolved constituents (e.g., NO_3-N) have a much more asymmetric annual chemograph and exhibit highest concentrations during periods of highest flow so that seasonal contrasts are enhanced. Other substances, transported in particle-associated form, are mobilized together with sedimentary material. Since suspended sediment transport is usually much more episodic and responds to extrema in high-flow conditions in the river basin, the chemograph of particle-associated constituents tends to be dominated by episodic transport induced by storm transients. Climatically-induced features of the river hydrograph can also affect the discharges of chemical constituents. Mountainous regions, supporting seasonal accumulations of snow or the formation and maintenance of glaciers, are often characterized by periods of intense river flow separated by more quiescent conditions. In such areas, the dissolved and particle-associated chemical fluxes may be concentrated into relatively short pre-breakup and breakup periods of ice and snow melting. Similarly, the areas having considerable seasonality in atmospheric precipitation, such as savanna and 'Mediterranean' regimes, will also be characterized with marked variations in river flux.

It is often possible to represent the general response of dissolved and particle-associated substances to changing flow in streams and rivers by means of a simplified 'rating relationship' which can take the form

$$C = aQ^b$$

where C is chemical concentration, Q is river flow and a and b are constants. Although the use of rating relationships has been developed and refined by subdividing data on the basis of season, stage conditions, and flow components, and by using more complex functions, recent work in this area has stressed the complexity and variability of storm-period sediment and solute responses. These responses are considerably more complicated by hysteresis and antecedent accumulation of materials in the drainage basin. The reservoir of material available for transport in a storm event is, to some extent, dependent on the length and season of antecedent conditions during which potentially-mobile or soluble material accumulates in the drainage basin. Thus the length of time during which the antecedent conditions persist, prior to the storm event, will have a direct influence upon the river composition during the storm event itself when previously accumulated material is transported in runoff. Hysteresis in storm-event mediated transport occurs because the reservoir of accumulated material in the drainage basin may be continuously and rapidly depleted during the storm and this results in asymmetry in the relationship between chemical concentration and flow during the storm. Similarly, the frequency of storms, and the variability of quiescent periods between storms, has an effect on the store of material available for transport and the basin may have 'memory effects' related to the number and intensity of previous extrema in storm-induced flow. Other factors contributing to hysterisis are the relative partitioning of runoff between surface and sub-surface flows, which may be a function of storm intensity and duration, and the effects of seasonality in biological activity within the basin.

There is a general tendency for fluvial transport to become more dominated by transients as catchment size (drainage basin size) decreases. Nevertheless, even large rivers can have major portions of their chemical constituent transport controlled by transient events and there is a need therefore to pay particular attention to the characterization of flow and constituent concentration during such events.

As the scale of the drainage basin increases and its climatic, geological, topographic, soil and vegetational regimes become more diverse, the variability in chemical concentrations in downstream locations of a river becomes more complex and fluxes more difficult to predict. However, such heterogeneity in conditions may also make the chemograph (and hydrograph) somewhat less susceptible to periodic extrema than in smaller basins. The presence of lakes and often-inundated floodplains in river systems can considerably modify the transport of particle-associated materials by providing temporary or permanent sinks for the deposition of suspended particulate material. In such situations sediment yields per unit area often decrease and sediment transport becomes a more discontinuous process involving periodic storage and remobilization of material as the size of drainage basins increase.

In a global context, chemical concentration and composition are known to be well differentiated according to climate (Meybeck, 1979; 1983) and data from 500 rivers (Walling and Webb, 1983a) reveal total dissolved solids concentrations and loads to be clearly correlated with mean annual runoff. Although mean total and individual solute concentrations tend to decrease with increasing runoff because of a dilution effect, the reverse trend is true for the flux of both total and individual dissolved substances. This clearly demonstrates that greater water flow through a basin results in increased flux of dissolved constituents. Other factors, most notably catchment lithology (Meybeck, 1981), introduce scatter into the above relationship between flux and runoff and the real representation of such relationships has been the subject of considerable debate. Similar uncertainties have complicated attempts to estimate global sediment fluxes and to link authoritatively particulate material transport with hydrological parameters. The continuing process of improved data acquisition means that estimates of regional and global runoff and particle transports to the ocean are in need of continuous revision. Current estimates of these values are 3.74 10^{16} $kg \cdot a^{-1}$ for global riverine water runoff (Baumgartner and Reichel, 1975) and 1.55 10^{13} $kg \cdot a^{-1}$ for suspended sediment discharge by rivers (Meybeck, 1977).

It should be appreciated that not only does fluvial transport vary spatially but also temporally. Some temporal variation in river composition may be a result of anthropogenic activities. One of the aims of this report is to determine how the human influences upon river transport of contaminants might be measured and an assessment made of the net effect on natural influxes of chemicals to the marine environment. These subjects are discussed in greater detail below (section 4) and in the Appendices to this report.

2.5 Needs for Improvement of Estimates of Regional and Global Gross River Fluxes

Estimates of the global runoff of trace constituents from rivers have generally been derived from scaling of the fluxes of chemicals from individual major rivers. Examples are estimates for cadmium and nickel derived from scaling of the Amazon discharge (Boyle *et al.*, 1976; Sclater *et al.*, 1976); and for a number of trace metals by scaling of fluxes in the Mississippi (Trefry and Presley, 1976) and the St. Lawrence Rivers (Yeats and Bewers, 1982). With similar aims, studies of other large river systems such as the Yangtze and Orinoco have been also conducted (Boyle *et al.*, 1982; Grant *et al.*, 1982).

While such projections of global runoff fluxes from individual rivers are useful and undoubtedly warranted, it is likely that they provide relatively inaccurate estimates of global river fluxes of chemicals. This is discussed in some detail in Appendix III. It only requires a small bias in the degree to which a single river is representative of world runoff to make the global estimate prone to serious error. Furthermore, the study of single rivers, especially large rivers having very diverse climatological, lithological, biological and demographic regimes, within their drainage basins is unlikely to provide the degree of insight into the actual features which control river composition and the discharge of chemicals, required for reliable global extrapolation. Clearly then, it might be reasonable to assume that a less biased basis for estimation of global fluxes of natural trace chemicals might be obtained by examining data from a number of major rivers. This approach, which has been employed by Martin and Meybeck (1979) and Shiller and Boyle (1985), must also be used with caution since as noted by Holland (1978) the aggregate runoff from the largest 20 world rivers only accounts for 31% of the estimated world runoff and the largest rivers, as might be expected, drain the wettest areas of the globe. It would seem far more suitable to approach the estimation of global runoff fluxes of chemicals by obtaining data from a number of rivers representing a range of climatic, geological and biological environments. If this approach were used it might be possible to scale the fluxes for regimes having similar drainage basin characteristics to obtain better representation of the diversity of continental conditions. Such an approach would also have advantages in focusing investigations on the factors which control the mobilization of substances in river runoff thereby allowing somewhat greater confidence in the scaling process. Furthermore, it appears that there may be reason to choose rivers and drainage basins for compositional and flux studies more on the basis of the degree to which they represent particular hydrological, climatic or geological regimes rather than on the basis of size. This assumes that there should exist discernible relationships between natural trace chemical compositions (specifically trace metals and nutrients) of rivers and the various characteristics of their drainage basins. Such relationships clearly exist for the major dissolved constitutents of rivers (Livingstone, 1963; Gibbs 1967; Reeder et al., 1972; Stallard and Edmond, 1983) and it appears reasonable to assume that there are similar controlling factors that determine trace compositional characteristics. It is thus concluded that detailed studies of the mobilization of natural trace chemicals in small river systems having geological, topographic, vegetational, and climatic regimes more representative of various continental conditions be increased. The emphasis on these studies should be to elucidate the natural riverine compositional features in terms of the drainage basin characteristics. Such studies could later be extended to comparisons between similar basins which are subject to differing anthropogenic influences, due to either population density or industrial activity, to investigate the nature and extent of anthropogenically-mediated chemical mobilization.

3. NET LAND-SEA FLUXES

3.1 General

In the previous Chapter we have defined the nature and location of the river/estuarine boundary at which measurements of concentration, flow and flux pertain to gross riverine transport. Many of the chemical constituents transported by rivers to the sea are transformed or removed from water during transport through the estuarine and continental shelf environments. Thus, to understand the transport of chemicals into various regions of the ocean, particularly the deep ocean, it is necessary to determine what the net fluxes of river-transported chemicals are at some offshore boundary. An equally valued product of the net flux determination, when complemented with a gross estimate, is the estimate of what proportions of river-transported materials that are retained within estuarine, nearshore or shelf environments. Such estimates allow for the assessment of the effects of such retention on amenities and communities of these areas.

River discharges are only one of several mechanisms of material input to the marine environment. Others include atmospheric deposition, air/sea gas exchange, sub-marine volcanic emanations and remobilization of material from marine sediments. However, the two major mechanisms of recent anthropogenic material transport to the marine environment are atmospheric transport and deposition and river discharge. Both of these pathways of contaminant introduction to the ocean are of considerable interest from both environmental protection and marine geochemical perspectives. From the geochemical perspective, particularly in relation to the study of the fluxes and processes of transport to the deep ocean, understanding the net transport of river-derived material to the ocean is essential.

3.1.1 Objectives of Net-Flux Measurements

The determination of net fluxes of river-derived materials across marine boundaries has a number of uses in both regulatory and scientific domains. From a scientific perspective it is useful to gain deeper insight into the processes controlling the transport and fate of materials. This insight is often aided by flux measurement and mass-balance construction for geochemical purposes. In environmental regulation, it is often valuable to gain an appreciation of the effects of discharging certain materials to the marine environment through rivers or pipelines. This requires insight into the transport and fate of materials as well as an appreciation of the manner in which the natural concentration field is disturbed by the introduction of anthropogenically-mobilized materials, thus allowing for an assessment of the effects of such changes on marine organisms and amenities.

3.1.2 Boundaries for Net Flux Determination

In order to deal with net fluxes it is necessary to define what a net flux is and the boundaries across which a flux measurement corresponds to a net transport rate. Net flux is the rate of transport of material, derived from river discharge, in an offshore direction across defined marine boundaries in units of mass/time. These boundaries are defined on the basis of identifiable marine regimes for which the influx and efflux of river-derived chemicals is of interest. The first such region is the estuarine environment. In general terms an estuary is a place where most of the mixing between river-derived freshwater and seawater occurs. A formal definition of estuaries has been offered by Fairbridge (1980) as "An estuary is an inlet of the sea reaching into a river valley as far as the upper limit of tidal rise, usually being divisible into three sectors; (a) a marine or lower estuary, in free connection with the open sea; (b) a middle estuary subject to strong salt and fresh water mixing and (c) an upper or fluvial estuary, characterized by fresh water but subject to daily tidal action." Closely related to estuaries hydrologically, but different in terms of physical geography, are sounds, lagoons, and deltas. Fairbridge (*op cit*) stressed that "the bulk of world's estuaries have only been in existence for the last 6,000 years, since then they have been progressively infilled, aided by an eustatically oscillating sea level and by sedimentation, furnished either from rivers, or by onshore and longshore drift. Where the fill has been principally from river-borne sediments, a delta grows at the expense of the estuary ... where longshore drift is dominant, a lagoon or sound (a larger equivalent) is created due to the growth of barrier islands..."

Perhaps the only major modification to this definition that would be useful in the context of this discussion is the replacement of tidal limits by specification of flow direction. The use of the 'limit of tidal rise' in Fairbridge's definition is insufficiently precise since tidal activities take place in all bodies of water no matter where they are located. We have, in Section 2.2 adopted a definition of the downstream region of a river as the point at which flow throughout a section is unidirectionally downstream under all tidal and flow conditions.

With such alteration to the landward limits of an estuary, Fairbridge's definition is a useful one. It should be noted that the downstream (offshore) units of an estuary are defined largely by geographical constraints and can be interpreted as the baseline between the offshore headlands.

Beyond estuaries, in most cases, the region becomes that of the continental shelf. Thus another definable region in terms of the net influx of contaminants to the ocean is the region between the offshore limit of the estuary and the continental shelf break. This is illustrated diagramatically in Figure 3. There also exists rather more loosely-defined regions such as the "coastal zone". In cases where this term is employed in this document, it will be generally used to cover the region between the river boundary (Section 2.2) and the continental shelf break. There are, however, several special cases which do not fit this generalized classification. Among these are oceanic islands which may have estuaries but instead of having continental shelves have only narrow island platforms. Other rather more important special cases are regional seas such as the North Sea, the Baltic Sea, the Mediterranean Sea and the Gulf of St. Lawrence which can be clearly defined in geographical terms but which often contain both estuarine and continental shelf components. In such cases it is possible to consider estimating net effluxes of river-borne contaminants from these systems at geographically or hydrographically-defined sections.

We therefore have the opportunity to define net fluxes as either those across downstream estuarine boundaries into continental shelf regions, those across geographically defined boundaries of marginal sea systems, or those across the continental shelf break into the deep ocean.

Fluxes across the first of these boundaries (i.e. the estuarine boundary) are often of the most interest to multilateral regulatory authorities, although in some cases fluxes across marginal sea boundaries are also of concern. In the interest of assessing changes in contaminant fluxes to the global ocean, it is most often fluxes across the last of these boundaries, the continental shelf break, that is of particular interest. The boundaries of marginal sea regions may often be of primary interest as sections across which fluxes can be more easily quantified and for providing insights into aspects of coastal zone modifications to land/sea fluxes of material.

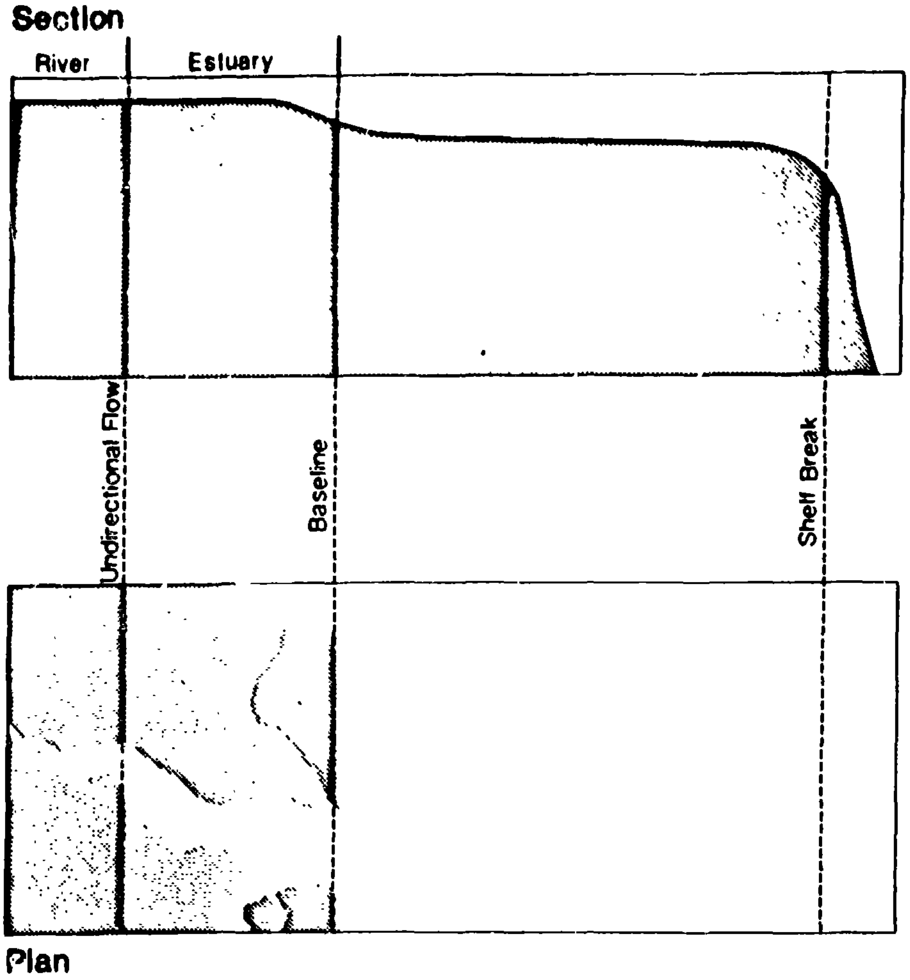

Figure 3. Schematic diagram of a cross-section and plan view of the "land-sea boundary".

3.2 Processes Controlling Net Fluxes

The processes occuring in estuarine and continental shelf environment that have direct bearing on the modes of transport, removal and augmentation of nutrients, trace metals and synthetic organic compounds are similar to processes occurring elsewhere in the marine environment. However, there are certain characteristics of estuaries and shelves that result in these processes assuming greater importance here than elsewhere. These characteristics that are typical of most estuarine/shelf environments are:

1. pronounced spatial gradients in the physico-chemical properties of water;

2. pronounced spatial gradients in the concentration of particulate matter;

3. pronounced changes in the types and composition of suspended particulate matter;

4. high biological activity; and,

5. intense mixing and advection.

Processes of major importance in terms of modifying the modes and rates of transport of chemical constitutents are discussed in Appendix VI and may be chemical, physical or biological in nature. Chemical processes include precipitation and dissolution, particle-water exchange reactions, photo- and chemical degradation and complexation with organic material. The dominant biological processes involve incorporation of chemicals into living material and the subsequent release of these constitutents during regenerative processes. Organisms can also cause effects due to the uptake and release, in chemically changed forms, of certain chemicals. Physical processes include advection, mixing, sedimentation and resuspension.

The specific affects of these processes and others on the net flux of the types of substances discussed in this report are described in detail in Appendices II, III and IV.

3.3 Methods of Estimating Net Fluxes

It has been pointed out above that in this report net fluxes apply to the transport of material across the boundary between the continental shelf environment and the pelagic ocean basins. Thus, the processes that are responsible for the removal of material in the coastal zone are those occurring both in estuaries and on continental shelves. However, the extent to which these processes modify river discharge fluxes is likely to vary from extreme, for minor river runoff into large slowly flushed shelf regions, to small, in the case of rivers having external estuaries on narrow continental shelves such as is the case of the Amazon. This argument is based upon the premise that the longer the residence time of water on the shelf, the greater is the time for removal to occur. There are also varieties of continental shelf environments that will have a pronounced effect on the nature and extent of coastal zone removal. Rivers discharging into constrained marginal seas having limited exchange with offshore shelf waters, such as the Baltic Sea and the Gulf of St. Lawrence, are likely to have smaller net discharges into the deep ocean than similar rivers discharging directly into narrow, well-flushed shelf areas. It is this very heterogeneity of conditions that makes the estimation of net riverine influxes so difficult. Simplifications can be made to obtain crude estimates of the relationships between gross and net riverine fluxes for particular types of environments such as has been done for the Gulf of St. Lawrence (Bewers and Yeats, 1977) and the Baltic Sea (Brugmann, 1984), but it will be necessary to obtain estimates for other types of coastal/shelf areas and river sizes. None of these approaches, will however, serve any purpose in the absence of reliable estimates of gross river fluxes of contaminants and sufficient insight to be able to scale such discharges to different hydrological and geological regimes (see Sections 2.3 and 2.4 and Appendices III and V). Therefore, it is absolutely essential that early attention be given to improving the present knowledge of gross river fluxes.

During the last decade there has been accelerated interest in the study of estuaries, and it is now possible to gain some idea of the extent of removal processes and the difference between gross and net riverine fluxes for a variety of estuarine types. However, the number of constitutents for which such information is available is somewhat limited and has not changed substantially since the assessment of the subject during the SCOR River Inputs to Ocean Systems (RIOS) Workshop in 1979 (UNEP and UNESCO, 1981). Furthermore, in defining net fluxes as those pertaining to transport across the shelf/deep ocean boundary, processes of removal on the continental shelves, beyond the estuarine regions, are also involved in the modification of gross riverine fluxes and are, for some constitutents, likely to be as important as, or more important than, processes in estuaries.

In its simplest form, the problem of relating gross and net river fluxes of chemical constitutents can be expressed in the following way. The global coastal zone has a number of influxes and effluxes which can be assumed to be in quasi steady-state over reasonably long periods of time for constitutents that have not had their fluxes systematically or episodically, augmented by natural or anthropogenic processes (this does not imply that it may be assumed that any particular coastal zone regime is in internal steady state). The influxes to the coastal zone comprise gross river discharge, sea water inflow, atmospheric deposition and release from estuarine and shelf sediments through remobilization processes (see Appendix VI). Effluxes from the zone comprise mixed water outflow, sedimentation and any volatilization or aerosol ejection to the atmosphere. There are thus seven fluxes involved in the mass balance and it would be necesary to quantify any six of these to derive the seventh. This is likely to be an intractable problem, even if some of the fluxes can be neglected on the basis of an assumption that they are insignificant relative to others. A gross assumption might be made that the difference between gross and net riverine fluxes is largely accounted for by net sediment accumulation within the coastal zone, but, in view of the heterogeneity of sediment deposition and composition, the mass balance would still be an extremely difficult equation to solve. It would, however, be worthwhile to attempt to quantify the fluxes of certain constituents by direct measurements in areas that are amenable to identification of the carrier water flows. In this respect, it would be more justifiable to give greater attention to marginal seas having well-defined hydrographic regimes, within which it might be possible to make direct measurements and comparisons between constituent fluxes. The recent improvement in the accuracy, precision and, above all, intercomparability, of the methods for determining certain contaminants (e.g. trace metals) would certainly justify renewed attention to marginal sea areas such as the Baltic Sea, the North Sea, the Irish Sea, the Gulf of St. Lawrence and the Mediterranean Sea, for which the major hydrographical fluxes have been defined. The type of model developed by Bethoux (1980) for water transports in the Mediterranean is very suitable for these purposes and justifies evaluation as a means of estimating chemical constituent fluxes in that sea. It may well be that the hydrographic understanding for these, and other similar, areas is qualified by uncertainties, but this should, in no way, be used as an excuse for not attempting preliminary estimation of the influxes and effluxes of contaminants taking due account of the uncertainties involved.

An alternative approach to the problem might be to examine salinity/contaminant and nutrient/contaminant relationships on continental shelves in an attempt to characterize the major variability within the coastal zone so that the relationships between contaminant concentrations and hydrographic features can be determined. This would then provide a basis for estimating net fluxes in terms of the hydrographic understanding of particular shelf regions and the broad-scale exchanges of water between the deep ocean and continental shelf areas. It is worth noting that coverage of the distributions of trace contaminants in the global coastal zone is not very extensive, especially when the likely heterogeneity of conditions is considered. In this respect, it should be remembered that while assumptions of steady-state conditions can often be made for the deep ocean, such conditions are unlikely to be general properties of continental shelf regions. Heterogeneities in shelf waters are both spatial and temporal and, in consequence, studies of shelf waters need to be much more intensive than those in the deep ocean. It is perhaps time for greater attention to be paid to the study of trace contaminants in shelf areas in relation to the effort devoted to the collection of high-quality chemical data from the deep ocean and localized studies of estuaries. It must, however, be stressed that the precisions and accuracies required for the inshore work are similar to those required for investigations in the deep ocean. With such new data it might be possible to construct some models for typical coastal zone types with which to at least estimate the magnitudes of net contaminant fluxes. The type of work undertaken by Kremling (1983) is an example of the kinds of study that would be useful in this connection. Similarly, extensions of the type of study carried out by Bruland and Franks (1983) and Windom and Smith (1985), with greater emphasis on the relationships between chemical substances and salinity and nutrients in continental shelf waters, would also be valuable.

Another method for the estimation of net fluxes which has received considerable attention in recent years is the global mass-balance approach. This procedure is necessarily rather crude and subject to a great deal of criticism because of the uncertainties involved in constructing such budgets. However, the approach does provide a means of assessing the reasonableness of results obtained from other methods of calculating net fluxes. It also provides a check on the overall geochemical consistency of such fluxes. For crude estimates of the net river flux to the pelagic ocean, the mass-balance equation can be reduced to three major terms: the gross river influx, the atmospheric depositional flux and the pelagic sedimentation flux. It is implicit in this approach, however, that a steady-state balance is assumed. This is unlikely to be an acceptable assumption for a wide variety of artifical organic comounds which have accelerated rates of dissemination in recent years or which degrade during transport within the ocean. Even for some of the inorganic contaminants, such as lead and cadmium, an assumption of steady-state is either untenable or questionable. The accumulation of additional gross river flux information would assist in determining whether elements like cadmium have significantly augmented fluxes caused by anthropogenic activity. Such increased dissemination, relative to the natural fluxes of the elements, should show up as systematic variablity in riverine concentrations when the geological and hyrologic characteristics of individual drainage basins are taken into account.

All three of the above approaches are valid for the increased understanding of geochemical cycles and net riverine fluxes to the ocean. The suitability of each approach will vary with the particular region of the coastal/shelf enviroment being dealt with. However, at this juncture, no one approach holds superior promise to another and each should continue to be used in the solution of this problem.

In this discussion, particular emphasis has been placed upon the processes of contamination removal on continental shelves in order to counterbalance the disproportionate attention devoted to the study of estuaries. Sedimentation outside the deep ocean basins does not all occur within estuaries. Removal of contaminants from dissolved and particulate phases in the coastal zone water column occurs both within estuaries and beyond them, on the continental shelf and slope. While considerable attention has been paid to process and mass-balances in estuaries, comparatively little attention has been devoted to the quantification of removal outside estuaries, which also has the effect of reducing the 'net' or residual fluxes of contaminants to the ocean from terrigenous sources. This is particularly critical for contaminants that are removed from the water column by association with accumulating sediment particles but which may subsequently be remobilized by regenerative and diaggenetic processes. Such remobilisation is probably of greater significance in regions of slowly accumulating sediments (i.e. low sedimentation rates) as exist in large areas of the continental shelf and slope.

Conditions in continental shelf waters should vary from those dominated by estuarine mixing, at the inshore end, to those dominated by deep oceanic biological processes, at the offshore end. The extent to which these differing regimes control the removal of land-derived materials needs to be defined, but it must be stressed that this is likely to be extremely difficult given the great heterogeneity of conditions in such regions.

4. ESTIMATES OF NET LAND/SEA FLUXES

4.1 General

In the following sections of this chapter attempts are made, where possible, at estimating net land/sea fluxes of three categories of contaminants; nutrients, trace metals and synthetic organic compounds. The estimates discussed below are generally for the global ocean but primarily are presented to demonstrate the applications of approach introduced in Section 3.3 and to indicate the type of information that is required to make such estimates. The discussions also serve to identify deficiencies in the quantity and quality of existing data that are required to make estimates of land/sea fluxes.

Although the focus of this report and the estimates of land/sea fluxes presented below are on river transport, direct land/sea fluxes also occur due to natural processes (i.e. runoff). On a global scale these are not quantitatively important but for some regions such as islands, where river systems are not developed, direct runoff will be the major natural transport mechanism for land/sea fluxes of contaminants. For this reason a brief discussion of two approaches to estimating land/sea fluxes due to runoff from islands is presented in the Section 4.5.

4.2 Nutrients

4.2.1 Introduction

Most of the early estimates of global river fluxes of nutrients are limited to an evaluation of the gross river fluxes obtained by multiplying average river concentrations by an estimate of the global river discharge (Livingstone, 1963; Turekian, 1971; Garrels et al., 1973; Stumm, 1973). These evaluations were rather satisfactory for dissolved inorganic nutrients. The general reliability of analytical measurement of nitrate, ammonium, reactive phosphorous and silicon is good and there is an extensive data base covering temporal and spatial variations for many regions, especially in developed countries. The data for dissolved organic N and P compounds and for the particulate forms which have to be considered for flux estimations are much less extensive and reliable. Furthermore, the fluxes of nitrogen and phosphorus through river estuarine systems have become greatly modified by the increased concentrations of these elements in runoff from agricultural land as a result of the use of fertilizers and the discharge of domestic and industrial wastes. Many of the existing estimates are based on a restricted number of rivers, do not consider some specific forms of N and P, (in particular the organic and particulate form) or do not take into account the influence of man's activities.

Van Bennekom and Salomons (1981) were the first to publish a rather complete world budget of N, P and Si based on a dozen major rivers, including some highly polluted ones. They estimated indirectly the fluxes of N and P due to specific activities of man (domestic, agricultural, industrial). Meybeck (1982) has published a more complete budget of N and P based on an extensive set of data. The natural levels considered in his calculations are based on major rivers for the subarctic and tropical zones and on small rivers for temperate zones which are still unpolluted. Extrapolation of the data to the global flux of nutrients was obtained by considering specific transport rates and drainage areas corresponding to various climatic and morphologic environments. The same typology was used by this author to evaluate the fluxes of dissolved silica (Meybeck, 1979). The increase of the concentration of nutrients in rivers due to man's activities was discussed by Meybeck in terms of per capita loadings in a given watershed.

Natural gross river fluxes, anthropogenic fluxes and net fluxes to the ocean based mainly on the data of Van Bennekom and Salomons (1981) and on those of Meybeck (1979; 1982) will be discussed successively in the following sections.

4.2.2 Natural Gross River Fluxes

4.2.2.1 Dissolved Nitrogen

The first estimate of the global nitrate flux was obtained by Livingstone (1963) by multiplying a mean concentration of NO_3 in rivers (220 ug $N.NO_3$/l) by a global river discharge estimated at $3.24 \cdot 10^{16}$ l/y which gives a flux of $7.13 \cdot 10^{12}$ gN/y. The effect of man's activities was minimized by considering only very early measurements of the concentration of nitrate in a few European and American rivers.

By selecting the data for dissolved inorganic nitrogen (DIN) concentrations in rivers of thinly populated regions, Van Bennekom and Salomons (1981) obtained a mean value of 15 umoles/l. Since the contribution of ammonium is negligible, this value corresponds roughly to the concentration of NO_3. This mean value (210 ugN/l) is similar to the one given by Livingstone. These authors considered an equal contribution of organic dissolved N as being likely. Meybeck (1982) calculated a weighted average concentration of nitrate by considering values for a more extensive set of unpolluted rivers, classified in five major climatic zones, and found 100 $ugN{\cdot}NO_3/l$. Natural concentrations of ammonium and nitrite were calculated by the same author indirectly by considering mean proportions of $N\text{-}NH_4$ and $N\text{-}NO_2$ in the dissolved inorganic fraction (DIN), estimated to be of the order of 0.15 and 0.015, respectively. The resulting concentrations calculated were 15 ug $N\text{-}NH_4/l$ and 1.5 $ugN\text{-}NO_2/l$).

The data concerning dissolved organic nitrogen (DON) in rivers are more limited and Meybeck (1982) used two parameters to estimate the mean value of this component: the C/N average ratios for dissolved organic carbon or the DON/DIN average ratios usually observed in various climatic regions. The weighted average obtained with the first parameter is 300 ugN/l and with the second parameter 260 ugN/l. Table 1 summarizes the data concerning export rates and fluxes of dissolved nitrogen in unpolluted rivers.

4.2.2.2 Particulate Nitrogen

The data concerning the concentration of particulate nitrogen in unpolluted rivers is limited to a dozen of cases. Besides a small and negligible amount of ammonia which may be fixed by clay minerals, particulate N is mainly present in the organic fraction. Therefore, Meybeck (1982) used his budget of particulate organic carbon (POC) as a basis of the estimation of the concentrations and fluxes of particulate organic nitrogen (PON). As shown in Figure 4, this author found a very good correlation between PON and POC indicating a C/N ratio of 8.5 in the river suspended organic matter. The average content of nitrogen in the suspended matter obtained by Meybeck was 1200 ppm, which corresponds to a mean concentration of PON equal to 560 ugN/l and a global flux of $21{\cdot}10^{12}$ gN/y).

4.2.2.3 Dissolved Phosphorus

Stumm (1973) has estimated the mean concentration of phosphorous in unpolluted streams mainly on the basis of chemical considerations and has proposed 20 ug $P\text{-}PO_4/l$ for orthophosphate and an equal amount of dissolved organic phosphate (DOP). Using the same approach as for N Van Bennekom and Salomons (1981) suggested a value of 0.2 to 0.3 uM for othophosphate and of 0.5 uM for the total dissolved phosphorus. Meybeck (1982) has estimated his budget of orthophosphate on a simple discharge-weighted average and obtained 12.5 ug $P\text{-}PO_4/l$. From an average estimated ratio of $P\text{-}PO_4/TDP$ (total dissolved phosphorus) 0.4 for the few rivers for which data exists, this author obtained a mean value for the concentration of dissolved organic phosphorus (DOP) of 15 ug P/l.

TABLE 1

EVALUATION OF NATURAL GROSS RIVER FLUXES OF DISSOLVED NITROGEN

	NO_3	NO_2	NH_4	DIN	DON	TOTAL	AUTHOR
conc. flux	220 7						Livingstone (1963)
conc. flux				210 7	 8	 15	Van Bennekom and Salomons (1981)
conc.	100	1.5	15	∿115	260	375	
export rate	-	-	-	40	100	140	Meybeck (1982)
flux	3.7	neg	0.6	4.3	9.7	14	

concentrations in μg N/l

export rates in $kg/km^2 \cdot y$

fluxes in 10^{12} gN/y

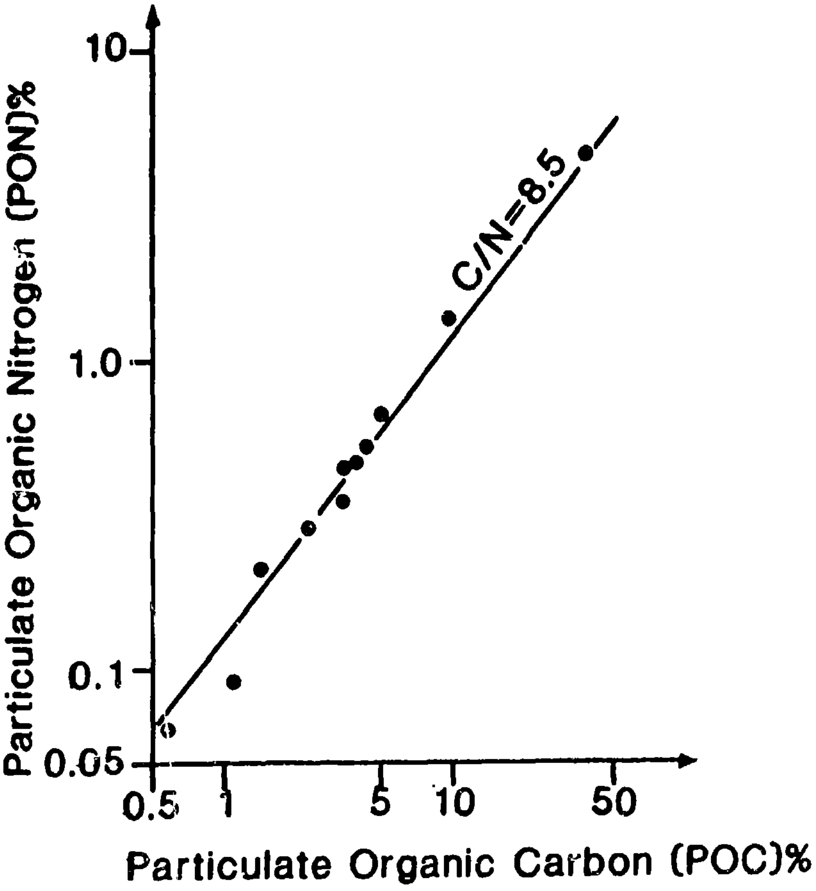

Figure 4. Contents of particulate organic carbon and particulate organic nitrogen in river suspended matter (from Meybeck, 1982).

4.2.2.4 Particulate Phosphorus

The concentration of particulate organic phosphorus (POP) was estimated by Meybeck (1982) on the basis of the very few existing measurements. The observed mean PON/POP ratio in rivers is around 2.5. A large amount of data exist for the concentration of total particulate phosphorus. The world average concentration is around 1150 ppm (Martin and Meybeck, 1979). Combining the data, 450 ppm is obtained for the concentration of organic P and 700 ppm for that of inorganic P in suspended matter. The mean concentrations, export rates and fluxes of the various forms of phosphorus discussed here are summarized in Table 2.

4.2.2.5 Dissolved Silicon

Dissolved silicon is one of the major dissoved elements in river water and its distribution is very well documented. Livingstone (1963) estimated a global mean value of 6.1 mg Si/l based on a weighted average river discharge. A more extensive set of data, especially from some large rivers, and the use of specific transport rates for various environments led Meybeck (1979) to propose a slightly lower value: 4.85 mg Si/l. This value gives a total gross river input of dissolved silica of $181 \cdot 10^{12}$g Si/y and corresponds to a mean continental export rate of 1800 kg Si/km^2·y. The extreme paucity of the data concerning suspended opal in the aquatic system does not permit any evaluation of the river flux of this component.

4.2.3 Anthropogenic Fluxes

The nutrient fluxes in rivers related to man's activities have been estimated by a variety of approaches including comparison of concentrations of N and P species in pristine and polluted streams, historical evolution of these concentrations in some large rivers or direct estimations of fluxes due to domestic, agricultural or industrial activities. Large discrepancies are found when these approaches are used on a global scale. They are briefly shown and discussed below.

The increase of dissolved inorganic N and P species in the river Rhine reported by Van Bennekom and Salomons (1981) is shown as an example in Figure 5. These authors attribute the gradual increase in nitrate and ammonium to the increase in the use of fertilizers between 1950 and 1979. They suggested that the subsequent increase of nitrate and decrease of ammonium observed after 1970 is due to the large-scale introduction of secondary treatment in sewage purification plants in Germany. The sudden increase in phosphate around 1960 was due to the introduction of detergent polyphosphate. Van Bennekom and Salomons (1981) claimed however that it is difficult to extrapolate the present-day river transport from the existing data and that better estimates may be obtained from an evaluation of the inputs related to various activities. Table 3 summarizes their estimates of the fluxes related to various pollutant sources. These figures must be viewed with appropriate caution because of the restricted amount of data available for many countries.

Figure 6 shows the mean concentrations of nitrate in relation to phosphate for important river systems (adapted from Kempe, 1982). In this diagram, the industrial rivers plot in the right hand upper corner and the tropical,

TABLE 2

EVALUATIONS OF NATURAL GROSS RIVER FLUXES OF DISSOLVED AND PARTICULATE PHOSPHORUS

	DISSOLVED			PARTICULATE			TOTAL	AUTHOR
	INORG	ORG	TOT	INORG	ORG	TOT		
conc.	20	20	40	-	-	-	-	Stumm (1973)
conc.	8	8	16	-	-	-	-	Van Bennekom and Salomons (1981)
flux								
conc.	12.5	15	28	320	210	530	560	Meybeck
export rate	4.5	5.5	10	120	80	200	210	
flux	0.4	0.6	1	12	8	20	21	

concentrations in μg P/l

export rates in kg P/km^2·y

fluxes in 10^{12} gP/y

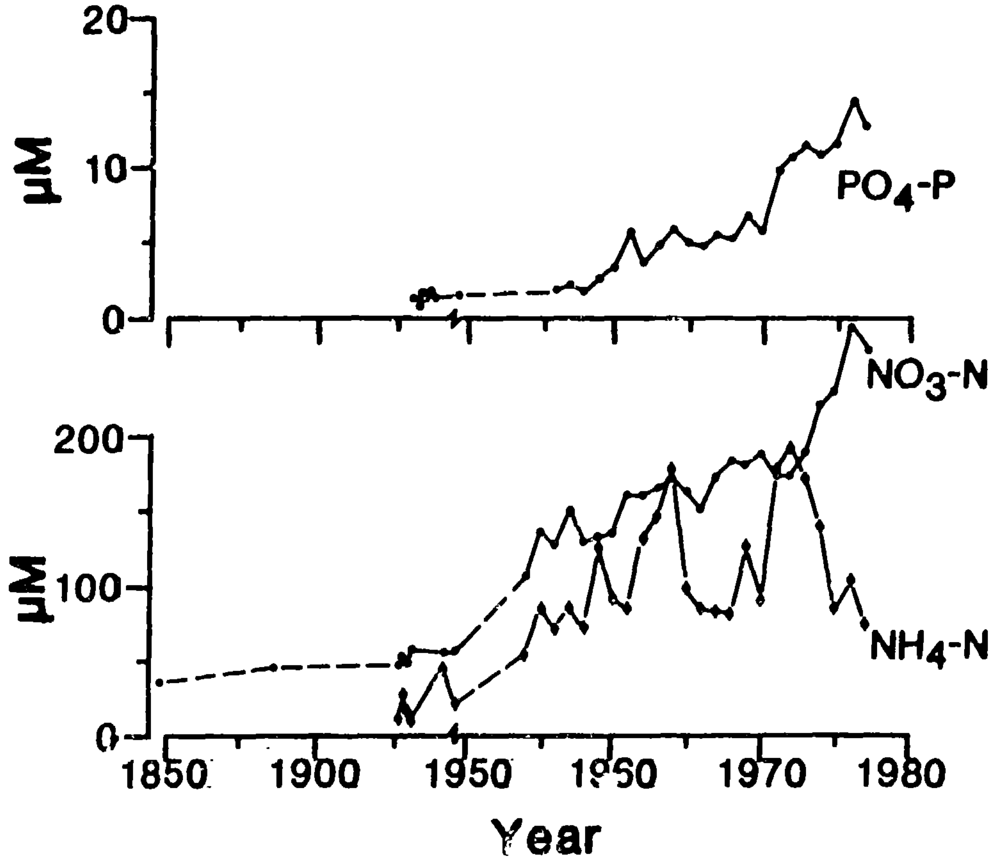

Figure 5. Evolution with time of the concentrations of dissolved inorganic N and P in the river Rhine. Annual averages measured at Rhenen, the Netherlands. After Van Bennekom and Salomons (1981).

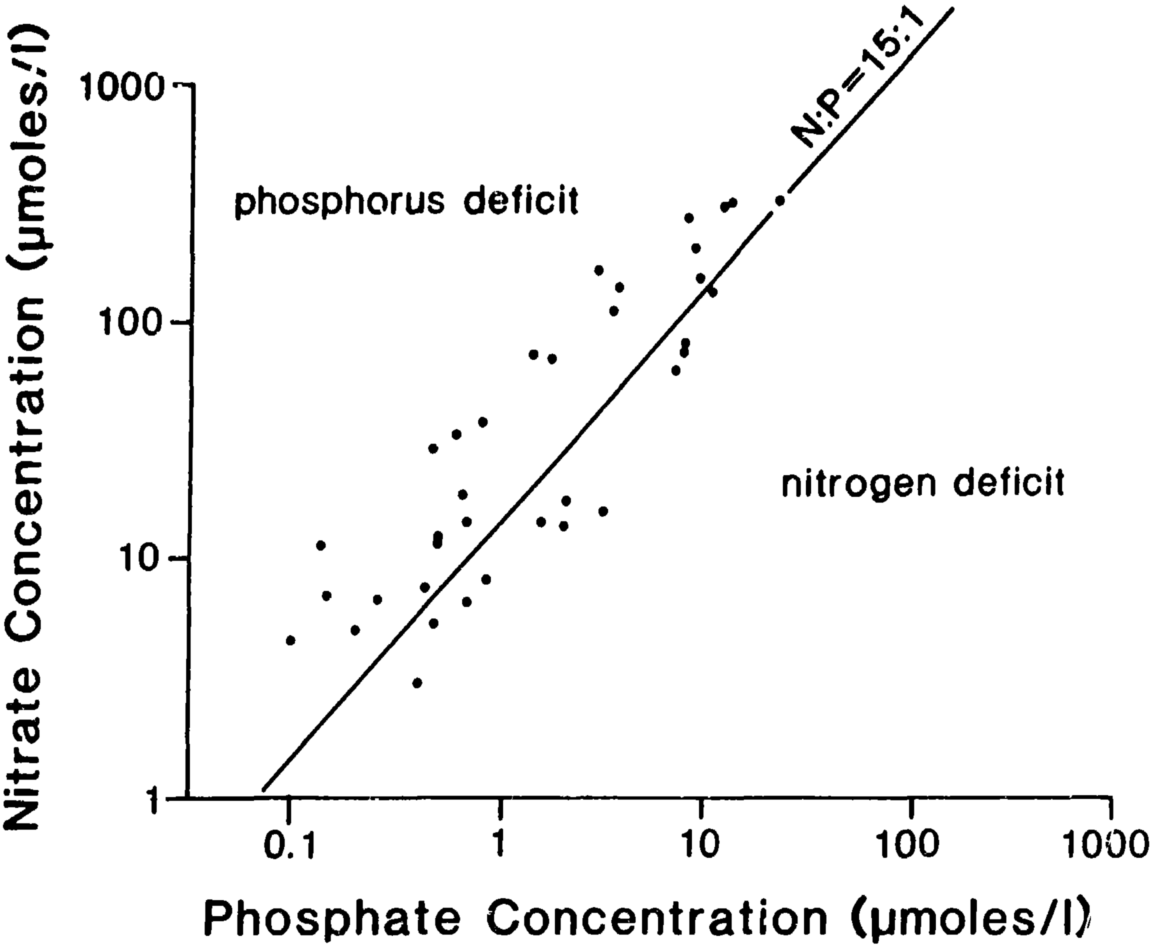

Figure 6. Comparison of the orthophosphate-nitrate relations for various rivers of the world (from Kempe, 1982).

relatively unpolluted, rivers plot in the lower left corner. It becomes evident that the nutrient transport through the small temperate rivers from highly industrialized regions plays a far more important role today than the world's largest rivers like the Amazon or the Zaire. It is on the other hand interesting to note that the increase of concentration of nutrients follows closely a N/P ratio equal to 15 which corresponds to the mean composition of organic matter in marine as well as in the fresh water phytoplankton (Redfield ratio).

The influence of man on the increased concentrations of nutrients can be analyzed in terms of per capita loading by dividing the increase in concentration in a given river by the total population in the watershed (Meybeck, 1982; Wollast, 1983). On this basis, Wollast (1983) obtained a mean extrapolated annual per captia load of 7 kg N/y and 0.2 kg P/y. However, this per capita loading reflects somewhat the state of development of each country and the water uses in each watershed. The highest values are calculated for Europe (10 kg N/y and 0.4 kg P/y) and the USA (8 kg N/y and 0.5 kg P/y) but much lower values are calculated for poorly developed regions like Java (0.4 kg N/y and 0.02 kg P/y). Meybeck (1982) used a correlation between a "demographic" index, based on the amount of energy used per capita in a given region, and the per capita loading of nutrients to evaluate more carefully the global nutrient fluxes due to man's activities. His extrapolations are given in Table 3.

Although there are still some large discrepancies between the estimates of the various authors it is obvious from a comparison of Table 3 with Tables 1 and 2 that the anthropogenic flux of dissolved nutrients is at least comparable to, and probably already significantly larger than, the natural fluxes. Except for the estimates of increased flux of particulate N and P due to soil erosion made by Van Bennekom and Salomons (see footnote Table 3) there are no other data available on a global basis.

4.2.4 Net Fluxes of Nutrients to the Open Ocean

As decribed in detail in Appendix II, the nutrients are extensively involved in biological, chemical and physical processes which can affect their transfer from rivers to the open ocean. The result of these processes is mainly the removal of the dissolved nutrients N, P and Si from the water column and their transfer to the sediments. A significant amount of nitrogen may also be lost to the atmosphere by the denitrification process. Thus only a small fraction of the river input of nutrients may be transferred across shelf areas to the open ocean. Net fluxes to the ocean are, however, difficult to evaluate due to the complexity of the mechanisms involved, but also because coastal areas are often upwelling zones, which constitutes, in addition to the river input, another source of nutrient supply, greatly complicating mass balance calculations.

A long term mass balance calculation of the N and P accumulating in open ocean sediments may give some insight into the possible mean net fluxes under steady-state conditions on a geological time scale. According to a recent review by Berner (1982), the rate of accumulation of organic C in pelagic sediments is $5.7 \cdot 10^{12}$ g C/y. Assuming a molar C/N ratio close to 15 for organic matter preserved in those sediments (Wollast, 1981), one obtains a rate of accumulation of organic N of $0.44 \cdot 10^{12}$ g N/y. This represents only 3% of

TABLE 3

ESTIMATIONS OF ANTHROPOGENIC FLUXES OF DISSOLVED NUTRIENTS IN RIVERS

(in 10^{12} g/y)

Authors	N	P
Stumm (1973)	-	0.6
Lerman *et al*. (1975)	-	1.8
Söderlund and Swensson (1976)	18	-
Delwiche and Likens (1977)	35	-
Van Bennekom and Salomons (1981)		
domestic	11	1.7
agricultural(*)	8	0.35
industrial	13	1.7
Total	32	3.75
Meybeck (1982)	7	1.0
Wollast (1983)	21	1.7

(*) Particulate N and P fluxes due to land erosion estimated as 28 x 10^{12} g N/y and 10 x 10^{12} g P/y by these authors.

the natural dissolved river input or approximately 1% of the total (dissolved plus particulate) river input.

According to Froelich et al. (1982) the mean $(C/P)_{org}$ molar ratio for deep-sea sediments is about 100 (close to the Redfield ratio). This would give an output flux of organic P of approximately $0.15 \cdot 10^{12}$ g P/y for the deep ocean. The inorganic phosphorus flux linked to the burial of phosphate bound to $CaCO_3$ skeletal material would represent, following the same authors, an equal flux giving a total flux of around $0.3 \cdot 10^{12}$ g P/y. This amount represents 30% of the dissolved river input, but only 1.5% of the total river input.

Similar calculations for silica are not possible due to the lack of data concerning the concentrations and fluxes of opal in the aquatic system.

Although there are very large uncertainties in the figures obtained in the above estimations, they nevertheless indicate that only a very small fraction of the river input of nutrients reaches the open ocean, as one may expect from the intense utilization of these elements by the biota in the estuaries and in the coastal zone. The river input thus accounts for a negligible fraction of the supply of nutrients required to support the primary productivity of the open ocean which is mainly supplied by upwelling processes or vertical turbulent mixing. The increase of the river input due to man's activities will probably have no marked influence on the the open ocean system on a short or medium time scale. It may on the other hand have a drastic effect on the coastal environment, although light seems to rapidly become the limiting factor of primary production in these eutrophicated environments.

4.3 Trace Metals

4.3.1 Gross Influxes

As outlined in Chapter 2.5 the use of individual river compositions to estimate global runoff fluxes for trace chemical constitutents is fraught with uncertainty. However, these uncertainties are usually not so great as to preclude order-of-magnitude (or better) estimates of gross global river discharge fluxes of trace metals. It should be noted that a great deal of insight into the overall flux of elements through the ocean has been gained from classical geochemical investigations (Clark, 1928; Horn and Adams, 1966, etc.) in which the geological evolution of sedimentary rocks has been quantified on the basis of weathering rates and excess volatile element emissions. This situation results from the early ability to conduct geochemical analyses of trace element constituents (i.e., in the ug/g concentration range) in rocks and sediments whereas the abilities for ultra-trace determinations of elements in aqueous carrier phases, such as rivers and seawater, has been a relatively recent development. Early attempts to quantify the dissolved trace element composition of river water (e.g., Livingstone, 1963) were limited by analytical inaccuracies. Even more recent compendia of dissolved river compositions of this kind (Martin and Whitfield, 1983) have also warranted revisions as the technology for elemental analysis of aqueous media has been further improved and applied to river water. This situation is less likely to apply to the case of compendia of the compositions of suspended particulate material discharged by rivers since such measurements do not usually involve such difficult ultra-trace analysis and sample contamination is less pronounced. Nevertheless, there are analytical errors associated with such measurements and revision of estimates based on them should also be undertaken as new and more reliable data are obtained. One additional point needs to be made before presenting estimates of gross riverine fluxes of trace metals in dissolved and particulate form. Most of the available data for riverine particulate matter composition pertains to total analyses based upon sample digestions with hydrofluoric acid in combination with other strong acids. A portion of the particulate forms of elements will be associated with the crystalline aluminosilicate lattice material (see Appendix III) and will essentially remain conserved within particulate material on time-scales far longer than those involved in transport to, and deposition in, the ocean. Such fractions are of no concern in terms of their effect upon the concentration field of elements in the ocean itself. The particulate fractions which are more loosely bound in various exchangeable forms are of direct concern in these respects since they also contribute, with the dissolved phase, to the supply of reactive chemical constitutents that can effect the concentration fields within the ocean.

If we use the data for mean dissolved and suspended particulate composition of rivers, modified by recently-reported dissolved data for As, Cd, Co, Cu, Hg, Pb, Ni and Zn shown in Tables A.III-1 and A.III-2, we can obtain estimates of the overall gross riverine influxes of elements to the marine environment. These flux estimates, together with dissolved transport index DTI and K_d values are given in Table 4. It must be noted however, that the K_d values will be larger than the true representation of equilibrium exchange partitioning because the detrital element fraction is included in the particulate values.

4.3.2 Net Fluxes

As stated in Section 3.3, there are several approaches that can be used for estimating the net fluxes of riverine transported materials to the ocean. The mass-balance approach has been used by various workers with some of the earliest attempts being, from an empirical modeling base, Horn and Adams (1966) and from field measurements and calculations Windom et al. (1971). Two of the regional sea areas that have received major attention for the development of mass-balances and for the estimation of net fluxes have been the Baltic Sea (Brugmann, 1986) and the Gulf of St. Lawrence (Bewers and Yeats, 1977; Yeats and Bewers, 1983). These latter authors first calculated that 94.5% of the suspended matter delivered by rivers to the Gulf of St. Lawrence is retained as semi-permanent sediments within the Gulf. They then constructed mass-balances for a number of trace metals for this system (Figure 7) taking account of both dissolved and particulate forms, to determine the fractions of riverborne metals that were retained and sedimented inside the Gulf or transported beyond the offshore boundary of the Gulf to the North Atlantic Ocean (Bewers and Yeats, 1977). The results for the Gulf of St. Lawrence were then scaled up to the global case by making an assumption that the Gulf of St. Lawrence was representative of average estuarine-continental shelf environments and that the St. Lawrence River was representative of world runoff composition. The results of these scaled up balances are presented in Table 5 and are compared with estimates of the accumulation rate of the metals in pelagic sediments. As can be seen from this Table there exists good agreement beween the net riverine discharge fluxes and pelagic sedimentation fluxes for SPM, Fe, Mn, Co, Ni, and Cu to within a fraction of 2. In

TABLE 4

GLOBAL GROSS RIVER FLUX OF TRACE METALS

	DTI	K_d	Gross River Flux ($kg \cdot yr^{-1}$) Dissolved	Particulate
As	12.8	$1.7 \cdot 10^4$	$1 \cdot 10^7$	$7.8 \cdot 10^7$
Cd	2.38	$1 \cdot 10^5$	$3.4 \cdot 10^5$	$1.5 \cdot 10^7$
Co	0.61	$4 \cdot 10^5$	$1.7 \cdot 10^6$	$3.1 \cdot 10^8$
Cu	0.73	$3.3 \cdot 10^5$	$1 \cdot 10^7$	$1.5 \cdot 10^9$
Fe	0.20	$1.2 \cdot 10^6$	$1.4 \cdot 10^9$	$7.4 \cdot 10^{11}$
Hg	2.38	$1 \cdot 10^5$	$3.4 \cdot 10^4$	$1.6 \cdot 10^6$
Mn	1.87	$1.3 \cdot 10^5$	$2.8 \cdot 10^8$	$1.6 \cdot 10^{10}$
Pb	0.15	$1.7 \cdot 10^6$	$2 \cdot 10^6$	$1.6 \cdot 10^9$
Ni	0.89	$2.7 \cdot 10^5$	$1.1 \cdot 10^7$	$1.4 \cdot 10^9$
Zn	0.16	$1.5 \cdot 10^6$	$5.8 \cdot 10^6$	$3.9 \cdot 10^9$

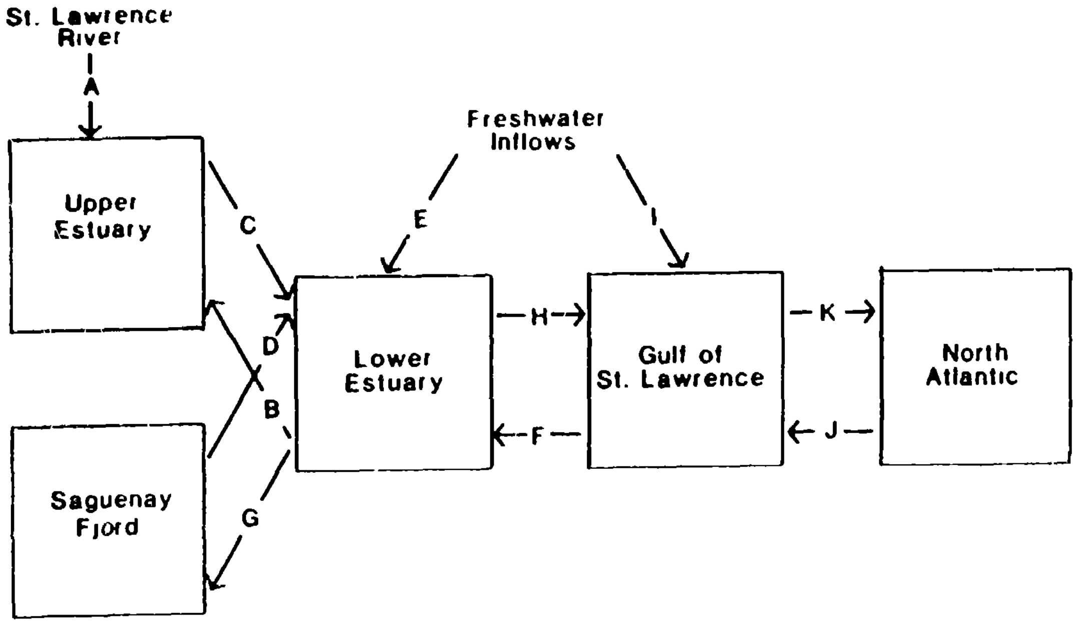

Figure 7. Model of the St. Lawrence system.

Table 5

MASS BALANCE CALCULATIONS

	Units	SPM	Fe	Mn	Co	Ni	Cu	Zn	Cd
Annual outflow from St. Lawrence River	kg yr^{-1}	4.4×10^9	3.8×10^8	1.0×10^7	1.4×10^5	7.6×10^5	1.4×10^6	2.2×10^6	1.2×10^5
River flux corrected for nearshore losses	kg yr^{-1}	3.08×10^6	4.18×10^7	5.3×10^6	1.05×10^5	6.69×10^5	1.25×10^6	2.20×10^6	1.02×10^5
Particulate fraction at Cabot Strait	kg yr^{-1}	100	65	11	4	1.3	0.7	0.2	0.02
Global dissolved flux	kg yr^{-1}	-	1.08×10^9	3.48×10^8	7.42×10^6	4.86×10^7	9.11×10^7	1.62×10^8	7.51×10^6
Global particulate flux	kg yr^{-1}	1.26×10^{12}	1.11×10^{11}	2.39×10^9	1.72×10^7	3.56×10^7	3.57×10^7	1.80×10^7	8.35×10^4
Sum of global dissolved and particulate fluxes	kg yr^{-1}	1.26×10^{12}	1.12×10^{11}	2.74×10^9	2.46×10^7	8.42×10^7	1.27×10^8	1.80×10^8	7.59×10^6
Oceanic sedimentation rate	kg yr^{-1}	1.5×10^{12}	1.0×10^{11}	2.0×10^9	3.9×10^7	1.7×10^8	8.0×10^7	7.8×10^7	6.3×10^5

Global dissolved flux based on scaling river water discharge to world river runoff of 3.24×10^{16} kg yr^{-1}. Livingstone (1963).

Global particulate flux based on scaling river particulate discharge to world river sediment discharge of 1.8×10^{13} kg yr^{1}. Haleman (1968).

contrast, the fluxes for cadmium differ by about an order of magnitude and those for zinc by about a factor of three. It was concluded by the authors that this might be due either to the localized increased Cd concentration of the St. Lawrence River due to anthropogenic activities or because the inaccuracy of the cadmium and zinc measurements in this river.

In a later paper (Yeats and Bewers, 1983) the net fluxes were re-evaluated using more comprehensive time-series measurements of the St. Lawrence River trace metal concentrations (Yeats and Bewers, 1982). In this case, a global mass balance was used to determine the extent of transformation of metals from particulate material sedimented on continental shelves to dissolved or water-transportable particulate forms (Table 6). In this latter work both Zn and Cd again show that the net effluxes from the coastal zone are considerably larger than the accumulation of other metals in pelagic sediments, again suggesting that either the St. Lawrence River concentrations of Cd and Zn are unrepresentative of global runoff or that considerable mobilization of these elements in the St. Lawrence drainage basin is occurring through anthropogenic activities.

Another approach to net flux calculations is the extrapolation of element/salinity ratios in surface ocean transects as discussed by Kaul and Froelich (1984). A number of such transects have now been analysed for various oceanic regions and the regressions of elements on salinity defined. The zero-salinity intercepts of a number of these regressions are shown in Table 7 covering the Arctic Ocean (Canadian Basin), Hudson Strait, Scotian Shelf-Sargasso, U.S. South Atlantic Bight, the central western Atlantic off the Amazon River, the Northeastern Atlantic, the Northeast Pacific and the Gulf of Thailand.

As can be seen there exists considerable variability in these zero-salinity intercepts although in most cases they are within an order of magnitude. The most extreme variations are for nickel, which has a comparatively high intercept for the northeast Atlantic and a comparatively low intercept for the Amazon plume, and cadmium for which the Arctic and Northeast Atlantic intercepts are relatively high. The general distribution of intercepts might suggest that the effective runoff end-member is highest in the eastern North Atlantic and that this seems to be most pronounced for Mn, Ni, Cu and Cd.

The average values for these intercepts have been used to calculate the net runoff fluxes of each of these elements on the assumption that the average value represents the effective composition of the freshwater end-member for mixing with global oceanic waters. These values are presented in Table 8 together with estimates of net runoff derived from the Gulf of St. Lawrence mass-balances and the accumulation rates of the elements in pelagic clay. It should be noted that such a comparison ignores the accumulation of the elements in other pelagic sediment phases such as carbonates, and polymetallic concretions.

It is interesting to compare the two independent estimates of the net fluxes of elements to the pelagic environment. For nickel, copper and cadmium the two estimates are essentialy identical but for manganese, cobalt and zinc the St. Lawrence mass-balance estimation yields values that are significantly higher than those calculated from the zero salinity intercept approach. When the two independent oceanic flux estimates are compared with the rates

TABLE 6

RESULTS OF GENERIC COASTAL ZONE MODEL
(After Yeats and Bewer, 1982)

Component	Global River Discharge Flux ($kg\cdot yr^{-1}$)	Net Efflux from the Coastal Zone ($kg\cdot yr^{-1}$)	Proportion Redistributed in the Coastal Zone (%)	Pelagic Sediment Concentration	
				Predicted	Observed
SPM	$1.8\cdot10^{13}$	$1.0\cdot10^{12}$	-	-	-
Al	$1.4\cdot10^{12}$	$7.8\cdot10^{10}$	0	7.8%	8.0%
Fe	$9.2\cdot10^{11}$	$5.5\cdot10^{10}$	0.2	5.3%	5.8%
Mn	$2.2\cdot10^{10}$	$7.9\cdot10^{9}$	31	5600	4000-12,500
Co	$3.0\cdot10^{8}$	$7.8\cdot10^{7}$	21	61	38-116
Ni	$1.5\cdot10^{9}$	$2.3\cdot10^{8}$	8	180	72-293
Cu	$2.5\cdot10^{9}$	$5.8\cdot10^{8}$	34	410	130-570
Zn	$5.4\cdot10^{9}$	$2.8\cdot10^{9}$	46	1900	130
Cd	$3.0\cdot10^{7}$	$1.3\cdot10^{7}$	31	8.5	0.5

TABLE 7

ZERO-SALINITY INTERCEPTS OF METAL-SALINITY REGRESSIONS

REGION	Mn ug/l	Ni ug/l	Cu ug/l	Zn ug/l	Cd ug/l	Pb ug/l	Co ug/l	REFERENCES
ARCTIC (Canadian Basin)	1.1	1.7	2.5	3.2	0.45			Yeats (private communication)
HUDSON STRAIT	4.0	0.8	2.0	3.3			0.06	Yeats (private communication)
SCOTIAN STRAIT	2.5	1.3	1.1	1.0	0.14			Yeats (private communication)
SARGASSO SEA	6.27	1.2	1.2	1.0	0.12			Bruland and Franks, 1983
SOUTH ATLANTIC BIGHT	6.05	1.5	2.1	0.4	0.08	0.04	0.03	Windom and Smith, 1985 Windom _et al_., 1985
AMAZON PLUME		0.23	1.6		0.01			Boyle _et al_., 1982
NORTHEAST ATLANTIC	7.7	9.4	5.8		0.65			Kremling, 1985
NORTHEAST PACIFIC		1.4	4.6		0.025		0.35	Knauer _et al_., 1982 Bruland, 1980, Maeda, 1987
GULF OF THAILAND	8.23	0.9	1.3	1.0	0.02	0.03	0.04	Windom _et al_. (unpublished data) Windom _et al_., 1987

of element accumulation in pelagic clays only in the case of cadmium do the fluxes greatly differ from the sedimentary removal rates. These data, as presented in Table 8 suggest that both the mass-balance and salinity regression approaches are valid means of estimating net riverine fluxes. There may well be differences in the flux values yielded by these independent methods if significantly greater removals of dissolved elements occur at higher, relative to lower, salinitities or if the regional sea mass-balances only partially represent the true element removal rates for the entire global continental shelf. In these respects the respective data for manganese are particularly interesting. While the mass-balance projection yields a net flux that is comparable with the removal rate to pelagic clays, the zero salinity intercept gives a flux that is an order of magnitude lower. Coarser riverine particulate material discharged over the Gulf of St. Lawrence can accumulate in sediments that are only oxidizing in a thin surface layer. Reducing conditions release manganese from sub surface sediments and permits the manganese in Mn^{2+} form to diffuse into the overlying water column. This manganese slowly oxidzes and precipitates on fine suspended particles which have low settling rates and are able to be transported out of the Gulf in water outflows (Yeats *et al.*, 1978). These conditions may be atypical of average shelf sediments which may be either coarser or lower in organic content resulting in a much thicker layer of oxidized sediments. This would explain the much higher net effluxes of manganese from the Gulf of St. Lawrence than from an "average" continental shelf area of equivalent size.

4.4 Estimation of Net Fluxes of Synthetic Organics

The following section attempts to describe to what extent the available data may be used to estimate the net fluxes of synthetic organics, particularly the neutral hydrophobic compounds in their dissolved and particulate associations.

Although most of the organic pollutants considered are persistent, microbiological or chemical degradation processes ultimately will serve to decay these compounds. The extent of these processes may depend on environmental conditions, e.g. temperature dependent microbial attack. The flux calculation should, therefore, take into consideration the half-lives of these contaminants (as in the case of radionuclides) if the residence times in the estuaries, shelves or marginal seas is a significant component in the flux calculation.

Within the limits of accuracy of determining the range of K_d's, and given the restrictions above, it is nonetheless possible to calculate the fluxes of riverborne persistent organic contaminants from the riverine end-member to the marine system on the basis of the % partitioned between solution and suspended matter, combined with the net fluxes of water and sediment load through the land-sea boundary.

4.4.1 Dissolved Fraction

An association of an organic contaminant with the DOC pool of river water may be the principal mechanism by which neutral hydrophobic substances display reasonably high concentrations in these solutions despite the presence of high amounts of potentially efficient particulate sorbants.

The behaviour of such synthetic organic constituents during initial mixing may therefore be analogous to the behaviour of DOC, which has been reported

TABLE 8

NET FLUXES OF TRACE METALS TO THE PELAGIC OCEAN

		Mn	Ni	Cu	Zn	Cd	Pb	Co
Mean zero-salinity intercept	µg/l	5.1 ± 2.6	2.0 ± 2.8	2.5 ± 1.6	1.6 ± 1.2	0.18 ± 0.23	0.03 ± 0.01	0.12 ± 0.15
Mean net flux to the ocean	$kg\cdot a^{-1}$	$1.9\cdot10^{8}$	$7.5\cdot10^{7}$	$9\cdot10^{7}$	$6\cdot10^{7}$	$6.7\cdot10^{6}$	$1.1\cdot10^{6}$	$4.5\cdot10^{6}$
Mean net flux to the ocean based on Gulf of St. Lawrence mass balance	$kg\cdot a^{-1}$	$2.7\cdot10^{9}$	$8.4\cdot10^{7}$	$1.3\cdot10^{8}$	$1.8\cdot10^{8}$	$7.6\cdot10^{6}$	-	$2.5\cdot10^{7}$
Accumulation rate in pelagic clays	$kg\cdot a^{-1}$	$2\cdot10^{9}$	$8.0\cdot10^{7}$	$8.0\cdot10^{7}$	$7.8\cdot10^{7}$	$6.3\cdot10^{5}$	-	$3.9\cdot10^{7}$

to behave conservatively in several estuaries. It should be recognized that a major component of DOC, the humic fraction, undergoes flocculation and removal in the estuary, whereas, the fulvic fraction survives passage through the estuary and its signature may be detected offshore.

Compounds with relatively high solubilities or low K_d's (e.g. lindane) have clearly been shown to behave conservatively. Compounds with much lower solubilities have a surprisingly high relative concentration in solution and in the few cases where these individual components have been studied, their solution transport appears convervative (Appendix IV).

The net flux for components exhibiting conservative mixing behaviour is simply represented by the gross riverine flux of dissolved material. Examples of constituents whose net flux may be equal to the gross (dissolved) contaminant flux include lower chlorinated hydrocarbons, lindane, selected PAH's and PCB's.

In addition to the generic processes affecting river fluxes as described under Section 2.4, Appendix V, a number of factors should be considered which may produce deviations from predicted conservative mixing behaviour of synthetic organics:

1. Atmospheric deposition along the mixing gradient including its marine end-member would result in an apparent positive deviation from linearity where as evaporation/co-distillation of volatile components would result in an apparent loss.

2. Degradation processes, such as photo and microbial degradation, chemical reactions and rearrangements along the mixing curve, if occurring over time scales comparable to the residence time in the coastal regions, would result in an apparent deviation. Less refractory materials would be influenced to a greater extent by these processes.

3. Remobilisation from bottom deposits as a result of POM (particulate organic matter) degradation could produce positive deviations from a linear mixing curve.

4. The change of K_d as a function of particle composition along the mixing curve (i.e. as a result of *de novo* synthesis, microbial colonization, bio packaging, etc.), and the time dependent reequilibration within estuary.

4.4.2 Particulate Fractions

The calculation of net fluxes of particle associated synthetic organics is fraught with problems such as variations in the rate of supply, variation in particle composition both in the river and estuary and variations in the many sources of allochtonous and autochtonous materials.

The use of sediment accumulation rates as a means of determining contaminant removal is a useful approach in the calculation of net fluxes where sediment accumulation is regular and the deposits are undisturbed (e.g. some fjords which act as very effective filters). In the absence of specific tracers for terrigineous particulate material, it is difficult to estimate how much land-derived material actually traverses an estuary. Such a tracer would provide a means of normalizing contaminant concentration in the organic fractions of particles to the actual gross flux (analogous to the use of crustal aluminum data).

An estimation of the net flux of particulate associated contaminants based on K_d's requires the following:

1. A knowledge of the concentration in solution and the Kd's of both the riverine and marine end-members.
2. An estimation of the fraction of riverine suspended matter load that escapes the shelf, which may be calculated from the deep-sea accumulation rate.

At present there exists a paucity of data to accurately determine the K_d of the offshore boundary and the deep-sea sedimentation rate of synthetic organics has only recently been studied (Knap et al., 1986; Burns et al., 1987).

An analogy may be made to the studies of river borne trace metals in making a rough assumption that approx. 5-10% of the gross river flux of particulate matter reaches the shelf break. The calculation relies heavily on the underlying assumption of true equilibrium in the partitioning of contaminants in a suspension which undergoes changes as a result of particle sorting, new production, bio-packaging, change of surface properties, etc.

In applying the approach using the data presented in Table A.IV-2 for the Rhine export of five PCB congeners to the central North Sea, it can be shown that the calculated and measured net flux are within an order of magnitude. The calculated net flux assumes a 10% efficiency in the transport of Rhine River suspended matter through the estuary. It should, however, be borne in mind that the Rhine does not constitute the sole riverine input, and that the North Sea (in fact a shelf sea) receives additional contributions of these congeners from atmospheric inputs.

4.5 Direct Land/Sea Fluxes

While a number of attempts at determining fluxes to the ocean through continental coastlines have been made, it is worth referring to two additional studies that have examined respectively gross and net runoff fluxes from an oceanic island (Jickells et al., 1986) and the nearshore distribution of contaminants issued from multiple point sources from beaches for civil engineering and public health protection purposes (French, 1986). The first of these studies deals with runoff from Bermuda, a small oceanic island in the Sargasso Sea with a relatively narrow platform compared with most Atlantic continental shelves. The authors estimated the gross runoff input and the sedimentary depositional fluxes of certain metals and nutrients in three coastal basins of Bermuda. By comparison between these fluxes the proportions of the input fluxes that were either trapped within sediments in the coastal zone or were transported offshore in water exchanges were estimated. The runoff from Bermuda is rather unusual since rivers are not involved; the types of land discharge considered by the authors are groundwater seepage, cooling water discharges (from hotel air-conditioning units), street runoff and atmospheric particle deposition. The results of this work show that large majorities of the nitrogen, phosphorus, copper, manganese, lead and zinc inputs are transported offshore by water exchange. Only iron, and to lesser extents, cadmium and nickel (for both of which the data are subject to more uncertainty), in the innermost depositional environments, are more susceptible to removal by sedimentation than offshore water transport. In the outer area of the platform, however, all constituents are predominantly transported offshore by water rather than sedimented presumably due to the less intensive sedimentation of particles in these regions.

The study by French (1986) was of a very different nature and was aimed at estimating the degree of dispersion of contaminants introduced from multiple underwater point-source inputs along a beach. The author assumed that if the density of point sources was large enough the source becomes a line source. The particular problem addressed in this study was the extent of littoral-zone contamination by sewage discharged from a series of resort hotels spread along a beach edge that discharge their sewage via underwater pipline to the littoral zone. On an assumption that multiple sewage discharges constitute a line source, the rate of sewage discharge in units of mass per second per meter of shoreline can be calculated. Seaward dispersion of the sewage was assumed to occur by waves, tides and currents with wave action being the predominant mixing agent within 100 meters of the shore, tidal exchange was based upon a simple prism analogy, and current induced mixing occurs by dispersive eddies generated by longshore drift. The analysis of the collective contributions of these dispersive processes can be used to construct concentration distributions in cross-sectional profiles of the shoreline that may be compared with field measurements. The removal of non-conservative species can be modelled by a decay rate that assumes first-order decay in the concentration of the species as a function of time. Such comparisons, although there exists wide scatter in observational values, show that, for conservative species, the theoretically derived distribution conforms approximately with experimental observation while, for non-conservative species, there appears to be reasonable conformity although higher concentrations than predicted can often be found offshore. Nevertheless, the theoretical prediction does conform to measured distributions to within an order of magnitude.

The latter study therefore serves as an example of small-scale mixing and dispersion modeling that describe the movement of contaminants offshore. This kind of treatment needs, however, to be more closely integrated with non-conservative processes of removal that represent not just a simplified removal rate but dissolved-particulate exchange reactions taking into account both the reactivity of the contaminant and the concentrations and types of particle which sequester the contaminant. Furthermore, the particulate-phase transport would also need to be modelled to account for the mixing and transport of contaminants in particulate forms.

5. CONCLUSIONS

5.1 Development of Comprehensive Strategies for the Assessment of Gross River Transport of Contaminants

There is a need for the development of comprehensive strategies for the measurement of river composition that satisfies internal national objectives for water quality measurements as well as providing data suitable for scaling to regional and global river fluxes. Meybeck (1982) discusses five different approaches for the development of global river discharge fluxes while Appendix VII of the present report describes procedures for more accurate and precise determination of individual river fluxes. An approach that attempts to obtain compositional data for a large proportion of the global runoff is largely untenable because of the large numbers of rivers that would need to be sampled intensively to yield reliable flux estimates. From the contents of Appendix VII it is clear that there will need to be compromises between the frequency of measurement in relation to flow variability and the regional accuracy and precision of the flux estimate. It is probably implicit that for such tradeoffs the best return on resource investment is to invest efforts into studies of single rivers rather than a large number in any one specific geographical regime. This, in turn, means that the greatest insights into large-scale runoff fluxes will be gained by carefully designed and intensive investigations in well-characterized rivers that attempt to discern the hydrological, geological, climatological, and demographic factors influencing river composition. This probably requires, in the first instance, intensive study of relatively small river systems with individually uniform characteristics but which among them, contain representatives of a diversity of hydrological, geological and climatological while being relative pristine in the context of human and industrial influences. Once the nature of the hydrological, geological and climatological influences on composition or rating relationships have been established, it would then be necessary to extend these investigations to similar systems having diversity in the intensity of demographic and industrial influences.

All these kinds of investigation would be presented best within an international framework in which a strategy is developed multilaterally and then implemented through individual national programs.

5.2 Cooperation Between Programs

Investigations of the composition of river water are actively and intensively pursued by a large number of national water authorities and major international programmes. While these investigations are primarily aimed towards establishing water quality and supply for human health needs and the management of human and agricultural resources, the large variety of compositional data collected in these programmes could potentially serve a wider purpose and benefit the marine scientists in their investigations of gross river fluxes of contaminants.

To achieve a degree of commonality between the objectives of the two types of investigation requires a strengthening of the cooperation between scientists to better understand the requirements of the marine scientist to make riverine flux estimates. For example, a body of literature exists on the occurrence of novel synthetic contaminants in river waters, where detection is facilitated often by localized increases in concentrations. Many of these may be source specific and suitable for use as tracers of the river's export to the seas.

To mesh the determinations of contaminants in river waters with those in the marine environment requires some standardization in the adopted analytical techniques. The marine science community recognizes the importance of the quality of the data base for a wide range of parameters. The importance of quality assurance in riverine data should be similarly recognized by individuals and/or organizations involved in such studies. Long term commitments to river transport studies by national and international agencies should be encouraged. At the present time these studies are conducted on an *ad hoc* basis. For the purpose of evaluating gross river fluxes to the ocean, long time series studies are necessary so that a data base will be obtained that is comparable to that established or being established for the oceans.

The riverine analyses most useful to the marine community, for purpose of evaluating river fluxes to the ocean, are those which are as specific as possible for individual constitutents (e.g., individual metals, specific organic compounds in either dissolved and particulate forms) and are conducted near to the mouths, but in the freshwater regime, of major rivers. These measurements should be accompanied with detailed hydrological data and concommitant measurements of major riverine characteristics.

5.3 Temporal Trend Monitoring of Contaminants in River Runoff

There has been considerable interest expressed by certain regulatory Commissions (e.g., the Oslo and Paris Commissions) in the development of procedures and protocols for detecting and quantifying temporal trends in the incidence of contaminants in the marine environment. As a result, organizations like ICES have been developing procedures for detecting trends in the incidence of contaminants in marine organisms and sediments and considering how similar trend monitoring might be achieved for contaminants in seawater. For marine embayments receiving a multiplicity of inputs, which would be difficult to characterize individually, coastal zone trend monitoring might be an expedient way of assessing overall trends subject to the adequacy of analytical precisions and the degree to which shorter-term variability can be characterized. However, for marine systems in which individual, or a small number of, rivers are likely to dominate the inputs of particular contaminants, there are reasons to consider monitoring of river compositions as a useful indicator of likely trends in the discharge of contaminants to coastal areas.

The attenuation of runoff contaminant signals by dilution, and the concomitant removal of particle-associative contaminants, during estuarine and nearshore mixing often means that changes in the concentrations of contaminants in the marine environment resulting from altered fluxes of contaminants in runoff are difficult to detect either because of the amplitude and frequency of natural variability or because of the precision limitations of current methods for the quantification of contaminants in seawater. The best signal-to-noise ratio for the detection of temporal trends, at least in terms of the concentrations of contaminants, occurs within rivers themselves and, although the consequnces of trends in the fluxes of contaminant discharge need to be determined independently in order to assess effects in the marine environment proper, it seems logical to use this enhancement of concentrations in runoff compared to the ocean to study temporal trends. It is, therefore, suggested that initial assessments of the trends in contaminant influx to the marine environment be gained through studies of the temporal variability and trends of contaminants in selected rivers. If trends are found to be systematic and substantial, or give rise to concerns regarding future effects on marine resources or amenities, the scale of such effects should be assessed on the basis of studies of the mechanisms of transport, the fate and the biological effects of these contaminants within adjacent coastal areas. It should be noted that such an approach could be combined with that discussed in 5.1 pertaining to the characterization of the gross riverine transport of contaminants. This would increase the cost effectiveness of resources devoted to the study of river composition by facilitating the application of the results of these studies to the elucidation of both short and long-term variability and its causes.

5.4 Regional Workshops and Intercalibration Exercises

To implement the strategies and approaches discussed in this report and above in 5.1, 5.2 and 5.3 there is a need to conduct regional Workshops and intercalibration exercises. The objectives of such activities would be to bring together scientists from regional academic institutions, regulatory agencies and other organizations concerned with river transport of contaminants to:

1. test methods and approaches to contaminant measurement in an effort to ensure accuracy, sensitivity and intercomparability.
2. agree on approaches for obtaining, using standardized techniques, time series data on the compositional characteristics and associated hydrologic information of rivers to estimate and compare gross chemical discharges from different rivers in the region.
3. agree on approaches to the interpretation of hydrologic and compositional data acquired during the time-series studies to gain a better understanding of the relationships between chemical discharges from rivers and drainage basin geology, climatology, demography and anthropogenic activities within drainage basins.
4. to establish suitable procedures for normalizing the fluxes of chemical substances, particularly contaminants (e.g. heavy metals, nutrients, synthetic organic compounds), in rivers to other factors such as major ion composition and components of organic carbon and drainage basin characteristics.

In the long term, the overall objective of these programmes is to collect, assemble and interpret data on the discharge of chemical constituents from world rivers in order to provide estimates of aggregate regional river discharge of chemicals into the ocean. This information can then be applied to the construction of mass balance assessments for ocean basins and marginal seas towards an assessment of the health of these systems.

5.5 Testing of Approaches to Determining Net Land/Sea Fluxes

This report gives several examples of approaches to estimating net land/sea fluxes of pollutants resulting from river transport. In all cases the examples used are based on limited data and it is therefore difficult to assess the comparibility of the different approaches. It is recommended that a limited number of case studies be conducted in different areas having different land/sea boundary characteristics. The objectives of these studies would be:

1. To assess existing limitations of data needed for different approaches.
2. To evaluate the comparability of approaches.
3. To evaluate the "cost effectiveness" of the different approaches.
4. To assess the influence of different land/sea boundary characteristics on net fluxes.

APPENDIX I

REGISTER OF RESEARCH GROUPS INVOLVED IN CHEMICAL STUDIES OF RIVERS AND ESTUARIES

1. GENERAL

One of the first activities of the Land/Sea Boundary Flux of Pollutants Working Group was to circulate a questionaire to a wide sector of the scientific community involved in studies of the fluxes of materials to the seas through rivers and estuaries. The objective of this questionaire was to obtain information to address the following questions:

1. Which organizations throughout the world are conducting studies of material (i.e. pollutant) transport by rivers?
2. Which river systems are being studied?
3. Which classes of pollutants are being studied, what are the nature of the studies and what are the approaches being used?
4. What are the major difficulties encountered?
5. How adequate are hydrologic data for the purpose of estimating fluxes?
6. What information exists on river transport studies other than that available from the published literature?

The questionaire was initially circulated by the UN agencies network. Additionally, members of the Working Group helped to identify other individuals and/or groups conducting river-estuarine studies to which the questionaire could be also sent.

Based on the responses to the questionaire the Working Group was able to take a broader perspective regarding the present state of understanding of land/sea pollutant fluxes. Although the results of this Working Group report reflects to a large degree the opinions of the Working Group members it also presents a wider perspective as a result of the questionaire.

Further activities related to river-estuarine transport may be enhanced by regional participation or correspondence among research groups from many nations. The Working Group feels that the list of individuals/groups responding to the questionaire may serve as a starting point for initial contacts. This register of research groups involved in chemical studies of rivers and estuaries, presented in this Appendix, obviously does not include a large number of such groups because of the mechanism used to circulate the questionaire. Nonetheless, it is hoped that this register will serve a useful purpose.

2. THE REGISTER

The following list of individuals and their addresses are presented alphabetically by country. Numbers after the individual's name refer to the nature of studies being conducted using the following scheme.

1. Water Quality Assessment/Pollution Studies

2. General Geochemistry
3. Nutrient Cycling
4. Organics Cycling
5. General Biological Studies
6. General Ecology
7. General Sediment Studies
8. General Water Chemistry
9. General Hydrology Studies
10. General Trace Metal Studies
11. Trace Metals - Sediments
12. Trace Metals - Solution/Suspended Particulate
13. Other

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APPENDIX II

RIVER AND ESTUARINE BIOGEOCHEMISTRY OF NUTRIENTS

1. NITROGEN

1.1 Speciation and Sources

Dissolved nitrogen occurs in many different oxidation states from -3 to +5 as inorganic constituents (NH_4^+, N_2, NO_2^-, NO_3^-) or organic ones. River water also contains organic nitrogen in living and detrital particulate matter. The most abundant form is elemental nitrogen N2 which is derived from solution of atmospheric nitrogen. Elemental nitrogen plays a rather insignificant role in natural waters since it cannot be easily utilized by phytoplankton and is in equilibrium with the atmosphere in surface waters. In the framework of the nitrogen cycle only NO_3, NH_4, and dissolved and particulate organic N have to be taken into account. The most abundant inorganic form is NO_3 which is the most stable N species in well oxygenated waters. However, dissolved organic nitrogen may be the dominant dissolved nitrogen component in rivers of the humid tropics or of the subarctic region. In temperate regions the fraction of dissolved N is more variable. It varies between 0.2 and 0.6 with a median value of 0.4 (Meybeck, 1982). Except in the cases of polluted rivers, ammonium is usually at very low concentrations. It should be noted that ammonium is often included in the so-called Kjeldalh nitrogen (N_{kj}) which measures the total reduced organic nitrogen.

Soil leaching and surface run-off are the principal sources of dissolved and particulate nitrogen in natural waters. Deforestation, soil fertilization, animal production, discharge of industrial (mainly from the food processing industry) and domestic waste waters have considerably increased the concentration of dissolved and particulate nitrogen in rivers.

1.2 Behavior in River and Estuarine System

The transfer of dissolved inorganic nutrients to the particulate fraction in aquatic systems is almost entirely biological. In river waters, the balance between production of organic matter and respiration is of primary importance. The production of organic matter is controlled by the concentration of available nutrients but is often dependent on light penetration, which is limited by the relatively high turbidity of river waters. In temperate and subarctic regions the productivity exhibits a strong seasonal variation due to temperature and light intensity fluctuations. The significance of nitrogen fixation is not likely to be very great except in some tidal freshwaters and estuarine subsystems such as saltmarshes (Nixon and Pilson, 1983) and in estuaries suffering from high phosphate input (Froelich et al., 1985).

The speciation of nitrogen in aquatic systems is further complicated by the changes which occur as a result of other biological processes. For nitrogen, in addition to the assimilatory reduction and formation of organic compounds, and the reverse bacterial process of ammonification and nitrification occurring in oxygenated environments, there are also speciation changes as a result of denitrification under suboxic and anoxic conditions, yielding N_2O and N_2. In rivers denitrification often occurs in the organic rich sediments which may induce a flux of NO_3 from the water column to the sediments. N_2 and N_2O produced during this process are transferred to the atmosphere and become unavailable for the aquatic system. Whereas denitrification is a well-documented phenomenon in many estuaries, much less is known about the alternative pathway of dissimilatory nitrate reduction to ammonia. The occurrence of this process has been demonstrated recently in estuarine and coastal marine sediments (Jorgensen and Sorensen, 1985), and deserves further investigations.

The biological processes described above may be enhanced in the estuarine and coastal zone due to the particular characteristics of these environments (see Appendix VI). For example, the anoxic or suboxic zone corresponding to the turbidity maximum may favour dentrification (Wollast, 1983). The decrease in turbidity in the more saline region associated with the presence of high concentrations of nutrients often induces a zone of high productivity where these nutrients are intensively consumed (Sharp et al., 1984).

The point within the estuary where productivity is at a maximum can vary widely relative to the river-estuary boundary. Where productivity is high the concentrations of dissolved forms of inorganic nitrogen are decreased by conversion to dissolved and particulate organic forms; the latter may be transported in suspension and rapidly remineralized (Nixon and Pilson, 1983) or may enter bottom sediments. As a result of the regeneration of soluble inorganic forms in sediments, diagenetically mediated fluxes of combined nitrogen across the sediment-water interface can be important (Vanderborght et al., 1977). The establishment of reducing conditions in sediments is facilitated by high productivity and rapid rates of sedimentation. In stratified estuaries, denitrification is common in the stagnant bottom waters which become anoxic due to the lack of exchange with the atmosphere and to the accumulation of detrital organic matter (Van Bennekom et al., 1978). Significant losses of combined nitrogen from the estuary by conversion to nitrous oxide and nitrogen gas can arise as a result of denitrification not only in the water column but also in sediments where the interface between the surface sediment and the overlying water is anoxic.

The main processes that may modify the speciation of nitrogen in the estuarine zone are demonstrated by the longitudinal profile of concentration of the dissolved inorganic nitrogen species in the Scheldt estuary (Figure A.II-1). Oxygen is depleted in the low salinity zone due to degradation of organic matter which is also responsible for the release of ammonia. Nitrate in this zone has been completely removed by denitrification and transferred as N_2 to the atmosphere. When aerobic conditions are restored in the estuary, NH_4 is oxidized to NO_2 and NO_3 by nitrifying bacteria. The concentration of NO_3 decreases when approaching the sea mouth by mixing of the river water with sea water and uptake of nitrate by the phytoplankton.

2. PHOSPHORUS

2.1 Speciation and Sources

Complications due to speciation are less for phosphorus which is mainly present in the aqueous phase as dissolved orthosphosphate PO_4^{3-}. In addition, however, dissolved organic and particulate phosphorus have to be considered for comprehensive flux calculations. In the case of polluted rivers receiving untreated domestic waste water, polyphosphate may represent a significant portion of the inorganic dissolved P. This component is however rapidly hydrolyzed and transformed into orthophosphate in the river itself.

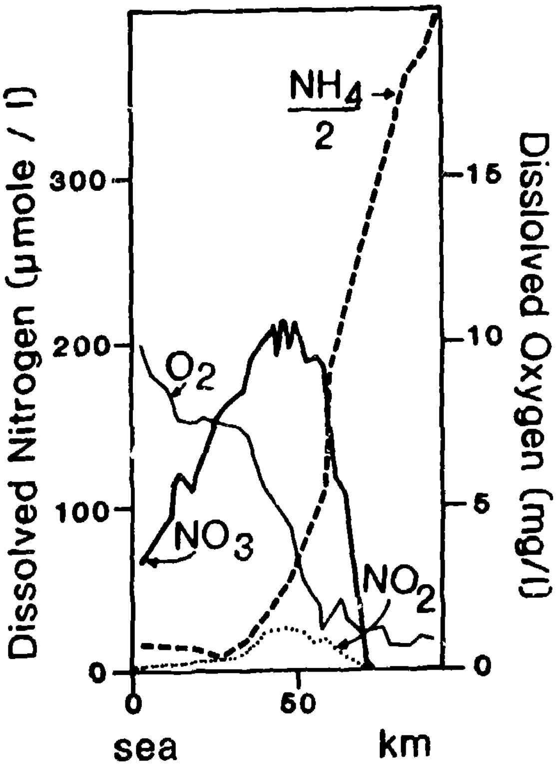


Figure A.II-1. Longitudinal profiles of dissolved nitrogen species and oxygen in the Scheldt estuary during the summer (from Wollast, 1983).

According to Stumm (1973) on the average one half of the dissolved phosphorus is in the inorganic form and its concentration corresponds to the solubility of phosphorus-bearing minerals (Ca, Fe or Al phosphates). An equal amount is present as organic phosphorus. It appears impossible to establish a trend between the concentration of phosphorus and environmental factors for unpolluted rivers (Meybeck, 1982).

2.2 Behaviour in River and Estuarine System

The behaviour of phosphorus is strongly controlled by the production and respiration of organic matter. It is often considered as the limiting nutrients in river systems if light is sufficiently available (Taft and Taylor, 1976; Fox et al., 1985). Phosphorus is also a very chemically active element and orthophosphate may be involved in various dissolution, precipitation or adsorption-desorption reactions. These chemical reactions seem to be reversible and have rather fast reaction rates. Stumm et al. (1980; cited in Stumm and Morgan, 1981) have shown that orthophosphate is adsorbed on hydrous oxide surfaces, especially Fe_2O_3 and Al_2O_3 and that this reaction is reversible. At higher concentrations, apatite may be precipitated as coatings on calcite surfaces (Morse and Berner, 1979).

In some river inputs, significant amounts of dissolved phosphates, as defined by conventional filtration procedures, can be associated with colloidal material and be subject, like 'dissolved' iron, to destablization and aggregation in the early stages of estuarine mixing (Bale and Morris, 1981). There is evidence that the behaviour of phosphate is at least partly decoupled from that of iron in such processes. Within the estuary there is also a tendency for phosphate to be converted to particulate forms by association with iron-rich oxide coatings or mineral particles. In a few estuaries, exchanges with suspended or bottom sediments appear to regulate the concentrations of dissolved phosphorus within a relatively narrow range, around one $\mu mol \cdot l^{-1}$ (Liss, 1976). More generally, some degree of phosphate scavenging by particles under oxygenated conditions and release under anoxic conditions, either in the water column or in sediments may be observed. The behavior of phosphorus has been studied by several authors using laboratory simulation of estuarine mixing. These experiments show clearly that the removal of phosphate is favored in the presence of colloidal iron especially under high pH conditions and in the absence of humic acids (Sholkovitz, 1976; Bale and Morris, 1981; Carpenter and Smith, 1984). Desorption of phosphate in solutions low in dissolved phosphorus has also been demonstrated in laboratory experiments.

The behavior of phosphorus in an estuary is illustrated, for example, by the case of Zaire where Van Bennekom et al. (1978) observed a maximum of PO_4 in the salinity range 0 to 25 o/oo, whereas the concentration of phosphate in particulate phases decreased with increasing salinity (Figure A.II-2). The increase of dissolved phosphate may be the result of a desorption mechanism. At salinities above 25 o/oo the concentration of PO_4 decreases as a result of the mixing process and phytoplankton growth.

3. SILICON

3.1 Speciation and Sources

Silicon in solution in natural waters is mainly in the form of silicic acid $Si(OH)_4$. Opal which constitutes the biological fraction of silicon is usually a minor mineralogical constituent of the suspended matter transported by rivers.

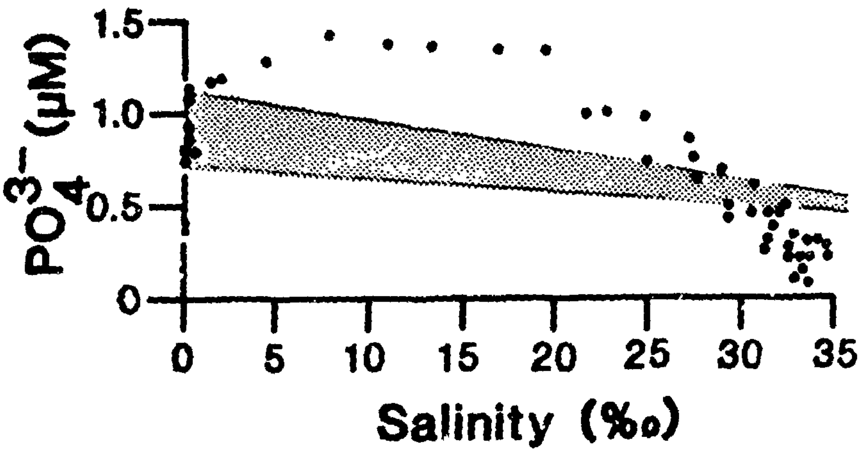


Figure A.II-2. Relationships of PO_4 with salinity in the upper 5 m of the water column of the Zaire river plume. Range expected from conservative mixing with subsurface seawater is hatched (after Van Bennekom and Salomons, 1981).

This creates a problem if the fluxes of biogenic and non-biogenic particulate silicon are to be differentiated. Silicon fixed in biogenic solid phases is more easily mobilized than that in lithogenous mineral particles such as quartz and aluminosilicates. There is a major problem in detecting the fluxes of biogenic silica against the large background of the more inert material. In this case, information is needed on the mineralogical form rather than on a particular fraction defined analytically.

Silicon is a major dissolved constituent and represents about 10% of the dissolved solids in average river water. It results from the weathering of a variety of silicate minerals. The role of weathering of these minerals is strongly dependent on temperature, rainfall and relief. According to Meybeck (1979) 74% of the dissolived silica transported by rivers originates from the tropical zone which represents only 35% of the drained continental surface area. The humid regions with high relief (12.5% of the drained continental surface area) are responsible for 43% of the dissolved silica transport. In contrast to nitrogen and phosphorus, anthropogenic sources of dissolved silicon are unimportant relative to natural weathering. On the contrary, it is well possible that the eutrophication of rivers and the construction of artificial lakes have resulted in a decrease of the natural river flux of dissolved silicon.

3.2 Behavior and the River and Estuarine System

The extent to which dissolved silicon is significantly removed by biological processes depends strongly on the activity of diatoms. This removal is usually limited in unpolluted rivers having a low biological activity. The development of diatoms is favoured in large rivers with low water velocities and in lakes. Opal is relatively soluble and redissolves as soon as the organic coating has been removed from the skeletons. This redissolution process may be an internal source of dissolved silica for the aquatic system. However, if the dissolution of opal occurs after deposition of the skeletons in the sediments the dissolved silicon may react with the clay minerals during early diagenesis (Wollast, 1974). Dissolved silica may thus be substantially removed from the water column when the diatom frustules are transferred to the sediments.

In many estuaries, especially in the unpolluted ones, biological processes have little discernible effect on silicon removal. In eutrophic estuaries, increased plankton activity may be responsible for the total removal of dissolved silicon during summer, while in the winter the extent of biological removal is almost absent (Figure A.II-3).

Slight removal, occurring under conditions of low biological activity and generally at low salinity and high turbidity, has been ascribed to chemical processes, mainly reverse weathering reactions of clay minerals (see review in Liss, 1976) or adsorption by amorphous hydroxides of iron and aluminum (Li, 1980). However, the occurrence of these reactions in estuaries has been questioned. For instance in the mixing zone of the Chiang-jiang (Yangtze), under winter time conditions when biological activity is minimal, silica behaves conservatively even in the presence of suspended matter concentration of several hundred parts per million (Edmond et al., 1984).

The creation of artificial lakes and the eutophication of large rivers have a drastic effect on the transport of dissolved silicon. For example after the completion of the Aswan Dam on the Nile River, a drop of 5 mg Si/l was observed

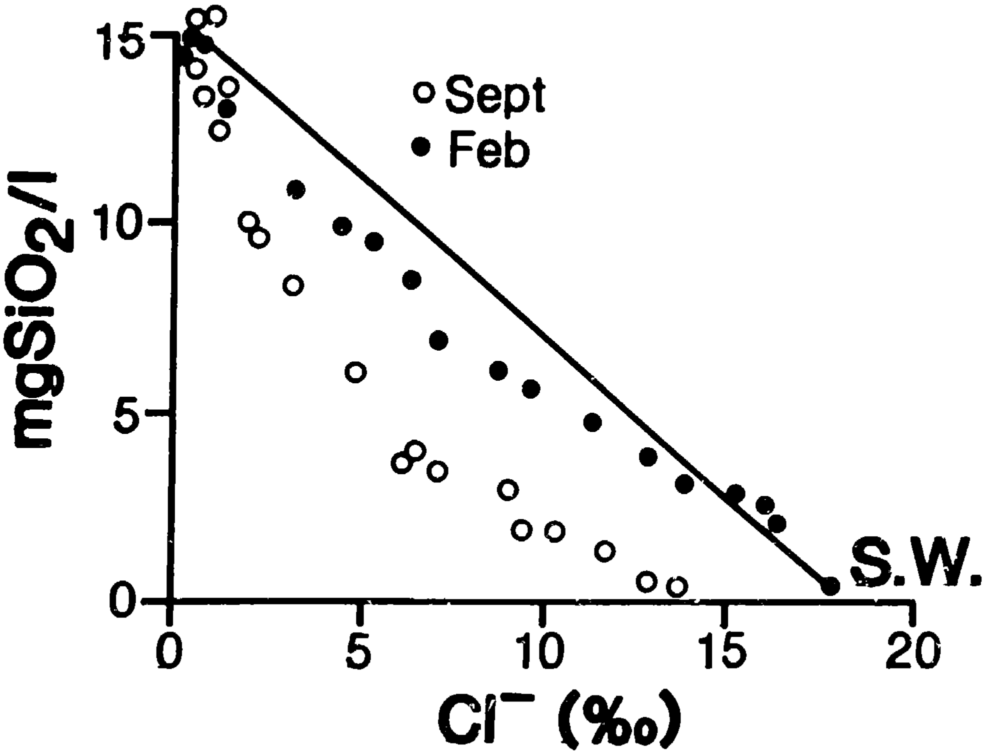


Figure A.II-3. Relationships between dissolved silica and salinity in the Scheldt estuary observed in February and September. Conservative mixing is represented by the straight line. (Wollast, R. and Beckers, O., unpublished data.)

(Wahby and Bishara, 1981). Also according to Van Bennekom and Salomons (1981) the river Rhine reflects a pronounced seasonal cycle of dissolved silicon: near the mouth the concentration of dissolved silicon in river water is 7.4 mg Si/l in winter and 3.8 mg Si/l in summer. It should be emphasized that the activity of diatoms in the Rhine and in lake Constance has been significantly enhanced by the input of excess N and P.

APPENDIX III

RIVER AND ESTUARINE TRACE METAL GEOCHEMISTRY

1. TRACE METALS IN RIVERS

The present understanding of the natural mobilization on land and transport of trace metals to the oceans by river systems is primarily descriptive. Very little attention has been given to the processes that govern the natural amounts of trace metals carried by rivers. Until these processes are understood it is difficult to compare natural with anthropogenic riverine contributions to the marine environment. Nonetheless the following discussion attempts to review the present state of knowledge concerning these processes.

1.1 Factors controlling concentrations

The weathering of continental rocks is the result of leaching mechanisms dominantly controlled by carbonic acid and organic acids produced by biological activity. To a lesser extent mineral acids may be the leaching agent in areas containing significant sulfide deposits or receiving acid rains as a result of atmospheric pollution (see Cronan et al., 1978). Depending on the geology of the catchment and the weathering regime, cations will be mobilized and transported in balance with various anions.

In the case of major elements a fairly clear understanding of the relationship between drainage basin geology and weathering regime, and river chemistry has emerged from recent studies. Much of this is summarized in Holland (1978), but the work of Stallard and Edmond (1983) on the tributaries of the Amazon is an example where this relationship has been established best.

Stallard and Edmond (1983) used the concept of transport limited and weathering limited denudation regimes to help understand river water chemistry. In a weathering limited regime transport processes remove weathered material from the drainage basin as rapidly as it is produced, allowing only a thin soil cover to develop. A transport limited regime is one where the weathering rate exceeds the rate at which material is removed. Drainage basins in which this regime dominates will develop deep, highly leached soils. Obviously the regime that develops will depend on climate, topography, geology and vegetation coverage. As pointed out by Stallard and Edmond (1983):

> "...in a drainage basin exhibiting transport-limited denudation, contributions to the river load by different lithologies should be proportional only to their area of exposure. For a weathering-limited catchment, however, contributions by various lithologies should be proportional to both their area exposed and to their relative susceptibility to weathering."
>
> "A principal difference between transport-limited and weathering-limited conditions is that the physical products of weathering have a much longer time to react with soil and ground waters in the former, while partially weathered solid material is eroded in the latter."

Using this concept Stallard and Edmond (1983) were able to demonstrate how major element composition and concentrations were related to catchment geology and weathering regime. They found that waters from the most intensely weathered (transport limited) catchments had the lowest (< 200 ueq/l) total cation charge, TZ+, and pH values and the highest Fe and Al levels. Silicon (as silica) occurred at levels comparable to other major elements. The chemistry of these waters are very similar to those of rivers which drain low-lying swampy regions of the southeastern U.S. Coastal Plain (Beck et al., 1974). Rivers draining catchments containing evaporite deposits had the highest TZ+ (> 3000 ueq/l) and were rich in Na and Cl. Rivers having TZ+ levels between 200 and 450 ueq/l drained siliceous terrains. Within this range, rivers that drained transport limited areas were rich in silica. This is similar to results on the Bang Pakong River in Thailand which drains a sandstone and granite terrain and has silica levels of ca 100 ueq/kg (Windom et al., 1987). Rivers having TZ+ values within this range and draining weathering limited catchments are enriched in Na over K and Ca over Mg. Rivers draining catchments containing marine sediments have TZ+ values of 450 to 3000. These rivers contain high levels of Ca, Mg and alkalinity, with Ca and Mg generally balanced by alkalinity. This is also similar to results on the Mae Klong River in Thailand (Windom et al., 1987) which drains a carbonate terrain. Cyclic salts (i.e. due to atmospheric input) appear to be only a minor contribution to total cations in the Amazon (Stallard and Edmond, 1981).

It appears that the relationships between major element river chemistry and catchment geology and weathering regime observed for the Amazon Basin are generally similar to those observed elsewhere (see Holland, 1979). It is also apparent that there should be similar relationships between trace element chemistry of river systems and drainage basin characteristics.

The geology of a drainage basin puts limits on the amounts of trace elements available for mobilization and transport. The geology and vegetation of the drainage basin along with climatology interact to determine the weathering regime which in turn determines the rates of trace element mobilization and transport. This also determines the relative efficiency of particulate and soluble material transport but the partitioning of trace elements between these phases is probably more influenced by the chemical nature of the weathering solution. For example, if the major weathering agent is organic acids the solubility of many trace elements may be increased due to formation of complexes with organic ligands. The importance of organic ligands in river chemistry has been demonstrated by several studies which show that organic anions account for a significant amount of the major cation balance (Beck et al., 1974; Cronan et al., 1978; Stallard and Edmond, 1983; Cronan and Aiken, 1985).

The work of Schnitzer and Skinner (1966, 1967) has shown the importance of fulvic acid complexes of many trace elements, and increased concentrations of natural dissolved organics (e.g., humic substances) apparently result in increased carrying capacities of metals such as iron and aluminum in natural waters (Beck et al., 1974, Moore et al., 1979). Increased lead (Windom et al., 1985), cadmium, zinc and iron concentrations (Windom and Smith, 1985) in river water have been observed with increased dissolved organic carbon (Figure A.III-1). Increased carrying capacity has been attributed to the greater solubility of organic complexes of metals (Perdue et al., 1976; Reuter and Perdue, 1977) and to stabilization of colloids containing the metals by organics (Boyle et al., 1977; Sholkovitz et al., 1978; Moore et al., 1979; Sholkovitz and Copland, 1981).

The residual acidity of the weathering solution may also have a major influence on trace element solubility regardless of the acid. Shiller and Boyle (1985)

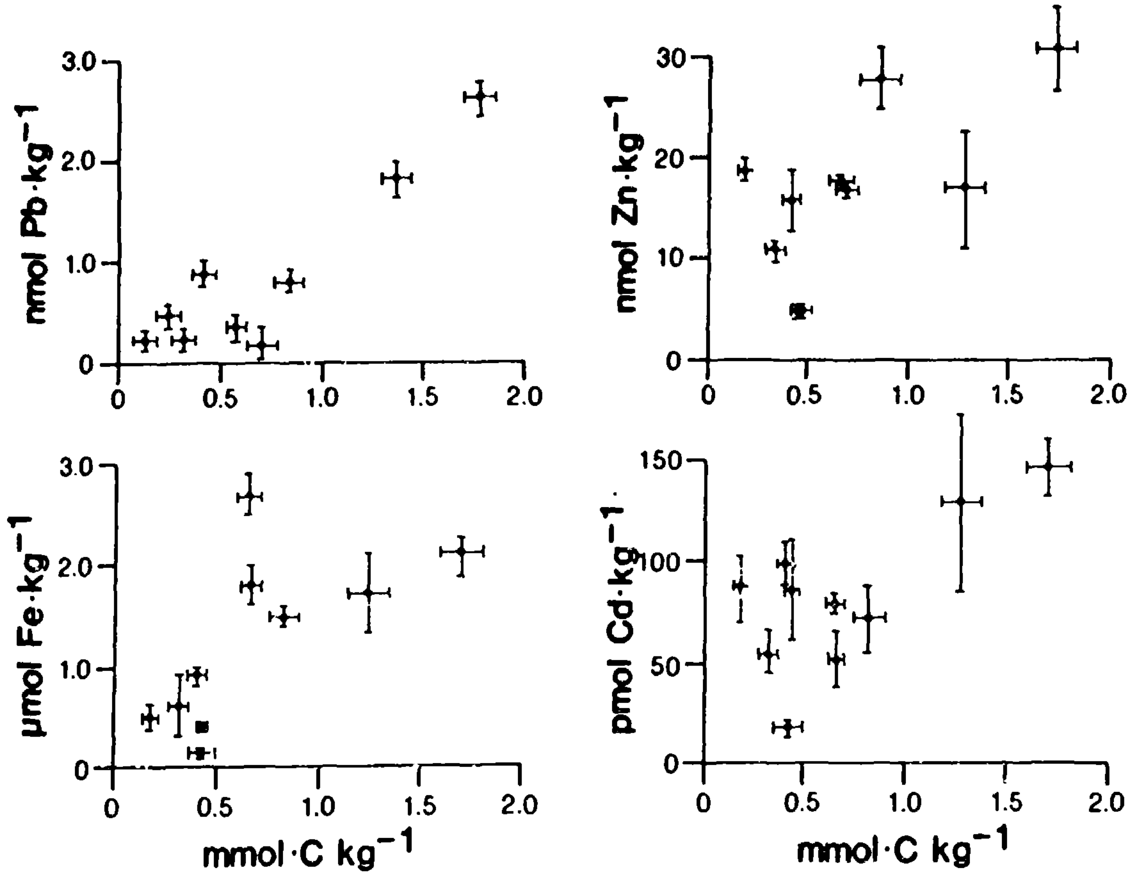


Figure A.III-1 Soluable trace metal concentrations versus dissolved organic carbon (from Windom and Smith, 1985, and Windom et al., 1985).

have shown that dissolved zinc concentrations in rivers throughout the world appear to be related to pH (Figure A.III-2). They also demonstrated that acidification of unfiltered Mississippi River water results in similar increases in dissolved zinc concentrations. The zinc-pH relationship is similar to isotherms for the adsorption of zinc on various natural and metal oxide surfaces. Results on Thai rivers (Windom et al., 1987) show similar relationships between dissolved iron and manganese concentrations and pH, but these could be explained by simple acid-base reactions.

Because of the strong relationship between pH and DOC (Cronan and Aiken, 1985) it may be difficult to deduce what process is operative based on concentration-pH relationships alone. It is possible that increased trace element concentrations with decreasing pH could be due to either adsorption-desorption, acid-base reactions or complexation with organic matter.

Parameters such as pH, composition and concentration of suspended sediment and major anions clearly influence the distribution of trace elements between particles and solution. In the case of anthropogenically introduced trace element pollutants the parameters will determine their fate in the riverine system and thus their delivery rate to the marine environment. Also, because natural concentrations of trace elements (e.g. Zn, Figure A.III-2) may vary considerably, the influence of these controlling parameters must be understood in order to improve our ability to resolve natural and anthropogenic loadings.

1.2 Dissolved concentrations

For the trace metals that are commonly introduced into rivers as pollutants (e.g. As, Cd, Co, Cu, Hg, Pb, Ni, Se, Sb, Sn and Zn) it is surprising how few credible data exist for river water concentrations. Table A.III-1 lists concentrations of some of these metals in selected rivers of the world. Table A.III-2 lists concentrations of some metalloids in selected rivers. Although other credible data certainly exist, those presented in these tables give a fair representation of the range in concentrations that have been observed. The highest concentrations are observed in the anthropogenically perturbed river systems such as the Rhine and the Hudson. More natural rivers, both large and small, have considerably lower concentrations.

The need for additional data on the concentrations of trace metals in rivers cannot be overstated. Data from river systems of differing geology, climatology, and physiography as well as differing anthropogenic influences are needed to better assess natural variability and to provide a basis for differentiating natural from unnatural concentrations. Obviously, data is needed from a significant number of rivers to adequately assess gross river flux on global or regional scales. Such strategies are discussed by Meybeck (1982).

Although the processes controlling river transport are not well understood numerous attempts have been made to quantify gross river fluxes of trace metals to the marine environment. Various recent estimates of the riverine contribution to the World Ocean are really estimates of gross riverine fluxes and have been based on studies of large river systems. For example, using concentrations in Amazon River water and scaling this to world runoff, total gross riverine fluxes of cadmium and nickel to the World Ocean have been estimated (Boyle et al., 1976; Sclater et al., 1976). Similar estimates have been made using the Mississippi (Trefry and Presley, 1976) and the St. Lawrence Rivers (Yeats and Bewers, 1982).

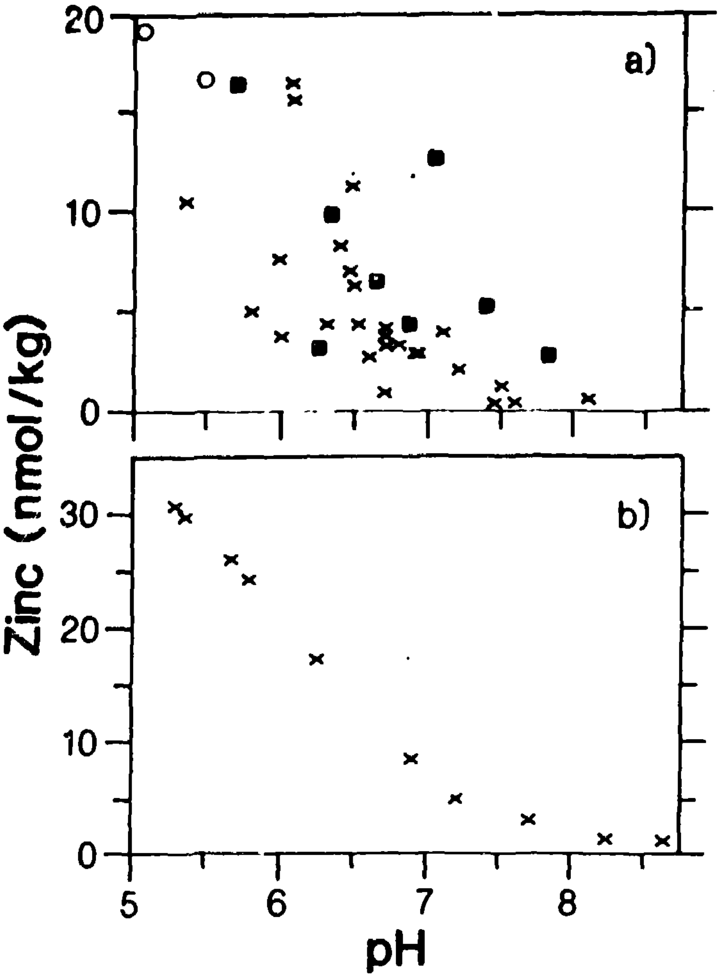


Figure A.III-2 Dissolved zinc versus pH. a) zinc in major rivers including the Yangtze and tributaries of the Amazon and Orinoco. Squares and circles are data for southeast U.S. rivers (Windom, unpublished data) and Thai rivers (Windom et al., 1987); b) zinc in pH-adjusted aliquots of Mississippi River water (after Shiller and Boyle, 1986).

TABLE A.III-1

DISSOLVED TRACE METAL CONCENTRATIONS IN SELECTED RIVERS

	Cd	Co	Cu	Hg	Pb	Ni	Zn
	nmoles/kilogram						
St. Lawrence (Canada)	1.0	0.9	40			30	130
Gota (Sweden)	0.08-0.22		20-25		0.4-0.9	10-20	90-110
Hudson (USA)	2.0		40			50	150
Savannah (USA)	0.08		8	0.1	0.1-0.4	5	10
Ogeechee (USA)	0.08		5	0.1	0.1-0.3	5	10
Atlamaha (USA)	0.05		10	0.1	0.2	5	11
Satilla (USA)	0.06		5	0.1	0.7	5	15
St. Marys (USA)	0.13		2		1.8-2.5	7	25
Rhine (Germany)	4.0		100				300
Conwy (UK)	4.0		30		24	50	700
Amazon (Brazil)	0.03		25			4.5	
Chanjiang (China)	0.22-0.34		17-21			4	
Mae Klong (Thailand)	0.05	0.3	10		0.3	10	5
Chao Phraya (Thailand)	0.05	0.3	20		0.3	15	8
Bang Pakong (Thailand)	0.08	0.4	10		0.3	15	10

REFERENCES: Bewers and Yeats (1978), Danielsson *et al.* (1983), Klinkhammer and Bender (1981), Duinker and Nolting (1978), Boyle *et al.* (1982), Elderfield *et al.* (1979), Windom and Smith (1985), Windom *et al.* (1987), Windom *et al.* (1985).

TABLE A.III-2

DISSOLVED METTALOID CONCENTRATIONS IN SELECTED RIVERS

	As nmol/kg	Ge nmol/kg	Sb nmol/kg	Se nmol/kg	Sn nmol/kg
Ochlockonee (USA)	-	55	214	-	10
Suwannee (USA)	-	89	-	-	9-71
Mississippi (USA)	-	366	148	1.4	7.2-320
Satilla (USA)	1.8-5.0	-	85	-	-
St. Marys (USA)	1.3	-	45	-	-
Susquehanna (USA)	3.9	59	-	4.1	12.0
Apalachicola (USA)	-	1086	450	-	8
Rhine (Germany)	-	28-165	1890	-	12-46
Main (Germany)	-	10	2250	-	-
Tamar (UK)	80	77	-	-	5.0
Amazon (Brazil)	-	67	-	2.7	-

REFERENCES: Andreae *et al.* (1981), Byrd and Andreae (1986), Froelich *et al.* (1985a), Kharker *et al.* (1968), Sanders (1985), Waslenchuk and Windom (1978).

With similar aims studies of other large river systems such as the Yangtze and Orinoco have been conducted (Boyle et al., 1982; Grant et al., 1982).

Studies of the concentration of trace elements in large river systems are clearly important in understanding riverine contributions to the oceans. They, however, provide an inadequate basis for evaluating the drainage basin processes which govern the mobilization and transport of trace elements. In fact, because of some, perhaps unique, features of the drainage basins of large river systems that have been used for estimating world river input to the ocean, estimates are biased and may be wrong. For example, average world runoff is ca 30 $cm \cdot yr^{-1}$ (0.3 $m^3 \cdot m^{-2} \cdot yr^{-1}$) (see Holland, 1978, p. 67) whereas the mean runoff for the Amazon is ca 115 $cm \cdot yr^{-1}$ (1.15 $m^3 \cdot m^{-2} \cdot yr^{-1}$). As shown in Figure A.III-3 this is atypical for continental runoff even for the major world rivers. Thus it is quite likely that the composition of water from a river system with an average discharge of ca 1.1 $m^3 \cdot m^{-2}$ of drainage basin will not reflect that for average world runoff of 0.3 $m^3 \cdot m^{-2}$ even if the composition of the drainage basin is similar to average continental material. The Mississippi River has a runoff of ca 17 $cm \cdot yr^{-1}$, or about half the world average, but probably a more unique characteristic of this system, which may lead to biases in extrapolation of data, is the extensive anthropogenic modification of its drainage basin. Likewise, data from the St. Lawrence River may be biased by the geology of its drainage basin which is dominated by the Canadian Shield.

Clearly data from a larger number of river systems provide a less biased basis for estimating global gross river fluxes of trace metals than do data from a single large river system. This approach has been used for particulate trace metal transport by Martin and Maybeck (1979) and for zinc by Shiller and Boyle (1985). Nonetheless there is also danger in this approach as pointed out by Holland (1978) who states:

> "It has been proposed that the computation of the total input of dissolved solids into the ocean requires only a knowledge of the chemistry of the 20 largest rivers of the world. Unfortunately this does not turn out to be true....The combined runoff (of the 20 largest rivers accounts for) only 31% of the estimated mean annual world-wide runoff. As might be expected, the rivers with the largest runoff tend to drain the wettest areas of the globe."

It would appear that trace metal data on a number of sufficiently diverse river systems (i.e. representative of a wide range of continental conditions) could provide perhaps the best basis for estimating world river fluxes. Such data would certainly help to evaluate whether estimates based on data from large rivers are significantly biased. If the river systems studied are not significantly perturbed by anthropogenic activities, and their drainage basins are adequately characterized, results might be weighted in proportion to the amount of continental area having similar characteristics (e.g., geology, climatology, vegetation). This approach was used by Schlesinger and Melack (1981) for estimating global river fluxes of carbon and yielded a value very similar to estimates based on seven of the largest rivers of the world, thus lending credibility to the latter estimates.

A statement on the quality of existing data on concentration of trace metals in rivers should be made at this point. In the past decade considerable advances have been made in the quality of metal data collected from the marine environment. The realization that there were problems was the outgrowth of intercalibration

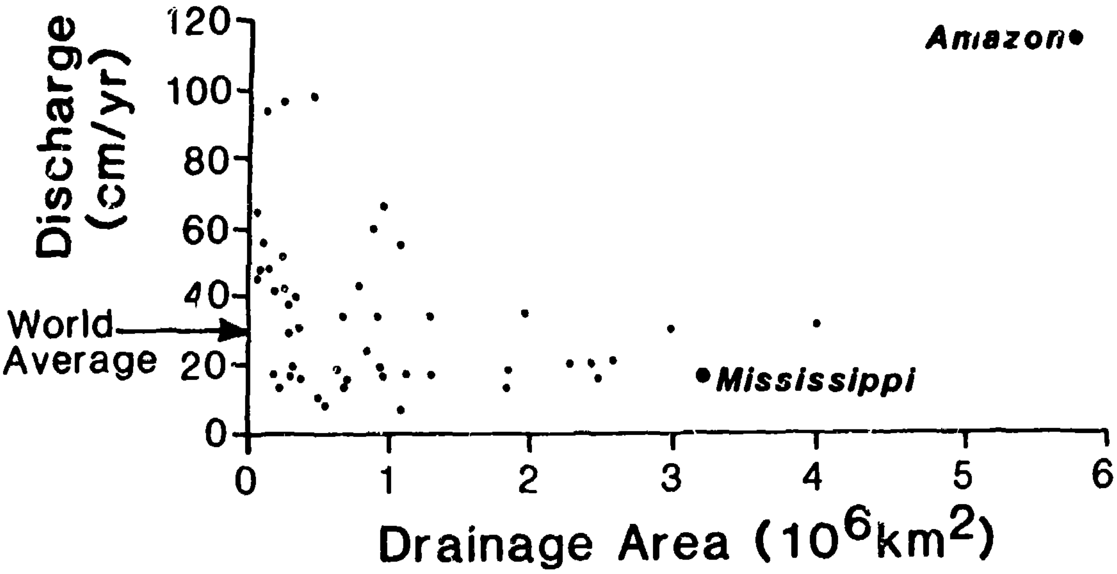


Figure A.III-3 Discharge versus drainage basin area for the fifty largest rivers of the world.

exercises which indicated great variability in results from different laboratories. Laboratories that carried out sampling and analysis with great care produced data that were "oceanographically consistent". This set some controls on the generation of data such that investigators were obliged to demonstrate that their results met certain quality criteria (i.e. they performed well in intercalibation exercises or their data were consistent with oceanographic features). There is every indication that the situation regarding data on concentration of trace metals in rivers is similar. Often high trace metal concentrations reported for rivers are accepted as indicating pollution when they could easily be the result of contamination of samples during handling. Like oceanic data, those resulting from the analysis of river samples should meet similar quality criteria. Either the laboratory should prove its ability through intercalibration exercises or should be able to demonstrate the environmental consistency of its data by being able to extrapolate it to sea water values through the analysis of samples collected along an estuarine transect.

1.3 Particulate concentrations

The gross river flux of trace metals on particles will be largely controlled by the geology and weathering regime (i.e. transport or weathering limited). These two factors will also influence the concentration of trace metals on particles but this will also be influenced by anthropogenic inputs of metals since most will rapidly equilibrate with particles.

Martin and Meybeck (1979) estimated the relative importance of trace metal transport by rivers in particulate and dissolved phases on a global scale. Although the data they used are of questionable reliability and are from only a few rivers they nontheless serve to demonstrate the relative importance of particulate phases in carrying trace metals. From the data they used they were able to calculate a dissolved transport index (DTI) for global river water. This index gives the percentage of the total metal transported in the dissolved form and is tabulated for several environmentally important metals in Table A.III-3. Recent results of Windom *et al.* (1987) for trace metals transported in Thai rivers were used to calculate *DTI's* and these are also given in Table A.III-3. As can be seen, using more recent data, of presumed good quality, values are similar to those used by Martin and Maybeck (1979) with the exception of Ni.

These results demonstrate that much, if not most, of the natural trace metal load transported by rivers is in particles, predominantly bound in crystal lattices. Increased loads due to anthropogenic inputs will be concentrated predominantly on particles as well but will be presumably more labile. Identification of anthropogenic increases on particles is probably facilitated best by use of an enrichment factor, EF, where metal ratios of particles are compared to natural abundances. For this purpose Al has been used by many investigators as an appropriate normalizer (Martin and Meybeck, 1979; Duce *et al.*, 1976; Windom *et al.*, 1984). Such enrichment factors are expressed by the following equation:

$$EF = \frac{(M/Al)_p}{(M/Al)_c}$$

where the numerator is the metal to aluminum ratio in the riverine particles and the denominator is the metal to aluminum ratio in average crustal material. The denominator could also be based on the natural abundances of metals within a drainage basin under study.

TABLE A.III-3

DISSOLVED TRANSPORT INDEX (DTI) FOR GLOBAL RIVER WATER
(After Martin and Meybeck, 1979)

DTI	
50-10%	Sb, As, Cu (45), Zn (16)
10-1%	Ni (48), Co (6), Mn (14), Pb (6)
1-0.1%	Fe (1)

Values in parentheses were calculated using average particulate and dissolved loads from four rivers in Thailand (Windom *et al*., 1987).

Although anthropogenic trace metal inputs are carried predominantly on particles, the fate of the metals upon delivery to the marine environment depends on the phase in which they are carried. In particular the exchangeability of the metal between suspended solids and solution in the estuarine environment will determine its fate and thus its net transport. This is discussed more fully in the following section and in Appendix VI.

2. ESTUARINE BEHAVIOR OF TRACE METALS

To be able to assess the input of trace elements to the oceans it is necessary to understand what processes affect their transport through estuaries. Both physical and biological characteristics of estuaries have major controls on processes affecting trace element concentrations and numerous studies have addressed this subject. The residence time or time of mixing of an estuary will depend on its physical characteristics as will turbidity (i.e. sediment resuspension) and redox conditions of the water column. Biological productivity of the estuary may affect trace element concentrations due to biological uptake (removal) or microbial degradation of organic matter (release).

The chemical characteristics of estuaries obviously also influence trace element transport. Important chemical features of all estuaries are the salinity gradient and the composition of the river end member (other chemical characteristics are predominantly controlled by physical and biological processes; see Appendix VI). Both of these features may influence trace element behavior during estuarine transport, yet the influence of the composition of the river water entering the estuary has generally received little attention in past studies except as one of two end members which are used to define the mixing pattern.

For many trace elements, strictly estuarine charateristics (i.e. physical, biological and the salinity gradient and its associated chemical characteristics) may control their mixing behavior. For other trace elements, however, the composition of the river end member may have a major influence on their estuarine behavior. It would therefore appear that if observed differences or similarities in the mixing behavior of trace elements in different estuaries are to be understood, the nature of the river end member and its influence must be taken into consideration.

Like the composition of rivers, the behavior of many materials in estuaries varies from system to system. For example, dissolved copper mixes conservatively in the Amazon Estuary (Boyle et al., 1981), is removed from solution in the Rhine and San Francisco Bay estuaries (Duinker and Nolting, 1977, 1978; Eaton, 1979a) and increases due to release from suspended and bottom sediments in southeastern U.S. Estuaries (Windom et al., 1983) and in the Patuxent River Estuary (Eaton and Chamberlin, 1980). The concentration of dissolved manganese in estuaries increases at lower salinities, usually followed by removal (Evans et al., 1977; Duinker et al., 1979). Conservative behavior has also been observed (Moore et al., 1979). The behavior of zinc during mixing also appears to differ between estuarine systems (Duinker and Nolting, 1977; Elderfield et al., 1979; Eaton, 1979a; Windom et al., 1985, Windom and Smith, 1985).

The distribution of trace elements (i.e. behavior) in estuaries is amenable to mathematical modelling. Approaches used by Li and Chan (1979) and Kaul and Froelich (1984) appear to be the most straightforward but the models are only useful in estimating the rates of trace element removal from, or release to the water column (i.e. dissolved) and net transport through the estuary. The processes responsible require additional consideration.

Given the complex nature of processes that influence the concentration of trace and, in some cases, major elements in estuaries it is not surprising that major differences have been observed. Gradients in ionic strength, pH and other parameters vary from estuary to estuary. Estuaries also vary in concentrations and distribution of particulate matter and show different degrees of Eh variability. Biological processes may also be more important in some estuaries than in others. And, of course, the composition of the zero salinity end member of estuaries varies from system to system.

The composition of the river end member may have significant influence on trace element transport through estuaries. For example, the concentration and composition of dissolved organic carbon of the river end member may have various effects on trace element behavior. Waslenchuk and Windom (1978) suggested that the formation of organic complexes stabilizes dissolved arsenic resulting in its conservative transport through southeastern U.S. estuaries. Non-conservative behavior of other trace elements during estuarine mixing has been suggested to be the result of cationic destabilization of colloidal humic substances with which the elements are associated (Sholkovitz, 1976; Sholkovitz and Copland, 1981) although Eaton (1979b) suggests that destabilization may also result from bacterial polymerization of the colloids (see Sholkovitz, 1980 and Eaton, 1980 for discussion of this controversy). Also, since the stability of metal-fulvic acid complexes are pH dependent (Schnitzer and Skinner, 1966, 1967) the behavior of a given trace element in an estuary will differ depending on whether or not it is transported in the river in such a form.

The pH of rivers varies considerably and may influence the estuarine transport of many trace elements. The mixing behavior of elements in estuaries whose river end member pH is lower than that of sea water (e.g., southeastern U.S. rivers) may differ significantly from estuaries whose river end member pH is similar to sea water (e.g., the Mackenzie River in Canada). For example, Graham et al. (1976) showed that the partitioning of manganese between soluble and particulate phases in rivers and estuaries of the eastern U.S. is related to pH. It therefore follows that variations in manganese will be greatest in estuaries with the largest gradient in pH. The beryllium concentration of rivers is also strongly related to pH (Measures and Edmond, 1983). The estuarine chemistry of beryllium varies according to the composition of the river end member and may depend on the chemical species of beryllium that is present at a given pH as well as the particle sites available for absorption (Measures and Edmond, 1983). Low pH rivers usually have high iron concentrations (Beck et al., 1974; Stallard and Edmond, 1983; Windom et al., 1985a). The low salinity region of estuaries of such rivers should be characterized by a steep gradient of increasing pH along which iron becomes increasingly insoluble.

Wollast et al. (1979), using the parameters of ionic strength, pH, dissolved oxygen and total dissolved carbonate, thermodynamically explained observed dissolved manganese concentrations in the Rhine and Scheldt Estuaries. Obviously this suggests that variations in gradients of these parameters, which are controlled by the river end member, can lead to differences in the estuarine behavior of manganese. Wollast et al. (1979) however found it surprising that dissolved manganese appeared to be in thermochemical equilibrium in estuarine waters given the kinetics of the reactions involved. They proposed that suspended particles and microbial activity may catalyze the reactions.

Suspended particles may also influence trace element concentrations in estuarine waters due to adsorption-desorption reactions. Li et al. (1984) found that the conditional partition coefficient, K_d, for several metals exceeds 10^4 for Hudson River water. This, according to a simple equilibrium sorption model proposed by Morris (1985), indicates that significant removal would take place in the low salinity region of the estuary. If, however, the K_d for the given trace element is less than 10^3, removal would be negligible even in estuaries having strongly developed turbidity maxima unless the particles are greatly depleted with respect to the given element. Desorption may occur at higher salinities depending on the variability of adsorption isotherms with increasing sa'inity and the relative saturation of particles with respect to exchangable trace element concentrations. Morris (1985) explained observed dissolved zinc concentrations in the Tamar Estuary by particle removal in the low salinity region followed by zinc desorption at higher salinities because of decreased K_d.

Differences in biological characteristics of the river-estuarine system also clearly influence the behavior of materials during estuarine transport. The speciation of some metalloids (e.g. As, Sb) may be changed, due to biological activity, to different oxidation states or oranic forms which could affect their estuarine behavior (Andreae, 1979; 1983). Morris et al. (1978) demonstrated the importance of biological processes in the very low salinity region of estuaries where apparently the demise of freshwater microorganisms is accompanied by increased DOC, and decreased DO and pH. These changes obviously affect the behavior of other trace elements.

In highly productive estuaries trace elements may be removed due to biological incorporation. Likewise, degradation of biogenic materials may lead to trace element releases which should correspond to nutrient regeneration. Knox et al. (1982, 1984) have shown that in addition to ammonium, manganese and arsenic are remobilized in the sediment pore waters of the Tamar Estuary and are released to the water column during sediment resuspension. The same sort of mechanism also affects the distribution of tin in the Tamar (Byrd and Andreae, 1986).

The processes discussed above will be manifested in the soluble concentration of trace metals along the salinity gradient of estuaries. Three types of distribution are observed and are referred to as the estuarine behavior of the metal. The types of behavior are conservative, net removal and net increase and examples of each are shown in Figure A.III-4. From such "mixing curves" an apparent zero salinity end member concentration (AZE) can be calculated. This is accomplished by determining the intercept on the vertical axis of the regression curve for data at the high salinity end of the mixing curve; or, to be mathematically rigorous, that part of the curve where the second derivative of the concentration with respect to salinity is zero (see Li and Chan, 1979). The AZE concentration multiplied by river discharge represents a net flux of the trace metal in solution through the estuarine system. Since most estuarine/coastal systems trap particles (see Appendix VI) the net soluble transport is probably a good estimate of total net flux.

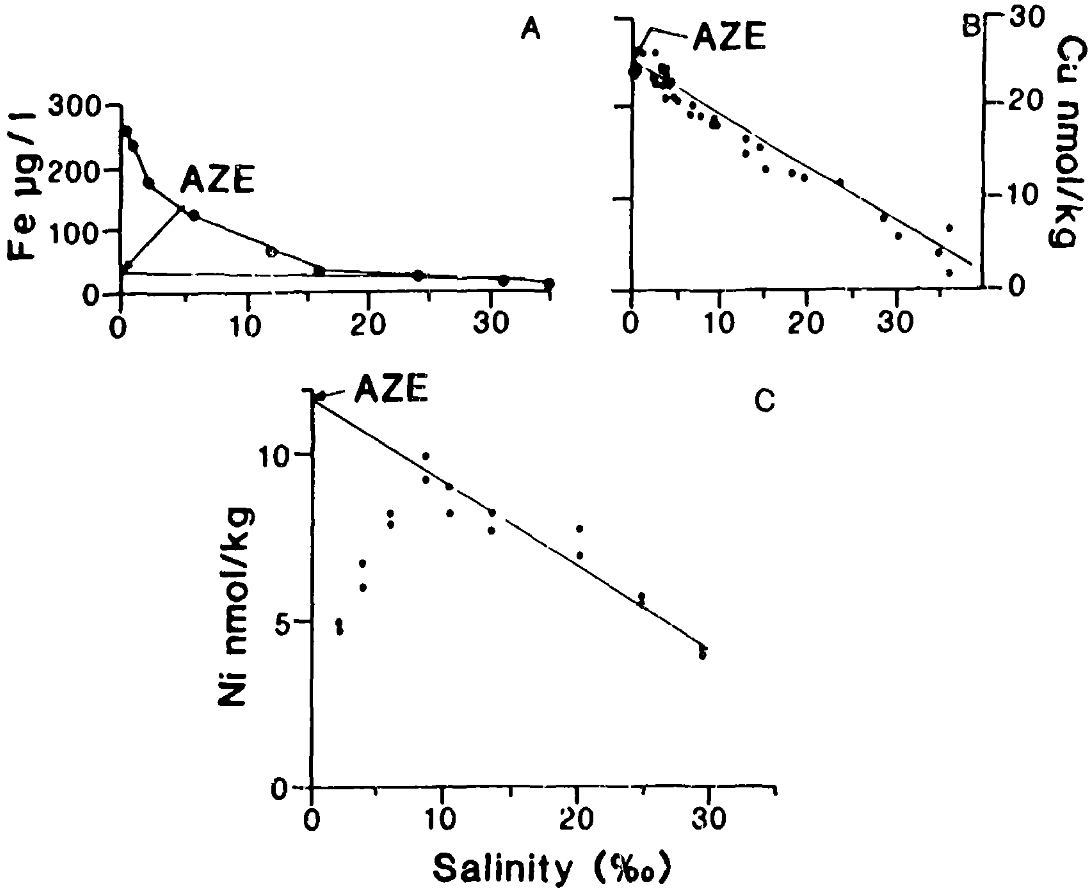


Figure A.III-4 Examples of different estuarine behavior of trace metals: a) removal (after Figueres et al., 1978); b) conservative (after Boyle et al., 1982); and c) release (Windom, unpublished data). AZE represents the apparent zero salinity end-member.

APPENDIX IV

RIVER AND ESTUARINE BIOGEOCHEMISTRY OF ORGANIC MATERIALS

1. NATURAL ORGANIC CONSTITUTENTS OF RIVER WATERS

1.1 Dissolved Organic Carbon

Riverine dissolved organic carbon is an important yet poorly defined and highly dynamic component of the global carbon cycle (Likens *et al.*, 1981). An understanding of the composition of the major constituents of DOC and their behaviour during river transport can give an insight into the sequestering of anthropogenically mobilized materials.

Riverine DOC has a weighted and worldwide concentration of 5.75 mg $C\cdot{}^{-1}$ and a global flux averaging 1.25 times that of particulate organic carbon (POC) (Meybeck, 1981, 1982). The riverine transport of organic carbon appears to be related to the annual production in the drainage basin (Mantoura and Woodward, 1983). The total export to the oceans has been extimated to be $6(\pm 4)\cdot 10^{14}$ g $C\cdot yr^{-1}$ (Meybeck 1982) and in contrast to most riverine suspended sediments, which are deposited at river mouths or in nearshore areas, riverine DOC has been suggested to behave conservatively in estuaries (Mantoura and Woodward, 1983) and thus has the potential to contribute to offshore marine environments.

Rivers integrate biogeochemical processes occurring in their entire drainage basins and thus contain organic matter synthesized and degraded in both the terrestrial and aquatic environments. Humic acids (acid insoluble) and fulvic acids (acid soluble) may make up 80% of DOC (Ertel *et al.*, 1986). Humic acids, as a group, have higher molecular weights and show a higher affinity towards particulate adsorption and removal mechanisms than the more degraded fulvic acid fractions. Whereas the humic acid fractions are adsorbed onto particles and undergo removal in estuaries, Ertel *et al.* (1986) conclude that the fulvic acids (representing up to 50% of the humic material), as characterized by their lignin derived phenols from terrestrial plants, are valuable tracers of riverine DOC and that the signature of the Amazon input of these materials should be clearly recognizable and represent a major portion of the terrestrial DOC input to the ocean.

The remaining DOC pool of rivers is thought to consist of potentially labile, autochthonous biochemical components (Degens, 1982) such as carbohydrates, polypeptides and fatty acids (Degens and Ittekott, 1983). This fraction is unlikely to survive the river-sea interface unlike the allochtonous compounds and any anthropogenically introduced fractions which are not degraded in the riverine environment. In summary, three major components of organic matter can be identified:

1. the refractory allochtonous material

2. the relatively labile autochtonous contribution

3. the anthropogenic input to the river.

1.2 Particulate Organic Carbon (POC)

The components of POC essentially mirror the sources of DOC. Most studies of biogenic materials in river particulates have been confined to bulk measurements of POC whose concentrations range from about 1 to 30 $mg \cdot l^{-1}$ with a world average of around 5 $mg \cdot l^{-1}$ (Meybeck, 1982). Typically POC levels rise with a rising hydrograph and most of the carbon flux is in the <50um or fine fractions.

Details of composition of particulate matter in rivers are scarce in the literature. The typical range of atomic C:N values for POM (10-12) closely matches that of soil organic matter, suggesting a predominantly allochtonous origin. Seasonally higher values ($C:N \geq 20$) are typical of relatively unaltered vascular plant detritus as are seasonal increases in photosynthetic plant pigments. Relatively few characterizations of major biochemical compounds such as carbohydrates, proteins and lignins have been made. However, Hedges et al. (1986) in a study of Amazon River particulate matter involving characterization of lignin fractions, stable carbon isotope and elemental analyses, concluded that vascular plant debris and soil humic material constitute the bulk of the POC transported in the lower river. They also concluded that degradation takes place primarily in the terrestrial environment yielding refractory material comprising most of the particulate flux. This is an important aspect when considering fluxes through the estuary and the relationships between distribution coefficient and an assumed constant fraction of organic carbon.

2. PHYSICO-CHEMICAL PROPERTIES AND PARTICLE/WATER PARTITIONING OF NEUTRAL HYDROPHOBIC COMPOUNDS

Many organic contaminants have low water solubility and are strongly adsorbed onto colloids as well as suspended and sediment particles. Many are persistent, being only slowly biodegradable and many have environmental half-lifes in the order of years.

Attempts have been made to develop models for describing the degree of sorption, or distribution ratios, for organic compounds with a sorbing substrate.

2.1 The Partition and Apparent Distribution Coefficients (K_p, K_d)

The sorption of PAH, halogenated hydrocarbons and certain pesticides can be described by an equilibrium model involving a constant ratio (the partition coefficient, K_p) of the concentrations of the compound in particulates and in water:

$$K_p = C_p/C_w$$

where C_p = concentration in g per g of particulates and C_w = concentration in g per g of water.

Assuming that the partition of an hydrophobic compound is determined mainly by the organic matter content of the particulates, K_p can also be written as:

$$K_p = f_{oc} \cdot K_{oc}$$

where K_{oc} is an organic carbon normalized partition coefficient and f_{oc} is the fraction of organic carbon. The controlling function of the organic carbon content in the partitioning in suspension and in sediments, involving natural particles, has been demonstrated for several compounds (an example is given in Figure A.IV-1).

Log K_{OC} or log K_p values appear to vary inversely with the log of solubility and directly with the log of the n-octanol-water partition coefficients (log K_{OW}) for a wide range of compounds (Chiou et al., 1979; Karickhoff et al., 1979; Schwarzenbach and Westall 1981 (Figure A.IV-2). The two physico chemical properties, solubility (S) and octanol-water partition coefficients (K_{OW}) may therefore be valuable quantitative indicators of the partition of hydrophobic organic compounds in river transport models. These properties have been listed for a number of compounds in Table A.IV-1. These data illustrate two major points: 1) the very low aqueous solubilities of many compounds, indicative of their affinity for surfaces in aquatic systems; and 2) the wide range of solubility for these, essentially hydrophobic compounds. In Figure A.IV-3 log K_{OW} - log S relations have been presented for a number of polychlorinated biphenyls (PCB) and polyaromatic hydrocarbons (PAH). It should be noted that the concentrations of contaminants are related to water discharge as illustrated in Figure A.IV-4 for dissolved organohalogen compounds in the Rhine. The relationship may be used to evaluate time trends in contaminant discharge at fixed discharge rates and to estimate the gross flux normalized to discharge and the relationship is expected to hold true in the case of suspended matter (see Appendix V).

2.2 River Water/Particle Partitioning

A limited data base is available for apparent distribution coefficients K_d (defined in the same way as K_p) to test the applicability of the simple equilibrium partitioning model and to describe the partitioning of hydrophobic compounds between particles and water under field conditions. It should, however, be borne in mind that even compounds with similar class properties (e.g., the chlorinated biphenyls) display widely ranging K_d's (Table A.IV-2). Even though there are marked compositional differences between particulate and dissolved, and the K_d's of lower and higher chlorinated compounds may vary by a factor of 100, it has been estimated (Duinker, 1986) that an average fifty percent of the PCB loading of river water is in the dissolved phase prior to passage through the estuary.

In the simple two phase equilibrium partitioning model (water + particulates), a linear relation is expected between K_d and K_{OW}. A complicating factor is introduced by the presence of small particles including colloidal fractions. As the concentrations of PCB congeners in particles, vary with particle size and since the separation of 'dissolved' and 'particulate' forms is operationally defined, apparent K_d values depend strongly on the relative contributions of these small particles to "water" and "particulates". Small particles in offshore waters (Duinker, 1986) and colloidal material in the interstitial waters of coastal marine sediments (Brownawell and Farrington, 1986) are found to be dominant carriers of PCB congeners. Apparent distribution coefficients will be strongly dependent on whether the small fractions are included in the 'dissolved' ($K_d \simeq 10^3$ as in the case of the interstitial waters) or in the 'particulate' fraction ($K_d \simeq 10^4$-10^6 as in the case of the offshore suspended small particles). In the case of interstitial waters with large contributions of colloidal material, three phase models (involving dissolved, colloidal and particulate forms) are required to represent the experimental distribution coefficients (Brownawell and Farrington, 1986). These more complex models may not be required in the riverine environment. For instance, application of a simple two phase model to the PCB data from

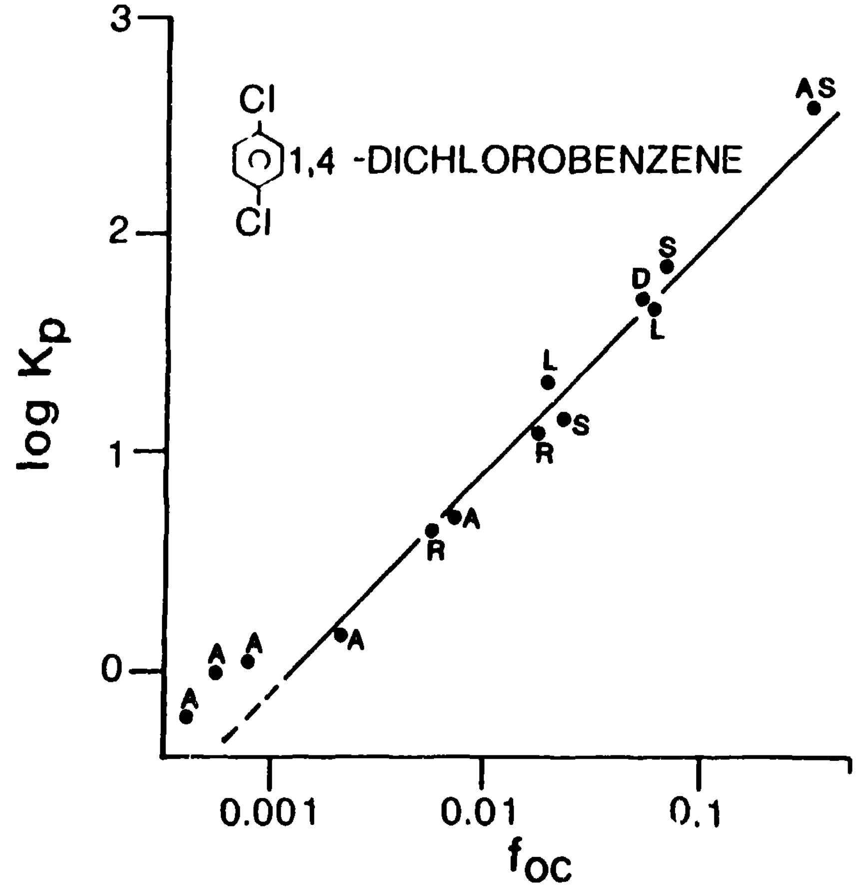


Figure A.IV-1. Solid/water partition coefficients of 1,4-dichlorobenzene as a function of the organic carbon content of the sorbent (A = aquifer material, AS = activated sludge, D = detritus, L = lake sediment, R = river sediment, S = sea sediment) (from Schwarzenbach and Westall, 1981).

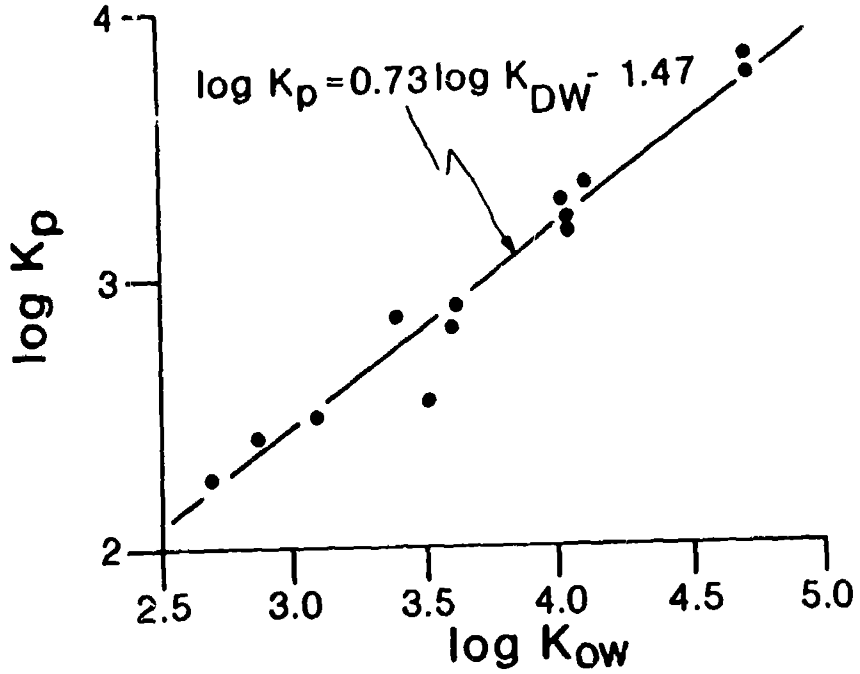


Figure A.IV-2. Linear free-energy relationships: Correlation between K_p and K_{ow}. The compounds used were methyl- and chlorobenzenes ranging from toluene to tetramethylbenzene and chlorobenzene to tetrachlorobenzene (from Schwarzenbach and Westall, 1981).

TABLE A.IV.-1

WATER SOLUBILITIES (S IN MOL DM-3) AND OCTANOL-WATER PARTITION COEFFICIENTS OF SOME COMPOUNDS

Compound	-log S	log K_{OW}
Chloroform	+1.24	1.57
Carbon tetrachloride	2.28	2.64
Benzene	1.98	2.13
Toluene	2.26	2.69
Monochlorobenrene	3.27	3.36
γ-HCH	5.19	3.66
Aldrin	7.45	5.52
Endrin	8.19	5.16
pp'-DDD	8.30	6.02
pp'-DDE	7.85	5.83
pp'-DDT	8.47	5.76
PCBs		
Biphenyl	4.28	4.10
2-Chloro-	4.66	4.56
3-	5.16	4.72
4-	5.32	4.69
2,2'-Dichloro-	5.45	5.02
2,4-	5.55	5.15
2,5-	5.58	5.18
3,3'-		5.34
4,4'-	6.60	5.28
2,2',5-Trichloro-	5.60	5.64
2,4,4'-	5.99	5.74
2,4,5-	6.44	5.77
2,4',5-		5.77
3,4,4'-	7.23	5.90
2,2',5,5'-Tetrachloro-		6.26
2,2',6,6'-		5.94
2,3,4,5-	7.18	6.39
2,3',4',5-		6.39
3,3',4,4'-	8.59	6.52
3,3',5,5'-		6.58
2,2',3,4,5'-Pentachloro-	7.86	6.85
2,2',4,5,5'-	7.89	6.85
2,3,4,5,6-	7.68	6.85
2,2',3,3',4,4'-Hexachloro-	8.91	7.44
2,2',4,4',5,5'-	8.47	7.44
2,2',4,4',6,6'-	8.60	7.12
2,2',3,4,5,5',6-Heptachloro-	8.92	7.93
2,2',3,3',4,4',5,5'-Octachloro-	9.19	8.68
2,2',3,3',5,5',6,6'-	9.37	8.42
2,2'3,3',4,4'5,5',6-Nonachloro-	9.61	9.14
Decachrobiphenyl	10.49	9.60

TABLE IV, continued:

PAHs		
Naphthalene	3.61	3.35
Fluorene	4.93	4.18
Anthracene	6.38	4.63
Phenanthrene	5.15	4.63
Fluoranthene	5.90	5.22
Pyrene	6.18	5.22
Chrysene	8.06	5.91
Benzo[a]pyrene	7.82	6.50
Benzo[g,h,i]perylene	9.02	7.10

Sources: Bruggeman et al., 1982 (PCB congeners and PAH) and various sources

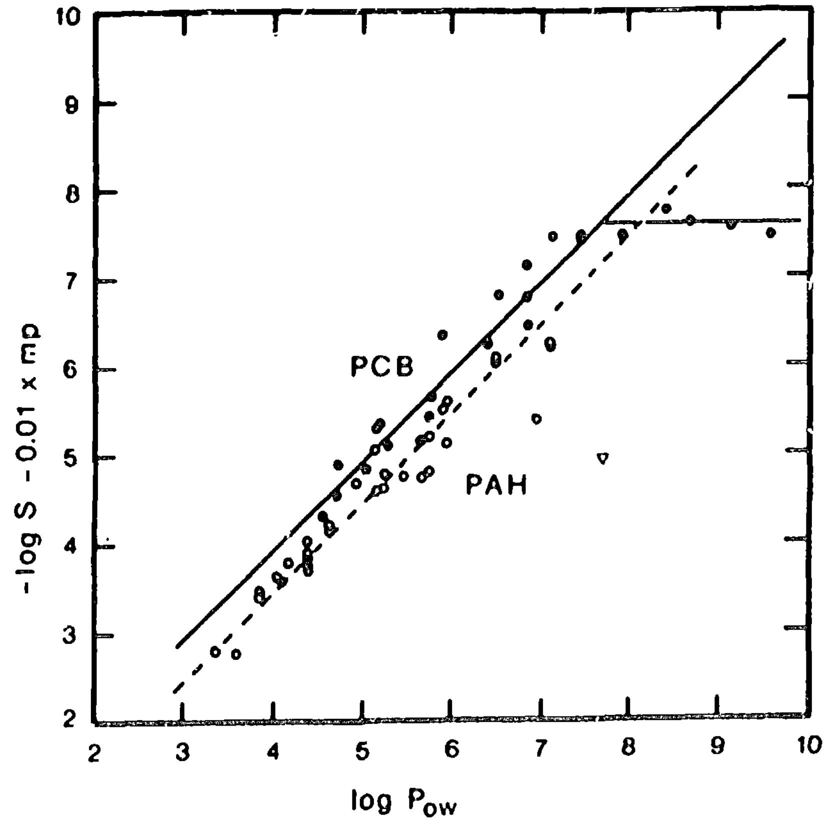


Figure A.IV-3. Relationship between octanol-water partition coefficient, P_{OW} and aqueous solubility, S (Mol/l) when corrected for melting point (m.p.). ●-●, PCBs; O---O, PAH's; ▽ , coronene (from Bruggemann et al., 1982).

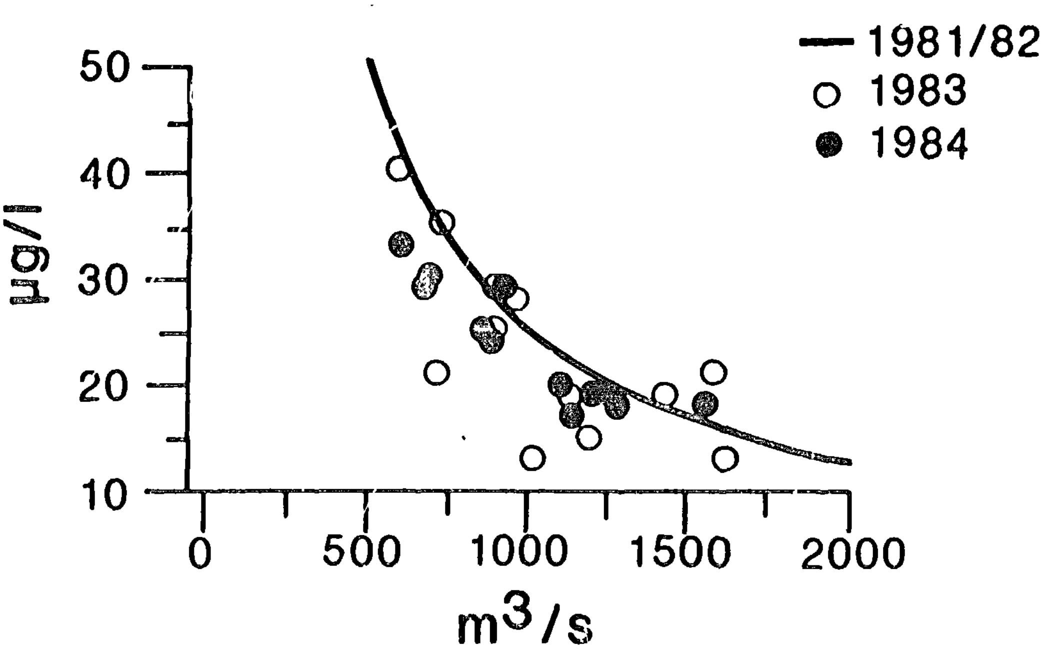


Figure A.IV-4. Concentration of organo halogen compounds adsorbed onto activated charcoal in relation to water discharge of the Rhine at Basel (from Meyers, 1985).

TABLE A.IV-2

PCB congener	Scheldt		Rhine		Ems		Weser		Elbe		Offshore North Sea	
	C_w	C_p	C_w	C_p	C_w	C_p	C_w	C_p	C_w	C_p	C_w	C_p
18	560	4.5	1010	25	220	4.0	170	2.8	290	5.6	24-90	2 -67
52	365	12.8	660	50	90	4.2	130	4.8	170	8.0	13-62	5 -76
101	190	15.6	220	22	30	1.8	60	5.9	70	7.3	5-56	0.4-20
149	160	21.3	180	149	30	4.0	70	13.1	60	13.7	4-70	3 -94
180	380	36.3	50	150	100	29	200	97.6	200	95.6	3-25	3 -34

A

PCB congeners	K_d Scheldt	Rhine	Ems	Weser	Elbe	Average Rivers	Offshore North Sea
18	1×10^4	2×10^4	2×10^4	2×10^4	2×10^4	1.8×10^4	4×10^4-2.9×10^6
52	4×10^4	8×10^4	5×10^4	4×10^4	5×10^4	5.2×10^4	9×10^4-5.9×10^6
101	8×10^4	1×10^5	6×10^4	1×10^5	1×10^5	8.8×10^4	7×10^4-3.3×10^6
149	1×10^5	8×10^5	1×10^5	2×10^5	2×10^5	3.0×10^5	1×10^5-3.8×10^6
180	1×10^5	3×10^6	3×10^5	4×10^5	5×10^5	8.6×10^5	1.7×10^5-3.2×10^6

B

TABLE VI/

A: Concentrations in solution (C_w, in pg·dm^{-3}) and contents of individual PCB congeners (identified by their IUPAC number according to Ballschmiter and Zell, 1980) in suspended particulates (C_p in ng·g^{-1}) in fresh water of the rivers Scheldt, Rhine, Ems, Weser and Elbe and offshore North Sea water.

B: Water-SPM distribution coefficients (K_d) for individual PCB congeners calculated from fresh water concentration data in A, for the rivers Scheldt, Rhine, Ems, Weser and Elbe (the average value is given in the last column) and offshore North Sea water (from Duinker, 1986).

five Western European rivers showed only minor variations of K_d values, despite considerable differences in PCB concentrations between river systems (Duinker, 1986). The dissolution of hydrophobic compounds into river water or seawater may in fact form pseudo-solutions associated with micelles or colloids or solubilized by association with components of the natural organic carbon pool, all of which in turn may alter the activity of an individual contaminant. The complex three phase models themselves are an oversimplification in the assumption of equilibrium and factors including microbial degradation, sorption kinetics and steric effects contribute to deviations from predicted distributions. The use of K_d rather than K_p already indicates that equilibrium is not assumed.

2.3. Effects of Estuarine Mixing

In the estuary, river-borne components are subjected to strong gradients in important properties (ionic strength, pH, dissolved O_2 and SPM concentrations). Water-particulate partitioning of a compound may be affected in response to changes in activities and suspended matter concentrations or as a result of chemically and biologically mediated reactions.

Hydrophobic contaminants tend to associate with lipid pools which themselves may be less refractory than the contaminants. Variations in the composition (e.g., lipid content) of estuarine DOC compared with the riverine source material may force a shift in the partitioning of the contaminants. This sorption behaviour may be more closely described by a multiphase equilibrium model.

Organic compounds with high hydrophobicity will, for the greater part, be associated with particles and thus be subjected to particle transport mechanisms in the estuarine and marine environments. Desorption of such compounds in estuarine water is not likely to be a quantitatively significant process. The combination of the persistence of these compounds and the long residence time of particles in the estuarine and shelf environments ensures that slow transport to offshore waters. Co-deposition of large amounts of high energy, labile organic compounds to sediments such as may occur in estuaries, favours abiotic degradation processes under reducing conditions or degradation as a result of increased microbial activity.

For hydrophobic compounds with relatively high solubilities, the dissolved phase assumes a more important transport function even at increased suspended matter concentrations. Examples of organochlorine compounds with high solubilities (high K_{ow}) are γ - HCH (lindane) and its by-product α-HCH. The major riverborne flux of lindane is therefore expected to occur in the dissolved phase and its net export beyond estuaries, shelves and marginal seas is likely to be significant (for example, Rhine Estuary, Duinker and Hillebrand 1979; Loire Estuary, Marchand <u>et al</u>. 1984). Dissolved riverborne PCB congeners have been reported to behave conservatively during estuarine mixing in the Rhine (Duinker and Hillebrand, 1979) Ems (Duinker <u>et al</u>., 1985) and Exe estuaries (Herrmann and Thomas, 1984). Hence it is likely that the dissolved fraction of PCB (around 50% of the input for these rivers) reaches the external estuarine boundary in solution. The remaining 50% of PCB, associated with river particles, comprises a larger fraction of higher chlorinated congeners (with higher K_d's, Table A.IV-2). Deposition of these refractory contaminants within estuarine sediments accounts for the removal of a significant fraction. A portion of the fine particulate load, however, may escape estuarine entrapment and determine the offshore end-member in the partitioning of PCB. The finer particulates have been found to have significantly higher K_d values (Duinker, 1986). Consequently, simple extrapolation of riverine partitioning to represent that in the open sea, with lower suspended matter concentrations, would inevitably misrepresent the relative distributions of the contaminants between the phases and thus predict a higher ratio in the dissolved relative to the observed case.

APPENDIX V

INFLUENCE OF RIVER HYDROLOGY ON MATERIAL TRANSPORT

1. Introduction

The chemistry and chemical flux of a river system is strongly related to its hydrology because the complex suites of pathways and storages involved in the translation of rainfall into runoff greatly influence the nature of fluvial transport. Figure A.V-1, for example, illustrates in a simplified form the rainfall/runoff processes operating in a drainage basin and their interaction with the mechanisms which govern the flux of dissolved material in streamflow. The influence of hydrology on river flux is evident at scales which range from that of the individual drainage basin to that of global patterns of fluvial transport, and the impact of different facets of river hydrology on chemical flux in dissolved and particulate-associated form may be isolated.

The following discusses important aspects of river hydrology that influence material transport.

2. Annual Regime

Rivers vary greatly in the distribution of flow throughout the year and considerable effort has gone into the characterization and classification of runoff regimes at global and more local scales (e.g. Ledger, 1964; Beckinsale, 1969; UNESCO, 1978). Many rivers also display a strong seasonal variation in chemical concentration, which may often be attributed to the dominance of runoff with contrasting origins at different times of the year (Skakalskiy, 1966), as data from the Pyalitsa River, U.S.S.R. indicate (Figure A.V-2A). Results from a much smaller catchment in Devon, U.K. (Walling and Webb, 1982a) reveal that the consequences of such annual cycles for river flux will depend on the detailed interaction of solute and flow regimes for a particular river. It is common for dissolved species to have an annual regime of concentration which is the simple inverse of flow (e.g. Mg in Figure A.V-2B) and this pattern tends to reduce the contrast in flux between wetter and drier seasons. In contrast, some solute species (e.g. NO_3^--N in Figure A.V-2B) have a more asymmetrical annual cycle and exhibit highest concentrations at times of greatest flow so that seasonal contrasts in flux are maximized. Substances transported in particulate-associated form are mobilized together with suspended sediment which tends to vary in the river system in a more episodic manner related to storm events rather than to any annual climatic or biological rhythm.

The nature of the annual cycle in concentration for a dissolved substance may also vary considerably over time at a particular station or over space between different sites for a particular time period. Data collected from the River Dart, Devon, U.K. (Webb and Walling, 1985) over an eight year period (February, 1975 - January, 1983) reveal the variability in NO_3^--N concentrations for a small (46 km^2) agricultural catchment (Figure A.V-3). Construction of 95% confidence limits around the average annual trend (Figure A.V-3) reveals the regime for NO_3^--N to be particularly variable in the early autumn period when the transition from low concentrations typical of the summer months to higher levels of the winter season varies in timing according to the sequence and character of early winter storms and the extent to which soil moisture is depleted in the preceding summer period. Data available more widely within the Exe Basin of Southwest England (Walling and

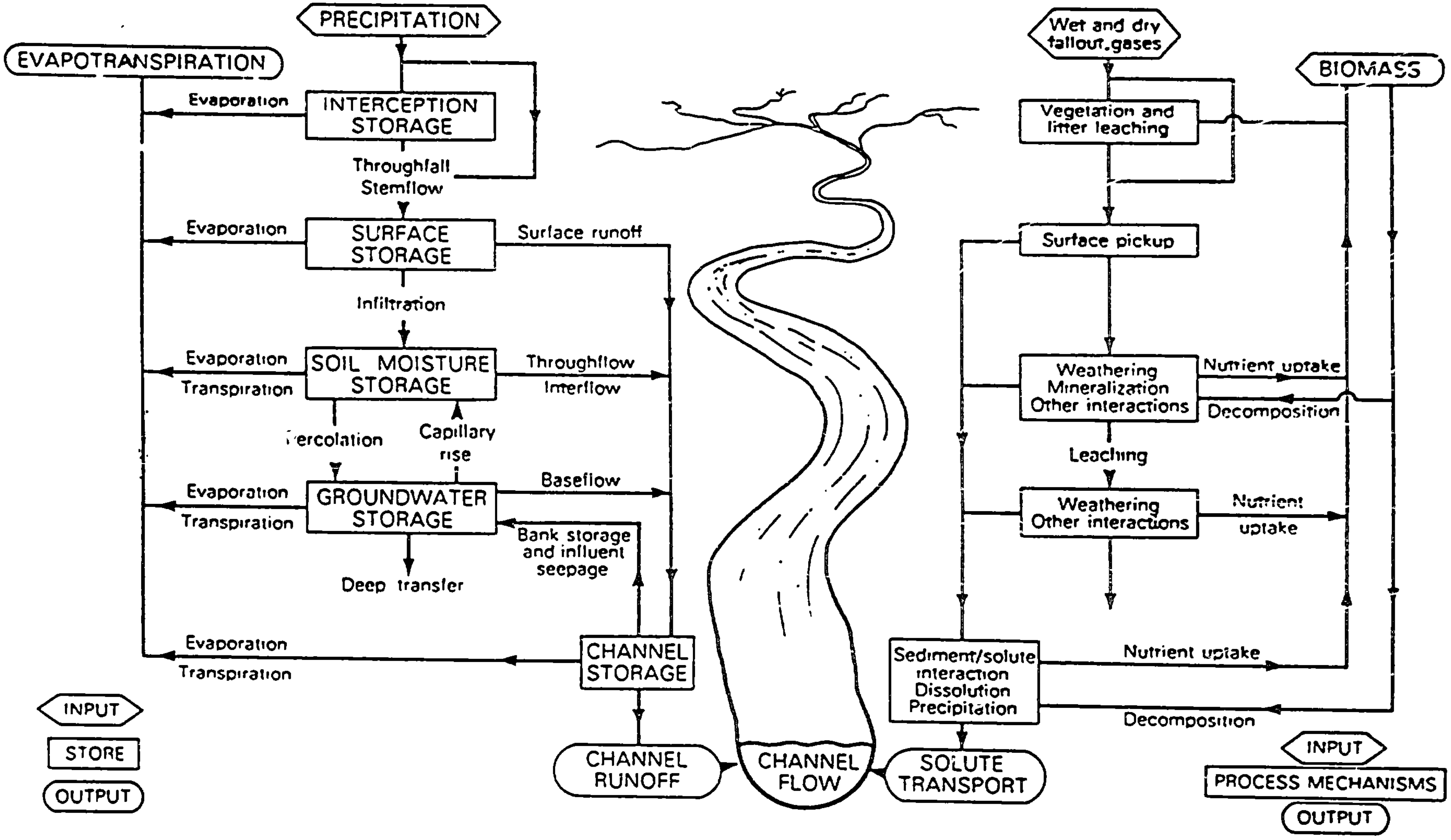


Figure A.V-1. Simplified representation of the rainfall/runoff processes operating in a drainage basin and associated mechanisms governing the flux of dissolved material in streamflow (after Walling and Webb, 1986a).

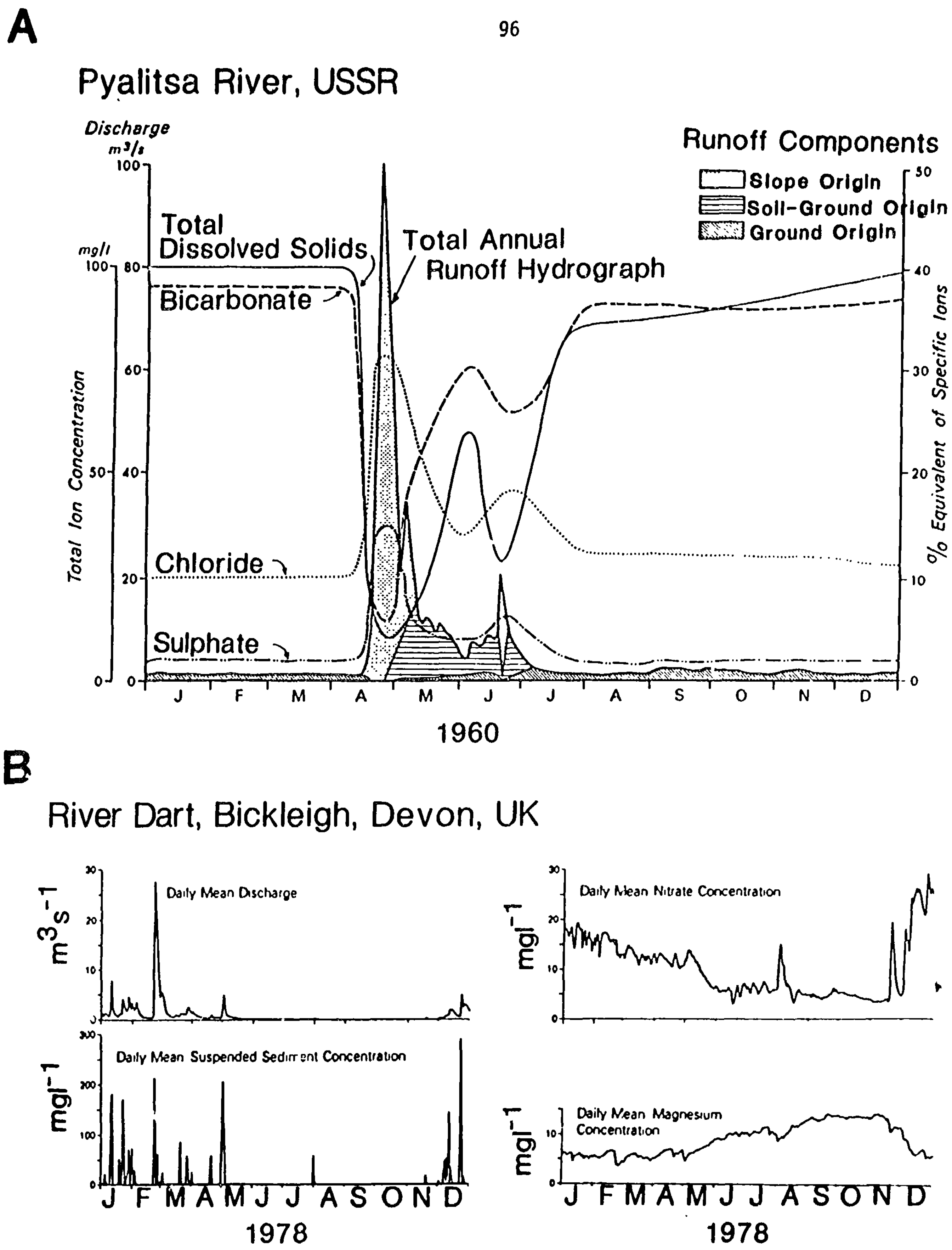


Figure A.V-2. Seasonal variation in river water chemistry (after Gregory and Walling, 1973 (A) and Walling and Webb, 1982a (B)).

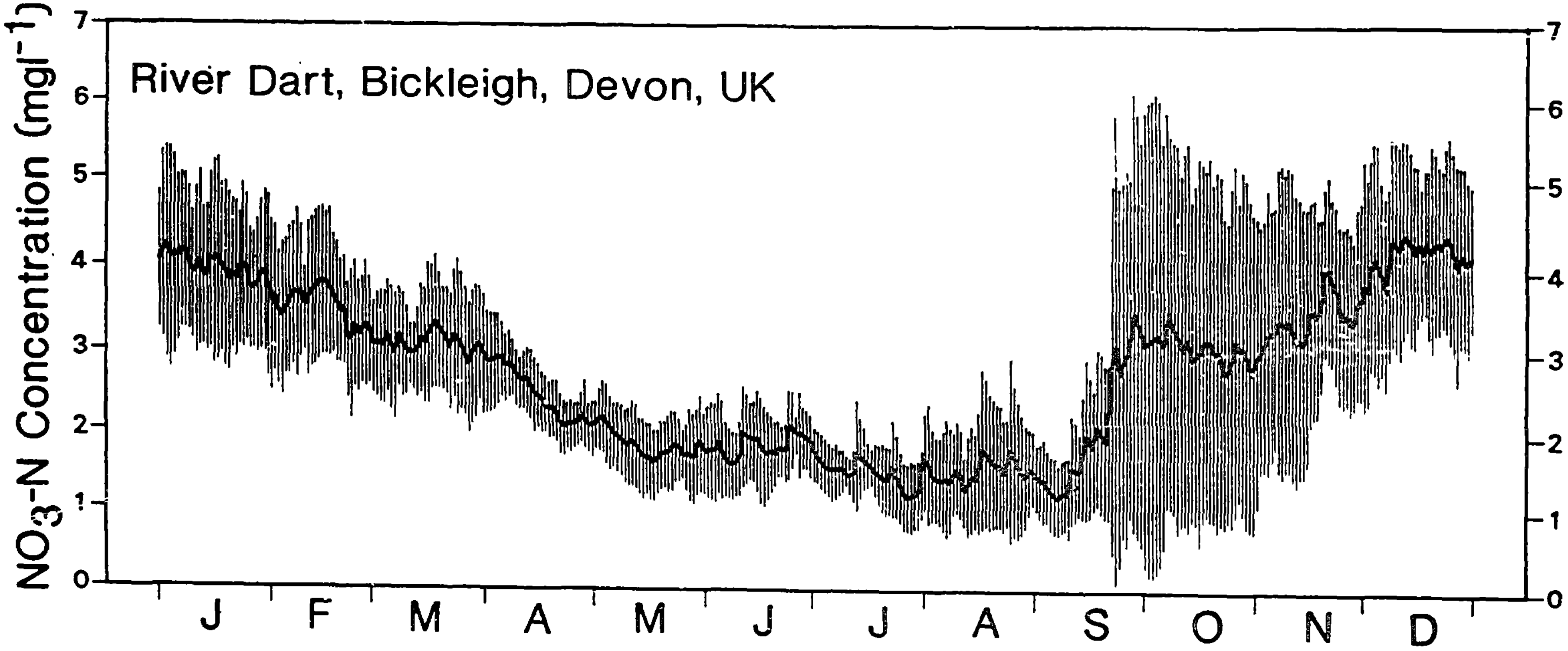


Figure A.V-3. Variability in the annual regime of NO$_3$-N concentration in streamflow (after Webb and Walling, 1985).

Webb, 1984) also reveal marked spatial variability in the form of the annual regime for NO_3^--N concentrations. Figure A.V-4 plots data collected over a four year period (January, 1980 - December, 1983) for three sites at which the average annual regime in NO_3^--N has been isolated by the fitting of simple harmonic functions (Walling and Webb, 1984). The catchments evidence a trend in land-use character from unenclosed heather moorland (Black Ball Stream) to pasture and woodland (River Batherm) to more intensively farmed arable areas (Jackmoor Brook) which is associated with an annual fluctuation in NO_3^--N of increasing amplitude.

Climatically induced contrasts in hydrological regime at regional and continental scales also strongly affect the annual pattern of flux in river systems. Mountainous regions supporting glaciers, zones of periglacial climate and regions where precipitation is dominated by snowfall are often characterized by episodes of intense river activity separated by periods of relative inactivity. Dissolved and particulate-associated flux may be largely concentrated into a short 'pre-break-up' and 'break-up' period of ice melting (Arnborg et al., 1967), into a series of floods associated with a snow and icemelt period (e.g. Ongley, 1976) or into a short summer season. The latter case is well illustrated by the seasonal variation in the transport of cations from the Gornergletscher Basin of Switzerland (Collins, 1983), where most of the cationic load was removed in the months of May-September (Table A.V-1). Other climates with a strong seasonal character, such as occurs in savanna and in 'mediterranean' regions, will also be associated with marked contrasts throughout the year in river flux, although existing data relating to suspended sediment regime (e.g. Gregory and Walling, 1973) revealed that fluvial transport often has a complex rather than a simple intra-annual variation (Figure A.V-5).

3. Storm-period Response

Superimposed on the annual regime of sediment and solute levels in river systems are pronounced shorter-term fluctuations related to the occurrence of storm events. It is often possible to represent the general response of dissolved and particulate-associated substances to changing flow in streams and rivers by means of a rating relationship (Figure A.V-6) of the form:

$$c = aQ^b \qquad (1)$$

where c is chemical concentration, Q is river discharge and a and b are constants (e.g. Nilsson, 1971; Turvey, 1975; Walling and Webb, 1983a; Walling and Kane, 1984). Although the use of rating relationships has been developed and refined (Figure A.V-7) by subdividing data sets on the basis of season (e.g. Foster, 1978a), stage conditions (e.g. Oxley, 1974) and flow components (e.g. Walling, 1974) and by the fitting of more complex rating functions (e.g. Hall, 1970; Foster, 1980), more detailed investigations of recent years have stressed the complexity and variability of storm-period sediment and solute responses (e.g. Walling and Foster, 1975; Miller and Drever, 1977; Foster, 1978b; Reid et al., 1981; Dupraz et al., 1982; Webb and Walling, 1983; Walling and Webb, 1986a, b).

The complexity of storm-period responses is evident from several events monitored in the Exe Basin, Devon, U.K. (Figure A.V-8). Different dissolved and particulate parameters often exhibit markedly contrasting behavior as the storm monitored on 6-7 October, 1979 in the River Dart at Bickleigh indicates (Figure A.V-8A). Mg concentrations showed a marked decrease during this event, and reached minimum values shortly after the flow peak. In contrast NO_3^--N levels increased

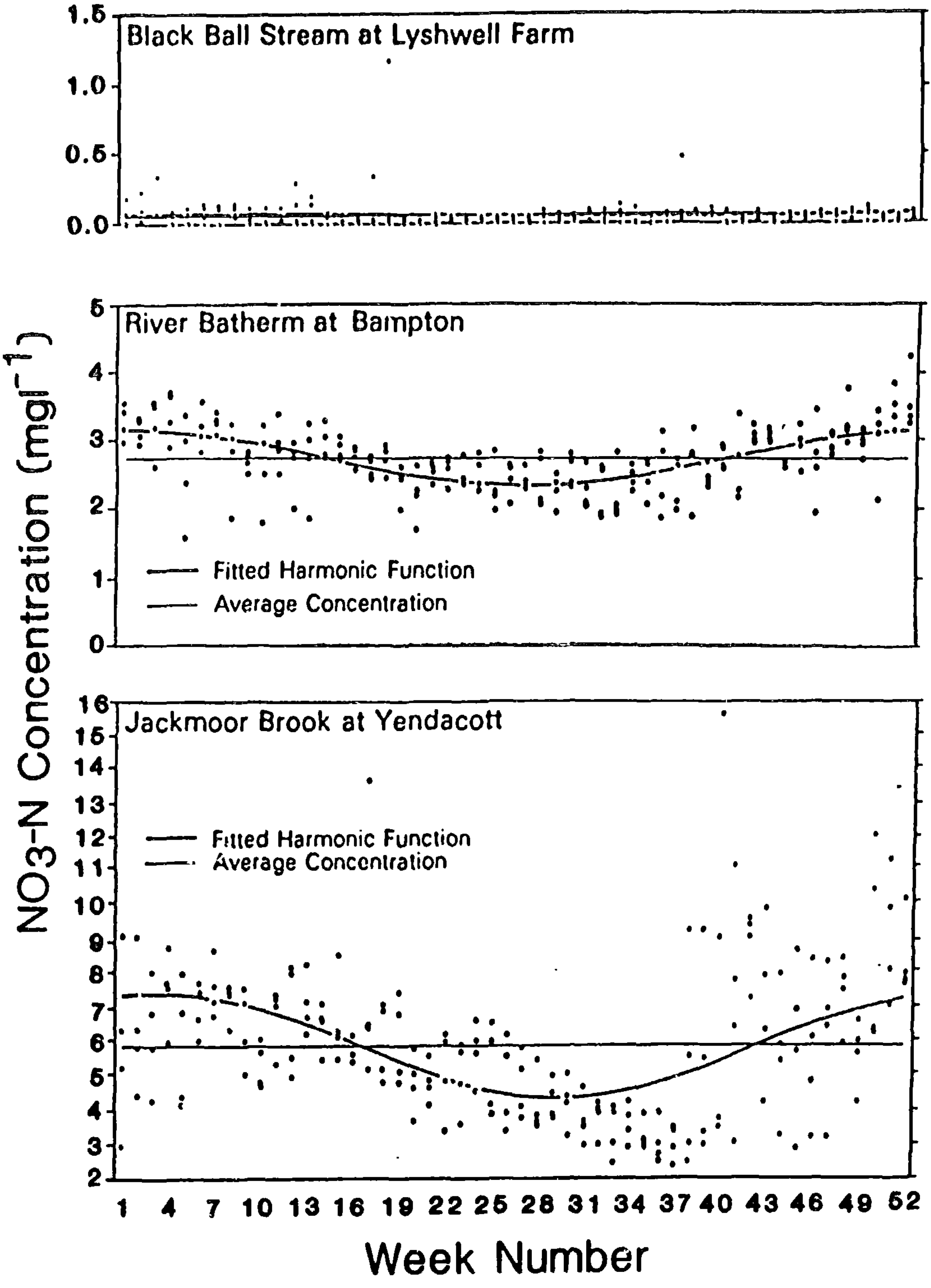


Figure A.V-4. The annual regime of NO_3^-N concentration at selected stations in the Exe Basin, Devon, U.K. (after Walling and Webb, 1984).

TABLE A.V-1

Seasonal variation in the transport of catonic load from the Gornergletscher Basin, Switzerland (after Collins, 1983).

Month	Cationic Load: (10^6 eq)	%
November	0.27	0.7
December	0.31	0.8
January	0.16	0.4
February	0.15	0.4
March	0.16	0.4
April	0.15	0.4
May	1.73	4.4
June	7.13	18.2
July	12.18	31.1
August	10.37	26.5
September	6.05	15.4
October	0.53	1.4
Total	39.21	

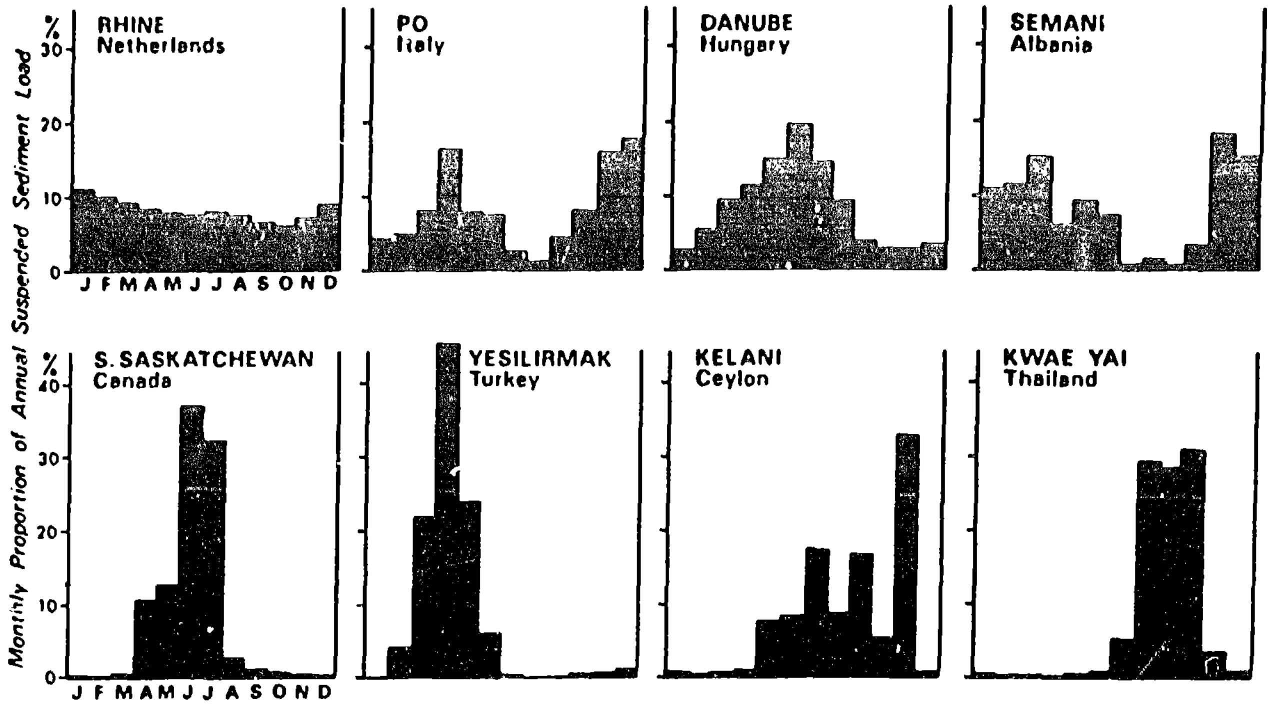


Figure A.V-5. Selected suspended sediment regimes (after Gregory and Walling, 1973).

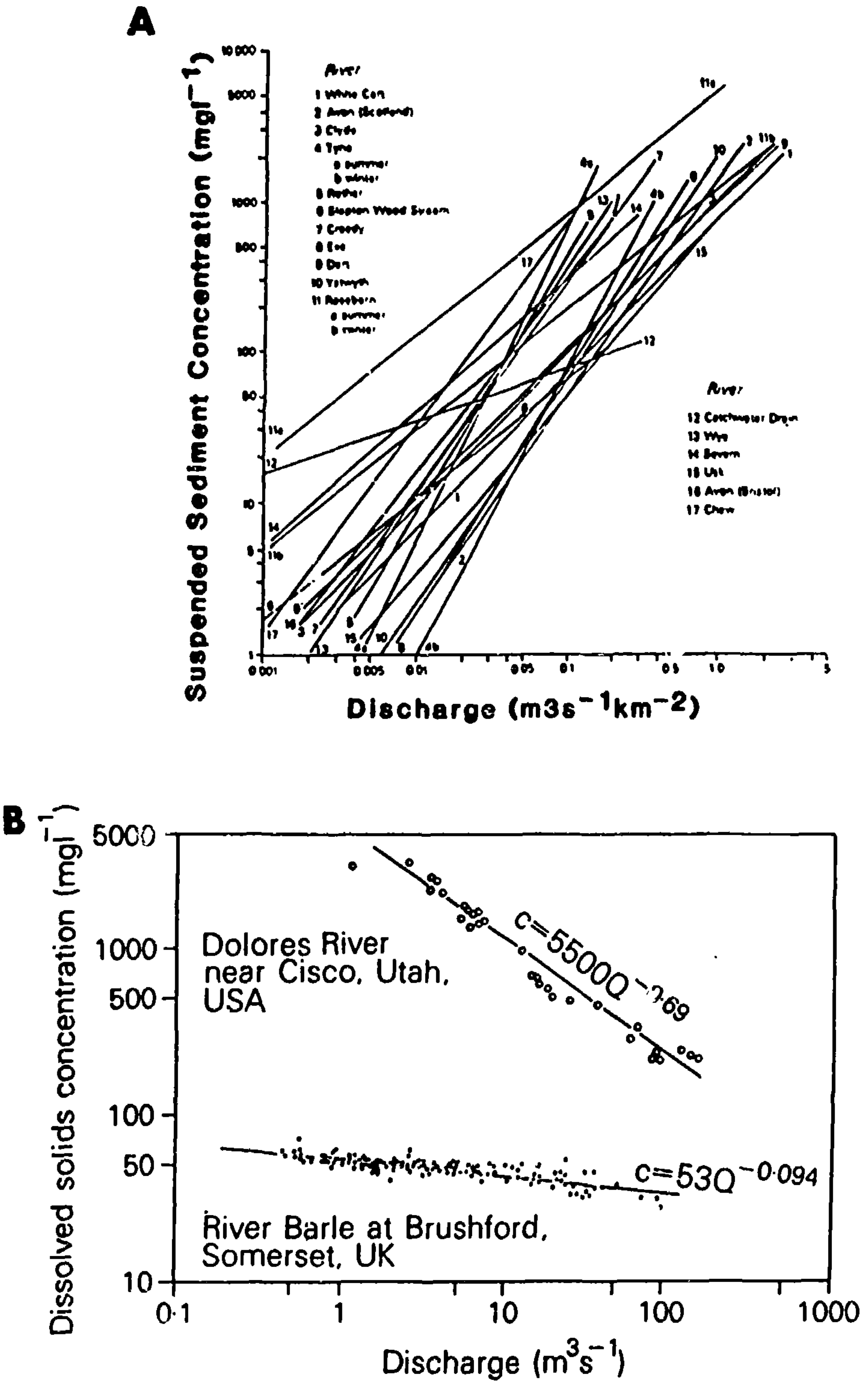


Figure A.V-6. Concentration-discharge rating relationships for dissolved, particulate and particulate-associated substances in river runoff (after Walling and Webb, 1983a (A) and Walling and Webb, 1981(B)).

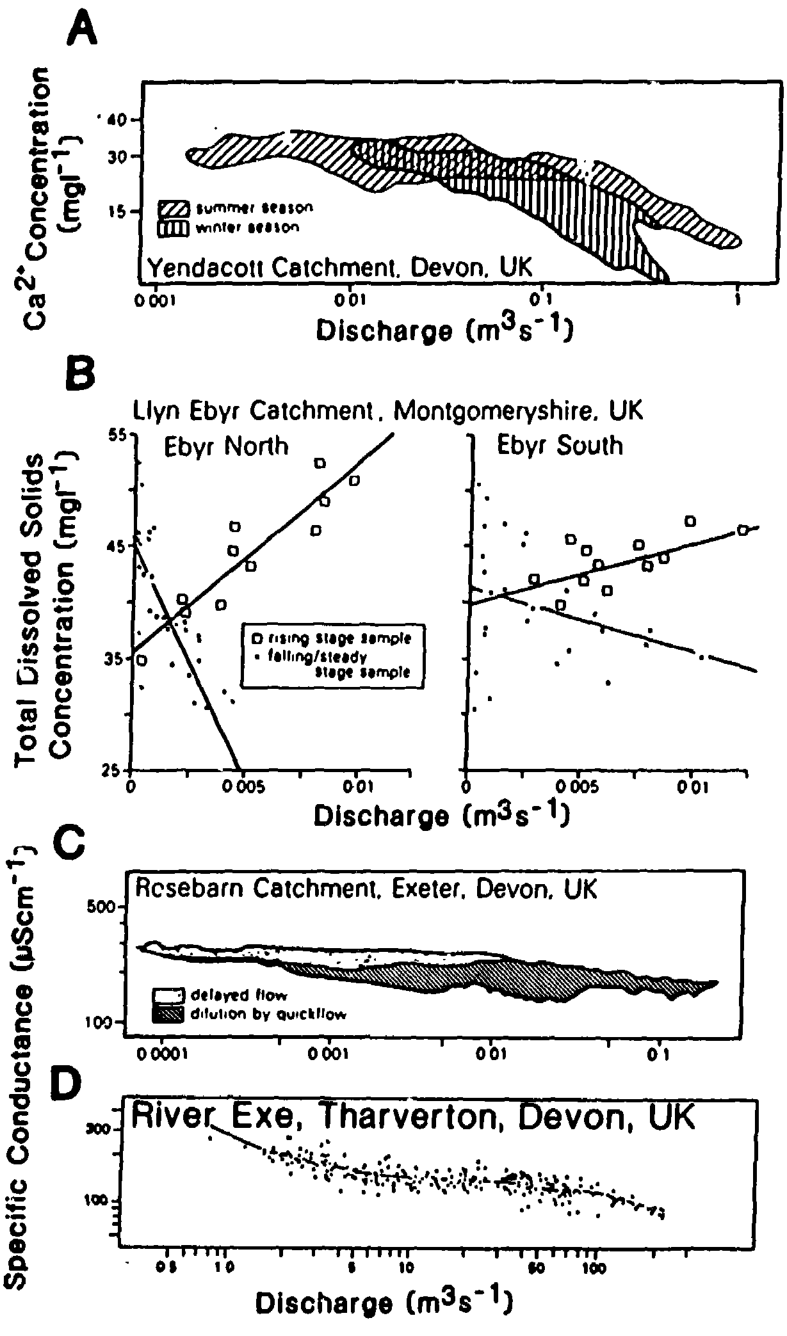


Figure A.V-7. Development of rating relationships through division on the basis of season (after Foster, 1978a) (A), stage conditions (after Oxley, 1974) (B), flow components (after Walling, 1974) (C), and through fitting of polynomial functions (D).

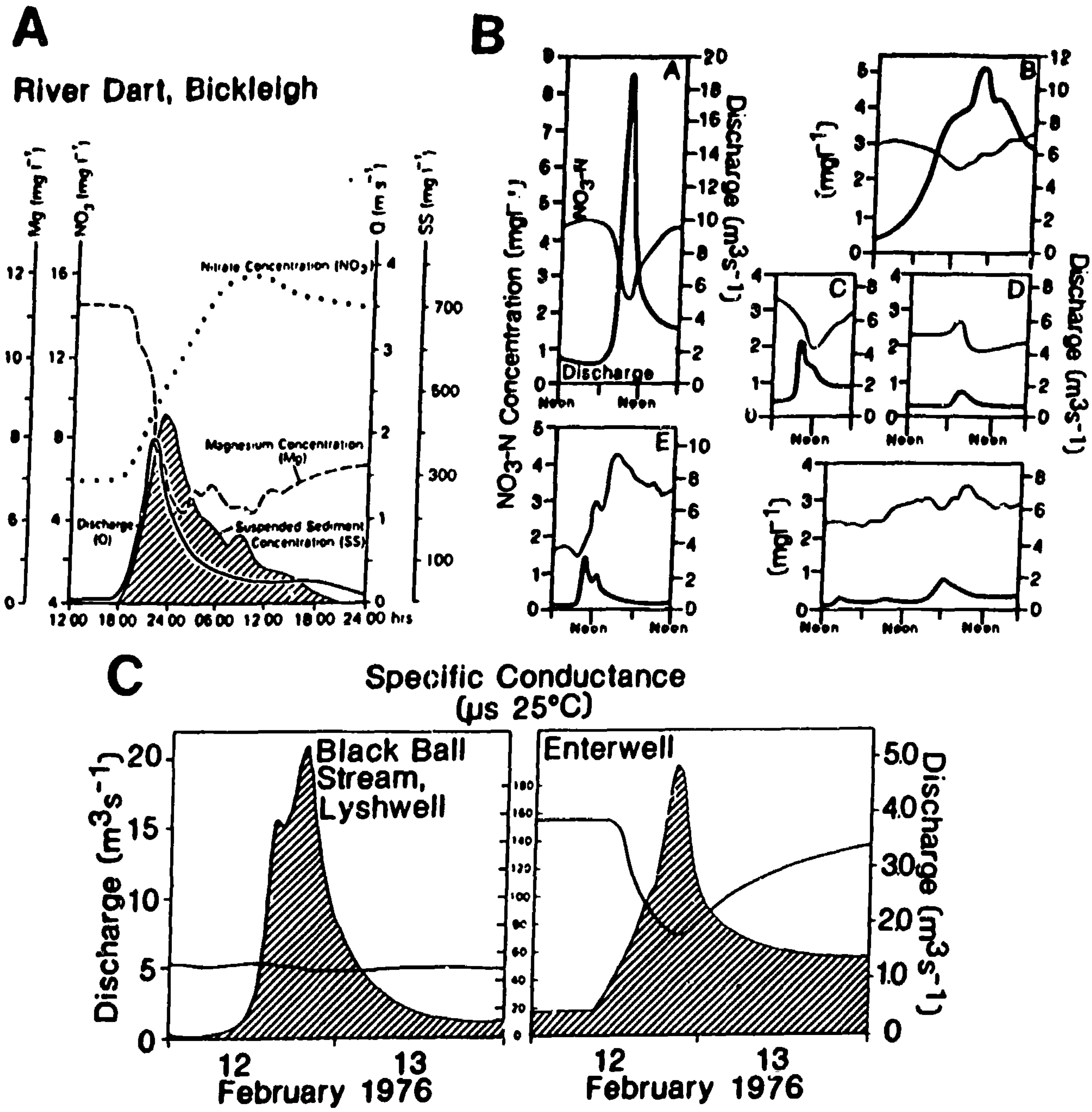


Figure A.V-8. Complexity of storm-period responses recosrded at stations in the Exe Basin, Devon, U.K., after Walling, 1978 (A), Walling and Webb, 1982a (B), and Webb and Walling, 1985 (C).

during the storm but did not attain maximum concentrations until some 12 hours after the peak in the hydrograph, whereas suspended sediment concentrations responded very rapidly to the increase in discharge and reached maximum values during the rising limb of the storm. Chemical, particulate and flow responses are clearly out of phase and in these circumstances it is extremely difficult to calculate flux estimates from discharge data alone.

Additional complexity arises in the case of some substances, such as NO_3^-N, which exhibit markedly contrasting responses in different storms at a single station (Webb and Walling, 1985). Data collected from the River Dart at Bickleigh (Figure A.V-8B) reveal that NO_3^-N concentrations are often diluted rather than increased by storms occurring in the winter months but chemographs exhibiting dilution vary greatly in their form and their timing with respect to the discharge hydrograph. Many substances will also vary in their behavior between different sites in a particular event. Walling (1978) presented data relating to the response of total dissolved solid concentrations (indexed by specific conductance) in two tributaries draining Exmoor in Devon, U.K. during the storm of 12-13 February 1976 (Figure A.V-8C). The site at Lyshwell is fed by a stream draining largely undisturbed moorland developed on resistant sandstones of Devonian age. Solute levels in this environment are generally low and the atmosphere provides the main source of dissolved material in streamflow so there is little contrast in the specific conductance of baseflow and stormflow in this catchment and storm events generate only small changes in stream chemistry. In contrast, the River Quarme at Enterwell largely drains an area of agricultural land developed on calcareous slates. This leads to higher solute concentrations in stream baseflows which provide a greater potential for dilution responses in storm events (Figure A.V-8C).

A further complication arises in the case of flux in particulate-associated form because data from several catchments in Devon (Walling and Kane, 1984) reveal that inter- and intra-storm variations in sediment chemistry may not always be predicted from data on sediment concentration.

4. Hysteretic Effects and Antecedent Conditions

The nature of chemical flux in storm events or over longer periods is made more complex by the occurrence of hysteretic effects whereby *a given flow level* occurring in different parts of a storm hydrograph (e.g. rising or falling limbs) or in different seasons of the year is associated with *a varying chemical concentration*. Traditionally, this phenomenon has been investigated through the construction of looped relationships between chemical concentration and river discharge (Figures A.V-9A and 9C) for specific storm events (Hendrickson and Krieger, 1964; Toler, 1965; Collins, 1979) or for particular years (Gunnerson, 1967; Davis and Keller, 1983). In the context of storm events, hysteretic behavior may be generated by the relative *timing* or the relative *form* of chemical and discharge responses (Walling and Webb, 1986a). Prowse (1984) has also distinguished *true* hysteresis, caused by the hydraulics of floodwave and floodwater transmission (Glover and Johnson, 1974), from *virtual* hysteresis, generated by other factors such as the balance of different surface and sub-surface flow components in storm hydrographs (Spraggs, 1976; Johnson and East, 1982). Virtual effects, including the influrence of seasonal variation in biological activity, also account for hysteresis on an annual time scale (O'Connor, 1976; Davis and Keller, 1983), and this phenomenon has been shown by Sundborg (1986) to be typical of particulate flux for rivers in a very wide range of environments (Figure A.V-9B).

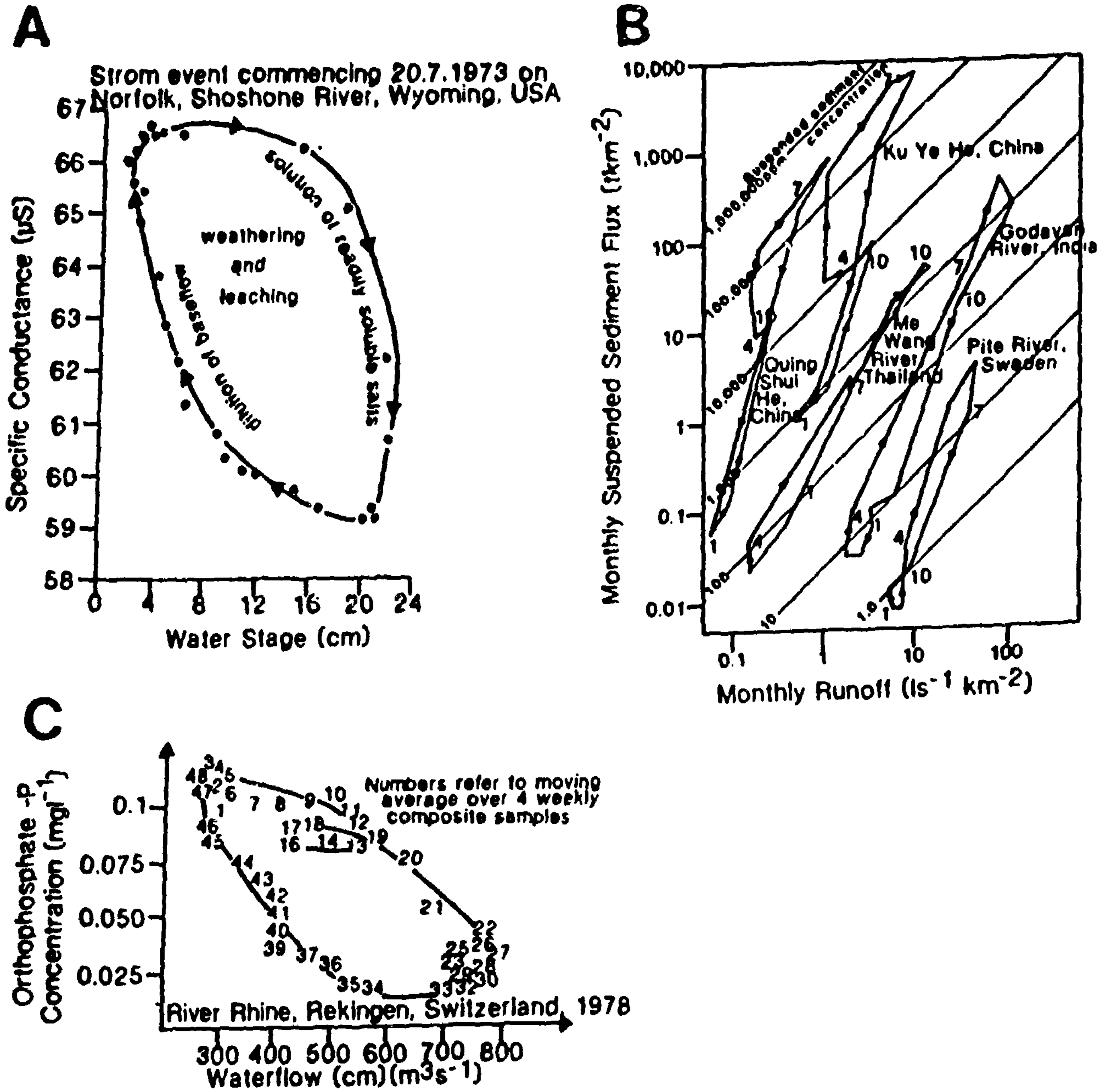


Figure A.V-9. Storm-period (after Miller and Drever, 1977) and annual (after Davis and Keller, 1983) hysteresis in solute levels (A and C) and annual looping in the relationship between suspended sediment flux and runoff (after Sundberg, 1986) (B).

Of the several factors which may generate storm-period hysteretic behavior through their influence on the form and timing of chemographs, conditions antecedent to the storm event are of particular importance. A 'flushing effect', for example, has been noted in many rivers (e.g. Hendrickson and Krieger, 1960; Edwards, 1973; Walling, 1974; Walling and Foster, 1975) through which soluble material accumulated in the period before a storm is mobilized and transported to the stream where it influences chemical concentrations during the early stages of a storm event. Evaporation of soil moisture, capillary rise and the build-up of dry fallout deposits from the atmosphere, leaf residues and dead plant material are processes which promote solute accumulation before a flood event (Walling and Foster, 1978), and flushing effects are particularly pronounced in autumn storms following such accumulation over the summer period. Chemical concentrations in surface and sub-surface flows have been found to be systematically related to the length of the dry period preceding a storm (Klein, 1981), and similar considerations of preparation and availability also apply to sediment concentrations and to substances transported in particulate-associated form. A study of suspended sediment dynamics during 98 storm events recorded in the River Dart. (Walling and Webb, 1982b) revealed that peak sediment concentrations in stormflow were more strongly influenced by the length of the period (recovery period) preceding an event than by the magnitude of peak stormflow runoff occurring in the event itself (Figure A.V-10). Storms which occurred at least 30 days after a preceding event were characterized by peak stormflow sediment concentrations of c. 2000 mgl^{-1} whereas this value fell to c. 400 mgl^{-1} for events occurring less than seven days after a preceding storm. Data for secondary peaks of multi-peaked stormflow events, where the recovery period was effectively zero, also generally plotted below the field of the main data set (Figure A.V-10). In the case of sediment transport, a longer period of time preceding a storm event allows physical and biological processes to increase the store of readily available sediment in a drainage basin (Imeson, 1977).

In contrast to the flushing effect, solute and sediment stores within a drainage basin may become depleted during a sequence of closely spaced flood peaks. This 'exhaustion effect' has been recorded for both dissolved potassium and suspended sediment concentrations over sequences of frequent storm events in the River Dart (Figure A.V-11), and progressive exhaustion of solute supplies has been shown to cause a systematic shift in the position of the hysteretic loop between specific conductance and discharge during a series of storms affecting the German's Creek catchment, New South Wales, Australia between April and June 1978 (Cornish, 1982).

5. Rare Events and Magnitude/Frequency Considerations

The occurrence of rare events, such as the incidence of severe drought may greatly exaggerate processes, such as flushing phenomena, which also take place under less extreme conditions. An example of such an exaggeration arose at the end of the 1976 drought in Britain when conditions of extreme dryness were rapidly changed by exceptional rainfall (Slack, 1977; Walling, 1980). Records of total and individual chemical concentrations collected from the Jackmoor Brook during September and October, 1976 (Figure A.V-12A) show the substantial and prolonged increases in many dissolved substances consequent upon the heavy rainfall in the period from 22 September to mid-October which terminated the drought in this catchment. Very striking increases in some constitutents, especially NO_3^-N, during the intermediate post-drought period were probably generated by changes in soil biochemistry, involving the interrelationship between organic and inorganic nit-

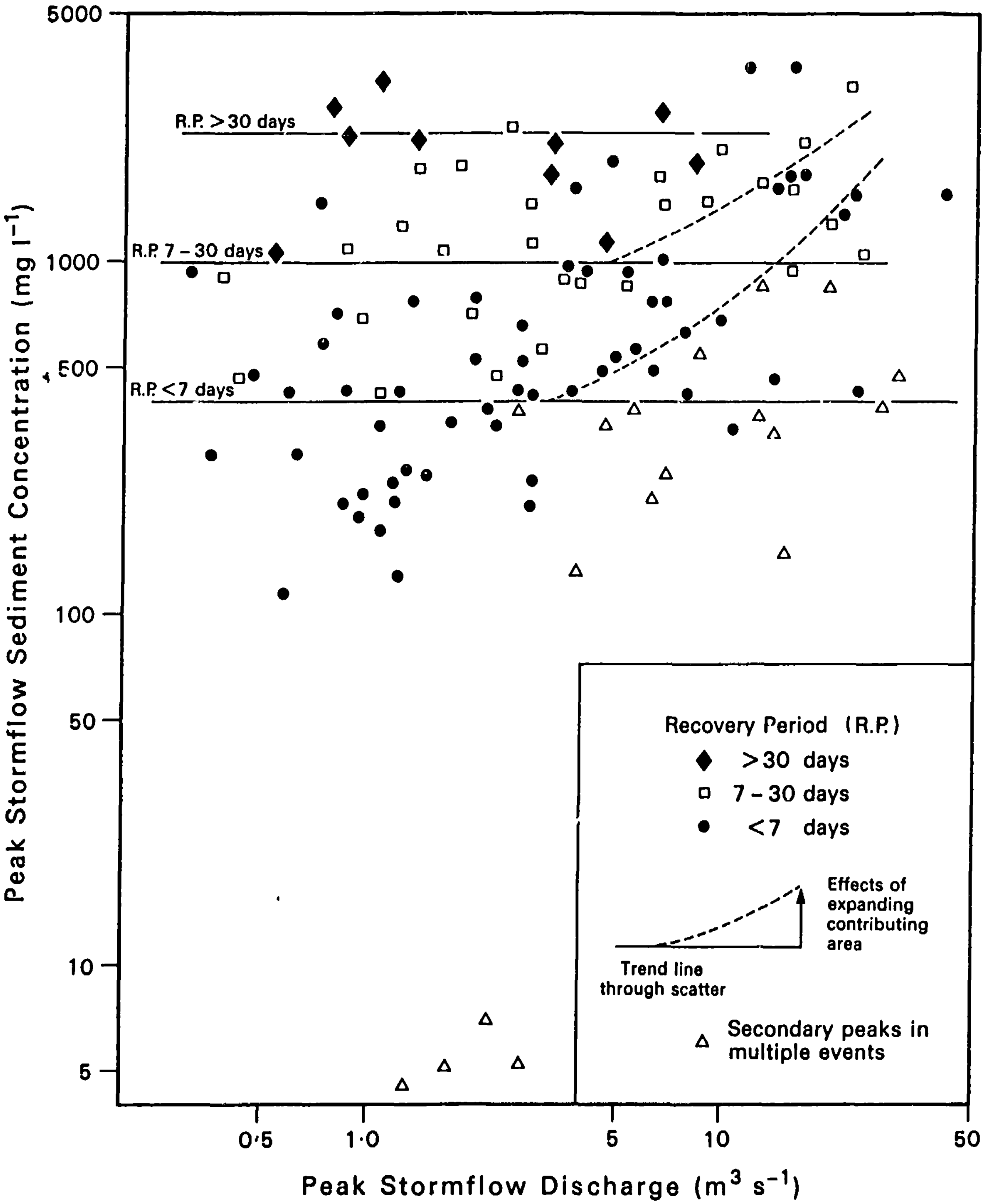
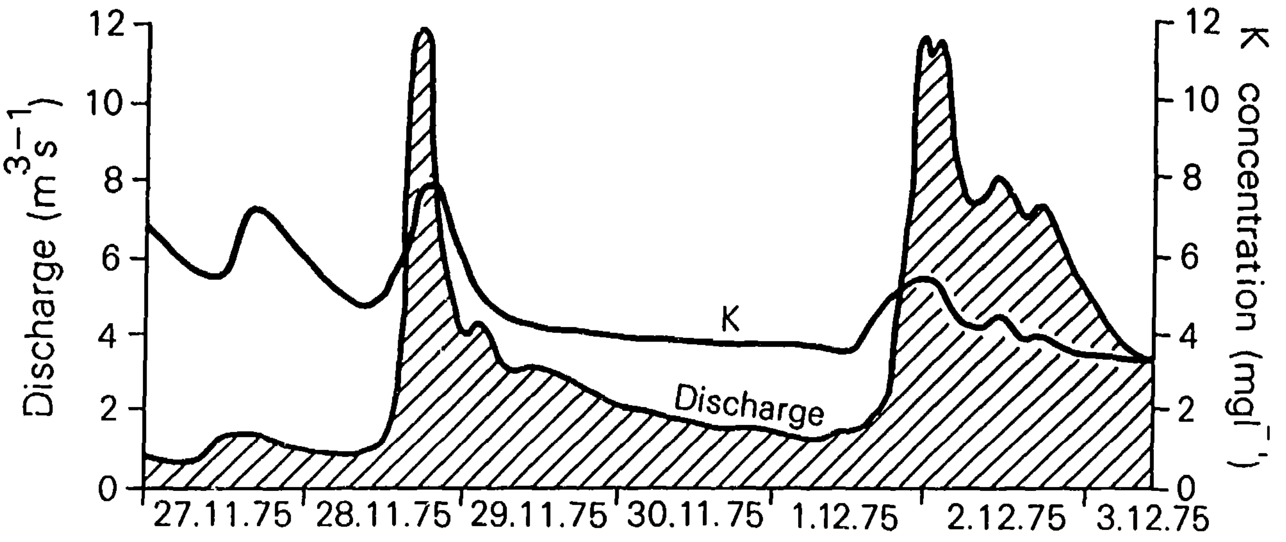


Figure A.V-10. The relationship between peak stormflow suspended sediment concentration and peak stormflow discharge for individual storm events classified by recovery period on the River Dart, Bickleigh, Devon, U.K. (after Walling and Webb, 1982b).



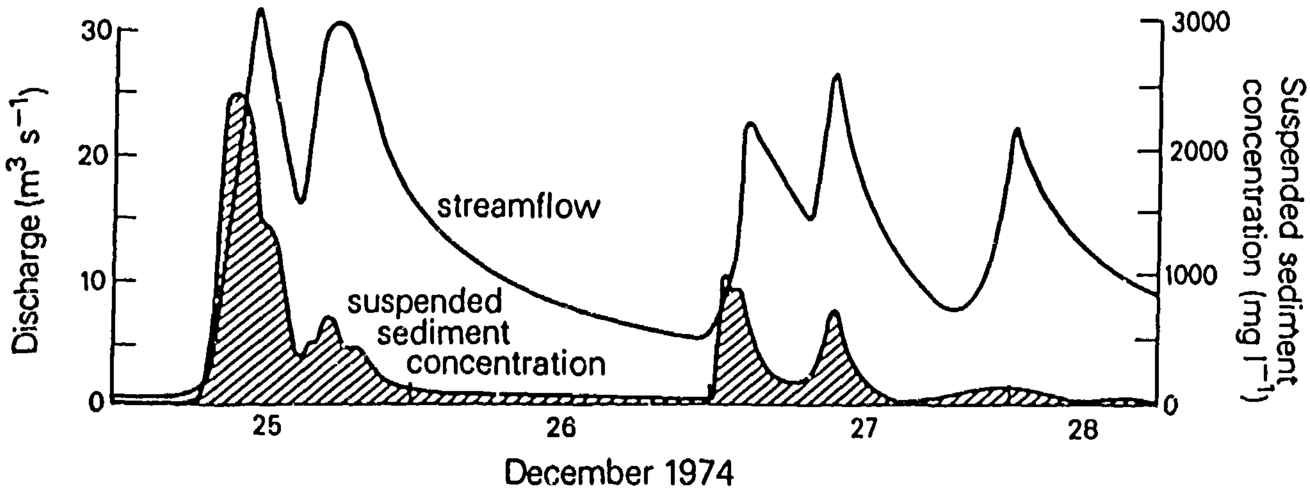


Figure A.V-11. An 'exhaustion effect' in potassium and suspended sediment concentrations recorded in the River Dart, Bickleigh, Devon, U.K. (after Walling and Webb, 1986a and Walling and Webb, 1981a).

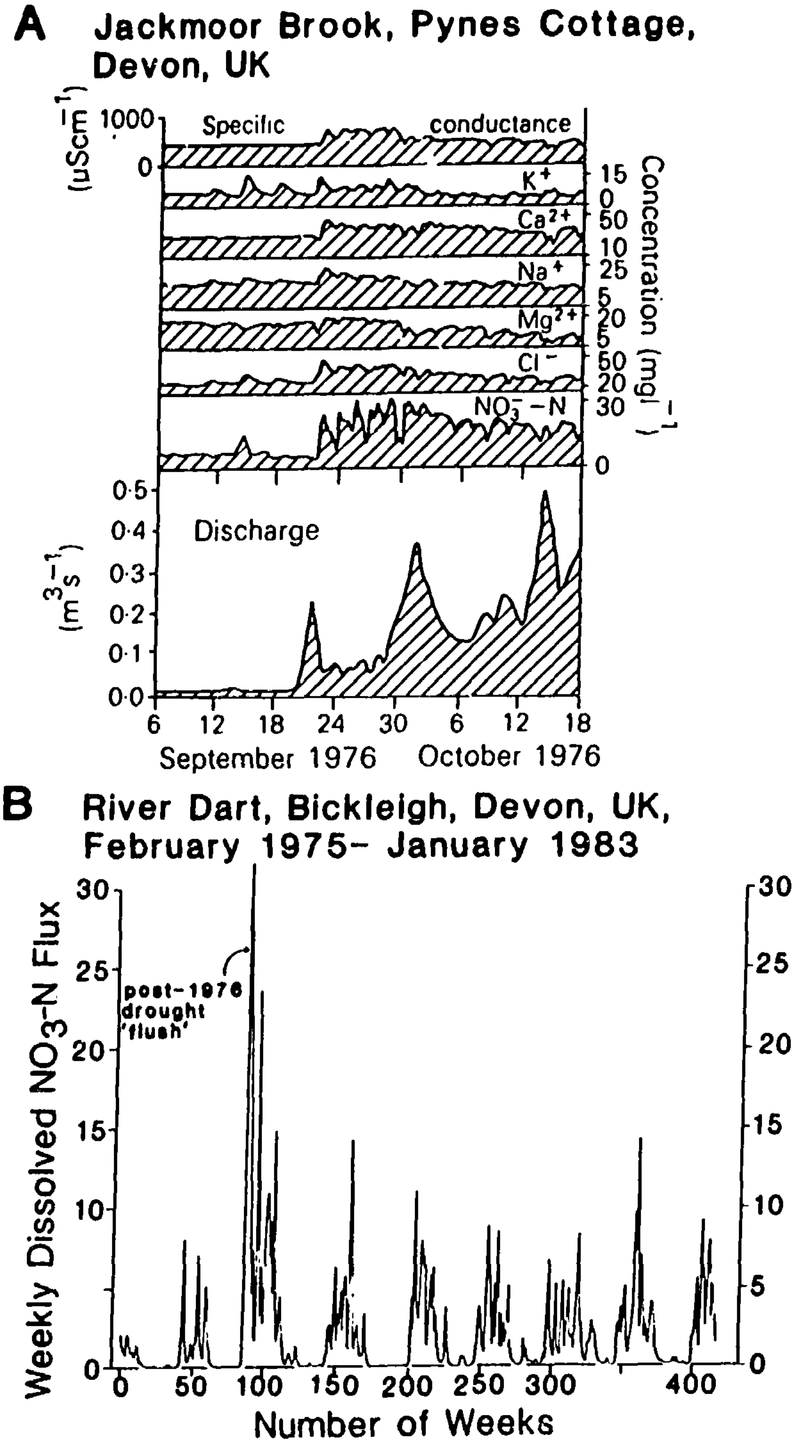
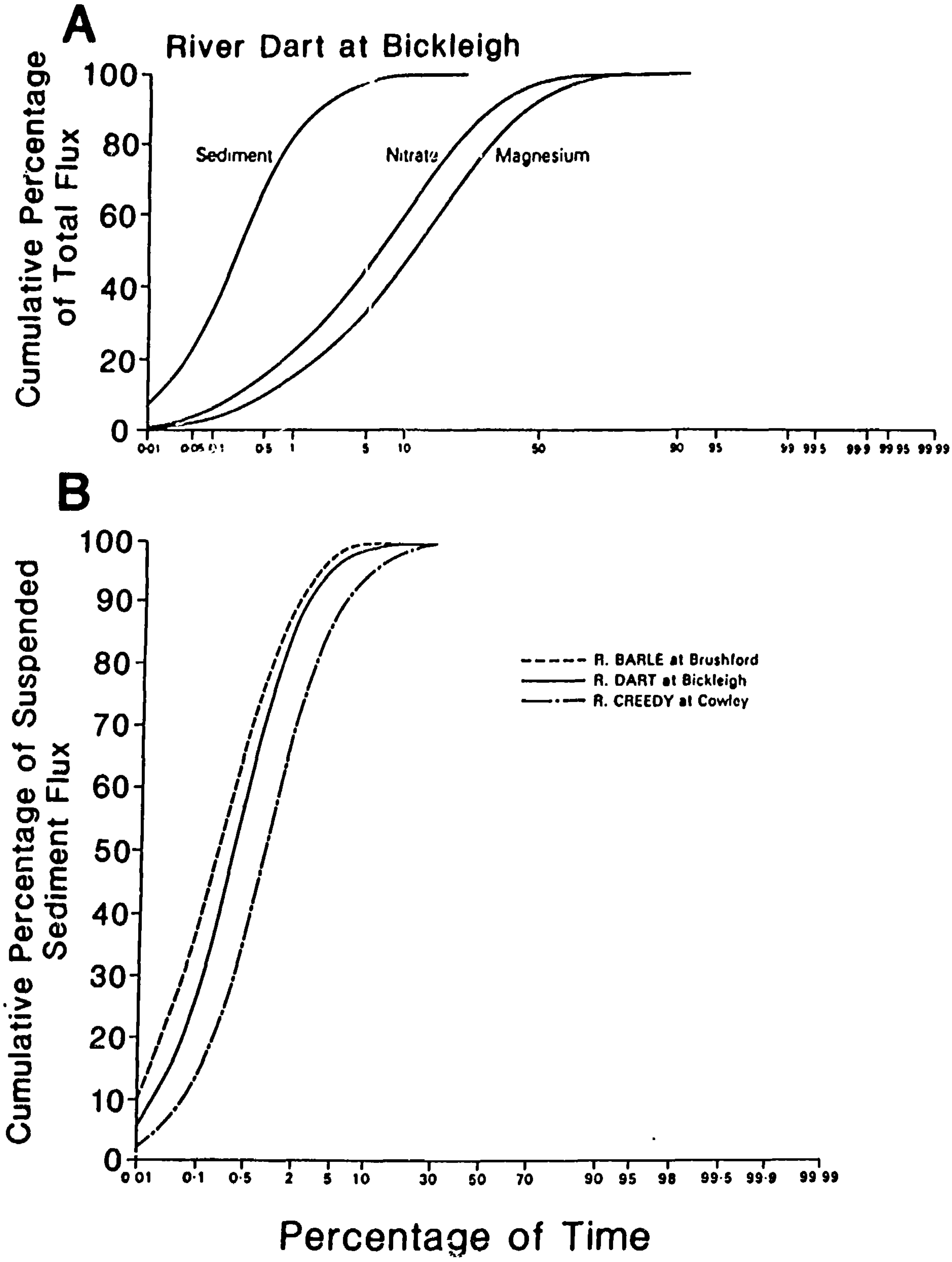


Figure A.V-12. Perturbations in solute concentratin and flux recorded in two Devon catchments during the immediate post-drought period in 1976 (after Walling and Webb, 1986a (A) and Webb and Walling, 1985 (B)).

rogen (Walling and Foster, 1978), as well as simple physical flushing processes. The large perturbation in NO_3^-N flux generated in the post-drought phase is readily apparent from an eight year record of NO_3^-N loads available for the River Dart (Figure A.V-12B).

The occurrence of extreme events such as catastrophic flooding (e.g. Stewart and LaMarche, 1967; USGS, 1979; South African Department of Environment Affairs, 1982) and the incidence of major mass movements (e.g. Pickup *et al.*, 1981; Watanabe and Ikeya, 1981) may also have an important impact on the transport of sediment and particulate associated substances. Colombani and Olivry (1984) have shown for small and large drainage basins in semi-arid and arid environments of the Maghreb of Tunesia and the Cabo Verde Archipelago that infrequent but heavy rainfalls can generate exceptional erosion and sediment transport, and even more spectacular was the 1980 eruption of Mount St. Helens, Washington, U.S.A. on sediment flux in the Toutle River. It has been calculated that approximately 10^9 t of unconsolidated ejecta and debris was made available for erosion and transport in this 1630 km^2 catchment as a consequence of the eruption (Nordin, 1985). The influence of extreme events on sediment flux may be especially marked when recovery of the fluvial system following a major storm is slow or when high magnitude floods cause critical geomorphic thresholds to be exceeded (Hadley *et al.*, 1985).

Although very rare events may be less effective over the longer term in transporting material from drainage basins than events of more moderate magnitude but more frequent occurrence (Wolman and Miller, 1960; Andrews, 1980; Webb and Walling, 1982a), *it must be emphasized that river flux is usually biased towards storm events and much of the fluvial transport in a study period takes place in a relatively small fraction of the total time available*. A five year series of hourly data on suspended sediment, NO_3^-N, and Mg concentrations available for the River Dart reveal that this tendency is most pronounced for particulate and particulate-associated substances and less pronounced for dissolved substances (Walling and Webb, 1982a). Cumulative frequency plots (Figure A.V-13A) indicate that 47.5% of the Mg load was transported in 10% of the study period but 83.3% of the suspended sediment flux occurred in only 1% of the total time available. The magnitude and frequency characteristics of fluvial transport not only vary between different substances but also between different tributaries of a single river system (e.g. Fisk, 1977; Webb and Walling, 1984). An example of the latter variation is provided by Figure A.V-13B which depicts cumulative frequency curves for suspended sediment yields in three sub-catchments of the Exe Basin. The plots refer to a five year period and reveal that 50% of the total flux took place in only 0.2% (88 hours) of the time in the River Barle, 0.35% (153 hours) in the River Dart and 0.75% (329 hours) in the River Creedy. There is a general tendency for fluvial transport to become more biased towards high magnitude events as catchment size decreases (Wolman and Miller, 1960), but even for major river systems a large proportion of the annual sediment flux may be transported in a relatively small number of days. Schmidt (1981) has shown for the River Ruhr in West Germany that > 25% of the average annual suspended sediment load may be transported in a single flood and Fisk (1977) calculates that 50% of the suspended sediment flux of the Mississippi River in the period 1970-1973 took place in < 100 days per year. In addition to basin size, other factors such as climatic conditions (Dickinson and Wall, 1978), catchment topography and the nature of sediment and solute sources in a drainage basin (Webb and Walling, 1984) will also have an important influence on the timing of fluvial transport.



igure A.V-13. Variability in cumulative load duration curves recorded in the Exe Basin, Devon, U.K., between sediment and solute parameters (after Walling and Webb, 1982a (A), and Webb and Walling, 1984 (B)).

6. Catchment Scale

The size of a drainage basin will affect several facets of river flux in addition to the magnitude and frequency properties of fluvial transport. As the scale of an upstream catchment area increases and its climatic, geological, topographic, soil and vegetational conditions become more diverse, the behavior of chemical concentrations at downstream stations may become more complex and fluxes less readily predictable (Hem, 1948; Silker, 1964; Walling and Webb, 1980). Sediment and solute fluctuations in large catchments will reflect the aggregation and downstream transmission of contrasting, and often unsynchronized, responses in different tributaries. Investigation of total dissolved solids concentrations (indexed by specific conductance) at a mainstream site (Thorverton, 600 km^2) on the River Exe (Webb and Walling, 1982b) has shown that the form of the storm-period chemograph is strongly dependent on the spatial origins of the storm runoff, most pronounced dilution occurring when northern tributaries are dominant (Figure A.V-14A). In contrast, sediment and solute behavior may become somewhat less complex in major river systems, such as the River Nile (Ball, 1939), where averaging and attenuation of contrasting responses in upstream tributaries produces a relatively simple seasonal regime of flow and flux at downstream stations.

Routing of flows through a sizeable channel network also gives rise to a kinematic differential between floodwave and floodwater velocities which causes sediment and solute responses to lag behind the flow response at downstream stations (Heidel, 1956; Glover and Johnson, 1974). The magnitude of this lag progressively increases with distance downstream, and this phenomenon is clearly apparent for an event monitored in the Exe Basin in March 1979 (Figure A.V-14B). The hydraulic effects of floodplain storage also complicate sediment and solute behavior in large catchments and may cause chemical responses to lead rather than lag the hydrograph (Walling, 1978).

The presence of large channels and well developed floodplains in major drainage basins will strongly affect the sediment conveyance or delivery processes operating in a catchment (Walling, 1983). These features provide significant temporary or more permanent sinks for particulates and particulate-associated substances with the consequence that sediment yields per unit area often decrease (Roehl, 1962) and sediment transport becomes a more discontinuous process, involving temporary storage and remobilization (Verhoff et al., 1979; Bogen, 1980), as drainage basins of increasing size are considered.

7. Patterns of Flux

Hydrological conditions play an important role in determining the patterns of fluvial transport that are apparent for the earth's surface at many different spatial resolutions. In a global context, chemical concentration and composition (Table A.V-2) are known to be well differentiated according to climate (Meybeck, 1979, 1983) and data from approximately 500 rivers (Walling and Webb, 1983a) reveal total dissolved solids concentration and load to be clearly related to mean annual runoff (Figure A.V-15). Although mean total and individual solute concentrations tend to decrease with increasing runoff because of a dilution effect, the reverse trend is true for the flux of both total and individual dissolved substances, indicating that greater moisture availability generates an increase in dissolved material released or available for transport. The effect of other factors, most notably catchment lithology (Meybeck, 1981), introduces considerable scatter into relationships between concentration or flux and runoff,

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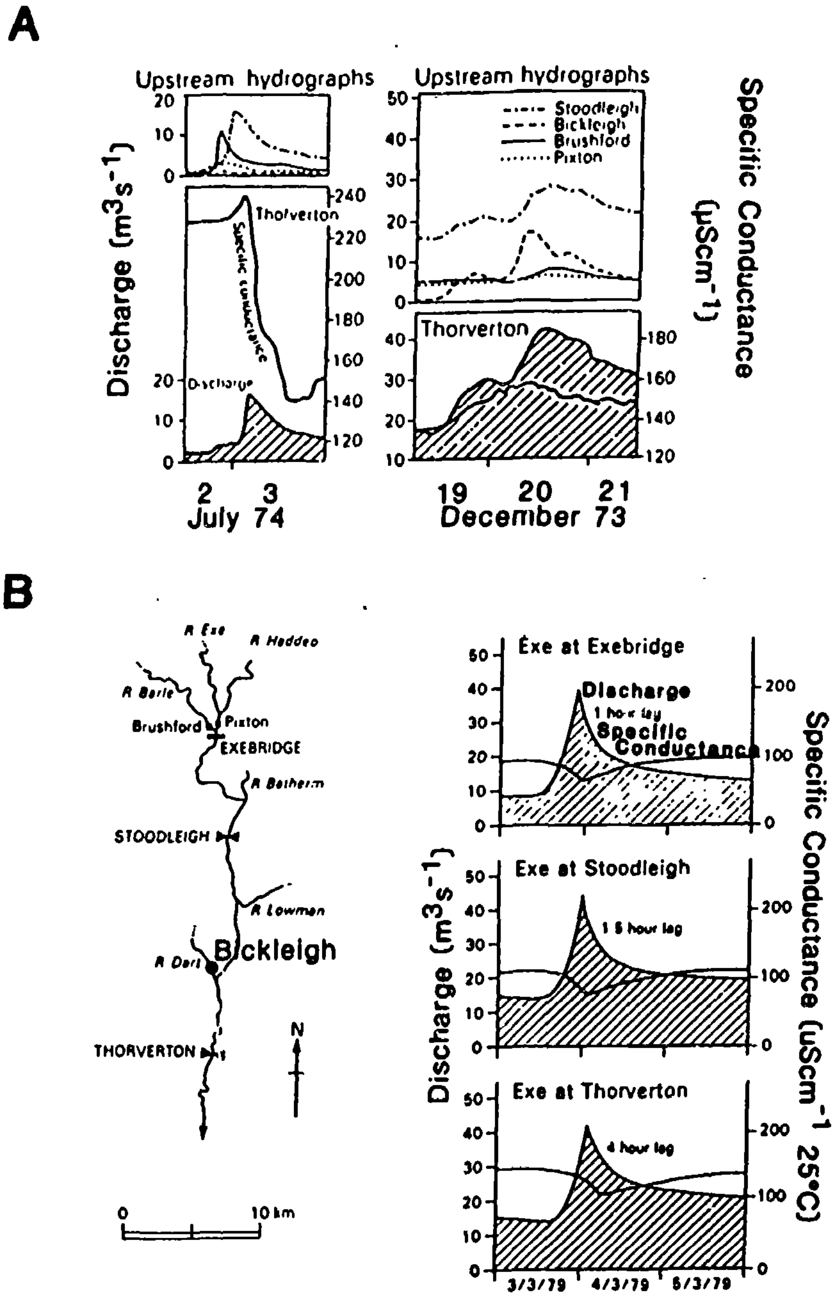


Figure A.V-14. The influence of aggregation (A) and routing (B) processes on solute behavior in the mainstream of the River Exe, Devon, U.K. (after Walling and Webb, 1980).

TABLE A.V-2

Suspended sediment and total dissolved fluxes in selected major rivers (after Meybeck, 1976).

River	Area (x 10^3 km^2)	Suspended Sediment Flux (t km^{-2} yr^{-1})	Total Dissolved Flux (t km^{-2} yr^{-1})
Colorado	635	870	23
Orange	1000	150	12
Brahmaputra	580	1370	130
Indus	950	500	65
Ganges	975	537	78
Zambezi	1340	75	11.5
Mekong	795	435	75
Amazon	6300	79	46.4
Congo	4000	13.2	11.7
Columbia	670	43	52
Don	420	13.6	33
Volga	1350	19	57
St. Laurence	1025	5.0	53

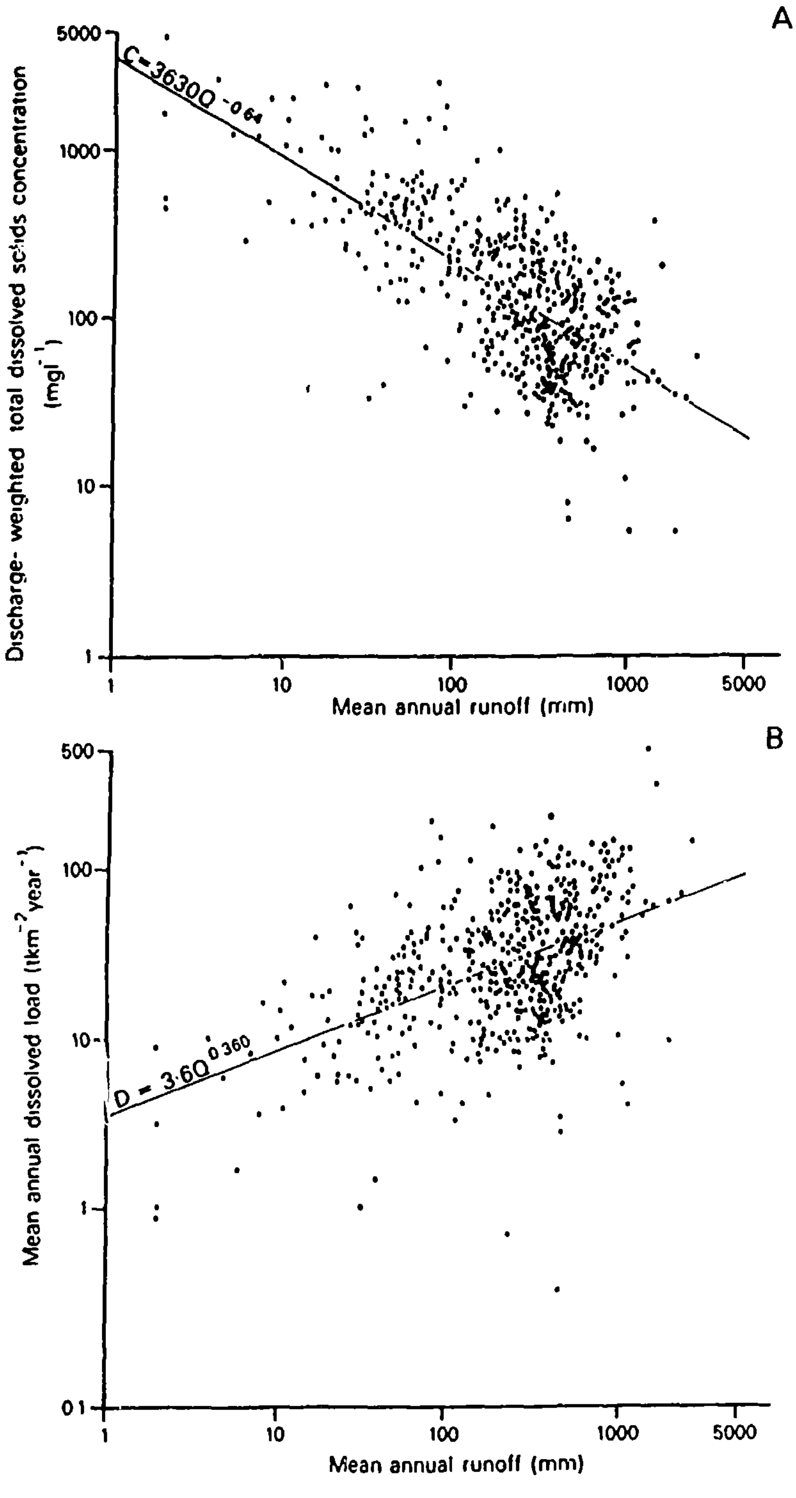


Figure A.V-15. Discharge weighted dissolved solids (A) and dissolved load (B) versus runoff (after Walling and Webb, 1983a).

and the precise form of these relationships in the absence of a comprehensive data set for world rivers has been the subject of some debate (e.g. Durum et al., 1960; Langbein and Dawdy, 1964; Holland, 1978; Walling, 1984).

Similar uncertainties surround attempts to quantify global patterns of sediment flux and to link particulate transport to hydrological parameters (Hadley et al., 1985). Early attempts to map world sediment yields based on limited numbers of monitoring stations (e.g. Fournier, 1960; Strakhov, 1967) led to results which were grossly conflicting in terms of both the magnitude and pattern of flux. Furthermore, more recent analyses based on more extensive compilations of sediment data (e.g. Walling and Kleo, 1979) suggest that long-standing relationships between yield and precipitation or runoff, such as that proposed by Langbein and Schumm (1958), are in need of further refinement (Figure A.V-16). The continuing process of data acquisition also means that estimates of global river flux to the oceans are in need of continuing revision. Values of suspended sediment and total dissolved loads in a number of major rivers based on the work of Meybeck (1976) are represented in Table A.V-3 and current estimates of total flux to the oceans are 13.5 x 10^9 t year^{-1} for suspended sediment (Milliman and Meade, 1983) and 3.718 x 10^9 t year^{-1} for dissolved solids (Meybeck, 1979).

At national, regional and more local scales, there is also a need to appreciate that patterns of river flux will reflect the interaction of chemical and hydrological factors. The distribution of NO_3^--N concentrations, runoff and NO_3^--N loadings in Mainland Britain provide an example of this interrelationship (Figure A.V-17). The countrywide NO_3^--N data relate to > 1500 sites on unpolluted small or medium-sized watercourses and are based on routine water quality surveys undertaken by Regional Water Authorities (Walling and Webb, 1981a). Mean concentration data show a gradient in NO_3^--N from low values in the wetter, upland and less intensively farmed areas of north and west Britain to high levels in the drier, lowland and more intensive agricultural areas of the south and east. A similar distribution, however, is not evident for NO_3^--N flux since high concentration values are offset in the south-east of the country by low runoff totals and high river discharges partly compensate the low concentrations encountered in north-west regions. Highest fluxes are found in the Midlands and along the south coast of South-West England where runoff and concentration values are both relatively high (Figure A.V-17).

8. Trends in Flux

Fluvial transport varies significantly through time as well as over space, but longer-term trends in river flux are often difficult to assess given that high quality data sets extending over long periods are only rarely available. Existing information suggests that the nature of trends in flux will depend on the chemical substances under consideration and may also vary in different river systems.

Continuous monitoring of suspended sediment and total dissolved solids concentrations together with discharge over a seven year period (Webb and Walling, 1982a) has shown for the River Creedy, Devon, U.K. that annual particulate transport is more variable and less strongly related to the annual volume of flow than is the case for dissolved flux (Figure A.V-18A). Annual sediment loads increase more rapidly with greater annual discharge than annual dissolved loads in this and other rivers (Walling and Webb, 1983a), but factors such as the number of major flood peaks in a year and the generation of runoff from either rainfall or

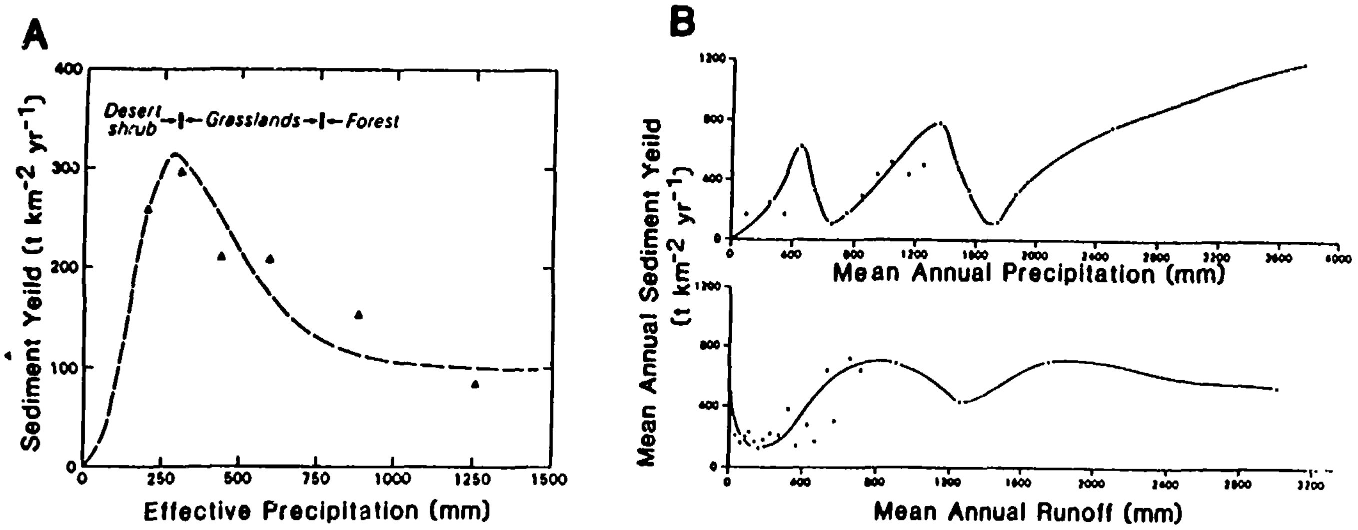
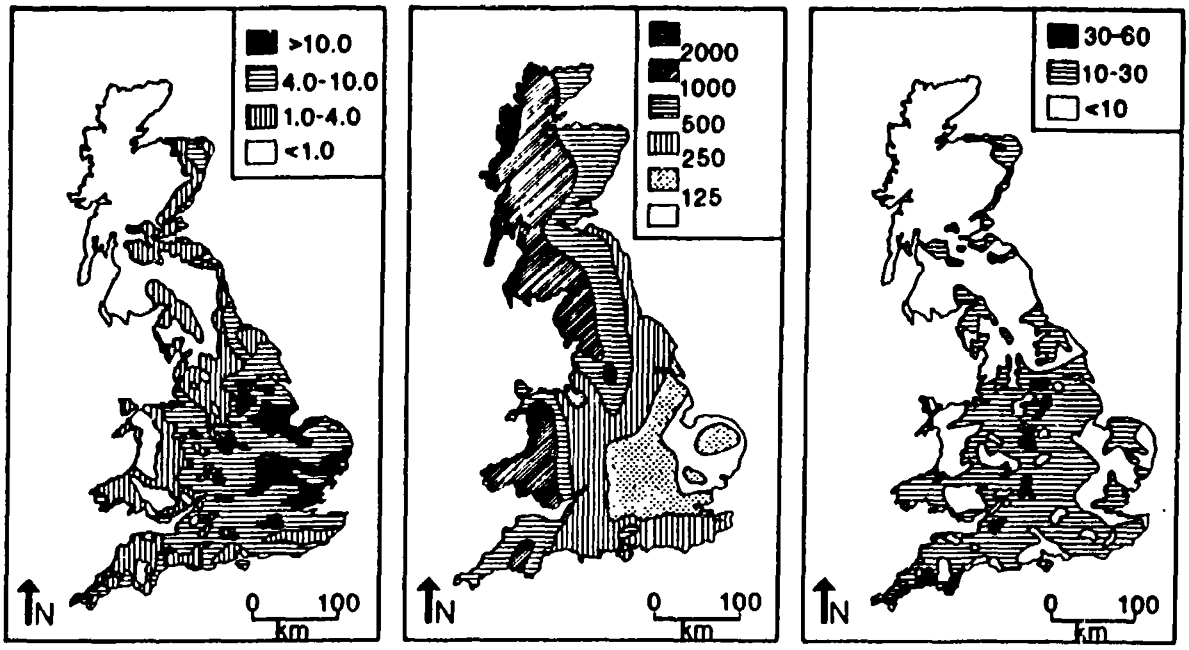


Figure A.V-16. Relationships between sediment yield, annual precipitation and annual runoff after Langbein and Schumm (1958) (A) and Walling and Kleo (1979) (B).

TABLE A.V-3

Average dissolved concentrations (mgl^{-1}) by morphoclimatic zone (after Meybeck, 1979).

Zone	SiO_2	Ca	Mg	NA	K	Cl	SO_4	HCO_3	ions
Tundra taiga	3.7	17.7	4.7	7.0	0.8	8.9	13.6	62.3	115
Humid taiga	4.0	9.7	2.1	2.8	0.6	2.7	9.3	31.9	593
Very humid taiga	5.3	5.2	1.4	3.8	0.6	3.6	4.7	22.2	414
Very humid temperate	8.0	14.0	3.5	5.0	2.0	5.9	6.9	56.6	938
Humid temperate	6.0	24.8	4.4	5.2	1.5	6.4	18.2	79.0	140
Temperate	7.1	37.6	9.9	12.2	2.2	14.3	30.2	126	234
Temperate semi-arid	7.0	54.0	10.8	24.8	1.9	26.2	74.5	140	332
Arid	15.4	38.3	13.5	64.5	5.5	63.4	54.9	153	393
Seasonal tropics	14.4	6.3	2.6	5.0	1.8	4.2	3.7	30.0	55.5
Humid tropics	11.4	8.3	3.5	4.9	1.7	4.2	4.0	45.4	71.8
Very humid tropics (lowland)	11.4	3.2	1.0	1.8	0.6	3.1	3.1	11.2	23.9
Very humid tropics (mountains)	14.5	15.4	3.2	5.4	1.4	7.7	6.5	61.8	102



NO_3-N Concentration
(mgl^{-1})

Mean Annual Runoff
(mm)

NO_3-N Flux
($kgha^{-1}\ yr^{-1}$)

Figure A.V-17. Pattern of mean NO_3-N concentration, runoff and NO_3-N flux in Mainland Britain (after Walling and Webb, 1981a).

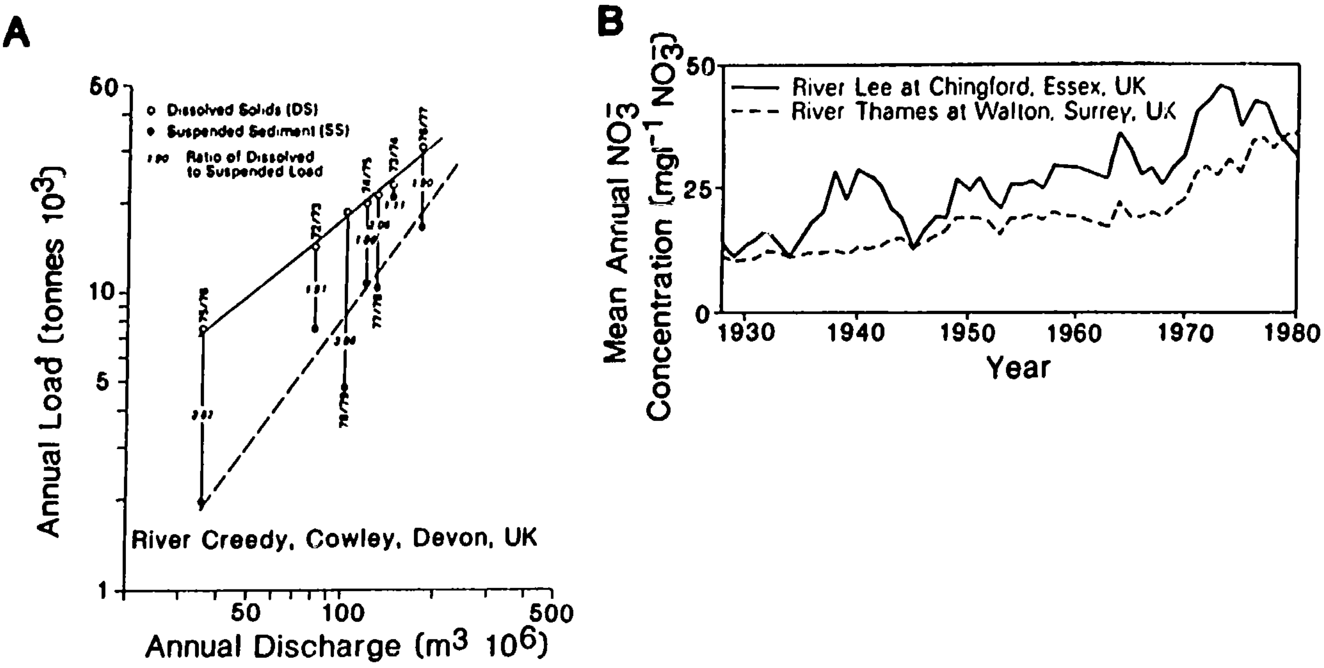


Figure A.V-18. Relationship of annual suspended sediment and dissolved solids loads with annual runoff in a Devon river (after Webb and Walling, 1982b) (A) and the upward trend of NO_3^-N concentrations in rivers of Eastern England over the last 50 years (after The Royal Society, 1983) (B).

snow-melt introduces considerable scatter into the relationship of sediment flux and flow. Analysis of > 250 stations in a wide range of climatic environments, which also had sediment records extending over more than seven years suggests that the coefficient of variation value of 70% is typical of annual sediment load data (Walling and Kleo, 1979).

In the case of many of the substances influenced by the activity of Man, river fluxes have not remained stationary over the longer-term. Nordin (1985) cites the example of suspended sediment transport in the Rio Grande at San Marcial, New Mexico where daily sediment records have been collected since before the turn of the present century, and where the time series of annual water and sediment discharge show a downward trend with time as a result of reservoir construction on the mainstream and tributaries of this river system and increased water use in the drainage basin. Non-stationarity of flux is also especially characteristic of chemical species influenced by non-point source pollution from agricultural areas, and there is considerable evidence in Britain and many other countries that intensification of farming practices has led to significant increases in the river concentrations and loadings of elements such as nitrogen and phosphorous over the last 50 years (e.g. Omernik, 1976; Hagebro et al., 1983; The Royal Society, 1983). Although an upward trend in concentration and flux of nutrients is clearly apparent in some catchments, such as the major river systems of eastern England (Figure A.V-18B), not all rivers which have experienced intensification of land use exhibit similar trends. For example, there is no clear rise evident in NO_3^-N flux in several catchments of South-West England (Figure A.V-12B) where increasing application of N-fertilizers has not yet reached a level to cause increased leakage of nitrogen from the soil system.

Some prospect of an improved understanding of natural and man-induced changes of river flux, and especially particulate transport, over the past 200-300 years has also emerged in recent years through studies of lake sediments (e.g. Oldfield, 1977; Foster et al., 1985; Walling and Webb, 1983b).

APPENDIX VI

ESTUARINE AND SHELF SEA PROCESSES AFFECTING NET LAND/SEA FLUXES OF CHEMICAL CONSTITUENTS

1. GENERAL CONSIDERATIONS

The net flux to the oceans of any chemical species is equal to the gross flux of that species crossing the river/estuarine interface corrected for gains and losses resulting from processes occurring within the estuarine and shelf sea regions. The effects of natural processes can be subdivided into:

(a) net exchange of the species across the air/water boundary,

(b) net exchange of the species across the water/sediment boundary,

(c) net consumption/generation of the species by internal chemical or biological activity.

Additionally, it is necessary to include direct anthropogenic additions to the estuarine and coastal environment through sewage and industrial waste disposal.

Routes for the transfer of chemical species within and through the estuarine and shelf sea regions are shown schematically in Figure A.VI-1. Fluxes, F, are subscripted to specify pathways between reservoirs (A = atmosphere; R = river; E = estuary and shelf sea; O = ocean; S = estuarine and shelf sea sediment). Thus, F_{R-E} represents the flux from the river into the estuary and shelf sea zone. Flux F_{M-E} refers to direct anthropogenic additions to the estuarine and coastal environment.

The next flux of any chemical species reaching the ocean, F_{E-O}, is given by the mass balance:

$$\begin{array}{ccccccccccc} \text{export} & & \text{input} & & \text{net exchange} & & \text{net exchange} & & \text{net internal} & & \text{anthro-} \\ \text{to} & = & \text{from} & + & \text{with} & + & \text{with} & + & \text{consumption/} & + & \text{pogenic} \\ \text{ocean} & & \text{river} & & \text{atmosphere} & & \text{sediment} & & \text{generation} & & \text{input} \end{array}$$

$$F_{E-O} = F_{R-E} + (F_{A-E} - F_{E-A}) + (F_{S-E} - F_{E-S}) + (F_G - F_C) + F_{M-E}$$

in which the terms subscripted G and C account, respectively, for internal generation and consumption processes. Steady state of the system may be assumed if the mean fluxes remain constant on the time scale considered (for example on an annual basis).

The relative importance of each individual pathway depends on the species type under consideration. Even in the simplest cases, it is preferable to consider dissolved and particulate forms separately. Conceptually, the best distinction for the present purposes is in terms of settlability. In the absence of chemical or biological transformation to particulate or colloidal forms having a significant settling velocity within the estuarine and coastal environment, the total flux of any dissolved non-volatile species introduced by rivers or any other source will inevitably be transported to the oceans. In contrast, transport routes and fluxes of settlable particulate mass are only partially controlled

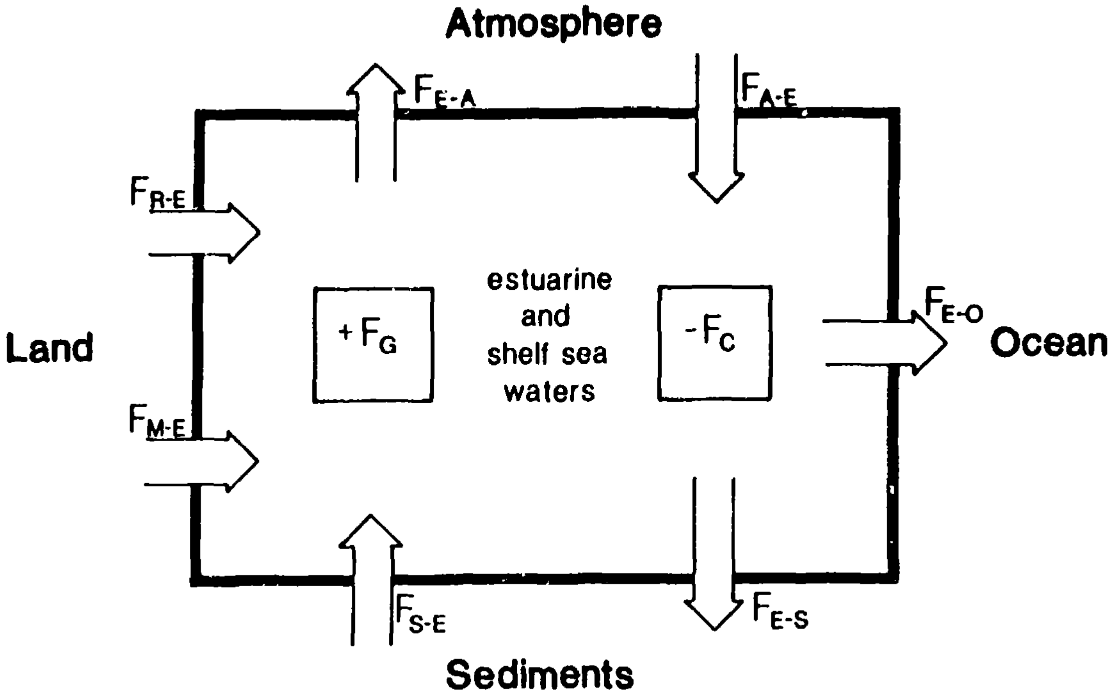


Figure A.VI-1. Transfer routes of chemical species within and through the estuarine and shelf region.

by passive transport in association with the aqueous phase. Unless altered by solubilizing processes, a major proportion of the riverine efflux of particulate chemical species will be transferred directly to the estuarine and shelf sediments by gravitational settling. One recent estimate is that less than 10% of the riverine particle input reaches the oceanic domain through continuous transport in suspension (Postma, 1980).

A major problem in considering separately the dissolved and particulate material in the riverine efflux to estuaries is their practical discrimination. As noted above, settlability (settling veolcity) is the most appropriate criterion from a theoretical viewpoint, although this is neither conveniently nor rapidly used in practice. Practical discrimination between dissolved and particulate states has most commonly been achieved on the basis of size by filtation (conventionally using a 0.45 um Millipore filter or, more recently, with 0.4 um Nucleopore membranes that maintain constant effective pore-sizes over larger load ranges), yielding operational information in the estuarine or shelf environment.

In this context, it should also be noted that there have been many attempts to distinguish chemical concentrations contained within the lattice structure of insoluble mineral grains, and therefore covalently transported as particulate entities, from concentrations associated with particles as sorbed species or as components of potentially soluble inorganic or organic solid phases, and therefore susceptible to the interchange with the soluble pool. These have been based either on chemical leaching techniques or on considerations of elemental ratios in the separated particulate material. However, despite their potential utility, these methods do not appear to have so far been applied extensively to precise flux calculations.

The environmental features of estuarine and shelf sea regions which contribute principally to the control of chemical speciation and chemical and biological reactivity are illustrated schematically in Figure A.VI-2. The most important characteristics are: (a) gradients in physico-chemical properties, (salinity or ionic strength, pH, and redox potential); in general, these gradients are steepest within the initial mixing zones of estuaries, decrease toward estuarine mouths and are much less significant in the shelf sea, (b) gradients in the concentrations of land-derived microconstituents, especially nutrient species, and (c) the gradient in water depth such that sediment-water column interactions are increasingly effective towards the river mouth where sediment disturbance by tides and wind stresses is most accentuated and where the volume of water overlying unit area of sediment is least.

In numerous estuaries, a region is present in the low salinity regime where suspended matter concentrations greatly exceed the values in the upstream and downstream waters. This turbidity maximum usually corresponds also to a zone of intense deposition of mud and silt. As soon as the turbidity drops, the estuarine waters are characterized by a high biological activity. The relatively high content of nutrients in fresh water promotes the development of high productivity zones.

In accord with these features, abiotic particle-water and sediment-water interactions affecting chemical speciation tend to decrease in significance relative to biotic interactions with distance seaward from the upper estuarine region. Correspondingly, the composition of suspended particulate material becomes increasingly controlled by the autochthonous biological component at the expense

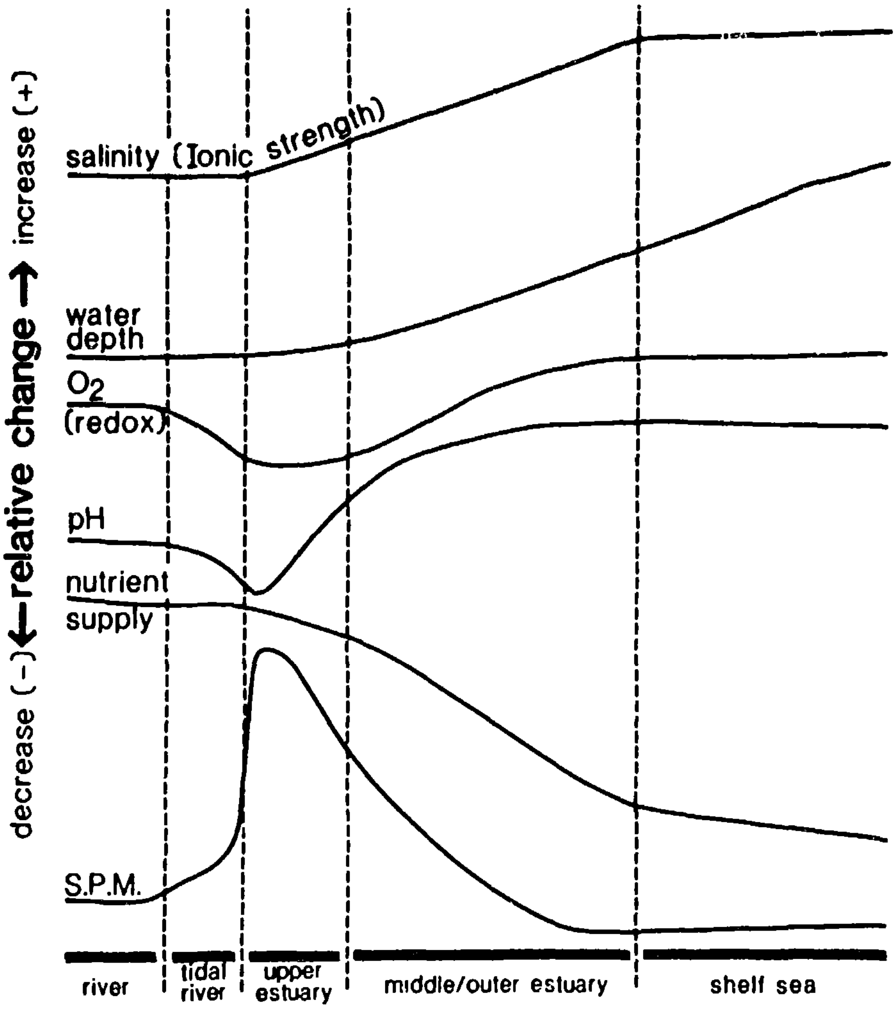


Figure A.VI-2. Relative changes in parameters controlling chemical and biological activity in the coastal zone. S.P.M. indicates suspended particulate matter.

of the riverine input augmented by mobilization of localized estuarine sediment (Abdullah and Royle, 1974; Sholkovitz and Price, 1980; Wollast and Duinker, 1982).

2. TRANSFERS ACROSS THE AIR-SEA INTERFACE

Gaseous transfer of volatile species is significant in the natural geochemical cycling of only a few elements. These include, importantly, the major biospheric and redox sensitive elements: carbon (as CO_2, CH_4, volatile organic compounds), nitrogen (as N_2, oxides, NH_3) and sulphur (as H_2S, dimethylsulphide). Other elements for which significant gaseous transport is suspected are mercury, iodine (as iodomethane?) and boron (as boric acid) (Liss, 1975).

A wide range of low molecular weight volatile synthetic organic compounds has been detected in the atmosphere. For these, the pathway through the atmosphere to the sea surface is possibly a principal route of pollutant entry to the marine environment (see, for example, Weiss et al., 1985). Conversely, river pollutant loadings of less volatile organic compounds are likely to be net transferred from estuarine and coastal waters by evaporation to the atmosphere (see, for example, Helz and Hsu, 1978; Schwarzenback et al., 1979). Many of the lower molecular weight organic compounds synthesized for industrial and domestic use are highly reactive in natural aquatic environments and have also been identified as products of natural biological activities, as intermediate chemical and microbiological degradation products and as products of natural photochemical reactions (Gschwend et al., 1982; Mantoura et al., 1982). More basic information on the occurrence and behavior, in the aquatic environment, of volatile organic compounds, of natural or anthropogenic origin is required.

Deposition (wet and dry) of particles from the atmosphere onto the sea surface is a significant route for the transfer of chemical material to estuarine, coastal and shelf environments. Particles in the atmosphere emanate from a diversity of natural sources including volcanic activity, fires, windblown dust and vegetative material, and seaspray. Anthropogenic emissions are also important contributors, especially in the vicinity of major industries. Indeed, for what is probably an extreme case - the North Sea, it has been calculated that atmospheric deposition exceeds all other sources, including contaminated river inputs, direct discharge and dumping, for copper (58% of total input), lead (58%) and cadmium (63%). A large proportion of the inputs of nickel (45%), zinc (35%), chromium (25%) and mercury (14%) to the North Sea are also atmospherically derived (data collected by Salomons and Forstner, 1984).

3. CHEMICAL TRANSFERS BETWEEN DISSOLVED AND PARTICULATE STATES

Significant transfers of chemical constituents between dissolved and particulate states within the water column of estuarine and shelf sea regions are brought about by physical, chemical and biological activities. Dissolved constituents may be sequestered by (a) adsorption reactions at the surface of preexisting particles, (b) precipitation of stoichiometric solid phases, and (c) incorporation into autochthonous biogenic material. Additionally, microcolloidal entities, which are effectively transported as solutes, may be sequestered by particles during flocculation processes (see later). Dissolved and microcolloidal constituents are generated from particulate material by reverse processes: desorption, dissolution of solid phases, aggregate breakup and degradation of organic detritus.

3.1 Sorption Process

Sorption processes at the surface of suspended particulate material are a principal non-biological cause of non-conservative behaviour of dissolved species in aquatic environments. Sorptive binding energies at surfaces are highly variable, ranging from relatively weak, non-selective (among like-charged solute ions), rapid and reversible non-specific electrostatic interactions to selective, often strong sorptions with restricted reversability, and are generated when other binding forces (e.g. covalent interaction, hydrogen bonding, dispersion forces 'hydrophobic bonding') are contributory. Adsorption is probably a necessary first step in the formation of stoichiometric solid phases since crystal growth at preexisiting solid surfaces is much more thermodynamically feasible than spontaneous nucleation and growth.

Augmentation of the riverine dissolved element flux at the expense of particulate sorbed forms following co-transport into the estuarine regime, especially during the intitial stages of mixing, appears to be favoured by relatively low seawater concentrations and by changes in conditional partition coefficients brought about by changes in environmental 'master variables', particularly ionic strength, pH, Eh and solution composition [see, for example, Kharkhar et al., (1968) or Li et al. (1974)]. Because of the uncoupling of particle and water transports and the variability of sediment movements in estuarine and coastal waters, the effects of sorptive exchanges can be highly complex, with considerable temporal and spatial variability in their net direction and intensity, especially in turbid systems (Duinker, 1980; Morris, 1986). Additional complexity arises from the variety of phases constituting the suspended particulate material in any natural waters and the heterogeneous structure of individual particles.

3.2 Precipitation of Stoichiometric Solid Phases

The homogeneous precipitation of significant quantities of small particles during the initial mixing of river water in an estuary has been reported (Eisma et al., 1980) but this isolated observation needs much further substantiation before its significance in a global context can be evaluated.

Thermodynamic equilibration of dissolved species with stoichiometric solid phase(s) is potentially a principal factor controlling the concentration of sparingly soluble constitutents in aquatic environments, and the distributions of a few dissolved species in estuaries have been interpreted as evidence of such a control. These include manganese (Wollast et al., 1979), phosphate (Fox et al., 1985) and aluminum (Mackin and Aller, 1984). However, the general relevance of this control mechanism has not been fully evaluated and distributions of these constituents recorded in other estuaries clearly reflect different controls. Kinetic factors are obviously important; stoichiometric reactions should increasingly counter more rapid sorptive controls as the time available for reaction increases and should therefore be expected to prevail in estuaries characterized by long water residence times. More information on the chemistry of larger estuarine and shelf sea regions is required to assess the potential for chemical control through stoichiometric equilibration reactions in these waters.

3.3 Aggregation of Riverine Particles in Estuaries

Significant amounts of many chemical species are introduced by rivers to the estuarine environment as microcolloidal species stabilized by surface adsorption, especially of organic material. These microcolloids are transported essentially as soluble components and are included in the soluble fraction by simple filtration procedures. In estuaries, destabilization and subsequent flocculation of these microcolloids into larger, filtrable and possibly settlable aggregates are brought about by a combination of partial charge neutralization through specific adsorption processes and double layer contraction, both engendered by a sharp increase in ionic strength. These destabilizing mechanisms are not however totally effective and a significant colloid fraction can be separated from estuarine waters (Sigleo and Helz, 1981; Sigleo et al., 1982). It is likely that this metastable colloid population is maintained dynamically by a balance between in situ generation and degradation.

The importance of colloid aggregation in altering the physical speciation of many riverine trace constituents was first highlighted by laboratory mixing experiments (Sholkovitz, 1976; Sholkovitz, 1978). However, subsequent field observations of trace constituents in estuaries have indicated that, with the notable exception of iron (see Mayer, 1982 and references cited therein), flocculation of microcolloids is not universally a major factor in controlling estuarine chemical distributions, since this process affects only a small proportion of the total riverine supply and/or is overwhelmed by other processes. The complete picture however is not yet fully resolved. Radiotracer experiments (Li et al., 1984) suggest that flocculation may be highly significant in the estuarine behaviour of tin, bismuth, cerium (and probably other rare earth elements: see Hoyle et al., 1984) and mercury, in addition to iron; more field studies of these elements are required to confirm this hypothesis. Indications that colloidal processes affect significantly the riverine phosphate input to estuaries have also been reported (Bale and Morris, 1981).

The subsequent fate of coagulated microcolloids is not well established. Recent field studies have indicated that newly aggregated iron-containing particles in estuaries behave more-or-less conservatively in the adjacent coastal waters (Mayer, 1982; Hong and Kester, 1985). That is, the increase in floc size may have only a minor effect on settlability and scavenging of microcolloids and flocculated entities.

3.4 Biological Processes

Anabolic and catabolic biological processes occurring both in the water column and in the sediment play an important role in the biogeochemistry of chemical constituents in estuarine and shelf sea environments. Their influence may be either direct, such as the uptake of dissolved nutrients and other trace constitutents during primary production of phytoplankton and macro-algae or indirect, through modifying the physico-chemical nature of their ambient environment, especially pH and redox potential, and thereby affecting the stability of chemical species. Indirect control of ambient conditions is most accentuated within the semi-isolated sediment environment and is mainly due to bacterial remineralisation of organic material.

Assimilation of dissolved constituents in primary production is an important mechanism for in situ generation of particulate material, a fraction of which subsequently settles to the sediment of estuarine and coastal waters. In estuaries with low turbidity (high ambient light), primary production may dominate over respiration through the entire system in summer. In energetic estuaries however, primary production within the upper regions is usually severely restricted by high suspended particulate loads and net summertime production is confined to the outer estuary or adjacent coastal sea. Temporal and spatial variability in primary productive activity is strongly pronounced, both within and between estuaries. In some estuaries, river flow dominates the distribution of nutrients throughout the year (although this is not to say that primary production is negligible); in others, primary production may be the most important influence on nutrient distributions. Most estuaries are intermediate, with nutrient distributions dominated by different controls at different times depending mainly on the season, tidal conditions and river flow (Cloern et al., 1983). Physical properties influencing the stability of summertime vertical stratification in the water column appear to be an important controlling factor for primary production in outer estuarine and shelf sea regions (Sinclair et al., 1981). Importantly, year-to-year changes in estuarine primary productivity are often pronounced (Peterson et al., 1985).

4. TRANSFERS ACROSS THE SEDIMENT WATER INTERFACE

Partial remineralisation of in situ generated organic material (and of river supplied allochthonous particulate organic material) occurs within the water column and may be chemically or bacterially mediated. However, in situ generated particles also combine with land derived particles to provide a continuous 'rain' of particulate material deposition on the sediment surface of estuarine and shelf seas. Gravitational deposition may be accelerated by the activities of filter-feeding benthos, by zooplankton pelletization and by particle aggregation processes (Edzwald et al., 1974; Hunt, 1982).

This deposition of particulate material represents the principal sink acting to reduce the flux of chemical species from riverine sources to the oceanic domain. However, the depositional flux is partially counteracted by remobilization of solutes to the water column following post-depositional diagenesis. The nature of chemical species liberated during remineralisation, their rates of generation and any subsequent diagenetic alterations are of course controlled by the ambient physico-chemical environment. Remineralised solutes may combine to form stable solid phases within the sediment or may accumulate in the sediment pore waters to be returned to the water column by diffusion across the sediment/water interface (see for example Elderfield and Hepworth, 1975), by bioturbation of the sediments (Aller, 1980; Christensen et al., 1984) and by physical resuspension of the sediment.

It is not surprising therefore that the composition of estuarine and shelf sea sediment pore waters and associated net fluxes of soluble species across the sediment/water interface are highly variable in space and time (Aller and Benninger, 1981; Hines et al., 1982; Hines et al., 1984; Watson et al., 1985). Bioturbation and physical resuspension of sediments complicate also the evolution of rates of accumulation of riverine material in the sediments of the estuarine and shelf areas.

5. SYNOPSIS

Although the pathways and mechanisms for internal chemical transformations within estuaries and shelf seas are reasonably well established, quantification of their effects on net throughfluxes of chemicals of riverine origin remains a problem. This arises from the multiplicity of processes influencing the partitioning of chemical constituents between dissolved and particulate phases, from the pronounced temporal and spatial variability in the effectiveness of these processes and from their rapidity relative to the water residence time within the estuarine and shelf sea environment. For example, trace nutrients and other bioaccumulated species probably pass many times through the primary production/remineralisation cycle and may undergo multiple temporary residences in the sediment before final sediment burial or transfer to the oceanic domain.

If it were possible to determine the aggregate accumulation of elements in estuarine or coastal/shelf area sediments, this would provide a means of estimating the difference between gross and net river influxes for many elements. However, because of problems of spatial heterogeneity in sediment accumulation and composition and processes of post-depositional change, application of this approach is usually untenable.

Carefully designed data collection schemes are necessary to distinguish how individual processes affect the behaviour of any particular chemical in a given estuary. This report has attempted to describe techniques for assessing net riverine influxes based upon various approaches to the problem.

APPENDIX VII

TECHNIQUES AND APPROACHES TO THE MEASUREMENT OF GROSS FLUXES OF CHEMICAL CONSTITUENTS IN RIVER DISCHARGE

1. The Problem

The assessment of chemical fluxes in rivers is complicated by the occurrence of pronounced and often complex temporal variations in the chemical concentration and composition of rivers, including sediment-associated parameters, which occur over various time scales including storm periods, annual cycles and trends over several years. Furthermore, marked inhomogeneities in chemical content with depth and lateral position in the channel may be present, especially in larger rivers.

The problem of channel inhomogeneity is relatively less acute than that of temporal variability and can be investigated by samplers designed to collect at specific points within the channel (Fig. VII-1A). The statistical significance of inhomogeneous chemistry within the channel cross-section may be tested by specially designed ANOVA procedures (e.g. Hilder and Wilson, 1972) which distinguish inhomogeneity from analytical variability and attribute it to variation with depth, position or the interaction of both (Table VII-1). Lateral and vertical variability in concentration will be an especial problem for sediment associated pollutants, and may be countered by collecting a series of samples across the river and weighting the results by the appropriate flows in different segments of the channel. Depth-integrating devices of the type frequently employed in measurement of suspended sediment concentrations (Fig. VII-1B) might also prove useful in sampling inhomogeneous cross-sections.

The flux or load of a chemical substance transported by a river is defined as the product of the chemial concentration and the water discharge. As such, instantaneous values of flux are relatively easy to derive for a particular river station from field exercises which combine water sampling with standard procedures for gauging river flow (e.g. WMO, 1974, 1979). Normally much more difficult is the assessment of flux (F) over longer time periods, such as a year or greater, since this objective requires the combination and integration of concentration (C) and river discharge (Q) records for the period (t) in question, i.e.:

$$F = \int_0^t CQ \cdot dt \qquad (1)$$

If detailed records (hourly intervals or more frequent) of river chemistry are available at a permanent river flow gauging station (Gregory and Walling, 1973) from continuous monitoring equipment, such as that frequently employed to detect electrical conductance, pH or suspended sediment concentration (Walling, 1984; Ward, 1984), or from commercially available or purpose-built automatic time-interval water samplers (Walling and Teed, 1971; Walling, 1984), the basic calculation of river flux is straight forward. Alternatively, discharge-integrating automatic sampling devices (Claridge, 1970), where timing or rate of sample collection is varied in direct proportion to river discharge, may be employed to yield a composite sample whose chemical concentration is the flow-weighted mean for the collection period. This value is simply multiplied by the mean flow for the period to determine the chemical flux.

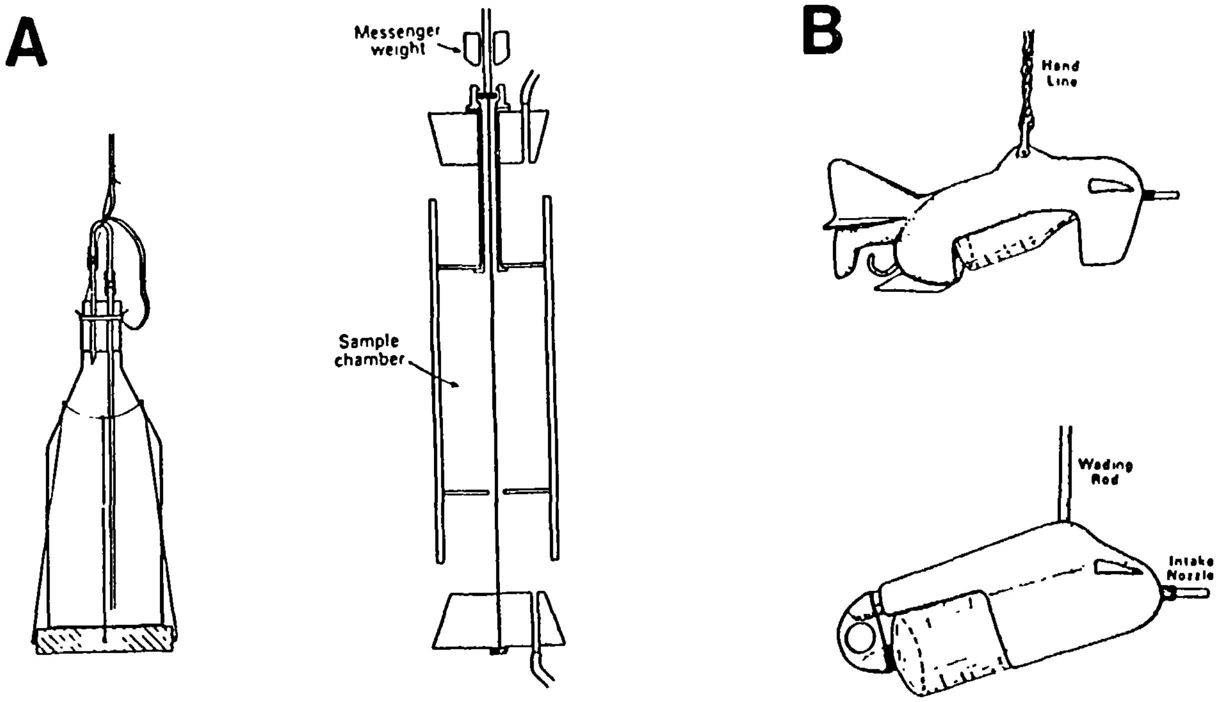


Figure A.VII-1. Samplers designed for collection at a particular depth (after Walling, 1986) (A) and for depth integration (after Gregory and Walling, 1973) (B).

TABLE A.VII-1

AN EXAMPLE OF STATISTICAL ANALYSIS OF CROSS-SECTION SAMPLES TO TEST FOR HOMOGENEITY

(Based on Hilder and Wilson, 1972 and after Walling, 1984)

A. Results

The following solute concentrations were measured:

Position	Replicate Result (mg l^{-1})	
Top left	55	65
Top middle	40	45
Top right	35	30
Bottom left	45	45
Bottom middle	50	45
Bottom right	35	30

B. Analysis of Variance Table

Source of Variation	Sum of Squares	Degrees of Freedom	Mean Square	F. Statistic
Depth	33.3	1	33.3	2.0
Position	816.7	2	408.4	24.4
Depth and Position	216.6	2	108.3	6.5
Residual	100.0	6	16.7	-
Total	1166.7	11	-	-

C. Critical F Statistic Values

	5%	1%	0.1%
Depth	5.99	13.74	35.51
Position	5.14	10.92	27.0
Depth and Position	5.14	10.92	27.0

D. Inference

There is evidence of lack of homogeneity in the cross-section related to positioning of sample (Significant > 99%).

Unfortunately, detailed river chemistry data are much less readily available than continuous records of river discharges which are maintained as part of most national hydrometric monitoring programs. Chemical flux in rivers is therefore commonly estimated by combining flow data with chemical information derived from relatively infrequent grab samples, and this procedure inevitably introduces uncertainties into the basic calculation (eqn. 1). No standard approach is available to overcome this problem, and those seeking to calculate chemical flux from many existing data sets or hoping to monitor river transport without the aid of automatic devices capable of collecting detailed chemical data, should realize that resulting estimates may be very unreliable.

2. Reliability of Flux Estimates

Evaluation of the reliability of river flux estimates must involve the concepts of both accuracy (bias) and precision (Dickinson, 1981; Dolan *et al.*, 1981; Walling and Webb, 1981b). The latter concept reflects the degree of dispersion in replicate flux estimates produced by a given approach (Fig. VII-2A) and indexes how consistently or otherwise flux is determined. In contrast, accuracy may be viewed as the difference between the actual or true load transported by the river and the mean of the replicate flux estimates (Fig. VII-2A), and it indicates the degree of systematic bias in load estimation associated with a given approach.

Methods of flux estimation which are accurate but suffer significantly from imprecision will jeopardize comparison of results between river stations since differences in loads recorded may only reflect chance variation (Fig. VII-2B). In contrast, methods associated with low accuracy but high precision will maintain the relative ranking of fluxes between sites (Fig. VII-?C) (cf Ongley *et al.*, 1977) but in the absence of knowledge of the true load involved, it may be impossible to suggest appropriate factors for correcting flux estimates. The tradeoff between the accuracy and precision in different methods for flux estimation can be usefully expressed by calculating the root mean square error criterion (Dolan *et al.*, 1981). This value is defined as:

$$\text{R.M.S.E.} = \sqrt{B^2 + S^2} \qquad (2)$$

where:

B is the bias of the method

S is the precision of the method represented by the standard deviation of replicate estimates.

The success of a particular approach to estimating chemical flux by rivers will depend on several factors. These include

i) the frequency of sample collection (e.g. daily, weekly, monthly)

ii) the sampling scheme (e.g. regular, random, rolling)

iii) the calculation procedure used for combining chemical and flow information.

Further discussion of chemical flux estimation will focus on the different calculation procedures commonly adopted to compute river loads and a convenient distinction may be made between interpolation and extrapolation methods. Some

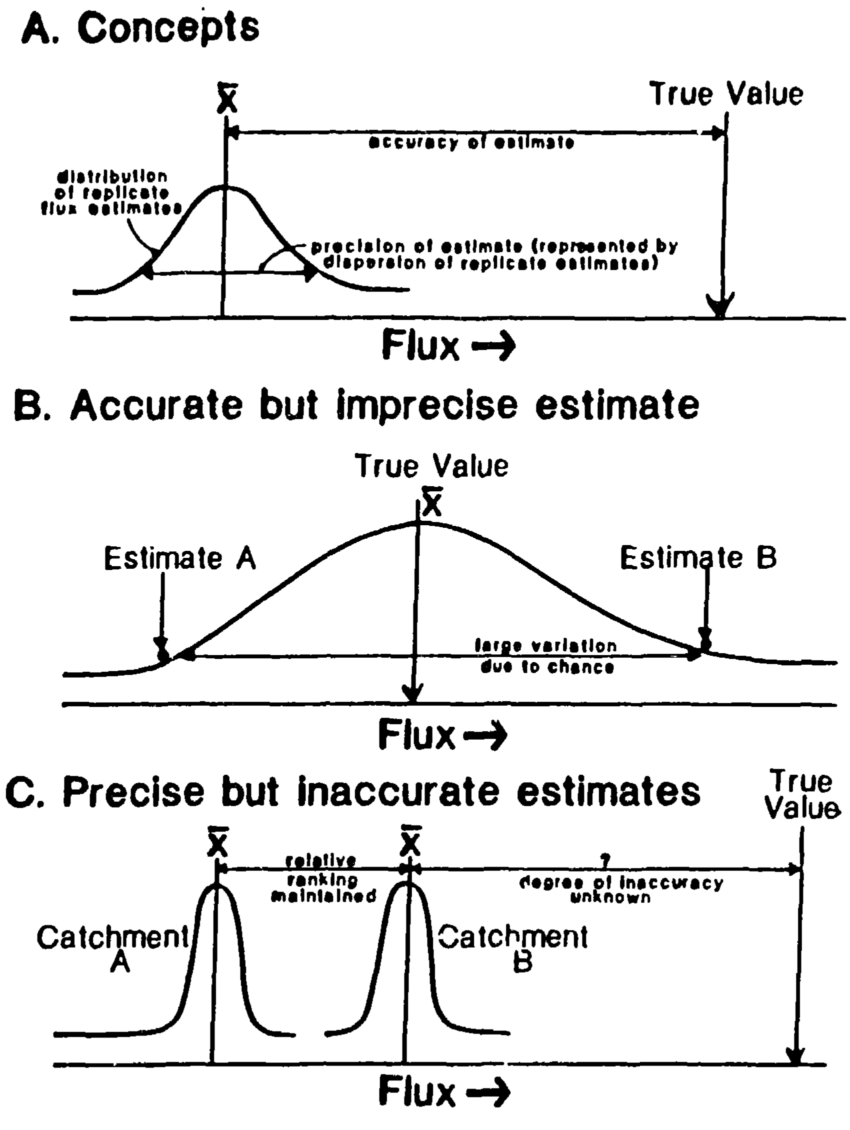


Figure A.VII-2. Accuracy and precision concepts in flux estimation.

examples of the relative success of these different approaches will be illustrated from analyses of detailed river chemistry and suspended sediment data available, in particular, for a number of sites in the Exe Basin, Devon, U.K. Results for suspended sediment flux are included because the problems of estimating this parameter are directly analogous to those of measuring the transport of particulate-associated substances in river systems (Walling and Webb, 1985). Detailed data series comprising hourly observations have been artificially decimated to simulate replicate flux estimates that would have been obtained for particular study periods from given sampling strategies and load calculation procedures, and the replicate values permit both the accuracy and the precision of individual approaches to be evaluated.

3. Interpolation Methods

These procedures make the assumption that the chemical concentration value associated with a water sample is *representative* of conditions in the river for the period between sampling. Chemical data from the samples may be manipulated and combined with discharge data in different ways, and five commonly used procedures are listed in Table VII-2.

The long-term chemical flux of a river may be effectively viewed as the product of the flow-weighted mean chemical concentration and the mean flow, and the various interpolation procedures differ in the extent to which they approximate this basic calculation. Methods 1 and 2 are based on time-weighted values of mean concentration and will tend to *underestimate* the discharge-weighted mean and hence the flux where the substance under consideration has a significant increase in concentration with greater flow volume, which will be the case with paticulate-associated parameters and some dissolved species. Conversely these methods will tend to *overestimate* where chemical concentrations are strongly diluted in increasing river flows, and the extent to which over- or underestimation occurs will depend on the range of variation in concentration involved. Methods 3 and, to a lesser extent, 4 employ discharge-weighting of the concentration values, whereas Method 5 conforms directly to the basic calculation referred to above. In the case of these methods, the reliability of flux estimate will depend on how representative is the flow-weighted mean concentration value derived from a relatively small number of water samples. The methods also differ with respect to the discharge information employed in the calculation procedure. Methods 2, 4 and 5 use the actual value of annual mean flow whereas Methods 1 and 3 are based on an approximation of the annual mean derived from instantaneous discharge values at the time of sampling.

The considerable variation in the accuracy and precision of flux estimates generated by these five interpolation procedures is illustrated by Figures VII-3A and VII-4. The estimates depicted in Figure 3A relate to loads transported in a 5 year study period by the River Dart, which is a relatively small (< 50 km^2) tributary of the Exe Basin. Fluxes were calculated on the basis of regular weekly sampling of chemical concentration, and 50 replicate estimates were generated by varying the day and time of sample collection. The distribution of the resulting flux estimates for each interpolation procedure has been plotted in an idealized form as a normal curve (Fig. VII-3A), which has been truncated at ± 2 standard deviations to give an indication of the 95% confidence limits of the replicate load estimates. The actual load transported in the River Dart has been calculated from hourly values of concentration and discharge, and results are presented for Mg, which represents dissolved substances with a relatively simple response to

TABLE A.VII-2

SELECTED INTERPOLATION METHOD OF FLUX CALCULATION

Method	Numerical Procedure
1	Total load $= K\left(\sum_{i=1}^{n} \frac{C_i}{n}\right)\left(\sum_{i=1}^{n} \frac{Q_i}{n}\right)$
2	Total load $= K\bar{Q}_r\left(\sum_{i=1}^{n} \frac{C_i}{n}\right)$
3	Total load $= K\sum_{i=1}^{n}\left(\frac{C_iQ_i}{n}\right)$
4	Total load $= K\sum_{i=1}^{n}(C_i\bar{Q}_p)$
5	Total load $= \frac{K\sum_{i=1}^{n}(C_iQ_i)}{\sum_{i=1}^{n}Q_i}\,Q_r$

K = Conversion factor to take account of period of record

C_i = Instantaneous concentration associated with individual samples

Q_i = Instantaneous discharge at time of sampling

Q_r = Mean discharge for period of record

Q_p = Mean discharge for interval between samples

n = Number of samples

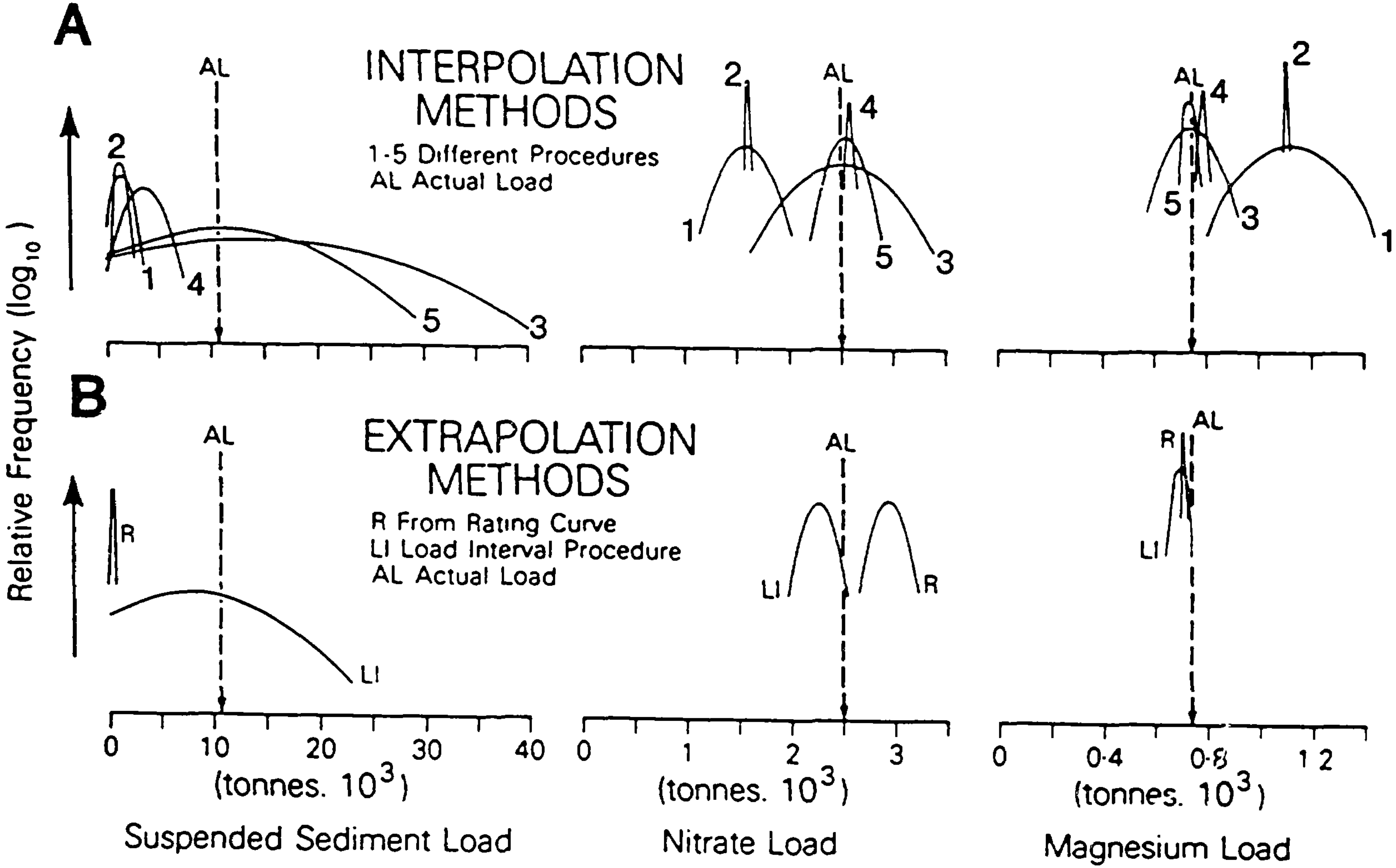


Figure A.VII-3. The accuracy and precision of estimates of nutrient flux for a 5 year period in the River Dart, Bickleigh, Devon, U.K., obtained using regular weekly sampling and various flux calculation procedures (after Walling and Webb, 1982a).

flow variation, for NO_3^-N, which represents dissolved substances with more complex responses to flow variation, and for suspended sediment, which models the behavior of particulate-associated substances. The estimates depicted in Figure 4 have been generated in a similar manner but relate to a mainstream station on the River Exe which receives runoff from a relatively large catchment area (> 600 km^2). A regular periodic sampling scheme has again been used, but estimates are presented for sampling frequencies of 7, 14 and 28 days and in this instance relate to suspended sediment flux alone. Results are presented in the form of simple histograms and the actual load again refers to transport calculated from hourly values.

Results from the Exe Basin study indicate that interpolation procedures based on calculation of time-weighted mean concentration values (Methods 1 and 2) produce flux estimates which are often precise but also are often very inaccurate. Dispersion in the estimates increases if the calculation procedure is based on spot values of flow (e.g. Method 1) and this tendency is most marked for dissolved parameters (Fig. VII-3A). Methods 1 and 2 overestimate those solutes that are diluted in increasing river discharge (e.g Mg) but underestimate dissolved substances which have more complex behavior related to flow (NO_3^-N). Results for suspended sediment flux indicate that Methods 1 and 2 would substantially underestimate the transport of particulate-associated substances. Data for the two-year period at Thorverton reveal that the degree of underestimation associated with these methods increases with less intense sampling, and produce load estimates averaging < 40% of the true value for sampling frequencies of 7 and 14 days but ca 25% if the sampling interval is increased to 28 days.

Introduction of discharge-weighting in the calculation of mean concentration values in the remaining interpolation procedures (Methods 3 - 5) greatly improves the accuracy of resulting flux estimates, but these methods are generally associated with a very marked lack of precision (Figs. VII-3A and VII-4). Imprecision is greatest if the complete flow record is not employed in the calculation procedure (Method 3) but Methods 4 and 5 in combination with a weekly sampling frequency produce relatively high accuracy and precision for solutes with simple and more complex flow responses (Fig. VII-3A). Substantial imprecision, however, characterizes estimates of particulate-associated transport when interpolation procedures based on the calculation of discharge-weighted mean concentrations are employed. Methods 3 and 5, for example, generate individual estimates of suspended sediment load at Thorverton which range between 10% and > 300% of the actual transport in the study period. Methods 3 - 5 all become more imprecise as samplng frequency decreases. However, Method 4, which involves the most limited degree of discharge weighting in the calculation procedure, provides estimates which are somewhat more accurate than those of the "time-based" approaches and rather more precise than those associated with Methods 3 and 5. Nevertheless, this procedure still produces estimates of particulate-associated transport which are of unacceptable reliability. Results from the River Dart study suggest, for example, that Method 4, even using a 2-day sampling interval, will only produce estimates of suspended sediment transport within ± 70% of the true value at the 95% level of confidence.

A further aspect of the reliability of different interpolation procedures for calculating particulate-associated transport is illustrated in Table VII-3A. This presents for the River Creedy, which is a west-bank tributary of the River Exe, the ratios between actual annual loads and the mean loads estimated by each of Methods 1 - 5. The mean loads have been obtained for the interpolation procedures

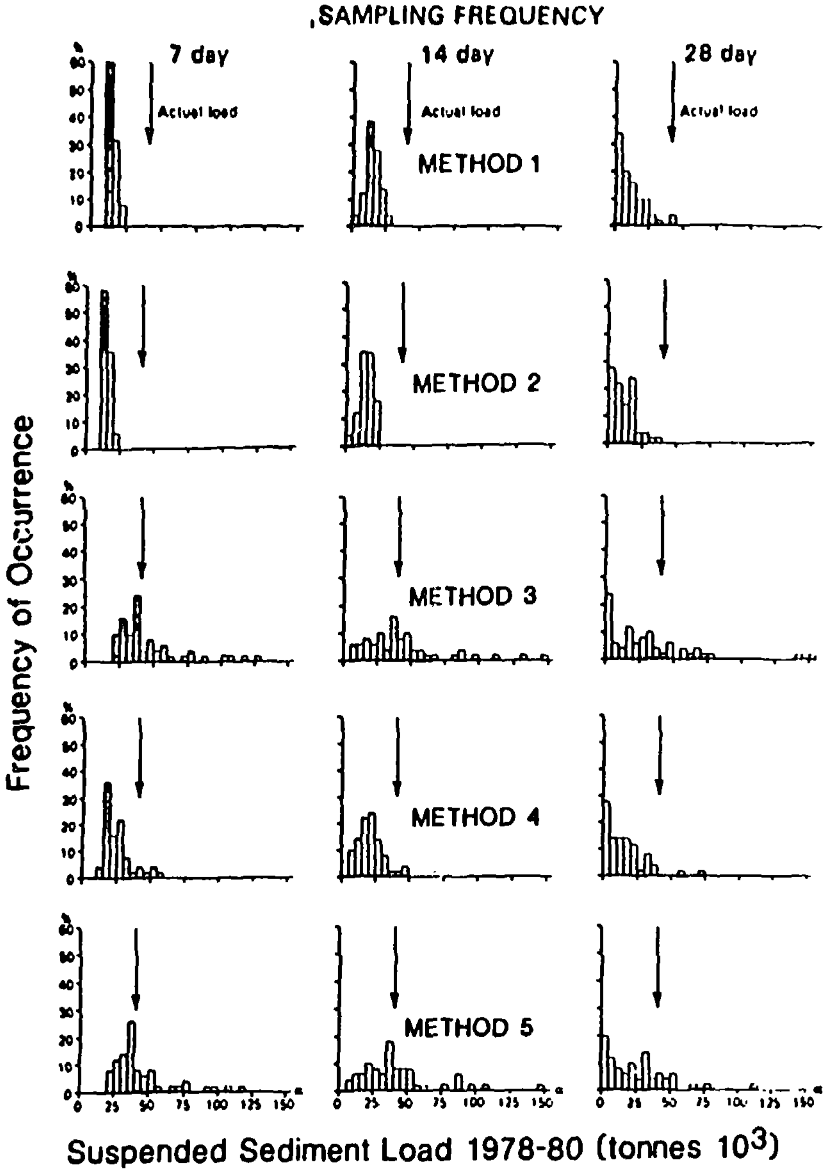


Figure A.VII-4. A comparison of estimates of suspended sediment flux in the River Exe, Thorverton, Devon, U.K., obtained using various sampling frequencies and interpolation procedures for flux calculation (after Walling and Webb, 1985).

TABLE A.VII-3

A COMPARISON OF THE RATIOS BETWEEN MEASURED AND ESTIMATED SUSPENDED SEDIMENT FLUXES IN INDIVIDUAL YEARS FOR THE RIVER CREEDY, COWLEY, DEVON, U.K. ESTIMATED VALUES WERE OBTAINED AS THE MEAN OF RESULTS FROM REPLICATE DATA SETS AND ARE BASED ON VARIOUS INTERPOLATION AND EXTRAPOLATION FLUX CALCULATION PROCEDURES (After Walling and Webb, 1981b)

	Ratio of Estimated/Measured Load							
	1972-73	1973-74	1974-75	1975-76	1976-77	1977-76	1978-79	1972-79
A. Interpolation Procedure								
1	0.22	0.23	0.22	0.32	0.35	0.16	0.27	0.21
2	0.28	0.20	0.20	0.17	0.26	0.22	0.25	0.21
3	0.48	1.12	0.90	3.13	1.18	0.83	1.10	1.02
4	0.48	0.55	0.48	1.53	0.59	0.47	0.63	0.53
5	0.49	1.02	0.84	2.10	1.10	0.82	1.05	1.00
Actual load (t)	7,482	20,619	10,547	1,941	16,234	10,214	4,717	71,754
B. Rating Relationship								
1	0.14	0.16	0.15	0.08	0.20	0.66	0.23	0.19
2	0.41	0.53	0.41	0.17	0.58	1.06	0.56	0.58
3	0.41	0.53	0.41	0.17	0.57	1.06	0.56	0.58
3A	0.50	0.78	0.52	0.18	0.69	1.32	0.59	0.74
4	0.52	0.68	0.50	0.19	0.72	1.36	0.67	0.73
4A	0.55	0.75	0.56	0.26	0.75	1.41	0.67	0.77

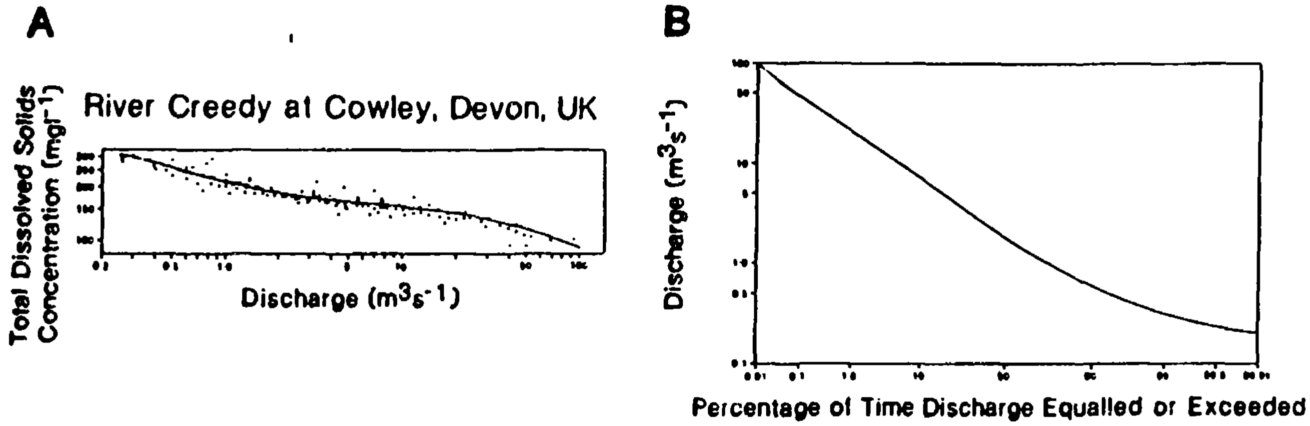


Figure A.VII-5. An example of the use of a rating relationship (A) in combination with a duration curve (B) (after Walling, 1984).

from replicate data sets and are based on a 7 day sampling interval. The "time-based" procedures are relatively consistent in their degree of underestimation of the true flux, but the "discharge-weighting" approaches produce estimates which are highly variable in their reliability between individual years.

4. Extrapolation Methods

These procedures seek to extrapolate the available data-base, classically by developing a rating relationship which links chemical concentration sampled at relatively infrequent intervals to river discharge at the time of sampling. Rating relationships are normally developed for sites with discharge monitoring facilities so that the rating function may be applied to a continuous flow record in order to extrapolate chemical concentration, and in turn flux, in the period between sample collections. Simple power functions of the form:

$$\text{Concentration} = aQ^b \qquad (3)$$

are often used to relate chemical or sediment concentration and flow. Fitting of such relationships is usually accomplished by least-squares regression techniques, although some authors (e.g. Jansson, 1985) argue that other methods of curve-fitting are more appropriate, and in some cases (e.g. Hall, 1970; Davis and Zobrist, 1978; Foster, 1980), the relationship between concentration and discharge will not be described by a simple power function.

The extrapolation procedure may be extended by employing rating relationships which have been subdivided (e.g. Loughran and Malone, 1976) on the basis of river stage conditions, a distinction being made betwen samples collected in rising and falling or stable flows, and/or on the basis of season of the year. Further refinement of rating relationships could also involve inclusion of several predictor variables in addition to river discharge in order to account for such effects as variations in rainfall intensity and preceding soil moisture conditions between storm events (e.g. Walling, 1974).

Rating relationships derived from instantaneous concentration and discharge data are not always combined with hourly or more frequent discharge values when extrapolating chemical flux. Daily mean flow series are sometimes employed but an instantaneous rating curve is theoretically not applicable to computation of daily flux from daily water discharges except for days on which the rate of water discharge is about constant throughout the day (Colby, 1956), and this procedure is likely to cause significantly inaccurate flux estimates (Walling, 1977). Rating relationships have also been used in conjunction with flow duration curves (e.g. Miller, 1951; Walling, 1977) in order to reduce the amount of computation involved. A duration curve is essentially a cumulative frequency diagram and displays the duration or frequency with which various magnitudes of flow in a study period are equalled or exceeded (Fig. VII-5). The flow duration-rating curve method of extrapolating load is based on subdivision of the flow duration curve into a large number (> 20) of duration classes (e.g. Piest, 1964; Collins, 1970; Murthy, 1977). The flux of each class is calculated (Table VII-4) as the product of the discharge associated with the mid-point of the duration class, the corresponding concentration value estimated from the rating relationship, and the total duration of flows in the class (Walling, 1984).

A further extension of extrapolating river loads by the use of rating relationships is the flow-interval method which was developed by the U.S. Army Corps

TABLE A.VII-4

FLUX CALCULATION USING RATING RELATIONSHIPS SHOWN IN FIGURE A.VII-5 (After Walling, 1984)

1	2	3	4	5	6
Duration Curve Interval (% time)	Interval Mid-point	Duration (% time)	Discharge (m^3 s^{-1})	Concentration (mg l^{-1})	Flux (tonnes)
0-0.05	0.025	0.05	72	103	116.9
0.05-0.2	0.125	0.15	43	120	244.1
0.2-0.5	0.35	0.3	31	130	381.3
0.5-1.0	0.95	0.5	23	138	500.5
1-2	1.5	1	17.5	143	789.2
2-5	3.5	3	12.2	150	1731.3
5-10	7.5	5	7.6	156	1869.5
10-20	15	10	5.4	163	2775.8
20-30	25	10	3.7	169	1971.9
30-40	35	10	2.7	176	1498.6
40-50	45	10	2.0	183	1154.2
50-60	55	10	1.6	191	963.7
60-70	65	10	1.2	202	764.4
70-80	75	10	0.98	215	664.5
80-90	85	10	0.73	231	531.8
90-95	92.5	5	0.52	254	208.3
95-98	96.3	3	0.425	273	109.8
98-99	98.5	1	0.35	286	31.6
99-99.5	99.25	0.5	0.31	299	14.6
99.5-99.8	99.65	0.3	0.27	306	7.8
99.8-99.95	99.875	0.15	0.24	312	3.5
99.95-100	99.975	0.05	0.22	319	1.1

Mean annual load for period of record 16,334.4 tonnes

Col. 4 = Discharge associated with interval mid-point (col. 2)
Col. 5 = Concentration derived from rating relationship for the discharge listed in col. 5
Col. 6 = Flux = col. 4 x col. 5 x col. 3 x 0.31536

N.B. In this example a limited number of duration curve intervals has been used, a greater number would provide a more accurate result.

of Engineers and has been used by several workers to estimate river fluxes (e.g. Verhoff et al., 1980). This procedure is based on the construction of a graphical plot of daily load versus daily discharge values which is then divided into uniform intervals of flow (e.g. Fig. VII-6). Mean load for each interval is calculated from the individual points, and the total mean load associated with each interval is calculated as the product of the mean load on the number of days during the study period with discharges in the flow interval.

The accuracy and precision of flux estimates produced by different extrapolation methods is illustrated in Figures VII-3B and VII-7 for catchments in the Exe Basin. The results shown in Figure VII-3B relate to flux in the River Dart during the same 5 year study period used to evaluate various interpolation procedures and they depict, again by means of idealized normal curves, the dispersion of estimates for Mg, NO_3^-N and suspended sediment based on extrapolation using simple rating relationships and the flow-interval procedure. Extrapolation has been based on regular weekly samples of concentration and 50 replicate estimates have again been generated by varyng the day and time of sample collection. The results for Mg flux indicate that the simple extrapolation using a power function rating relationship produces a flux estimate with a high precision and only small inaccuracy (c. 5% underestimation) for dissolved parameters with simple response to flow. Precision and accuracy are somewhat less when this approach is used to estimate the flux of solutes, such as NO_3^-N, which have a more complicated relationship with flow, and rating curve extrapolation may produce an overestimate of flux in these circumstances (Fig. VII-3B). Estimates of suspended sediment and particulate-associated transport based on rating relationships are very precise but are also inaccurate and may be less than 20% of the actual load when weekly sampling is involved. The flow-interval approach generally results in flux estimates which are less precise than those produced by rating relationships (Fig. VII-3B). In the case of suspended sediment, flux estimates generated by the flow-interval method are more accurate but very much more imprecise than those produced by the use of rating relationships, whereas for NO_3^-N the flow-interval approach tends to underestimate rather than overestimate flux (Fig. VII-3B).

Figure VII-7 presents results relating to suspended sediment transport alone in the River Creedy during a 7 year period. In this study, extrapolation procedures were applied to four data sets of 50 replicates which represented not only regular weekly collection of samples but also sampling schemes where an improved coverage of sediment concentrations during storm events, based on random aperiodic sampling of flows exceeding certain thresholds (Table VII-5), was included. The more intensive of these methods also allowed extrapolation by means of rating relationships subdivided according to season and stage conditions to be considered. The accuracy and precision of suspended sediment flux estimates for the River Creedy based on the combination of the various rating relationships with an hourly flow series and with daily flow data are depicted in Figures VII-7A and B, respectively. The use of daily mean flow values exacerbates the degree of underestimation associated with all of the rating curve estimates, although incorporating of storm-period samples in deriving rating relationships substantially improves the accuracy of flux estimation. The use of subdivided rating relationships in combination with hourly flows also produces an increase in the accuracy of the estimated flux (Fig. VII-7A). The precision of rating curve estimates is relatively high and increases as rating relationships are derived from a greater number of samples. Subdivision of the rating relationships may lead to a loss in precision because insufficient data may be available to closely define some of

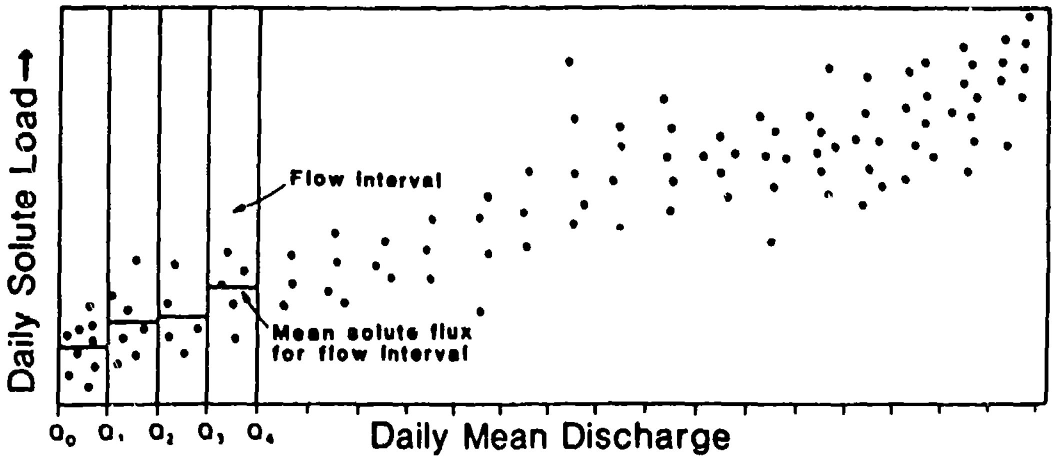


Figure A.VII-6. A representation of the flow-internal method of flux calculation (after Walling, 1984).

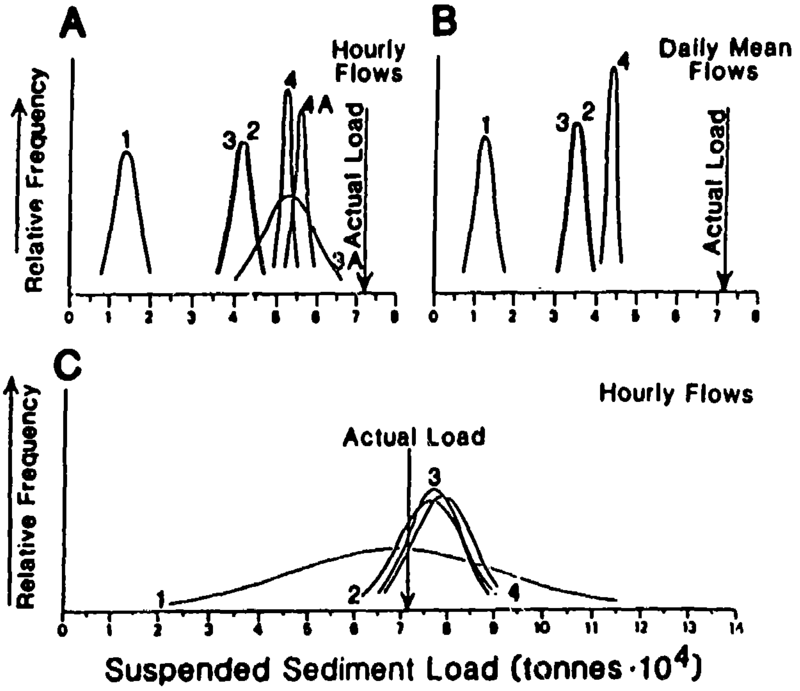


Figure A.VII-7. A comparison of estimates of suspended sediment flux in the River Creedy, Cowley, Devon, U.K., using extrapolation by means of rating curves in combination with hourly (A) and daily mean (B) river flow data and by means of the flow-interval procedure (C) (after Walling and Webb, 1981b). Number adjacent to curves refers to sampling strategy given in Table A.VII-5.

TABLE A.VII-5

SAMPLING STRATEGIES USED FOR RATING CURVE DURATION

Strategy	Sampling Program
1	Regular weekly sampling
2	Strategy 1 plus 200 random samples collected when discharge $> 15\ m^3s^{-1}$
3	Strategy 1 plus 150 random samples collected when discharge $> 15\ m^3s^{-1}$ and 50 random samples when discharge $> 30\ m^3s^{-1}$
4	Strategy 1 plus 750 random samples collected when discharge $> 15\ m^3s^{-1}$ and 250 random samples collected when discharge $> 30\ m^3s^{-1}$
3A 4A	Strategies same as above but rating relationships divided on the basis of season and stage conditions

TABLE A.VII-6

ESTIMATES OF SUSPENDED SEDIMENT FLUX IN THE RIVER CREEDY, COWLEY, DEVON, U.K., BASED ON THE COMBINATION OF RATING RELATIONSHIPS WITH DURATION CURVES (AFTER WALLING AND WEBB, 1981b)

Rating Type		Applied to Hourly Flow Series	Applied to duration curve based on hourly discharge data and following duration increments			
			Miller	Piest	Murphy	Collins
1	x	13,799	12,659	13,630	8,115	14,144
	s	3,092	2,798	3,046	1,549	3,186
4	x	52,243	47,026	51,383	23,964	53,920
	s	1,534	1,372	1,506	682	1,586

x = mean of replicate results (t)
s = standard deviation of replicate results (t)

the individual rating lines, for example that relating to rising limbs of hydrographs in the summer period. The results for the type 3A rating relationship (Fig. VII-7A) reveal this tendency even though the sampling strategy is based on an additional 200 storm-period samples.

The ratios between actual annual suspended sediment flux in the River Creedy and loads calculated by the different rating relationships in combination with an hourly flow series are presented for individual years in Table VII-3B. The calculated loads have been taken as the mean value of the replicate estimates derived for each sampling strategy and rating type (Table VII-5). Table VII-3B reveals that rating curve extrapolations are associated with errors which are highly variable from year to year. Inconsistencies are marked even for the rating relationships based on a large number of additional storm-period samples and type 4 ratings, for example, are associated with ratios which vary from 0.19 to 1.36 (Table VII-3B), and indicate the occurrence of substantial over- as well as underestimation in flux estimates for individual years. These results show that although rating curve estimates of sediment load are often highly precise there are considerable difficulties in applying a general correction factor to compensate for their substantial lack of accuracy.

An example of the effects on flux estimates resulting from using duration curves rather than a time series of discharge values in rating curve extrapolation procedures is presented in Table VII-6. Flux estimates for the 7 year period in the River Creedy are given for type 1 and type 4 rating relationships in combination with duration curves based on hourly observations of flow but using the different flow duration intervals suggested by different workers. Table VII-6 shows that use of duration curves has little effect on the precision of the flux estimates but produces rather less accurate load values when compared with extrapolation based on a time series of flows. Furthermore, it is clear that the accuracy of the flux estimates is highly sensitive to the flow duration intervals used.

Some further information on the reliability of the flow-interval method is provided in Figure VII-7C which plots, in the form of idealized normal curves, the replicate estimates for a 7 year study period in the River Creedy derived from the use of this extrapolation procedure in combination with hourly flows and concentration data yielded by different sampling strategies (Table VII-5). Figure VII-7C again reveals the greater accuracy but lesser precision of this procedure in comparison with rating curve estimates, but also reveals that the degree of imprecision of the flow-interval method may be substantially reduced if additional storm-period data are available. The flow-interval procedure gives more weight in the calculation to high suspended sediment concentrations occurring at high discharges, and results from the River Creedy show that this may lead to a small overestimation of load in relation to actual transport.

5. Developments in Flux Estimation

A number of recent developments in procedures for estimating river flux offer the prospect of improved load estimates, especially for particulate-associated substances, although in many cases the potential of thes advances has not been fully assessed.

Walling (1984), for example, argues that a combination of interpolation and extrapolation procedures provides considerable scope for an improved flux estimation procedure. One possible combined approach would use observed values of concentration to adjust estimates obtained from a generalized rating relation-The procedure could involve collection of samples at approximately weekly intervals from which a rating relationship with flow would be obtained. Actual concentration values in field samples would then be compared with the rating relationship estimate of concentration at the time of sampling in order to adjust rating estimates for periods between field collection. If the rating relationship was of the form expressed in eqn. 3 above, the adjusted estimate of concentration for a particular instant in time is calculated by:

$$C = \left[\frac{C_1}{aQ_1^b} + \frac{t}{T} \times \left(\frac{C_2}{aQ_2^b} - \frac{C_1}{aQ_1^b} \right) \right] \times aQ^b \qquad (4)$$

where:

C = estimated concentration

C_1 = concentration of previous field sample

C_2 = concentration of next field sample

Q_1 = instantaneous discharge at time of sampling C_1

Q_2 = instantaneous discharge at time of sampling C_2

T = time interval between samples C_1 and C_2

t = time interval between sample C_1 and the estimation point

Q = discharge at time concentration estimate required

a,b = constant and exponent in rating relationship

This approach is considered particularly useful where annual hysteresis in the relationship between concentration and flow is well developed or where a catchment is prone to flushing effects during autumn months.

Application of more sophisticated statistical techniques, such as the use of Box-Jenkins transfer models to derive relationships between chemical substances and discharge, also offers the prospect of improved flux estimates. This is especially so for certain environments, such as proglacial areas, where a major problem of serial autocorrelation in the residuals from rating relationships leads to unreliable estimates of suspended sediment flux (Gurnell and Fenn, 1984) which cannot be easily removed by fitting standard rating models to data from partial periods of record or to data filtered according to diurnal and seasonal river stage fluctuations, climatic conditions and major process events (Fenn _et al._, 1985).

Detailed examination of the statistical considerations underlying the use of rating relationships fitted to logarithmically transformed data has allowed Ferguson (1986) to propose a method for correcting the underestimation of river fluxes which commonly results from this simple extrapolation procedure. The bias arises because least-squares fitting leads to estimated values that are based on an *arithmetic* averaging of the scatter in the logarithmically transformed concentration data which is equivalent to *geometric* averaging for the antilogged regression. Since the geometric mean is lower than the arithmetic mean, it is inevitable that this procedure will cause underestimation of the true flux. The bias involved has been calculated to be an almost constant factor, and corrected flux estimates may be computed by:

$$L_c = L_r \times \exp(2.65s^2) \qquad (5)$$

where:

L_c = corrected flux estimate

L_r = load from rating relationship extrapolation

s = standard error of the estimate for the rating relationship

Testing of this correction factor with river data from Britain has given encouraging results, but it should be noted that the method does not correct for imprecision in rating estimates nor does it easily accomodate the annual variability in inaccuracy (bias) that is present in some data sets.

A somewhat different approach to the calculation of unbiased river flux estimates has been suggested by Dolan *et al.* (1981) who make use of the ratio estimator developed by Beale (1962). In this case, the estimate is derived from the ratio of the mean of the measured loads to the mean of the flows when loads were measured, which is then multiplied by the mean of the actual flow over the study period and corrected for bias by an additional term. The estimator is thus defined as follows:

$$\tilde{\mu}_y = \mu_x \frac{m_y}{m_x}\left(\frac{1+\frac{1}{n}\cdot\frac{S_{xy}}{m_x m_y}}{1+\frac{1}{n}\cdot\frac{S_x^2}{m_x^2}}\right) \qquad (6)$$

where:

$\tilde{\mu}_y$ = estimated flux

μ_x = mean daily flow for study period

m_y = mean daily loading for days on which concentrations were determined

m_x = mean daily flow for days on which concentrations were determined

n = number of days on which concentrations were determined

$$S_{xy} = \frac{1}{(n-1)} \sum_{i=1}^{n} x_i y_i - n m_x m_y$$

$$S_x^2 = \frac{1}{(n-1)} \sum_{i=1}^{n} x_i^2 - n m_x^2$$

3. as storm-period behavior of chemical concentration becomes more varied and increasingly divorced from simple correlation with flow

4. as changes in concentration become more dramatic with flow, time-weighted mean values will increasingly depart from discharge-weighted mean values with this trend

5. as chemical composition becomes more variable through time in response to heterogeneity in upstream catchment area, which is especially significant for large drainage basins

6. as sampling frequency becomes less intensive.

Simple extrapolation or interpolation procedures in combination with sampling at regular weekly or fortnightly intervals will be adequate in many cases to produce reliable flux estimates where transport is dominated by the dissolved phase. Sampling intervals of one month or greater are likely to introduce more uncertainty, and weekly sampling is regarded as being desirable in the case of dissolved parameters exhibiting a more complex response to discharge.

None of the commonly implemented sampling strategies and/or calculation procedures can be relied upon to produce estimates of sediment and particulate-associated transport which are both accurate and precise. Time-weighted interpolation procedures and rating curve approaches tend to give precise estimates which may be useful if time trends in fluxes of particular stations need to be evaluated, whereas discharge-weighted interpolation procedures and the 'load' interval method are often associated with less bias and may be useful if there is a need to calculate loads for large areas containing many stations. In the latter circumstance, errors associated with the estimates for individual stations may cancel each other out (Walling and Webb, 1985).

Flux estimation can often be considerably improved if a sampling program is directed towards monitoring flood events, and installation of continuous monitoring equipment for turbidity in most cases will greatly enhance the assessment of suspended sediment and particulate-associated transport, although in some rivers a good correlation between suspended sediment concentration and turbidity may not exist. In cases where resources for flux estimation are limited a short trial period of detailed monitoring may prove invaluable.

Recent developments of monitoring and calculation procedures offer the prospect of improved and more easily obtained river flux estimates in the future but some problems remain including:

1. quantification of the amount and significance of the saltation and bedload components of river fluxes and of the properties of suspended sediments, such as mineralology and particle size characteristics

2. the effects of sampling schedule are not as yet fully known

3. testing of procedures for flux estimation has been restricted to only a few climatic zones, most notably humid temperate and proglacial areas.

4. few detailed records are in existence to enable longer-term average chemical fluxes of rivers to be confidently established.

x_i = individual measured flows

y_i = daily loading for each day on which concentration was determined.

The method was regarded as being ideally suited to the calculation of flux when an abundance of flow data but relatively little concentration information are available, and this approach was found to give the best overall results, in comparison with several interpolation and extrapolation procedures, for estimation of total phosphorous transport in the Grand River feeding Lake Michigan.

Dolan et al. (1981) in fact used a ratio estimator which was stratified to account for contrasts between high and low flow conditions, and Yaksich and Verhoff (1983) have shown that focusing of sampling activity on high flows in relatively few flood events throughout a study period may be equally or more successful in flux estimation than fixed interval sampling, especially in drainage basins defined as event response rivers where suspended sediment and particulate-associated parameters increased markedly with flow. Results based on studies of several event response rivers in Ohio suggested that estimates of suspended sediment and particulate associated loadings with an error estimated at 10-20% could be produced by sampling approximately two to three of the largest events per year with 15 to 20 grab samples collected over each hydrograph. An additional five to ten samples during steady flow periods were also required, and the calculation procedure recommended was the flow-interval technique discussed earlier. In the case of certain predominantly dissolved parameters, such as NO_3^-N, the occurrence of marked seasonal variation in concentrations leads to overestimation of annual flux if event-based sampling is employed, and fixed interval collection of samples was recommended for this and other parameters with similar behavior.

Further sophistication has recently been introduced into the estimation of suspended sediment flux with the application of strategies based on variable probability sampling. Thomas (1985), for example, describes a 'Selection at List Time' (SALT) scheme where the probability of taking a sample is proportional to its estimated contribution to total suspended sediment flux. The SALT scheme requires a pumping sampler, a stage sensing device and a small battery-powered computer for collection of samples, but testing of the approach in Caspar Creek, California revealed that it underestimated the actual flux of suspended sediment by less than 1%, so that installation of the necessary equipment at gauging stations could provide an attractive alternative to the setting up of continuous monitoring facilities.

6. The Prospect

In general terms, the reliable assessment of chemical fluxes in rivers becomes more problematical with the following conditions:

1. as an increasing proportion of material is transported by a smaller percentage of the higher flows within a catchment, generally this tendency becomes more extreme as catchment size decreases but other controls, such as relief and distribution of sediment and solute source areas in a drainage basin, may also be significant

2. as hydrological and chemical/sediment regime become more variable from year to year

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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.

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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

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

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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.

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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

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