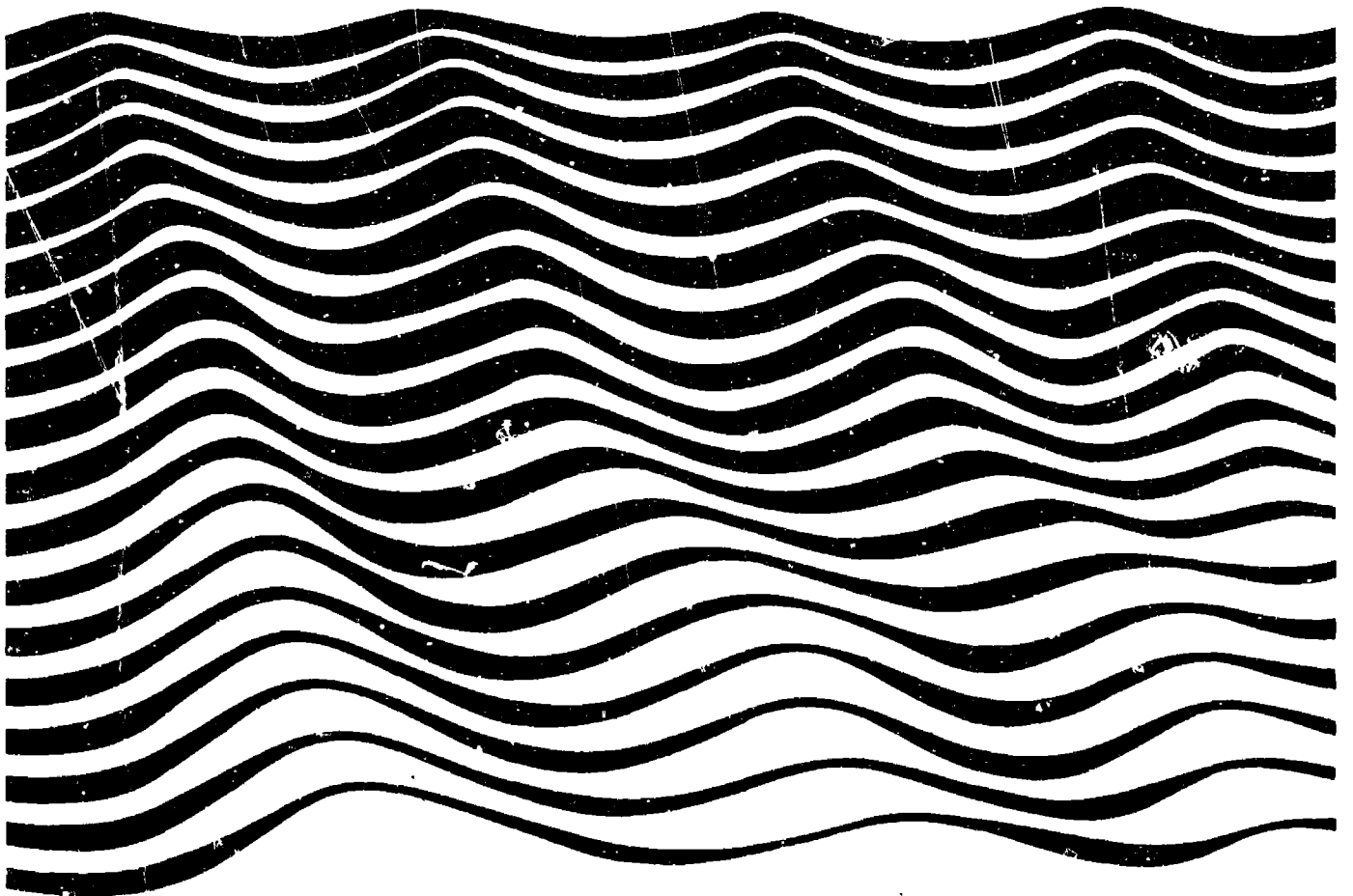


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**River inputs to ocean systems:  
Status and recommendations  
for research**

Final Report of  
SCOR Working Group 46



Unesco 1988

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25	1976	—	44	1983	—
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26	1976	—	45	1985	—
<p>Marine science in the Gulf area-Report of a consultative meeting, Paris, 11-14 November 1975</p>			<p>The International System of Units (SI) in Oceanography Report of IAPSO Working Group on Symbols, Units and Nomenclature in Physical Oceanography (SUN)</p>		
31	1980	—	46	1986	WG 70
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32	1981	—	47	1986	—
<p>Coastal lagoon research, present and future. Report and guidelines of a seminar, Duke University Marine Laboratory, Beaufort, NC, U S A August 1978 (Unesco, IABO).</p>			<p>Research on coastal marine systems Report of the third meeting of the Unesco/SCOR/IABO consultative panel on coastal systems October 1984</p>		
33	1981	—	48	1986	WG 65
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34	1980	WG 62	49	1986	—
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35	1980	—	50	1987	—
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36	1981	WG 10	51	1987	—
<p>The practical salinity scale 1978 and the international equation of state of seawater 1980 Tenth report of the Joint Panel on Oceanographic Tables and Standards, (JPOTS) Sidney, B.C., Canada, 1-5 September 1980 Sponsored by Unesco, ICES, SCOR, IAPSO Available in Ar, Ch, F, R, S</p>			<p>Thermodynamics of the carbon dioxide system in seawater Report by the carbon dioxide subpanel of the joint panel on oceanographic tables and standards</p>		
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39	1981	WG 10	<p>The acquisition, calibration and analysis of CTD data. A report of SCOR Working Group 51</p>		
<p>International Oceanographic Tables, Vol. 3</p>					
40	1982	WG 44			
<p>International Oceanographic Tables, Vol. 4</p>					
41	1982	WG 44			
<p>Ocean-Atmosphere Materials exchange (OAMEX) Report of SCOR Working Group 44, Unesco, Paris, 14-16 November 1979</p>					
42	1983	—			
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Prof. J.D. Burton

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## PREFACE

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### Abstract

A review of estimates of the river discharge of dissolved constituents indicates that, despite recent improvements in the data base, information remains inadequate for the accurate estimation of riverborne fluxes of many important constituents. The limitations of estimates of mean annual loads of suspended sediment are also discussed. Contemporary changes in land use and river management can have major influences on river discharges, particularly on the fluxes of suspended sediment to estuaries. For the estuarine environment key questions arise concerning (i) interactions between particles and dissolved constituents and their consequences for the modification of fluxes of the latter to the ocean, (ii) chemical speciation, (iii) flocculation of particles and the characteristics of colloids. These and related topics are discussed and recommendations made regarding research objectives.

### Résumé

L'examen des estimations du débit des constituants dissous dans les cours d'eau montre que, malgré les améliorations apportées récemment aux bases de données, les informations demeurent insuffisantes pour estimer avec précision le flux de nombreux constituants importants charriés par les cours d'eau. Les limites de l'estimation des charges annuelles moyennes de sédiments en suspension sont également analysées. Les modifications actuelles de l'utilisation des terres et de la gestion des cours d'eau peuvent exercer une forte influence sur le débit de ces derniers, et en particulier sur les apports de sédiments en suspension aux estuaires. Pour l'environnement estuarien, des questions fondamentales se posent au sujet (i) des interactions entre particules et constituants dissous et de leurs conséquences sur la modification des flux de ces derniers vers l'océan ; (ii) de la spéciation chimique ; (iii) de la flocculation des particules et des caractéristiques des colloïdes. Ces questions et d'autres qui s'y rattachent sont analysées et des recommandations faites concernant des objectifs de recherche.

## Resumen

El análisis de los cálculos de las descargas fluviales de componentes disueltos indica que, a pesar de que se hayan perfeccionado recientemente las bases de datos, la información sigue siendo insuficiente para poder evaluar de manera correcta los flujos transportados por los ríos en muchos de los componentes importantes. También son objeto de discusión los cálculos de las cargas medias anuales de los sedimentos en suspensión. Los cambios actuales del uso de las tierras y de la gestión de los ríos pueden influir bastante en las descargas fluviales, sobre todo en el flujo de los sedimentos en suspensión que van hacia los estuarios. En cuanto al medio estuarino, hay cuestiones esenciales que siguen sin resolverse: i) las interacciones entre partículas y componentes disueltos y sus repercusiones en la modificación del flujo de estos componentes hacia el océano, ii) la especiación química, iii) la floculación de las partículas y características de los coloides. Estos y otros asuntos afines son objeto de debate y se formulan recomendaciones sobre los objetivos de la investigación.

## Аннотация

Обзор оценок растворенных в расходуемой воде веществ показывает, что несмотря на усовершенствованную в последнее время базу данных, информация по-прежнему остается неадекватной для точной оценки содержащихся в расходуемой воде многих существенно важных веществ. Рассматривается также вопрос о том, что мешает оценкам средних ежегодных значений объема взвешенных наносов. Происходящие в настоящее время изменения в характере землепользования и рационального использования рек могут оказывать существенное влияние на расход воды, особенно на поступление взвешенных наносов в эстуарии. С точки зрения окружающей среды эстуариев возникают ключевые вопросы, касающиеся (i) взаимодействия между частицами и растворенными в воде веществами и последствия этого для изменения поступления последних в океан, (ii) химических видов, (iii) флоккуляции частиц и характеристик коллоидов. Рассматриваются указанные выше и связанные с ними вопросы и вносятся рекомендации относительно целей проведения исследований.

## خلاصة

يتضح من دراسة تقديرات تصريف الأنهار من المواد المذابة أنه ، بالرغم من التحسينات الحديثة التي طرأت على قاعدة البيانات ، لا تزال المعلومات في هذا الشأن غير كافية لاجراء تقدير دقيق لحمولة مياه الأنهار من العديد من المواد الهامة. ويناقش التقرير حدود التقديرات السنوية الوسطية لحمولة الأنهار من المواد المعلقة في مياهها ، ويدرس نتائج ما طرأ في عصرنا من تغيير في أساليب استغلال الأراضي وتنظيم مياه الأنهار مما أثر تأثيرا كبيرا على تصريف الأنهار ولا سيما على تدفق المواد المعلقة نحو مصابها . ويثير فيما يتعلق ببيئة المصاب الخليجية أسئلة هامة تخص (١) التفاعلات بين الدقائق والمواد المذابة وأثارها بالنسبة لتعديل تدفقات المواد المذابة صوب المحيط ؛ (٢) التمايز الكيميائي ؛ (٣) تدمج الدقائق وخصائص المواد الغروانية . فيتناول التقرير هذه الموضوعات وموضوعات متصلة بها ويقدم توصيات خاصة بأهداف البحوث .

## 摘 要

一份评估被河流带走的溶解物质的审查报告表明，尽管数据库近期有了改进，但有关河流带走的许多重要物质的准确估量方面的信息仍不充足。对悬浮沉积物年平均运载量的评估的局限性问题也进行了讨论。当代的土地使用和河流管理方面的变化对河流流量可能产生重大影响，尤其是对悬浮沉积物通向河口弯的通量产生重大影响。关于河口弯的环境问题，主要涉及：( i )微粒和溶解物质的相互作用及它们在改变溶解物质流入海洋的通量方面所具有的影响，( ii )化学物种的形成，( iii )微粒的沉积及胶体特点。这些问题及有关题目已经讨论并对有关研究目标提出了建议。



## TABLE OF CONTENTS

	<u>Page</u>
INTRODUCTION	1
RIVER INPUTS	2
Discharge of water and dissolved material	2
Discharge of particulate material	4
Human influences on rivers	5
ESTUARINE PROCESSES	6
Fate of river inputs in the estuarine zone	6
Particle size and aggregation	10
RECOMMENDATIONS	12
REFERENCES	13
TABLES & FIGURES	18-23
APPENDICES	24-25

## INTRODUCTION

The original SCOR Working Group 46 on River Inputs to Ocean Systems (RIOS) was established, with ECOR, ACMRR, IAHS and UNESCO, in 1973; CMG, IAPSO and IABO were affiliated organizations. The terms of reference, as developed at its first meeting and the final membership of the group are given in Appendix 1. The Working Group met in Paris in June 1974 and in New Haven in March 1975. Following the latter meeting a Steering Committee, consisting of J.D. Burton (Chairman), D. Eisma and J.-M. Martin, undertook the detailed planning for a Review and Workshop on RIOS. This was held, with the collaboration of IOC and the support of UNEP, in Rome in March 1979, under the Chairmanship of Professor D. Lal. The proceedings were published by UNEP and UNESCO in 1981.

After completion of this phase of its activities, and following a proposal by Professor Lal, Dr. Burton was appointed Chairman, and SCOR subsequently reconstituted the Working Group, with the membership and terms of reference shown in Appendix 2. The reconstituted WG46 met in Lisbon in December 1982. The meeting was held there at the invitation of the Portuguese National Commission of the Environment, following a Scientific Workshop on Estuarine Processes: an Application to the Tagus Estuary. Working Group members had been invited to participate in this workshop, which was organised by the Portuguese national authorities, with technical support from IOC, UNESCO and UNDP.

The following attended the meeting:

- (i) Members of Working Group 46  
J.D. Burton (Chairman), D. Eisma, R.F.C. Mantoura, J.-M. Martin, J.P. O'Kane, J. Richey.
- (ii) Invited Experts  
R. Dawson (IOC) attended the whole meeting. Parts were also attended by: H.L. Windom (representing IOC as Acting GEMSI Chairman), D. Krause (UNESCO), and T.R. do Espirito Santo (Comisao Nacional de Ambiente, National Director of the Tejo Project).

A report of this meeting was submitted to SCOR and has been published in SCOR Proceedings (1983, vol. 19, p. 36-42). The Working Group considered, however, that its final report should consist of a somewhat expanded version of material included in the report of the Lisbon meeting.

Under its terms of reference the Working Group was concerned with two primary scientific questions:

- (i) The input by rivers of water and dissolved and particulate material, with reference also to the processes determining these inputs.
- (ii) The modification of fluxes to the shelf seas and open ocean by processes occurring in estuaries.

The fuller account that follows of the Working Group's considerations of these topics has been updated by the Chairman in the light of some more recent developments.

### RIVER INPUTS

There are considerable deficiencies in the information available for evaluation of river inputs, especially limitations in geographic coverage and availability of time-series data. There have, however, been continuing advances in both the quality and geographical range of the information available. For example, more detailed studies have been made on the Zaire (Eisma and van Bennekom (1978) and contributions following this paper) and the Amazon and its tributaries (Stallard and Edmond, 1981, 1983). New data have become available on Chinese rivers, as in the studies by Hu *et al.* (1982), Li *et al.* (1984), Milliman *et al.* (1984), Edmond *et al.* (1985) and Aller *et al.* (1985). Extensive data for nutrients and carbon have become available from the SCOPE/UNEP programme on rivers (Degens, 1982; Degens *et al.*, 1983, 1985). Critical overviews of the literature on river inputs have been provided recently by Gordeev (1983) and Meybeck (1988).

In order to obtain adequate estimates of dissolved and particulate load it is necessary to have detailed records of the concentrations of dissolved and particulate material and of water discharge, and there are relatively few systems for which all this information is available with an adequate sampling frequency. The product of mean annual values for these parameters is an inadequate basis for estimation of load, leading generally to significant over-estimation in the case of dissolved load (Walling and Webb, 1983a). Sampling programmes must be designed with full consideration of the errors associated with the interpolation and extrapolation procedures that have to be applied to derive loads from non-continuous records. A detailed critique of these procedures is given in GESAMP (1987). These problems are greater for calculations of particulate load than for those of dissolved load, because of the generally greater temporal variability in the concentrations of suspended sediment.

### Discharge of water and dissolved material

The global discharge of water from rivers is estimated as  $3.74 \times 10^{19}$  g/yr (Baumgärtner and Reichel, 1975). Extensive data on water discharges of rivers have been compiled by UNESCO (1972, 1974, 1979). The contributions of the world's major rivers to the global input are shown in Table 1.

A recent overview of dissolved loads of rivers has been made by Walling and Webb (1983a) using data for 490 relatively unpolluted rivers in various parts of the world. Mean annual dissolved loads ranged from 0.34 to  $311 \times 10^6$  /km<sup>2</sup>/yr. The frequency distribution is shown in Fig. 1. The mean load for these rivers was  $39 \times 10^6$  /km<sup>2</sup>/yr, a value similar to the global mean value of  $33 \times 10^6$  /km<sup>2</sup>/yr derived by Meybeck (1979). Although there is considerable scatter in the relationship, mean annual dissolved load tends to increase with mean annual runoff. As regards temporal variability, the concentration of total dissolved

material generally shows an inverse relationship to discharge as a result of the dilution of base-flow with surface runoff.

Information on the concentrations of individual major constituents in river waters was critically examined by Meybeck (1979). His estimate for the global mean concentration of total dissolved material, excluding anthropogenic components, was 100 mg/l, corresponding to a global flux of  $3.7 \times 10^{15}$  g/yr. The estimate was based upon data for rivers which account for over 60 % of all drainage. Subsequently, Meybeck (1983) revised the estimates of atmospherically recycled salts to take account of the influence of these inputs in the sections of rivers near to the coasts. On this basis the global flux, excluding the anthropogenic component, is  $4.0 \times 10^{15}$  g/yr. A comparison of his estimates with those of Livingstone (1963), with data also for the concentrations of individual major constituents, is shown in Table 2. A detailed review of these and other estimates is given by Meybeck (1988).

There is wide variability in the composition of dissolved material in individual rivers, reflecting the relative importance of weathering and inputs in precipitation as sources of solutes, the geological and physiographical characteristics of the drainage area, and the geochemical processes within the river system. Anthropogenic influences must also be considered. According to Meybeck (1979) they may account for a further 10 mg/l, with the contributions of sodium, chloride and sulphate being particularly important relative to the concentrations arising from natural weathering processes (Table 2).

Both the quantity and quality of data for the less abundant inorganic constituents in rivers are much less good than for the major constituents. Analyses of the quality now regularly attained for trace metals in seawater are still relatively few for freshwater systems. Average values suggested by Meybeck (1988) for certain of these metals are listed in Table 3. These values may be subject to considerable revision in the light of further studies.

Analyses of inorganic forms of the micronutrient elements, phosphorus and nitrogen, are more readily available and are generally of higher reliability, although there are very wide gaps in regional coverage and good time-series data are relatively scarce. Anthropogenic influences are major for these elements. Wollast (1983) has summarized the more recent estimates of the pristine and modified inputs to the ocean (Table 4). While there is considerable uncertainty quantitatively as to the impact of man's influence, a substantial effect is apparent. It appears that the rivers of Europe and North America, which are not major contributors to the total global fluxes of material to the oceans, are now a major source of these elements as a result of intensive urban, industrial and agricultural development (Meybeck, 1982). The information in Table 4 is for the inorganic forms of phosphorus and nitrogen. Data are sparse on the organic forms but estimates suggest that for phosphorus the natural fluxes of inorganic and organic forms may be approximately equal (van Bennekom and Salomons, 1981; Meybeck, 1982) while the natural flux of dissolved organic nitrogen may be more than twice that of combined inorganic nitrogen according to Meybeck (1982).

Information on individual organic constituents in rivers, from natural sources and as pollutants, is extremely sparse. For total dissolved organic carbon (DOC) estimates of the global riverine flux have varied by an order of magnitude, from  $1-10 \times 10^{14}$  g C/yr. A summary of these estimates is given by Mantoura and Woodward (1983) who have emphasized the problems of estimating the global flux given the high variability of the concentration of DOC in river waters. On the basis that about 1 % of terrestrial production of organic carbon may be exported from catchments as DOC they suggested a global flux up to about  $8 \times 10^{14}$  g C/yr. Recent estimates (Degens and Ittekkot, 1985; Meybeck, 1988), based on the results of the SCOPE/UNEP carbon programme, have, however, been in the range of  $1.1-2.5 \times 10^{14}$  g C/yr, closer to the majority of earlier estimates.

It is evident that data are at present inadequate for the accurate estimation of the riverborne fluxes of many important dissolved constituents and that the need remains for systematic surveys, particularly on globally important systems. If these surveys are to be of value they must be based on strategies for sampling which minimize the errors due to temporal variability in discharge and solute concentrations.

#### Discharge of particulate material

A larger amount of weathered material is transported globally to the ocean in the form of suspended sediment than is carried in solution. Milliman and Meade (1983) have estimated that rivers with annual discharges of sediment exceeding about  $1.5 \times 10^{13}$  g provide an input to the ocean of  $7 \times 10^{15}$  g/yr, and that the total riverborne flux of suspended sediment is about  $1.35 \times 10^{16}$  g/yr. Bedload transport and discharge under flood conditions are difficult to estimate. The amounts contributed in these ways were considered by Milliman and Meade (1983) to represent globally up to perhaps some 15 % of the total carried in suspension under the normal range of discharge conditions, suggesting a total input of  $1.6 \times 10^{16}$  g/yr. The data of Milliman and Meade for major regions are presented in Table 5. A very striking feature is the dominance of S.E. Asia and the large western Pacific islands as a source of sediment. Prior to this work, the estimates made by Holeman (1968) were widely used in considering sediment inputs to the ocean. A comparison of the estimates is provided in Table 5. The differences which have the most important consequences for the estimates of total sediment discharge are the lower sediment yield taken by Milliman and Meade for Asia, reflecting the fact that large areas of the continent have much lower sediment yields than the Himalayan and Chinese systems, and the omission of the Pacific islands in Holeman's study. Individual catchments vary extremely widely in sediment yield. Data summarized by Walling and Webb (1983b) range from less than 10 to more than  $10^{10}$  g/km<sup>2</sup>/yr. It is apparent that rivers transport globally about four times as much material in the form of sediment as that carried in solution. Between individual rivers the relative importance of these fractions can vary greatly and there are systems in which dissolved load exceeds the suspended particulate load. Walling and Webb (1983a) have recently considered the relationship between mean dissolved and particulate loads for individual rivers, a matter on which there has been disagreement in

the literature. From the data on 302 rivers they found no clear trend but some indication of a positive relationship. The wide differences in the behaviour of individual elements in their distribution between solution and solid phases have been discussed by Martin and Meybeck (1979).

Apart from uncertainties concerning the importance of transport under extreme flood conditions, there are problems in estimating the mean loads of suspended sediment, carried by rivers, which are analogous to those described for dissolved constituents. Data are considered inadequate for many systems of obvious importance, such as the Ganges-Brahmaputra and the Amazon. Moreover, even where data are apparently more adequate, problems associated with the design of sampling programmes, particularly the frequency of sampling, still exist and for the estimation of fluxes to the ocean the locations of some sampling stations may be unsatisfactory. The problems of estimating mean annual loads are discussed by Walling and Webb (1981). In extreme cases the use of different methods of calculation can lead to differences in estimated load of at least an order of magnitude. The estimation of mean suspended sediment loads over extended periods is greatly complicated by the different time-scales on which material may be stored in locations such as flood plains between erosion and transport to river mouths, such storage involving the major fraction of eroded material in some regimes (Meade and Parker, 1985).

Thus, despite the considerably improved data base for the particulate loads of rivers, as compared with a decade ago, major gaps in information remain, as for the dissolved loads, and there continues to be a need for coordinated programmes on major systems, and for improvements in analytical procedures and quality control for many constituents. International organizations can contribute substantially in these areas, particularly by sponsoring field workshops and intercalibrations.

#### Human influences on rivers

Improved knowledge of river inputs is not, however, merely a matter of improved data acquisition. Basic understanding of processes in rivers is essential, as shown by the examples already quoted. Such an understanding is also vital for assessment of the substantial impact of many of society's activities involving changes in use of the environment. Knowledge of the origins of water (in surface runoff and groundwater, as a function of elevation and rainfall regime), origins of sediment, and of river processes, is necessary to predict, for example, how river inputs will alter with changes in land-use, river management and climate. Important contemporary changes, such as intensive agriculture, deforestation, and damming, modify river processes through alterations in floodplain area and nutrient balances, with their effects on storage and on fertility. Detailed basic knowledge of river dynamics and chemical behaviour during tributary mixing is needed to evaluate the consequences of such processes for fluxes to estuaries and their seasonal variability. The scale of man's intervention is, however, often apparent. Meade and Parker (1985) report that the amount of sediment transported by the Mississippi to the delta region has been reduced by

one-half as a consequence of the effects of dams and reservoirs and the seaward transport of sediment by the Colorado and Rio Grande almost wholly stemmed.

Working Group 46 has been particularly concerned with the implications of river processes for the fluxes of material entering estuaries, but changes in river conditions also influence other transport pathways in the environment, for example by changes in fluxes of trace gases to the atmosphere as a result of changes in redox conditions in rivers and floodplains.

Attention has been given to the consequences for marine systems of some human modifications of rivers, such as the construction of the Aswam High Dam (Wahby and Bishara, 1981). Marine scientists have, however, given little attention generally to the implications of the widespread changes which are occurring in the nature of many river systems. A detailed evaluation of this topic will need the collaboration of scientists concerned with river hydrology and those concerned with the marine environment.

### ESTUARINE PROCESSES

Estuaries have a central importance as regards RIOS for two principal reasons. First, because of the marked horizontal and vertical gradients in major physicochemical parameters (ionic strength and composition, pH, pE), they are zones of exchange between dissolved and particulate phases and thus, with respect to dissolved constituents, an estuary may act as a filter or an amplifier for the river supply. Secondly, they can be important areas for the deposition of particles, derived from both riverine and marine sources, which have different relative importance in different estuaries. The importance of marine inputs in estuarine sediment budgets has long been recognised. Little is known, however, of the sink functions of estuaries for dissolved material entering in seawater and the potential role of such a process in, for example, the transport of pollutants between estuaries.

#### Fate of river inputs in the estuarine zone

Some estuaries retain very little of the sediment delivered to them because their capacity to store sediment is fully utilized. For others, sediment trapping efficiency is high. For the estuaries and coastal marshes on the eastern coast of the United States trapping is virtually complete and additional sediment may be accumulated from the shelf (see, for example, Meade (1982)). Globally, deposition in estuaries and the submarine fans of some major sediment-carrying river plumes may account for at least 90 % of the river supply. All the material initially incorporated in sediments is not necessarily retained, however, even in areas of long-term deposition, since diagenetic changes in sediments can lead to a redistribution of material between particles and solutions and diffusive fluxes of solutes to overlying waters can be set up as a result of the concentration gradients which are created. Bioturbation and, especially, turbulent resuspension of sediments and associated pore waters, can greatly increase the diffusion coefficients.

Those dissolved constituents in the river input which are geochemically unreactive will behave essentially conservatively during estuarine mixing, showing distributions which are determined by the extent of mixing of freshwater and seawater. In these cases, the river input is balanced by export from the estuary. There are many constituents, particularly trace metals and nutrients, the behaviour of which has been studied in a few estuaries but only a limited number have been examined in sufficient detail, and over a sufficiently wide range of contrasting environments, to enable generalizations to be made. Where the concentration of the constituent in the river input is considerably higher than that in seawater the occurrence of removal is quite readily identified but for constituents which are of higher abundance in seawater the signals from river inputs become impossible to resolve at low salinities.

Non-conservative behaviour arises from exchanges between solutions and particles, and by biological uptake. Removal may occur as a result of the formation of new solid phases, as from the destabilization and aggregation of microcolloidal forms of iron (conventionally analyzed as "dissolved") on mixing of iron-rich river waters with seawater, or by scavenging on particle surfaces. It is known that particles remain negatively charged over the whole range of estuarine salinities, possibly as a result of coatings of organic material on the surfaces (Hunter and Liss, 1982; Loder and Liss, 1985). The nature of the surfaces affects particle reactivity and there is evidence for the role of micro-organisms on particle surfaces in at least one important estuarine reaction, namely the oxidative scavenging of manganese (see, for example, Vojak *et al.* (1985)). Release from particles by dissolution or desorption has been less unequivocally demonstrated than removal processes but some instances have been established.

A very substantial effort has gone into the study of estuarine chemical processes by environmental surveys and laboratory simulation experiments. Reviews include those by Duinker (1980), Aston (1978), Morris (1985) and Burton (1988). This effort has led mainly to improved understanding of the cycling of material within estuaries and little is known about the overall effects of processes in terms of modification of fluxes to the ocean. This is well exemplified by work on iron and manganese, the two most studied metals in these systems. The removal of micro-colloidal iron has been extensively documented but the fate of the flocculated iron has not been established. From the substantial literature on manganese it is often not possible to assess the overall modification of the flux of the dissolved metal in the estuaries studied. This is because studies specifically to evaluate export fluxes have been undertaken only infrequently and the design of most surveys is inadequate to enable conclusions on this aspect to be drawn. Net fluxes can be estimated from extrapolation of the relationships of salinity and concentrations of individual elements shown in oceanic transects of surface waters (Kaul and Froelich, 1984); such calculations will often indicate the flux from a drainage region rather than an individual estuary. Mass balance calculations, such as those made by Yeats and Bowers (1983) also enable conclusions to be drawn concerning modification of fluxes in the estuarine zone. An account of these approaches is given in GESAMP (1987).



In studying estuarine chemical processes the low salinity region has received special attention since it is the location of important reactions relating to rapid changes in composition (Morris *et al.*, 1978) and, in many cases, of turbidity maxima with high, though variable, particle concentrations and release of reactive species from sediments. Emphasis on this region is thus appropriate in the study of cycling processes within estuaries but from the standpoint of estimating the export of dissolved material from estuaries there is a need for more intensive studies of mixing relationships over extended salinity ranges.

Present efforts to develop predictive models for the behaviour of chemical constituents in estuaries are directed essentially to single systems. While each geochemical reaction of interest will occur to some degree in every estuary, the extent can vary greatly, depending upon the residence time in the system and the rate of the reaction, which is dependent in turn upon the availability of reaction sites. This is well illustrated by the seasonal variability in the removal of dissolved silicon in some estuarine systems, for example in the Yaquina Estuary (Callaway and Specht, 1982). Nevertheless, case studies on selected systems would enable the usefulness of various approaches to evaluation of export fluxes to be tested.

In addition to changes in the flux of dissolved elements through estuaries, substantial alterations in chemical speciation may occur, resulting in some cases from biologically mediated changes in oxidation states and molecular form, but also from differences in complexation reflecting the changes in the major complexing ligands along salinity gradients. The principles of equilibrium modelling of ion associations are well established. Major discrepancies in models have been largely attributable to deficiencies in the equilibrium data base. Many of these problems have been resolved by a more critical evaluation of the existing data and the model of Turner *et al.* (1981) represents a good description of the changes in inorganic speciation in the range of compositions of river waters and seawater. The position regarding organic complexation is less well defined theoretically and variable degrees of complexation are indicated by operational analytical procedures; recent electrochemical developments appear capable of providing more refined approaches to the measurement of such associations (Van den Berg, 1986). More information is certainly needed on the nature of non-labile complexes and the extent of their formation. The many departures from equilibrium predictions, observable analytically, emphasize the need also for experimentally derived information on the rates of environmentally important reactions.

An important requirement, especially in speciation studies, is a knowledge of pH and its variation during estuarine mixing. Considerable difficulties have arisen in marine chemistry through the use of several different pH scales. The problem is accentuated for estuaries with their wide range in ionic strength. Several workers are already addressing this problem. It would be of great value if standardized measurement procedures and a common pH scale could be adopted as early as possible by estuarine scientists. Any consideration of the pH problem in river

and estuarine waters should take account of the role of the acid-base properties of the dissolved organic compounds.

The practical study of organic chemical processes in estuaries, as well as in rivers, is underdeveloped, principally because of methodological limitations and uncertainties of strategy in the approach to a system containing a huge number of molecular entities. Even for total particulate and dissolved organic carbon, data are inadequate for budget calculations. The application of thermodynamic concepts to organic speciation and prediction of transformations of organic species is an area which warrants greater attention. The origins and characteristics of organic coatings on particles are little understood, despite their likely importance on surface properties and reactivity, as indicated above.

Biological processes, especially the major cycling of carbon by autotrophic production of organic material and by microheterotrophic processes, are of direct importance particularly in modifying the fluxes of micronutrients in estuaries. They also influence other trace constituents that become involved in the major biogeochemical cycles and may significantly modify chemical speciation as a result of cycling through biota. For example, arsenic (V) can undergo reduction to arsenic (III) and methylation under seasonally favourable conditions in temperate estuaries (see, for example, Howard *et al.* (1982)). More generally, the production and decomposition of organic material is important in the oxygen budgets of estuaries and respiration using a sequence of terminal electron acceptors is a primary control on the oxidation-reduction conditions in bottom sediments and, in some cases, bottom waters.

The accurate measurement of chlorophylls and other plant pigments in such waters is a key requirement in productivity studies. Investigations using high performance liquid chromatography have shown that in environments where plant material is being produced and decomposed at high rates the accuracy of standard spectrophotometric procedures for measurement of chlorophyll can become grossly inadequate (Mantoura and Llewellyn, 1983). Re-evaluation of methods is urgently needed.

Hydrodynamic features in catchment areas are important in relation to the mass transport of material into estuaries. Insufficient attention has been given to statistical methods in the design of sampling to determine inputs. For the modelling of the behaviour of chemical constituents in estuaries much more information is needed on the rates of exchange between dissolved and particulate material and on conversions between different chemical forms. There is often considerable lack of appreciation of the limits of the capabilities of a model, because of confusion as to objectives. Models constructed in response to management requirements for an estuary and which provide satisfactory simulations for the behaviour of specific constituents in this context may nevertheless be inappropriate when applied to a very different set of conditions or to another constituent which enters into reactions of a different type. Information on processes is essential if

responses to changes in input forcing functions are to be adequately predicted for a range of components and conditions.

#### Particle size and aggregation

Data on the particle size distribution of suspended particulate material are of central relevance to the study of processes involved in sedimentation and sediment transport in estuaries. The size and the surface characteristics of suspended particles are also major determinants of their chemical reactivity. Standard methodology involves sampling of suspended matter with some form of bottle or a bucket and subsequent size analysis by several possible methods: by eye with a standard light microscope, a reversed light microscope (as used in plankton studies), or a scanning electron microscope (SEM) after filtration on a fine filter, usually Nuclepore or Millipore; by Coulter Counter, HIAC particle counter or other electronic particle counting system; and by pipette analysis (using Nuclepore filters and microbalance). Size analysis has to be done soon after sampling - within half a day or so - before the particles start to break apart or clog together, or become attached to the wall of the container wherein the suspension is kept. Preparation for SEM analysis also has to be done as soon as possible after sampling. Particle size distributions, determined by these methods, are reproducible and, in so far as intercalibrations have been done, give similar results (particularly Coulter Counter and pipette analysis data).

A large number of suspended particles is present as flocs of mineral grains, organic matter and biogenic carbonate and opal particles. In estuaries and in most coastal seas, mineral particles dominate, bound together into flocs by organic matter, whereas further out on the shelf and in oceanic waters organic matter and biogenic particles dominate. The flocs found after the normal procedures of sampling and handling the samples, are rather strongly held together: it requires ultrasonic treatment or removal of the organic matter by oxidation to reduce their size. The suspended matter found after sampling is, at least partly, not in the same state as that in which it was present in situ in the water. There are many observations of larger flocs in the ocean in the form of more or less round flocs of up to several mm diameter called marine snow, or of up to 10-15 cm long stringers, the latter occurring in the quiet waters below the thermocline in nearshore waters. Both marine snow and stringers are fragile and easily broken up during sampling, if no elaborate precautions are taken. Marine snow is collected in sediment traps; stringers have been collected by SCUBA divers using glass or perspex tubes and handling them very carefully. Both marine snow and stringers have been observed from submersibles. Collectively they have been called "large amorphous aggregates".

Similar flocs as "marine snow" of up to several mm diameter (macroflocs) have been observed in estuaries and coastal waters (up to now only in temperate waters). They can be seen by eye from the surface when sunlight comes obliquely into the water and they have been photographed by in situ photography with a Benthos planktoncamera. They consist mainly of mineral particles glued together by organic matter,

which occurs in the estuarine flocs in relatively small amounts (5-20 %) as compared with the oceanic flocs. Where it could be checked, it was found that the macroflocs are made up of the smaller but more strongly bound flocs found after sampling and of single mineral grains (and some biogenic particles).

The fragility of the large flocs, which has been known since 1953 from Japanese observations (Suzuki and Kata, 1953), has led to attempts to measure the size of suspended particles in situ in the water. An in situ Coulter counter (Maddux and Kanwisher, 1965) and similar electronic counting device did not suffice because of floc breakage during the measurements or because of the turbulence created by the instrument itself. Recent developments are holographic size measuring (Carder et al., 1984) and direct photography (Eisma et al., 1983; Kranck, 1984; Honjo et al., 1984). Holography has successfully been used in combination with a freefloating sediment trap in quiet oceanic waters with low suspended matter concentrations. Particles of 15-250  $\mu\text{m}$  were recorded, showing in situ size, shape, orientation and settling rate. Direct photography in oceanic water yielded pictures of particles down to 200  $\mu\text{m}$  diameter (Honjo et al., 1984) and in estuarine waters down to ca. 50  $\mu\text{m}$  (with a Benthos planktoncamera; Eisma et al., 1983; Kranck, 1984). In the latter case the data down to 100  $\mu\text{m}$  were sufficient to estimate a size distribution down to that size. In estuaries the suspended matter concentration puts an upper limit to the use of direct in situ photography: at concentrations higher than 150-180 mg/l reliable results could not be obtained because of overlapping particles. From these attempts it is evident that a need for apparatus than can record in situ a size range from ca. 2  $\mu\text{m}$  upwards to several mm or cm, and that can be adapted to record in oceanic waters down to deep ocean depths as well as in estuaries and coastal waters at current speeds of 1 m/s or more and at concentrations up to 150 mg/l. Such recordings give size, shape and orientation of the suspended particles and allow estimation of the in situ size distribution. Such results will give a better understanding of suspended matter transport and deposition as well as of all processes related to suspended particle surfaces.

Methods are also needed for the collection and characterisation of particles extending into the colloidal range ( $<1 \mu\text{m}$ ), because of the importance of this fraction in terms of its surface reactivity. Limited information is available on the chemical composition of estuarine colloids (Sigleo and Helz, 1981).

Another key problem in this field is the role of organisms in particle aggregation and in alteration of surface sediment composition and micro-relief with consequent effects on sediment erosion and movement, and the seasonal variability of bottom boundary conditions. The lack of direct methods for realistically measuring bottom sediment transport is a major limitation on our understanding of the fate of sediment supplied to an estuary. Where large amounts of sediment enter and leave an estuary during a tidal cycle, estimates of net flux from measurements across the estuarine boundaries are subject to large uncertainties. As with dissolved substances, there is thus inadequate information as to how much of the material entering estuaries is eventually exported.

### Recommendations

Following its meeting in Lisbon, the Working Group made a number of recommendations which are listed below.

Recommendations (1)-(4) were for actions specific to SCOR, (5) & (6) required interorganizational action, (7) related to the follow up to the work of Working Group 46.

- (1) That SCOR re-evaluates the methods appropriate for the determination of the concentrations of chlorophylls and other plant pigments in estuarine and coastal waters with a view to the publication of revised recommended procedures. Similar problems exist for freshwater and SCOR may wish to affiliate with other appropriate bodies in this re-evaluation.
- (2) That SCOR considers the question of a pH scale suitable for estuarine waters, and the problem of practical measurements of pH in such waters, and recommends suitable procedures.
- (3) That SCOR critically evaluates techniques for particle size analysis in river, estuary and coastal systems, with reference also to colloidal particles, and with a view to development of reliable in situ techniques.
- (4) That SCOR should take the initiative in forming a group to deal explicitly with the analysis of the effects of land-use changes and dams on the downstream flux of water and materials within rivers and to the marine receiving waters. The specific terms of reference should include:
  - (i) retention by dams
  - (ii) input and routing of sediments and dissolved material
  - (iii) contact with "client" groups (e.g. those concerned with problems ranging from terrestrial erosion to management of mangrove and other near-shore ecosystems) and a synthesis of expertise in the diverse problem areas.

The group should include expertise on chemistry, hydrology, biology and sedimentology, focussed on a common model. The assessment of these problems should be brought to the attention of UNESCO with a view to implementation of a long term cooperative research programme.

- (5) That intercomparison and training workshops are held in selected estuaries adjacent to regional seas, to evaluate the methods for the measurement of important pollutant substances in river and estuarine waters. This objective could appropriately be pursued through IOC and UNESCO.
- (6) That a field experiment workshop be held to establish a strategy for the measurement of major sources of pollutants and other selected materials for a single estuarine system and the export of these materials from the estuary to the coastal zone. The planning

and execution of this programme should be pursued through IOC and UNESCO agencies with the cooperation of SCOR.

- (7) That SCOR continues to review the need for working groups to consider specific priority topics concerning RIOS. The working group suggests that one such topic is the dynamics of cycling of material in estuaries and that a group should address the following issues in relation to it: the surface chemistry and reactivity of particles in estuaries; the source and sink functions within estuarine waters and sediments; the characteristic time scales for biochemical and geochemical processes and their implications for the design of programmes of estuarine measurements.

Several of these recommendations have led to new initiatives by SCOR. WG 78 has been established to address the question of improved procedures for the determination of chlorophylls and other plant pigments. WG80 is to consider the role of phase transfer processes in the cycling of trace metals in estuaries.

There has also been an increased involvement of IOC, through GESAMP, in matters relating to RIOS. In particular, GESAMP Working Group 22 on Land/Sea Boundary Flux of Pollutants has considered (GESAMP, 1987) the requirements for estimating gross river fluxes of pollutants and the net flux of pollutants across the land-sea boundary. While the work of that group is primarily directed to fluxes of pollutants the considerations which arise are common to the evaluation of baseline fluxes of material.

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Table 1. Mean water discharge of major rivers

Rivers in rank order of discharge	Mean discharge m <sup>3</sup> /s	Cumulative discharge 10 <sup>3</sup> m <sup>3</sup> /s	Cumulative percentage of global discharge
1	Amazon	175,000	
2	Congo	39,640	
3	Orinoco	33,950	
4	Yangtse Kiang	22,000	
5	Brahmaputra	19,200	
6	Mississippi	17,800	
7	Yenissei	17,800	
8	Lena	16,300	
9	Paraná	14,900	
10	Mekong	14,900	372
11	Saint Lawrence	14,160	
12	Irrawady	13,560	
13	Si Kiang	12,500	
14	Ob	12,200	
15	Ganges	11,600	
16	Tocantins	11,000	
17	Aur	10,300	
18	Mackenzie	9,710	
19	Columbia	7,960	
20	Indus	7,550	482
21	Magdalena	7,500	
22	Zambezi	7,080	
23	Danube	6,530	
24	Yukon	6,220	
25	Niger	6,090	
26	Uruguay	5,500	
27	Ogoove	4,710	
28	Huang Ho	3,900	
29	Sepik	3,800	
30	Frazer	3,540	537
31	Northern Dvina	3,380	
32	Pechora	3,360	
33	São Francisco	3,070	
34	Godavari	2,690	
35	Pyasina	2,550	
36	Koksoak	2,550	
37	Neva	2,540	
38	Rhine	2,535	
39	Fly	2,450	
40	Purari	2,450	564
50	Cagayan	1,740	585
60	Shatt el Arab	1,450	602
80	Cuenza	950	625
100	Murray	737	642
120	Aux Feuilles	589	656
150	Dong Nai	473	671
200	Grey	294	690

From Martin *et al.* (1981).

Table 2. Global average concentrations of dissolved major elements in rivers

		SiO <sub>2</sub>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Na <sup>+</sup>	K <sup>+</sup>	Cl <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	HCO <sub>3</sub> <sup>-</sup>	Total
Livingstone (1963)	C <sub>d</sub>	13.1	15	4.1	6.3	2.3	7.8	11.2	58.4	118
Meybeck (1979)	C <sub>d</sub>	10.4	14.7	3.65	7.2	1.4	8.25	11.5	53	110
	C <sub>m</sub>	0	1.3	0.3	2.05	0.1	2.5	3.25	1	10
	C <sub>r</sub>	0	0.05	0.2	1.5	0.07	2.7	0.4	0	5
	C <sub>w</sub>	10.4	13.4	3.15	3.65	1.25	3.05	7.85	52	95
Meybeck (1983)	C <sub>d</sub>	10.4	14.9	3.85	8.45	1.50	10.5	12.3	53	117
	C <sub>r</sub>	0	0.25	0.38	2.75	0.13	4.95	1.2	0	12

All values are in mg/l.

C<sub>d</sub> - Material from all sources.

C<sub>m</sub> - Contribution from anthropogenic material, estimated as in 1970.

C<sub>r</sub> - Contribution from recycled marine aerosol.

C<sub>w</sub> - Contribution from continental weathering processes.

Table 3. Global average concentrations of some dissolved trace elements in rivers

Element	Concentration
Aluminium	40 ± 20
Chromium	0.8 ± 0.3
Copper	2 ± 1
Fluorine	100 ± 20
Iron	50 ± 30
Manganese	10 ± 5

Values (in µg/l) from Meybeck (1988).

Table 4. Global river fluxes of dissolved inorganic phosphorus and inorganic combined nitrogen

		Phosphorus	Nitrogen
van Bennekom and Salomons (1981)	$F_n$	0.5	5
	$F_m$	1.9	19
Meybeck (1982)	$F_n$	0.43	4.4
	$F_m$	0.4-1.0	7
Wollast (1983)	$F_n$	0.45	2.6
	$F_m$	1.7	21

$F_n$  - flux attributed to natural processes.

$F_m$  - flux attributed to anthropogenic material.

Fluxes in units of  $10^{12}$  g/yr.

For unpolluted systems inorganic phosphorus consists essentially of orthophosphate, and inorganic combined nitrogen is mainly present as nitrate.

Table 5. Global sediment budgets of Holeman (1968) and Milliman and Meade (1983)

Area	Drainage area 10 <sup>6</sup> km <sup>2</sup>		Sediment Yield 10 <sup>6</sup> g/km <sup>2</sup> /yr		Sediment Discharge 10 <sup>12</sup> g/yr	
	Holeman	Milliman & Meade	Holeman	Milliman & Meade	Holeman	Milliman & Meade
North & Central America	20.48	17.50	87	84	1780	1462
South America	19.20	17.90	57	97	1090	1788
Europe	9.2	4.61	32	50	290	230
Eurasian Arctic		11.17		8		84
Asia	26.6	16.88	543	380	14480	6349
Africa	19.7	15.34	25	35	490	530
Australia	5.1	2.20	41	28	210	62
Large Pacific Islands		3.00		1000		3000
Total	100	88.60	183	150	18300	13505

From Milliman and Meade (1983).

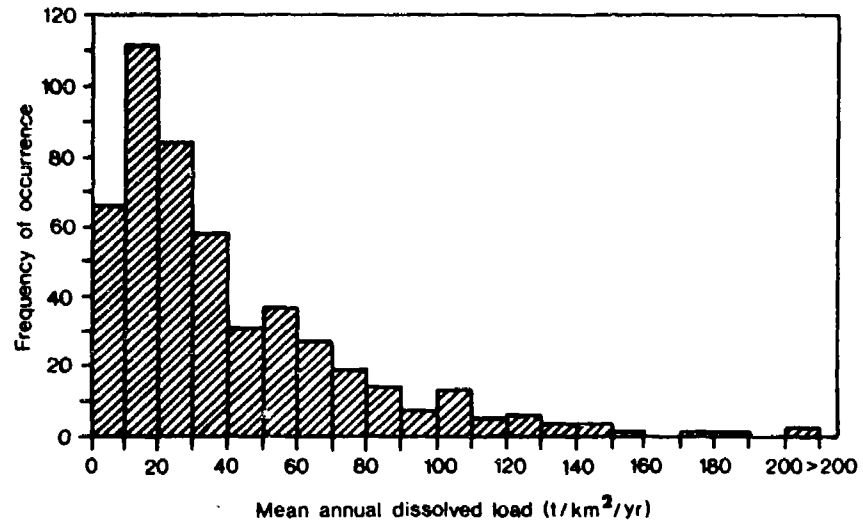


Fig. 1. Frequency distribution of values of mean annual dissolved load for 490 rivers (Walling and Webb, 1983).



Appendix 1Terms of reference and membership of the original Working Group 46

The questions with which the group was concerned were:

- (i) How do river water and its sediment load acquire their chemical qualities in response to climatic, geological and cultural factors?
- (ii) What transformations occur when a river meets the sea?
- (iii) What is the ultimate flux of constituents to the open ocean via river systems?

Members of the Working Group as at March, 1979, were as follows:

Chairman	D. Lal
	J.D. Burton
	R. Chesselet
	J.A. da Costa
	D. Eisma
	E. Eriksson
	F. Fournier
	A.L.H. Gameson
	V.V. Gordeev
	J.-M. Martin
	S.O. Stanley
	P.N. Storrs
	K.K. Turekian
	A. Walton
Corresponding Members:	L. Bruegmann
	C.D. Vara
Observer:	Y. Kitano
Executive Reporter:	H. Postma

Appendix 2Terms of reference and membership of the reconstituted Working Group

The terms of reference for the reconstituted Working Group were:

- (i) To review and evaluate knowledge of (a) factors which govern the input of materials by rivers to estuaries, and (b) the estuarine processes which modify the composition and flux of materials entering the ocean, including substances influenced by human activities.
- (ii) To identify priorities for further work in this area, including the accurate estimation of river fluxes, and to promote international co-operation in the study of river-estuary-ocean systems.

Members of the Working Group as at December, 1982, were as follows:

Chairman	J.D. Burton
	D. Eisma
	V.V. Gordeev
	R.F.C. Mantoura
	J.-M. Martin
	J.P. O'Kane
	J. Richey
	S. Stanley
	K.K. Turekian
Corresponding Members:	L. Bruegmann
	C.D. O'Vara
Executive Reporter:	R. Chesselet

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6	1967	WG 20	21	1975	WG 27
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10	1969	—	27	1976	WG 10
11	1969	WG 21	28	1978	WG 10
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13	1969	WG 15	30	1979	—
14	1970	WG 10			