[AMERICAN JOURNAL OF SCIENCE, VOL. 282, APRIL, 1982, P. 401-450]

American Journal of Science

*APRIL 1982*

# CARBON, NITROGEN, AND PHOSPHORUS TRANSPORT BY WORLD RIVERS

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ABSTRACT. The various forms (dissolved and particulate, organic and inorganic) of carbon, nitrogen, and phosphorus in world rivers are reviewed from literature data. Natural levels are based mainly on major rivers for the subarctic and tropical zones which are still unpolluted and on smaller streams for the temperate zone. Atmospheric fallout is also reviewed. Natural contents of dissolved organic carbon (DOC) are mainly dependent on environmental conditions: DOC varies from 1 mg $l^{-1}$ in the mountainous alpine environments to 20 mg $l^{-1}$ in some taiga rivers. The world DOC average is 5.75 mg $l^{-1}$. Particulate organic carbon (POC) is inversely related to the river suspended matter, $C_s$, and varies from 0.5 to 40 percent of total suspended matter with a weighted average of 1 percent. However, most rivers carry suspended material richer in organic carbon (between 1.6 and 6 percent). The DOC/TOC ratio (TOC = total organic carbon) is highly variable, ranging from 10 to 90 percent and it decreases with $C_s$. An average DOC/TOC = 0.6 is likely, but much lower ratios are found in highly erosive environments. The TOC transport rates by rivers are generally only 1 to 2 percent of the net primary production of the terrestrial ecosystem for any kind of environment. Nitrogen forms include dissolved organic nitrogen (DON), dissolved inorganic nitrogen (DIN = $N - NH_4^+ + N - NO_3^- + N - NO_2^-$), and particulate organic nitrogen (PON). Natural levels are very low: DIN = 120 $\mu$g $l^{-1}$ of which only 15 percent is present as ammonia, and 1 percent as nitrite. DON is much less often measured than DIN; its average level in world rivers is estimated to be 260 $\mu$g $l^{-1}$. In the subarctic zone, where the dissolved organic contents are highest (DOC $\geqslant$ 10 mg $l^{-1}$), DON represents between 60 and 90 percent of total dissolved nitrogen. However most river-borne nitrogen (55 percent) is linked to particulate matter, as PON. The C/N ratio in river particulate matter is very constant, mostly between 8 and 10 (wt ratio). This ratio is very similar to values found in surficial soil layers which are probably the main source of organic detritus in rivers although internal production of organic matter is known in some major rivers. Phosphorus is naturally present in very low amounts: around 10 $\mu$g $l^{-1}$ for $P\text{-}PO_4^{3}$ and 25 $\mu$g $l^{-1}$ for total dissolved phosphorus (TDP which includes the organic form). However, TDP may be overestimated in unfiltered samples. Particulate phosphorus represents 95 percent of P naturally carried by rivers, of which 40 percent is in organic forms (POP).

The average nutrient content of rains has been estimated with a set of unpolluted stations: $P - PO_4 = 5$ $\mu g$ $l^{-1}$, TDP = 10, $N - NO_2 = 5$, $N - NH_4 = 225$, DON = 225, and $N - NO_3 = 175$ $\mu g$ $l^{-1}$. TOC levels are probably around several mg $l^{-1}$. These contents are very similar to those found in unpolluted rivers. When considering the world water balance (1 m of rain over the non-glaciated exoreic part of the ocean corresponds only to 0,37 m of runoff) the precipitation fallout rates of dissolved nutrients on the terrestrial ecosystem are much higher than the river output rates. However, if the river particulate nutrients (particulate inorganic forms excluded) are considered, the fallout rates become three times lower than export rates by rivers for C, ten times smaller for P, but still remain twice as high for N. When comparing the river nutrient loads to the average primary production of the continents, they represent a very minor part of the amount of N, P, and C annually involved in the biological cycle: 1 percent for C, and about 15 percent for N. This proportion is only 4 percent for phosphorus which is actively picked up by vegetation from the parent rock and partly exported as POP. This process could explain the relative P enrichment (with respect to Al) previously noted in river particulate matter (Martin and Meybeck, 1979).

Man's influence on surface waters has now greatly increased natural nutrient levels. Total dissolved P and N have globally increased by a factor of two and locally (Western Europe, North America) by factors of 10 to 50. These increases were found to be directly proportional to the watershed population and to its energy consumption. The corresponding additional loads to the oceans represent about 8 percent of the N and P produced by mining and industry. The rest is still stored at the continent surface or exchanged (nitrogen) with the atmosphere.

River transport of material has been considered for over a 100 yrs in geochemical budgets (Forel, 1892). It gives essential information both on processes affecting the continental surface (weathering, plant production, pollution . . .) and on the amount and nature of material carried to water bodies such as lakes, seas, and oceans (Garrels and MacKenzie, 1971; Garrels, MacKenzie, and Hunt, 1973). The first well-documented review of river transport was made by Livingstone (1963) and mainly concerned the major dissolved elements. Since then many other world-wide budgets have been published taking advantage of the ever-increasing studies of river dissolved and particulate material (Alekin, 1978; Gordeev and Lisitzin, 1978; Martin and Meybeck, 1979; Meybeck, 1979). However none of these works has considered the major nutrients, nitrogen, phosphorus, and organic carbon. Measurements of organic carbon levels in rivers are still unusual; as a result estimates of this input to the ocean vary from 100 $10^{12}$ g $yr^{-1}$ according to Duce and Duursma (1977) to at least 1000 $10^{12}$ g $yr^{-1}$ (Richey and others, 1980). The same uncertainty is noted for nitrogen and phosphorus for which average contents in rivers are even more variable for two reasons: the chemical speciations of N and P are multiple, and the influence of man has greatly modified surface waters quality, particularly in the temperate zone. (Vollenweider, 1968; Stumm, 1973).

Previous budgets of N, P, and sometimes C have been based most of the time on crude estimates and no basic data or budget details have been published (except for Livingstone's review). Over the past decade the amount of basic material has rapidly increased, and many major rivers have now been studied: Amazon (Williams, 1968; Schmidt, 1972; Richey and others, 1980), Zaïre (van Bennekom and others, 1978), MacKenzie (Brunskill and others, 1975). Regional budgets have been published for the White Sea watershed (Maksimova, 1978), Black Sea (Manheim and Chan, 1974), Sweden (Ahl and Oden, 1972), et cetera. Regular river quality networks are now considering N and P species and sometimes organic carbon (Environment Canada; Service Hydrologique National de la Suisse; Briggs and Ficke, 1977, for the United State network). Environments now being studied range from the humid tropics (Brinson, 1976; Howard-Williams and others, 1977) to the Arctic (Brunskill and others, 1975; Schindler, Welch, and others, 1974). On the basis of these new data the following questions will be examined:

1. What are the *natural levels* of N, P, and organic C, and what are the relative proportions of their specific forms in river waters?
2. Is it possible to relate these levels to *environmental factors* (vegetation, water runoff, lithology, et cetera)?
3. What is the *amount of nutrients carried by rivers* compared to *precipitation input and to plant production?*
4. To what extent have nutrient levels and loads suffered from the *influence of man's activities?*

For organic carbon a detailed budget (including all basic data) has already been published (Meybeck, 1981); the summary of these results will be presented here and compared to the budgets of the other nutrients. At the same time Schlesinger and Melack (1981) have published another fully documented carbon budget which will be compared to ours.

## 1. BASIC DATA AND PROCEDURES USED IN RIVER TRANSPORT BUDGETS

### *1.1. Forms of N, P, and C in natural waters*

The distinction between dissolved and particulate material is operationally realized by most authors by use of a filter, usually of 0.45 or 0.5 $\mu$m pore size (for organic carbon studies this filter is of fiberglass). However some of the colloidal material may still pass through this type of filter, for instance, organic carbon (Lock, Wallis, and Hynes, 1977). Therefore the term "dissolved" matter, which will be still used here, might be inappropriate, and "filtered" or "non particulate" would be more convenient at least for organic carbon.

The nitrogen forms commonly found in river waters are: $NO_3^-$, $NO_2^-$, $NH_4^+$, dissolved organic nitrogen, and particulate organic nitrogen. These forms will all be reported here as nitrogen and will be referred to as $N\text{-}NO_3$, $N\text{-}NO_2$, $N\text{-}NH_4$, DON, and PON. The dissolved inorganic nitrogen, DIN, is the sum of $N\text{-}NO_3 + N\text{-}NO_2 + N\text{-}NH_4$. Total dissolved nitrogen, TDN, refers to all forms, and Kjeldhal Nitrogen, $N_K$, to the sum $DON + NH_4^+$.

The phosphorus forms discussed here are orthophosphate $PO_4^{3-}$, (including $H_2PO_4^-$ and $HPO_4^{--}$) expressed as $P\text{-}PO_4$, and total dissolved phosphorus, TDP, which includes the latter plus the polyphosphate originating from detergents, and dissolved organic phosphorus, DOP. Particulate organic phosphorus, POP, and particulate inorganic phosphorus, PIP, will also be considered.

The forms of organic carbon taken into account will be dissolved organic carbon, DOC, particulate organic carbon, POC, and total organic carbon or TOC which is the sum of the previous forms. They will be compared to dissolved inorganic carbon, DIC, sum of $HCO_3^-$ and $CO_3^{--}$ and to particulate inorganic carbon, PIC, which corresponds to debris of carbonate minerals.

### *1.2. Previous Budgets*

Livingstone published in 1963 the first world-scale review of river water quality. Concerning the nutrients, he considered only $NO_3^-$. The effect of man on river quality was minimized by use of early measurements of dissolved elements in European and some North America rivers. Turekian (1971) used this value (220 $\mu$g/l $N\text{-}NO_3$) in his review and referred to it as nitrogen, and for phosphorus he used an arithmetic mean of $P\text{-}PO_4$ on the Columbia river as possible world average. Livingstone's estimate has also been considered in other world budgets (Garrels, MacKenzie, and Hunt, 1973). Total dissolved phosphorus has been estimated to be 55 $\mu$g P/l by Stumm (1973) who attributed 20 $\mu$g/l to $P\text{-}PO_4$, based on solubility products of phosphorus-bearing minerals, and an equal amount for organic phosphorus. He estimated additional phosphorus due to man's activities to 15 $\mu$g/l. All these figures were author's estimates. Garrels, MacKenzie, and Hunt (1973) also adopted a value of 50 $\mu$g P/l without giving more details. Delwiche and Likens (1977) estimated river input to the ocean to 35 $10^{12}$ g N $yr^{-1}$, corresponding to about 950 $\mu$g N/l for total nitrogen, although it is not stated which forms are considered.

The most complete N and P budget so far realized is by van Bennekom and Salomons (1981) who present data on a dozen major rivers including some highly polluted ones. According to these authors, man's activities have increased five times the P load of rivers and three to four times the N load. Their natural river inputs to oceans are 5 $10^{12}$ g N $yr^{-1}$ and 0.5 $10^{12}$ g P $yr^{-1}$ while the present day inputs are estimated to be 24 and 2.3 $10^{12}$ g $yr^{-1}$, respectively, which corresponds to levels of 670 $\mu$g N/l and 70 $\mu$g P/l; particulate fluxes are estimated to be 8 $10^{12}$ g N $yr^{-1}$ and from 4.6 to 13.7 $10^{12}$ g P $yr^{-1}$.

The estimates of Garrels, MacKenzie and Hunt (1973) concerning the organic carbon are often quoted: 130 $10^{12}$ g C $yr^{-1}$ for DOC, corresponding to a content of 3.5 mg C/l, and 200 $10^{12}$ g C $yr^{-1}$ for TOC. Richey and others (1980) estimate the TOC transport to the ocean to be at least 1000 $10^{12}$ g C $yr^{-1}$ mainly on the basis of recent measurements of the Amazon. A recent estimate by Schlesinger and Melack (1981) is around 400 $10^{12}$ g C $yr^{-1}$ for TOC.

As can be seen, most of these estimates are based on a restricted number of rivers, which generally do not cover all types of environments. Effects of man's activities are generally not taken into account or are indirectly estimated. Very few details on computation methods and on basic data are given except by Livingstone (1963), van Bennekom and Salomons (1981), and Schlesinger and Melack (1981). Specific forms of N and P, particularly the organic and/or particulate ones, are generally not detailed.

### *1.3. Computation Methods used in Budgets*

Most studies present both an average river concentration and an estimate of river inputs to the ocean. The two figures are not exactly derived one from another because a fraction of river runoff flows into inland drainage basins (endoreic runoff) such as the Caspian Sea or Lake Chad. The corresponding drainage area is 33.2 $10^6$ $km^2$. The glaciated continental area is around 15.8 $10^6$ $km^2$. Therefore, out of 148.9 $10^6$ $km^2$ of continental area, only 99.9 $10^6$ $km^2$ are drained by rivers to the oceans (exoreic runoff) which corresponds to a water input of 37 400 $km^3$ $yr^{-1}$ (Baumgartner and Reichel, 1975). Other water balances have been proposed in recent years, but they are close to this one. The work of Baumgartner and Reichel (1975) will be preferred, as it also gives water inputs by latitudinal zones which can be used for estimating inputs by climatic zones (Meybeck, 1979). The nutrient transport by rivers to the oceans will be based on the figures of exoreic runoff (37 400 $km^3$ $yr^{-1}$ ans 99.9 $10^6$ $km^2$). Average river nutrients levels may also take into account some of the few rivers flowing into inland basins such as the Volga river.

Extrapolation of data is an unavoidable step in any budget since it is very difficult to get information on more than half the river water discharging to the ocean: this proportion already corresponds to the first 60 world rivers ranked according to their water discharge. A 10 percent increase of this proportion would imply the study of 200 additional rivers (Unesco, in press). Similar proportions are noted for the drainage areas. Two major forms of extrapolation can be performed through consideration of either dissolved contents and water discharges as used by Livingstone (1963) or of *specific transport rates* and drainage area as used by Alekin and Brazhnikova (1968) and by Meybeck (1979). The specific transport rates, noted as $N - NO_{3exp}$, $DOC_{exp}$ et cetera are obtained by multiplying the average content (in mg/l or $\mu$g/l) by the specific runoff q of rivers (in l $s^{-1}$ $km^{-2}$). They are usually expressed in metric tons $km^{-2}$ $yr^{-1}$ or in kg $km^{-2}$ $yr^{-1}$ by geomorphologists, in kg $ha^{-1}$ $yr^{-1}$ by agronomists, and in g $m^{-2}$ $yr^{-1}$ by ecologists.

Depending on the amount of available data various types of budgets (that is, of extrapolations) are:

A. *Simple extrapolation (sufficient and representative data).*—Collected data represent at least 25 percent of water discharged to the ocean (or 25 percent of drainage areas) from all types of environments considering different climatic characteristics, vegetation types, bedrock lithology, et cetera. The proportion of these types should be similar to that observed

for the remaining continental area. A good check can be realized by consideration of the specific discharge of the whole 25 percent sample which should be close to the world average: 11.8 l $s^{-1}$ $km^{-2}$ for the exoreic runoff. Weighted averages of concentrations and specific transport rates are computed from the collected data and extrapolated to the rest of the world through hypothesis of either the same average concentration (for the remaining discharges) or the same specific transport rate (for the remaining area).

B. *Use of typology (sufficient but non-representative data).*—The sample of collected data is not representative. This often occurs when all data originate from North America or from the Soviet Union and wet tropical environments are lacking. It happens to be the case also when the Amazon is considered because of its enormous influence (15 percent of the water discharged to the ocean, around 6 percent of the drainage area) which is usually not counterbalanced by a similar discharge from other rivers. If significant differences are noted from one type of river to another, for instance between the temperate and tropical zones, then the collected data are biased. The collected data are then used as a basis to define a typology of the concentrations (or transports) according to the various characteristics above-mentioned. The detailed account of the water discharges (or drainage area) of each type of environment must be known. The extrapolation is made inside each type. This kind of budget has been used for silica which was found to be directly linked to temperature (Meybeck, 1979).

C. *Use of support parameter (insufficient data).*—The collected data are too scanty and not representative. The relationship between the poorly studied element and a well known parameter of water quality is looked for and used to support the extrapolation. The support parameter can be environmental (watershed temperature, river runoff) or another characteristic of water quality (such as salinity, suspended solids, or calcium for which river budgets are better known).

D. *Use of small representative watersheds (insufficient data, no support parameter).*—The estimate of world average is entirely realized through a typology based on the study of smaller watersheds representative of a given environment. This implies that size effects between smaller and greater rivers are negligible, which may not be the case for nutrients because of internal production of organic matter particularly in greater rivers, as it has been observed in the Amazon (Richey and others, 1980).

E. *Direct estimate of additional inputs due to man's activities.*—Additional loads are calculated on well-studied large rivers by subtracting natural levels from present-day concentrations. It is then assumed that the additional loads are proportional to the number of people living on the watershed and to their state of development. This is defined as the energy consumption *per capita* divided by the basic per capita energy requirement, that is the *Demophoric Index* of Vallentyne (1978). This author also defines the demophoric population of a given country as the product of its actual population and its demophoric index, expressed in

demophoric units. For each given river the additional loads can be related to the demophoric population, and specific additional loads per demophoric unit can be calculated. The total additional load is eventually obtained by considering the total demophoric population of the world at a given time. This type of budget can only be realized if the size of the sample of man-influenced rivers is large enough to include all types of human activities directly or indirectly affecting water quality (agriculture, major cities, mines, industries, et cetera). It has already been used for $Cl^-$ and $SO_4^{--}$ (Meybeck, 1979).

### *1.4. Origin of Basic Data*

As can be seen from budget considerations, the extrapolation of data obtained on major rivers involves a good knowledge of the natural variation of nutrient contents. Therefore, many smaller representative streams have been considered in this review, particularly in the temperate regions where major rivers are somewhat polluted. All basic data are presented in table 1 and app. 1 and 2. The average contents given are generally annual means, although it is not always stated in the literature whether they have been discharge-weighted or not. Important exceptions must be pointed out for some tropical rivers (Amazon, Zaire, Orinoco, Niger) for which the average content is based on only a few samples per year or even on a single sample. However, these data have been measured by the various authors practically in the field and are more reliable. This is not always the case for data found in Water Quality Yearbooks: in these regular monitoring activities, laboratory facilities are sometimes far away from the sampling stations. For these reasons the data found in the scientific literature have generally been preferred to those reported through regular water quality surveys. Another major difference between research papers and Water Quality Yearbooks is the reporting of nutrient speciation: regular surveys do not generally analyze all forms of nitrogen or organic carbon. Most often only TOC and Kjeldhal nitrogen ($N_K$ = DON + N − $NH_4$) are reported. The most complete surveys are the Canadian (Environment Canada) and the Swiss ones (Service Hydrologique National). Very useful data, although not complete, are found in US Geological Survey reports (Briggs and Ficke, 1977), in French reports (Ministère de l'Environnement), and in some others. Water quality surveys of international water bodies (Rhine Commission; Commission du Léman) also provide very interesting case studies.

It is striking to note that the particulate nutrients (POC, PON, and POP) are almost never surveyed, although they constitute a major form of nutrient transport. Only a few studies are found in the scientific literature (Brunskill and others, 1975, Malcolm and Durum, 1976). As regards the dissolved forms of nutrients the most commonly analyzed are $NO_3^-$ and ortho $PO_4^{3-}$. These forms will be used as support parameters in the budget of the other speciations ($NO_2^-$, $NH_4^+$, DON; total dissolved phosphorus).

The greatest world river, the Amazon, has been split into its major components, Rio Negro and Rio Solimoes (the latter constitutes the

TABLE 1

Nutrients concentrations in some major unpolluted rivers ($\mu g\ l^{-1}$)

| | $P\text{-}PO_4$ | TDP | $N\text{-}NO_2$ | $N\text{-}NH_4$ | $N_K$ | DON | $N\text{-}NO_3$ | TDN | DOC | TOC | A | Q | Ref |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Arctic rivers** | | | | | | | | | | | | | |
| Kazan and Back (1969-1973) | 2 | | | | | | 16 | | | 4500 | 0.312 | 59 | (A) |
| **Subarctic rivers** | | | | | | | | | | | | | |
| Ob | | 30 | | | | | | | | 10900 | 2.5 | 385 | (B) (C) |
| Mackenzie (1972-1973) | 10 | 64 | | | 600 | | 150 | 750 | | 12000 | 1.8 | 306 | (A) |
| Nelson (1972-1976) | 4 | 19 | | | 600 | | 126 | (725) | 8000 | 9000 | 1.07 | 74 | (A) |
| Churchill (1972-1976) | 2 | 18 | | | 600 | | 70 | (670) | | 9000 | 0.28 | 49 | (A) |
| White Sea | 5.0 | 45 | | | (60) | (1100) | (60) | (1250) | | (13200) | 0.585 | 184 | (D) |
| Yukon | | | | | 596 | | 130 | (730) | 8400 | 9700 | 0.77 | 195 | (E) (F) |
| Iceland | 20 | | 0.7 | 25 | | | 23 | | | | 0.1 | 110 | (G) |
| **Temperate rivers** | | | | | | | | | | | | | |
| Gloma | 6.8 | 20 | | | | | 212 | 340 | | | 0.04 | 19 | (H) |
| Columbia | | 15 | | | | | 168 | | | 2900 | 0.67 | 249 | (I) |
| Fraser | | | | | | | 70 | 200 | | | 0.22 | 112 | (A) |
| Quebec | | | | | | | 200 | | | | 0.88 | 494 | (J) |
| Stikine | | | | | 160 | | 85 | (250) | | | 0.05 | 35 | (F) |
| Sweden | 10 | | | | | (175) | 60 | 250 | | (5000) | 0.25 | 117 | (K) |
| Finland | | 55 | | | | | | 700 | | (13800) | 0.23 | 67 | (L) |
| Volga | 11 | | | | | | | 400 | | | 1.35 | 260 | (M) |
| **Tropical rivers** | | | | | | | | | | | | | |
| Sumatra-Borneo | 7 | | | | | | 175 | | | | 0.15 | 213 | (N) |
| Niger | 13 | | 1.4 | 14 | | | 100 | | | | 1.21 | 191 | (O) |
| Zaire | 24 | 60 | 3 | 7 | | | 90 | | | 8800 | 3.82 | 1253 | (O) (P) |
| Orinoco | 6.2 | | | | | | 90 | | | | 1.0 | 1069 | (O) |
| Zambezi | 10 | | | | | | | | | | 1.34 | 224 | (Q) |
| Purari | 1.5 | | | 40 | | | 40 | | | | 0.03 | 75 | (R) |
| Mekong | | | | | | | 240 | | | | 0.8 | 472 | (S) |
| Solimoes | 15 | 25 | 1 | (40) | | 150 | 50 | (240) | 2000 | | (3.0) | (2400) | (T) |
| Negro | 6 | 8 | 1 | (25) | | 300 | 25 | (350) | 6300 | 8360 | 0.755 | 1400 | (T) |
| Amazon | 12 | (20) | 1 | (35) | | 200 | 40 | 275 | (5000) | (10000) | 6.3 | 5500 | (U) |
| **Desert rivers** | | | | | | | | | | | | | |
| Orange | 9.1 | | | | | | | 41 | | | 1.02 | 12 | (V) |

Amazon upstream of Manaus), because of the marked differences between the so-called black waters and white waters. For these rivers a combination of several works has been used in the average content estimate (Williams, P. J. L., 1968; Schmidt, 1972; Howard-Williams and others, 1977; Richey and others, 1980; Gibbs, 1972).

## 2. ORGANIC CARBON IN RIVERS

Only major findings on organic carbon levels and loads will be presented here; all detailed data and discussion are to be found in Meybeck (1981).

### *2.1. Dissolved Organic Carbon (DOC)*

The dissolved organic carbon in world natural river waters is commonly between 1 and 20 mg/l (table 1). The median value is 5 mg C/l. When looking at geographic variations (table 2) it seems that DOC levels are linked to climatic features: taiga rivers present a relatively higher DOC value (median 10 mg/l) than those in the wet tropics (median 6 mg/l) and in the temperate zone (median 3 mg/l) while lower contents can be found in tundra rivers (some mg/l). Maximum natural DOC values — around 25 mg $l^{-1}$ — are observed in rivers draining swamps or poorly drained soils. Minimum values less than 1 mg C/l are noted in some mountain rivers of the French Alps or in New Zealand.

The specific transport rate, here noted as DOC exp, varies between 0.2 and 14 t $km^{-2}$ $yr^{-1}$. Since DOC content is less variable for a given climatic zone than river specific discharge q, its transport rate is mostly influenced by q: lowest DOC exp values are reported for arid and semi-arid environments, highest ones are noted in rain forests (such as along the coast of British Columbia or in Amazonia).

### *2.2. Particulate Organic Carbon (POC)*

Particulate organic carbon can be expressed in river water either in terms of mass of particulate carbon per unit volume of water (POC in mg C/l) or as a percentage of the suspended material, here reported as $POC_s$ = POC/Cs where Cs is the amount of suspended matter in mg/l.

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TDP = Total dissolved phosphorus; DON = dissolved organic nitrogen; TDN = total dissolved nitrogen; DOC = dissolved organic carbon; TOC = total organic carbon; $N_K$ = Kjehldahl nitrogen.

All concentrations are expressed in $\mu g$ $l^{-1}$. Drainage area A is in $10^6 km^2$, water discharge Q is in $km^3$ $yr^{-1}$ (most data taken from Meybeck, 1979). ( ) author's estimates. More data on organic carbon in major rivers is found in Meybeck (1981).

(A) Environment Canada (1978), downstream stations; (B) Nesterova (1960); (C) Tarasov, Maltsera, and Smirnov (1977); (D) Maksimova (1978); (E) Briggs and Ficke (1977); (F) Nordin and Meade (1981) for DOC and TOC; (G) 6 rivers, from Armannsson and others (1973); (H) Holtan (1976); (I) Park, Osterberg, and Foster (1972), TOC from USGS quoted in Unesco (1980); (J) Ministère des Richesses naturelles, Québec; (K) Ahl and Oden (1972); (L) from J. Wartiowaara, personal commun. and Wartiovaara (1978); (M) Maksimova, Katunin, and Yeletskyi (1978); (N) avg of 5 rivers, from Kobayashi and others (1974); (O) van Bennekom and others (1978) and Venezulian internal report; (P) van Bennekom and Salomons (1981); (Q) Coche and Balon (1976); (R) Viner (1979) at Wabo damsite; (S) Carbonnel and Meybeck (1975); (T) These values are author's estimates from the following works: Williams (1968), Howard-Williams and Junk (1977), Schmidt (1972), and Sioli (1969); (U) based on Williams (1968), Gibbs (1972), Richey and others (1980); (V) M. J. Orren, oral commun. (1979).

As shown in figure 1, $POC_s$ is highly variable in rivers: from 0.5 to 40 percent. The minimum content is measured in highly turbid waters (Cs > 1000 mg/l) such as the Redstone in the Canadian Rocky Mountains (Wagemann, Brunskill, and Graham, 1977) or in the Brazos and Missouri rivers in the United States (Malcolm and Durum, 1976). The maximum values are noted in lowland rivers, where the suspended material is very low (Cs < 10 mg/l) such as the Sopchoppy river in Florida (Malcolm and Durum, 1976) or the Zaire river (Eisma, Kalf, and Gaast, 1978). In these cases almost all particulate material is organic, since it is generally accepted that organic carbon represents half the organic matter.

$POC_s$ is inversely related to the suspended matter content Cs (fig. 1). If river POC is mainly autochthonous this behavior means that phytoplankton, periphyton, et cetera are diluted by land-derived mineral material. This may happen in very large rivers. For the smaller ones the river organic matter is mainly allochthonous, and this debris is transported less at the higher erosion rates than mineral material.

Variation of POC content in rivers results from two opposite trends: the decrease of $POC_s$ with Cs increase and the better-known increase of Cs with water discharge Q. The latter process is always dominant and POC increases with Q. In the less turbid rivers (5 < Cs < 5000 mg/l) usually found in lowland regions, the POC contents are usually between 1 and 30 mg/l. This range is valid for about 99 percent of world rivers (see table 5). A similar range can be observed from the data of Malcolm and Durum (1976) on USA rivers where 80 percent of measured POC values are between 1 and 10 mg/l (median 2.5 mg/l). Maximum POC values can be as high as 100 mg/l for the very turbid waters. This has effectively been observed by Malcolm and Durum (1976) during a Missouri flood (POC = 190 mg C/l; Cs = 3068 mg/l; $POC_s$ = 6.25 percent).

TABLE 2

DOC levels in rivers, range of TOC export rates compared to terrestrial primary production, and TOC budget to the ocean

| Environment | Total* area $10^6$ km$^2$ | DOC mg l$^{-1}$** | Average TOC export rate g m$^{-2}$ yr$^{-1}$ | Total TOC load $10^{12}$g C yr$^{-1}$ | Mean net primary production*** g C m$^{-2}$ yr$^{-1}$ |
|---|---|---|---|---|---|
| Tundra | 7.55 | 2 | 0.6 | 4.5 | 65 |
| Taiga | 15.85 | 10 | 2.5 | 39.6 | 360 |
| Temperate | 22.0 | 3 | 4.0 | 88 | 225-585 |
| Tropical† | 37.3 | 6 | 6.5 | 241 | 315-900 |
| Semi-arid | 15.5 | 3 | 0.3 | 4.6 | 32 |
| Desert | 1.7 | | 0 | 0 | 1.5 |
| Total of the exoreic runoff | 99.9 | | 3.8 | 378 | 480 |
| Tropical rain forest only‡ | 15.9 | | 10 | 159 | 900 |

* Meybeck (1979), based on Baumgartner and Reichel (1976).

** Meybeck (1981).

*** Whittaker and Likens (1973), average production for exoreic continental area only.

† from savanna to tropical rain forest.

‡ specific runoff exceeding 20 l/s$^{-1}$/km$^{-2}$; TOC according to Amazonia rates.

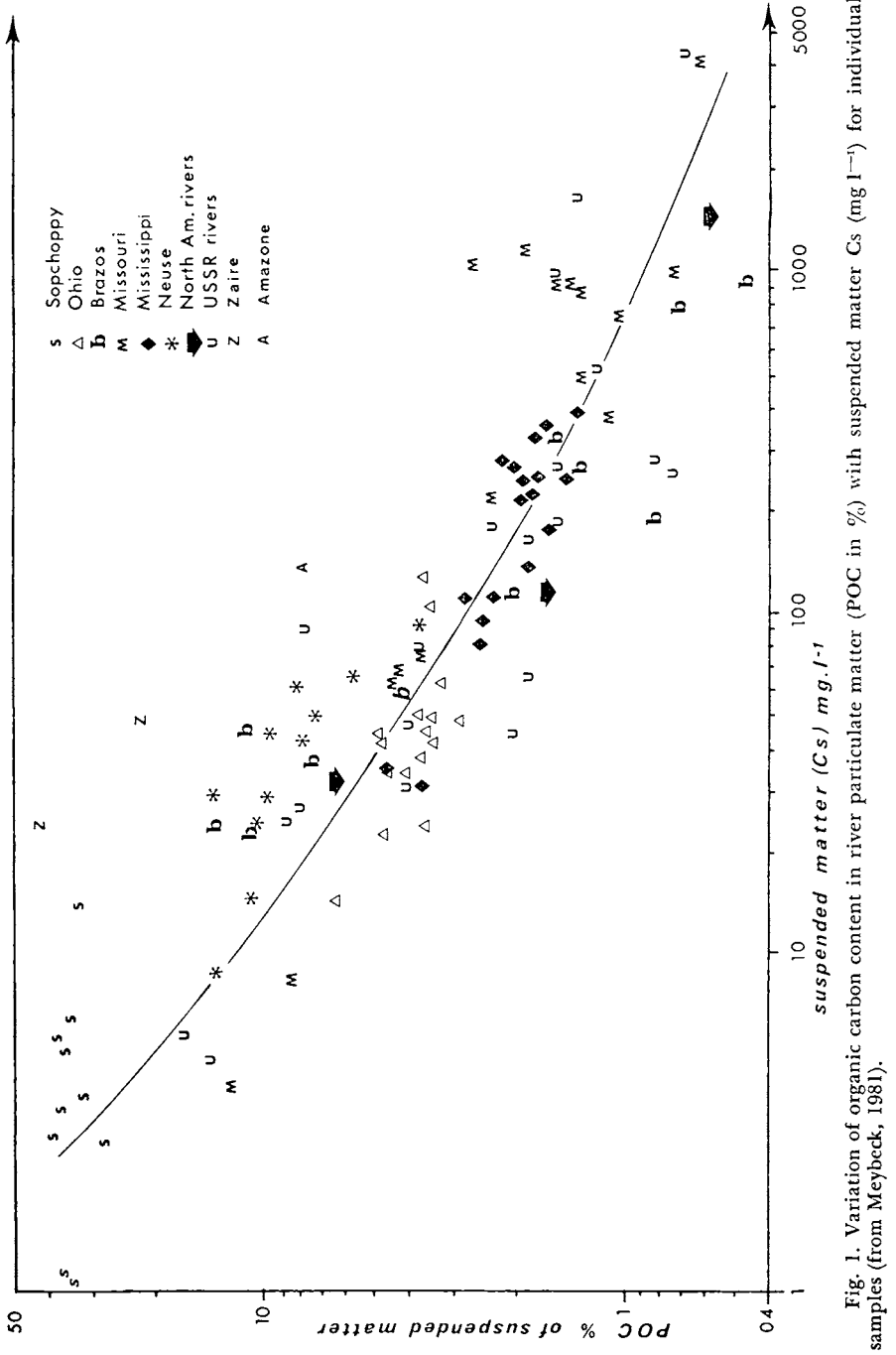



Fig. 1. Variation of organic carbon content in river particulate matter (POC in %) with suspended matter Cs (mg $l^{-1}$) for individual samples (from Meybeck, 1981).

According to available data the POC specific transport rate would vary between 0.2 and 5 t $km^{-2}$ $yr^{-1}$. Higher values are likely to be found for Southeast Asia rivers where both plant production and erosion rates are high.

### *2.3. Total Organic Carbon and Relative Importance of POC and DOC*

In many surveys DOC and POC are not analyzed separately but are combined in a single measurement of total organic carbon (TOC) on unfiltrated water as is done in Canadian and Swiss surveys (Environment Canada; Service Hydrologique National). There are therefore more data on TOC than on its components. For more than 100 rivers, mainly located in lowland areas, TOC was found to be generally between 2 and 30 mg/l with a median value of 10 mg/l. Higher TOC contents are likely to be found in rivers draining areas of higher relief where POC contents are higher.

Export rates of TOC are closely related to river runoff; as shown in table 2 maximum rates (10 t $km^{-2}$ $yr^{-1}$) are again found in the rain forests of the temperate (British Columbia) or tropical zones (Amazonia). Lowest rates (0.4 t $km^{-2}$ $yr^{-1}$) are noted for semi-arid region. There is also a climatic influence already remarked for DOC. When comparing these figures to the terrestrial net primary production of each type of environment, it is striking to note that the organic matter exported by rivers is always a very low fraction (around 1 percent) of the production (table 2). Schlesinger and Melack (1981) have also attempted to present estimates of TOC export rates in various environments. Their estimates are very similar to ours, and both average world values are identical (around 4 t $km^{-2}$ $yr^{-1}$). The only major discrepancy is noted for the

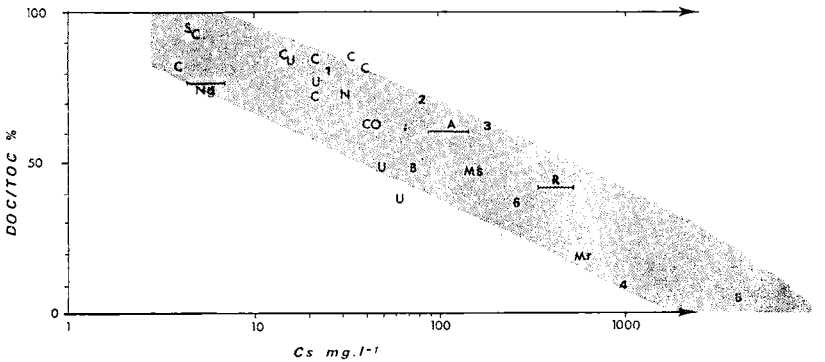



Fig. 2. Variation of average DOC/TOC ratio in some world rivers with suspended matter concentration $C_s$; S = Sopchoppy; O = Ohio; N = Neuse; Ms = Mississippi; Mr = Missouri; B = Brazos (data from Malcolm and Durum, 1976); Ng = Negro (data from Williams, 1968); A = Amazon (data from Williams, 1968; Richey, 1981; Richey and others, 1980); R = Rhone (data from Zobrist, Davies, and Hegi, 1977); U = USSR rivers (data from V. E. Artemeev [V. V. Gordeev, personal commun.]); C = Manitoba rivers (data from Environment Canada, 1978). 1. Dniepr, 2. Don, 3. Danube, 4. Kuban, 5. Rioni, 6. Chorokh (all from Shimkus and Trimonis, 1974). Shaded area: world range.

boreal forest: 5 t $km^{-2}$ $yr^{-1}$ for their value as compared to 2.5 t $km^{-2}$ $yr^{-1}$ here. However the details of calculations are different.

Relative proportions of dissolved and particulate organic carbon in rivers is a debated question: most authors have followed Wetzel's statement (1975) that there is approx 10 times more DOC than POC. This assumption is based mainly on lowland rivers, where erosion rates and POC levels are low. It is not verified when considering available data from various environments: average value of DOC/TOC varies between 0.1 and 0.9. This ratio is inversely related to the amount of suspended matter Cs. The trend is obviously derived from the variation of POC content with Cs and can be defined either for individual measurements for a given river or for yearly averages of DOC, TOC, and Cs computed on different rivers (fig. 2). Lower DOC/TOC ratio are measured in highland rivers; higher ratio are observed in lowland regions. For some rivers such as the Mississippi (Malcolm and Durum, 1976) DOC dominates POC at low stage while the contrary happens at high stage, but for others DOC may always be dominant as for the Sopchoppy. The most commonly measured DOC/TOC ratios in lowland rivers are between 0.6 and 0.8; for highland rivers this ratio is lower than 0.5.

## 3. NITROGEN IN RIVERS

### *3.1. Dissolved Nitrogen*

The study of dissolved nitrogen levels in rivers is more difficult than for dissolved organic carbon for three reasons: (1) there are four major forms of nitrogen species in waters ($NH_4^+$, $NO_2^-$, $NO_3^-$, and organic nitrogen or DON), (2) these forms are reactive in the framework of the nitrogen cycle, and (3) the natural levels may be badly affected by man's activities. We shall first concentrate on $NO_3^-$ which is the most frequently analyzed form.

Natural levels of *nitrate* in world major unpolluted rivers and some regional averages are reported in table 1. Although a careful screening of suspicious data has been done the levels vary widely from 16 $\mu$g N/l to 240 $\mu$g N/l. No doubt, part of this variation is due to the transformation to other nitrogen forms. The natural variability of total dissolved nitrogen (TDN) is probably much lower, but available data cannot confirm this assumption. In the temperate zone much higher levels are found in most major rivers probably as a result of pollution (app. 2). But low levels can also be found in smaller watersheds of this zone which are chosen for their pristine state (see app. 1).

It is very difficult to link nitrate levels with environmental parameters. In major rivers, highest levels (around 200 $\mu$g N/l) are found in some temperate rivers (Gloma in Norway, Quebec rivers, Columbia river), lowest (less than 25 $\mu$g N/l) are found in subarctic environments (Kazan and Back for the Canadian tundra, Iceland rivers) and in Amazonia (Rio Negro). Relatively higher levels (more than 200 $\mu$g/l) in the Magdalena (app. 2) and Mekong (table 1) rivers may reflect the influence of agriculture. As will be seen later, an average $N\text{-}NO_3$ natural value close to 100 $\mu$g/l is likely (table 6).

As regards the export rates of $N\text{-}NO_3$ they vary from less than 10 kg $km^{-2}$ $yr^{-1}$, in the subarctic environment where both $N\text{-}NO_3$ level and water runoff are low (Nelson, Kazan, and Back), up to more than 200 kg $km^{-2}$ $yr^{-1}$ in the wet tropics (Sumatra and Borneo rivers, Magdalena river in Columbia, Purari river in Papua New Guinea).

*Dissolved organic nitrogen* (DON) is very seldom analyzed despite its importance. Unfortunately DON is sometimes not differentiated from $NH_4^+$, for both forms are measured by the same method and reported as Kjeldahl nitrogen, $N_K$ (see for example the US network, Briggs and Ficke, 1977). However in natural waters the ammonia content is generally low, and the $N_K$ reported is mainly DON. Some estimates of the DON/TDN ratio can be proposed. For the humid tropics this ratio is 62 percent for the Rio Solimoes and 86 percent for the Rio Negro. For the subarctic region it is even higher: 90 percent for the White Sea watershed, according to Maksimova (1978). This value is confirmed by the Canadian rivers: Nelson (82 percent), Churchill (90 percent), and Mackenzie (80 percent) assuming that ammonia content here is negligible with respect to DON. Natural values of DON/TDN in the temperate zone cannot be based on major rivers for lack of data but can be estimated from the smaller watersheds and some less polluted rivers, such as the Swiss ones (see app. 1 and 2). For eight rivers (Lindaret, Brevon, Dranse in France; Mamai in New Zealand; and Ticino, Aare, Alpine Rhine, and Alpine Rhone in Switzerland) the DON/TDN ratio varies between 0.2 and 0.6 with a median value of 0.4. The importance of dissolved organic nitrogen seems to be linked to the average level of dissolved organic carbon (DOC = 3 mg/l in temperate zone, 6 mg/l in the humid tropics, and 10 mg/l in the taiga regions). In the tundra region the DON/TDN ratio should be lower since the DOC content is very low, a few mg/l. As a matter of fact the value found for the arctic Char Lake inlet is 0.25 (Schindler, Welch, and others, 1974). As concerns the polluted rivers of the temperate zone the DON/TDN ratio is not different from the unpolluted ones and lies between 0.2 and 0.7 for nine rivers with a median of 0.4 (most data in app. 2).

Some simultaneous measurements of DOC and DON have been realized in a few unpolluted rivers (see table 3). The DOC/DON ratio varies between 8 and 41, an average of DOC/DON = 20 can be chosen as a first estimate.

TABLE 3

Dissolved organic forms of nutrients ($\mu g\ l^{-1}$)

| | DOC | DON | DOP | DON/DOC% | DOP/DOC‰ | Ref. |
|---|---|---|---|---|---|---|
| Amazon | 3500 | 140 | 1.9 | 4 | 0.54 | (A) |
| Solimoes | 2030 | 130 | 3.7 | 6.4 | 1.8 | (A) |
| Negro | 5900 | 144 | 1.9 | 2.4 | 0.32 | (A) |
| Danube | 4800 | 600 | 35 | 12.5 | 7.2 | (B) |
| Como Creek (Colorado) | 2830 | 159 | 2.5 | 5.6 | 0.88 | (C) |

(A) Williams (1968); (B) Academia Romania (1967); (C) Lewis and Grant (1979b).

*Ammonium* measurements in major unpolluted rivers are uncommon (see table 1). These levels vary between 7 and 40 $\mu$g/l. If additional data obtained on smaller pristine watershed (app. 1) are included, this range extends from 7 to 60 $\mu$g/l, if one higher value found in some Alberta streams is discarded. In natural waters the ratio $N\text{-}NH_4/DIN$, where DIN is the total dissolved inorganic nitrogen ($N\text{-}NH_4 + N - NO_2^- + N - NO_3^-$) presents an extended range between a few percent up to 80 percent. These variations seem to be linked to the global level of mineral nitrogen: the $N - NH_4/DIN$ ratio is higher (between 25 and 80 percent) in rivers containing the lowest amounts of mineral nitrogen ($DIN < 50$ $\mu$g/l) (see fig. 3). In rivers presenting average DIN levels, this proportion generally drops below 25 percent, a median 15 percent value is likely. For higher DIN levels ($DIN > 300$ $\mu$g/l), which are encountered in rivers affected by man, this ratio is highly variable ranging from a few percent to 100 percent (fig. 3). This dispersion is due to the various sources of additional nitrogen (urban wastes are rich in ammonia, while agricultural runoff is high in nitrate) and to the influence of redox conditions found in heavily polluted rivers where deoxygenated waters are sometimes observed, as in the Sheldt river in Belgium (Van Bennekom and others, 1975).

*Nitrite* measurements are seldom obtained. From the few combined analyses of $NH_4^+$, $NO_2^-$, and $NO_3^-$ it clearly appears that nitrite is never abundant in rivers. When considering 45 rivers and streams, unpolluted and polluted (see app. 1 and 2, Commission du Léman, Service Hydrologique National of Switzerland, Department of the Environment of Great Britain), $NO_2^-$ is never more than 7 percent of the total dissolved inorganic nitrogen (DIN), and the median value is 1.5 percent.

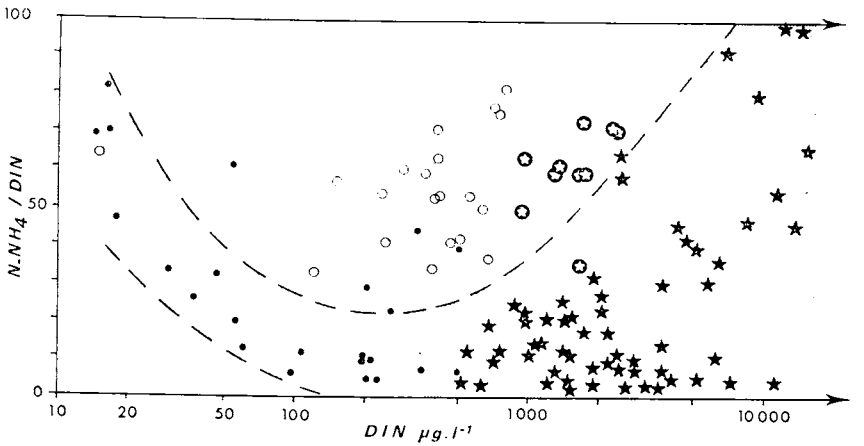



Fig. 3. Variation of the proportion of ammonium in dissolved inorganic nitrogen (DIN) in rivers and in atmospheric precipitation with DIN (note the logarithmic scale for DIN). Common range found in rivers. Dots, uncontaminated rivers (table 1 and app. 1); black stars, contaminated rivers (app. 2); open circle, uncontaminated atmospheric precipitation; white stars, contaminated precipitations (table 8).

Nitrite behavior is similar to that of ammonia, and the $N\text{-}NO_2^-/N\text{-}NH_4^+$ ratio is between 5 and 20 percent. Therefore the higher $N\text{-}NO_2^-/DIN$ ratios (> 3 percent are essentially noted for higher $N\text{-}NH_4^+/DIN$ ratios (> 30 percent).

### *3.2. Particulate Nitrogen*

The particulate nitrogen measurement involves three forms of nitrogen: particulate organic nitrogen (PON), adsorbed ammonia, and adsorbed organic nitrogen on the finest particles. It is believed that PON is by far the dominant form in river suspended material. Most of the available data shown in table 4 is given by Malcolm and Durum (1976) on United States rivers. With the exception of the Sopchoppy river in Florida, in which organic material constitutes the bulk of the suspended

TABLE 4

Organic nitrogen and phosphorus in river particulate matter (in percent)

| | POC | PON | POP | C/N | C/P | N/P | Ref. |
|---|---|---|---|---|---|---|---|
| Redstone (Canada) | 0.58 | 0.06 | | 9.7 | | | (A) |
| Mackenzie (Canada) | 1.58 | 0.20 | | 7.9 | | 2.15 | (A) (F) |
| Brazos (USA) | 4.67 | 0.65 | | 7.2 | | | (B) |
| Mississippi (USA) | 2.28 | 0.28 | | 8.1 | | | (B) |
| Missouri (USA) | 3.12 | 0.35 | | 8.9 | | | (B) |
| Neuse (USA) | 9.0 | 1.3 | | 6.9 | | | (B) |
| Ohio (USA) | 3.93 | 0.49 | | 8.0 | | | (B) |
| Sopchoppy (USA) | 35.3 | 4.04 | | 8.7 | | | (B) |
| Nile (Egypt) | 1.14 | 0.09 | | 12.7 | | | (C) |
| Purari (Papua New Guinea) | | 0.086 | 0.035 | | | 2.45 | (D) |
| Solimoes (Brazil) | | | | 8.5 | 24 | 2.8 | (E) |
| Negro (Brazil) | | | | 12 | 17 | 1.5 | (E) |
| Amazon (Brazil ) | | | | 13 | 51 | 4.0 | (E) |
| Iton (France) | 3.5 | 0.46 | | 7.6 | | | (G) |
| Eure (France) | 3.8 | 0.45 | | 8.5 | | | (G) |
| Char Lake inlet (Canada) | | | | | | 1.9 | (H) |

POC= particulate organic carbon; PON = particulate organic nitrogen; POP = particulate organic phosphorus.

Contents are in %; C/N, C/P, N/P are weight ratio.

(A) Wagemann, Brunskill, and Graham (1977); (B) Malcolm and Durum (1976); (C) FAO-UNESCO (1973, p. 181), deposited silt; (D) Viner (1979), deposited sediment; (E) Williams (1968); (F) N/P according to Brunskill and others (1975); (G) Iton and Eure are two small chalk streams in France (A. Dessevre and F. Lelong, personnal commun., 1980), deposited mud, (H) Schindler and others (1974).

matter, the PON content in percent of dry weight of solids is between 0.1 and 1.3 percent.

It is of special interest to look at the POC/PON ratio in river particulate matter. This ratio is remarkedly constant: half of POC/PON data presented in table 4 are between 8 and 10 (wt ratio). This relationship between N and C is rather independent of environmental factors and of POC levels in the river (fig. 4): the same figure is found for the Rio Solimoes (POC/PON = 8.6), the Mackenzie (POC/PON = 7.9), the Mississippi (POC/PON = 8.1). It is of particular importance to note that POC/PON is the same at higher contents of suspended material; the PON budget can therefore be based on this relationship. Also for a given river this ratio does not vary much as can be seen in the data of Malcolm and Durum; for instance, in the Ohio river POC/PON ratio is between 7.0 and 9.9 for 12 of the 14 measurements.

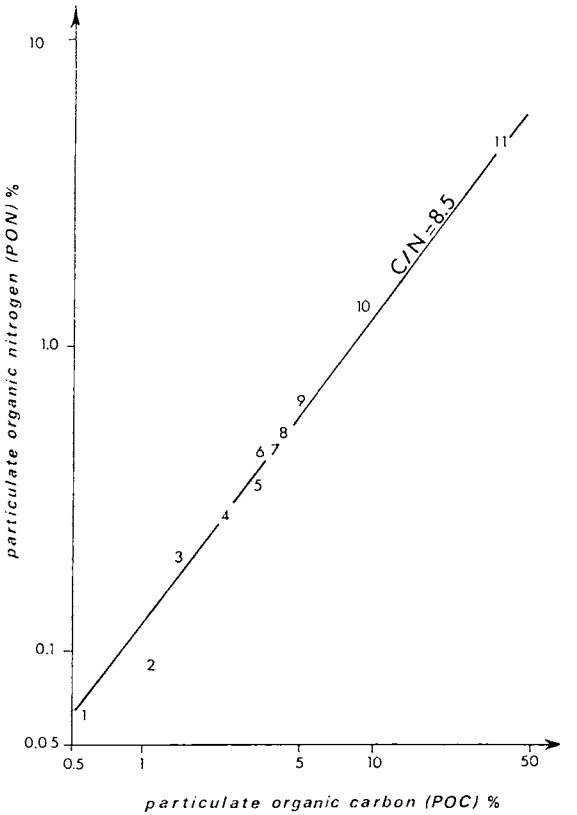



Fig. 4. Contents of particulate organic carbon (POC in %) and particulate organic nitrogen (PON in %) in rivers, yearly averages. (1) Redstone (Canada); (2) Nile (Egypt); (3) Mackenzie (Canada); (4) Mississippi (USA); (5) Missouri (USA); (6) Iton (France); (7) Eure (France); (8) Ohio (USA); (9) Brazos (USA); (10) Neuse (USA); (11) Sopchoppy (USA). Complete references in table 4.

## 4. PHOSPHORUS IN RIVERS

### *4.1. Dissolved Phosphorus*

Only two forms of phosphorus will be considered: orthophosphates, generally expressed as $P - PO_4$, and total dissolved phosphorus (TDP). Total phosphorus is sometimes measured on unfiltrated waters. In this case the total phosphorus reported refers to the total dissolved phosphorus plus an unknown part of particulate phosphorus — mostly the particulate organic phosphorus released to solution by the acid attack. This type of measure is reported routinely in the United States rivers survey (Briggs and Ficke, 1977). Orthophosphates are more commonly analyzed and will serve as a basis for the P budget.

*Orthophosphate* levels in natural waters are low, between 1 and 24 $\mu$g/l (see table 1 and app. 1). The most commonly encountered values are around 8 $\mu$g/l. In view of the sparse available data it has not been possible to link the $P\text{-}PO_4$ level to environmental parameters; average levels for subarctic (taiga), temperate, and wet tropical rivers are 9, 11, and 12 $\mu$g P/l and are not significantly different. The tundra rivers present the lowest values (few $\mu$g P/l). Similar trends have been noted for the other nutrients (N and organic C) in this very low productivity environment. The specific transport rate of $P - PO_4$ is generally between 0.5 and 10 kg P $km^{-2}$ $yr^{-1}$. Maximum specific transport occurs in wet tropical rivers (Zaire, Indonesia, Amazonia) and minimum in the subarctic rivers (0.35 kg P $km^{-2}$ $yr^{-1}$ for the Nelson, Kazan, and Back rivers in Central and Northern Canada). The Iceland value of 22 kg P $km^{-2}$ $yr^{-1}$, is an exception for natural rivers and results from both high phosphate level and high runoff ($q = 35$ l s $km^{-2}$). It is nearly two orders of magnitude higher than the export rate measured in northern Canadian rivers and probably reflects the influence of active volcanism and of volcanic rock weathering.

Orthophosphate is probably not the dominant form of dissolved phosphorus in natural waters. When considering available data for the unpolluted rivers (16 rivers and small representative watersheds, table 1 and app. 1), the ratio $P - PO_4/TDP$ is generally between 0.2 and 0.7 with a median value of 0.4. The same ratio is obtained for 10 contaminated river waters (see app. 2). However, as noted previously, these results must be considered with caution as many authors do not specify whether water is filtered or not prior to TDP analysis. In Amazonia, where waters have been filtered, Williams (1968) found that $P - PO_4$ was the dominant dissolved phosphorus species ($P - PO_4/TDP = 0.75$ for the Rio Negro and 0.77 for the Rio Solimoes).

As concerns the *dissolved organic phosphorus* (DOP), very few simultaneous measurements of the dissolved organic forms of nutrients, DOC, DOP, and DON have been made for river waters (table 3). The DOC/DOP ratio varies between 140 and 3000. As a very first estimate a typical composition of the dissolved organic matter would be $C_{1000}N_{50}P_1$ in weight.

### *4.2. Particulate Phosphorus*

Particulate organic phosphorus (POP) has been even less studied than PON. According to the few measurements (table 4) the PON/POP ratio is around 2.5. The composition of the organic particulate matter in rivers is, therefore, close to $C_{22}$ $N_{2.5}$ $P_1$ in weight.

Total particulate phosphorus (TPP) in rivers is much widely determined. From a previous review of TPP in major rivers (Martin and Meybeck, 1979) the world average is around 1150 $\mu$g per gram of solid. This value is much higher than that of Gordeev and Lisitzin (1978), for which no details are given, but is confirmed by Loubtchenko and Belova (1973) who found an average of 1100 $\mu$g/g for five major USSR rivers.

## 5. WORLD AVERAGES OF NATURAL NUTRIENT LEVELS AND RIVER NUTRIENT TRANSPORT

### *5.1. Dissolved Forms*

*Dissolved organic carbon* is known in only a very few major rivers (table 1). Therefore the world average must be computed by the typology method (method B) on the basis of the average DOC contents in various climatic zones and of the respective water contribution of these zones to the ocean (table 2). Runoff data of Baumgartner and Reichel (1975) rearranged by Meybeck (1979) are used here. Full details are given in Meybeck (1981). The average DOC is 5.75 mg/l, which corresponds to a global transport to the ocean of 215 $10^{12}$ g C $yr^{-1}$ and to a specific transport of 2150 kg C $km^{-2}$ $yr^{-1}$.

*Nitrate* is the most commonly measured form of nitrogen. Average nitrate content is also computed by the second method. The available data are not representative: the average specific discharge of the sample of unpolluted rivers listed in table 1 is 15.7 l $s^{-1}$ $km^{-2}$ (10800 $km^3$ $yr^{-1}$ for 22 $10^6$ $km^2$ out of a total of 37400 $km^3$ $yr^{-1}$ and 99.9 $10^6$ $km^2$). This is much higher than the world average (11.8 l $s^{-1}$ $km^{-2}$) for exoreic runoff. Tropical rivers, and particularly the Amazon, are over-represented, while temperate ones are under-represented because most rivers in this climatic zone have been discarded due to their obvious contamination. World runoff has been divided into five major climatic zones: tundra, taiga, temperate, tropical (wet and dry), and arid to which have been respectively attributed average $N - NO_3$ contents of 15, 125, 160, 75, and 20 $\mu$g N/l computed from data listed in table 1 and app. 1. The latter value is based only on the Orange River, and the true concentration may be higher. However change in this value would not affect the world average because of the relative amounts of water discharged to the ocean from these regions, respectively 1200, 4300, 10300, 21400, and 200 $km^3yr^{-1}$.

From this data the weighted average nitrate concentration is 100 $\mu$g N $l^{-1}$ corresponding to a worldwide river transport of 3.7 $10^{12}$ g $yr^{-1}$.

*Ammonia and nitrite* natural contents are based on the $N - NH_4$/DIN and $N - NO_2$/DIN ratios which were previously estimated to be of the order of 0.15 and 0.015 at DIN contents commonly found in natural waters (between 50 and 250 $\mu$g/l) (see fig. 3, table 1, and app. 1). The re-

sulting $N\text{-}NH_4$ and $N\text{-}NO_2$ concentrations are of the order 15 $\mu$g/l and 1.5 $\mu$g/l corresponding to river transports of 0.5 $10^{12}$ g $N\text{-}NH_4$ $yr^{-1}$ and 0.05 $10^{12}$g $N\text{-}NO_2$ $yr^{-1}$.

*Dissolved organic nitrogen*, DON, can be estimated by method C using DOC as a support parameter. Assuming that DOC/DON is equal to 20 (see table 3), the average DON content is around 300 $\mu$g N/l, and the river input is 11 $10^{12}$ g N $yr^{-1}$.

The average DON content can also be estimated by consideration of the relative proportion of the inorganic (total inorganic nitrogen DIN = $N - NO_3 + N - NH_4 + N - NO_2$) and organic forms of nitrogen. DIN can be estimated to 180 $\mu$g/l in the temperate zone; 90 $\mu$g/l in the tropical zone; 140 $\mu$g/l in the taiga; and 30 $\mu$g/l in the tundra (computed from table 1). The ratios DON/DIN are equal to 0.65 for the temperate zone, 2.3 for the tropical zone; 5.5 for the taiga; and 0.4 for the tundra (avg computed from data listed in table 1; for the tundra the estimate is based on Char lake inlet only, see app. 1). The corresponding DON values would be 120 $\mu$g/l, 210 $\mu$g/l, 800 $\mu$g/l, and 15 $\mu$g/l. The weighted world average DON obtained by this method is 260 $\mu$g N/l which is close to the previous method giving 300 $\mu$g/l N/l. The world average total dissolved nitrogen (TDN) is 375 $\mu$g/l corresponding to an export rate 140 kg $km^{-2}$ $yr^{-1}$, of which 100 kg $km^{-2}$ $yr^{-1}$ is organic, and 40 kg $km^{-2}$ $yr^{-1}$ is inorganic, mostly nitrate.

The *dissolved phosphorus* budget is based mainly on orthophosphate which is by far the most commonly analyzed form of phosphorus. As it has not been possible to see any trend between $P\text{-}PO_4$ and environmental factors, a simple discharge-weighted average is computed and extrapolated to the remaining rivers (method 1). The total sample of studied rivers corresponds to 22.3 $10^6$ $km^2$ and 10,200 $km^3$ $yr^{-1}$ ranging from the Kazan and Back rivers to the Orange (see table 1); its average runoff is 14.5 l $s^{-1}$ $km^{-2}$, which is somewhat higher than world average (11.8 l $s^{-1}$ $km^{-2}$). Because a satisfactory proportion of environmental types is realized, this sample is considered as representative. The average $P\text{-}PO_4$ content is 12.5 $\mu$g/l, and the global transport to the ocean is 0.45 $10^{12}$ g P $yr^{-1}$ corresponding to an average export rate of 4.5 kg P $km^{-2}$ $yr^{-1}$. It must be noted that the endoreic Caspian Sea basin is included in the determination of the world average content.

The average Total Dissolved Phosphorus (TDP) in rivers is based on the ratio $P\text{-}PO_4$/TDP, previously estimated to be 0.4. TDP is 25 $\mu$g P/l corresponding to a global transport of around 1.0 $10^{12}$ g $yr^{-1}$. The resulting dissolved organic phosphorus is 15 $\mu$g/l. As said before, these figures must be considered with caution since TDP can be overestimated if waters are not filtered. However the high level of DOP is confirmed when considering the DOC/DOP ratio which ranges from 140 to 300 (table 4); at such ratios the corresponding DOP content is of the order of 10 $\mu$g/l.

### *5.2. Particulate Forms*

The budget of particulate organic carbon (POC) is the basis of the other POP and PON budgets. Since the POC content in rivers (mg $l^{-1}$)

is directly dependent on Cs, the POC budget must take into account variations in Cs.

For this purpose a preliminary sediment budget (table 5) has been first calculated in order to distribute the amount of particulate material carried to the oceans into 9 classes of suspended matter Cs, from 5 to more than 50,000 mg $l^{-1}$. This grouping has been set up on a sample of 46 major rivers (Meybeck, 1976) corresponding to 44 percent of the world water discharged to the oceans and 55 percent of the drainage area. This sample has been considered as representative of the $10^8$ $km^2$ drained to the ocean. In table 5 the 46 rivers have been arranged into sets according to their average $C_s$. The Amazon (avg $C_s$ = 160 mg $l^{-1}$; Meade and others, 1979), since it is represented by two very different rivers, has been divided one third into the 50 to 150 class and two thirds into the 150 to 500 mg $l^{-1}$ class. To give an example of the calculation, the rivers in the 50 to 150 mg $l^{-1}$ class correspond to 32 percent of the water discharge of the sample and to 5.5 percent of sediment discharge. These proportions have been extrapolated to the total drainage area. Therefore a total water discharge of 37 400 $km^3$ × 0.32 = 11 970 $km^3$ has been attributed to this class for an average $C_s$ of 80 mg $l^{-1}$, corresponding to a sediment discharge of 960 $10^{12}$ g $yr^{-1}$. This computation has been performed for each of the 8 $C_s$ classes to which the Huang Ho (Yellow River), a unique case, has been added.

The total load to the ocean estimated by this method is 17 500 $10^{12}$ g $yr^{-1}$ which is fairly close to another estimate based on sediment transport typology (Meybeck in preparation) and to other values found in the recent literature (Alekin, 1978).

An average $POC_s$ content is assigned to each class according to the $POC_s$-$C_s$ relationship (fig. 1). For example, for the class of rivers in the 50 to 150 mg $l^{-1}$ turbidity range, the average $POC_s$ is 3 percent, resulting in a POC discharge of 28.8 $10^{12}$ g C $yr^{-1}$.

Several observations from table 5 can be made:

The weighted average suspended load in rivers is probably between 400 and 500 mg $l^{-1}$ (470 mg $l^{-1}$ here), but 75 percent of river waters carry less than 500 mg $l^{-1}$, and 50 percent less than 150 mg $l^{-1}$. This confirms previous remarks (Meybeck, 1976) on the relative importance of dissolved and particulate mineral transport, the dissolved transport being dominant in about 35 percent of the world rivers.

More than 40 percent of the world particulate load is carried by highly turbid waters ($C_s$ > 1500 mg $l^{-1}$), which represent only 2.3 percent of the water discharge. These rivers are found mainly in the arid and semi-arid zone (Indus, Orange, Rio Grande, Colorado, Huang Ho). The mountain rivers (Irrawady, Mekong, Yangtze, Ganges, Brahmaputra, Magdalena, Rhone, Mackenzie) carry 40 percent of the suspended load, in the $C_s$ range 500 to 1500 mg $l^{-1}$. The rest of the suspended load (about 20 percent is transported by lowland rivers with headwaters flowing from mountainous areas (Amazon, Amur, Indigirka, Parana, Danube, Zambezi). These rivers have $C_s$ contents between 50 and 500 mg $l^{-1}$ and correspond to 52 percent of the water discharged to the oceans.

TABLE 5

Loads of suspended material and of particulate organic carbon from rivers to ocean (Meybeck, 1981)

| Cs Range (mg $l^{-1}$) in world rivers | 5-15 | 15-50 | 50-150 | 150-500 | 500-1500 | 1500-5000 | 5000-15000 | 15000-50000 | Huang Ho* | Total |
|---|---|---|---|---|---|---|---|---|---|---|
| Water discharge % of total | 3.8 | 18.2 | 32 | 20.2 | 23.4 | 1.8 | 0.07 | 0.15 | 0.3 | 100% |
| Water discharge $km^3\ yr^{-1}$ | 1420 | 6800 | 11970 | 7550 | 8750 | 670 | 26 | 56 | 48 | 37400 |
| Average Cs mg $l^{-1}$ | 8 | 30 | 80 | 300 | 800 | 3000 | 8000 | 30000 | 65000 | — |
| Particulate load $10^{12}$ g $yr^{-1}$ | 11 | 204 | 960 | 2260 | 7000 | 2010 | 208 | 1680 | 3180 | 17500 |
| Particulate load % of total | 0.07 | 1.2 | 5.5 | 12.9 | 40.0 | 11.4 | 1.2 | 9.6 | 18.2 | 100% |
| $POC_s$ content in % of particulate load** | 15 | 6 | 3 | 1.6 | 0.9 | 0.6 | 0.5 | 0.5 | 0.5 | — |
| POC load $10^{12}$ g $yr^{-1}$ | 1.65 | 12.2 | 28.8 | 36.2 | 63 | 12 | 1.0 | 8.4 | 15.9 | 179 |
| POC load in % of total | 0.9 | 6.8 | 16.1 | 20.2 | 35.2 | 6.7 | 0.5 | 4.7 | 8.9 | 100% |

* Considered separately, avg Cs > 50000 mg/$l^{-1}$; ** from figure 1.

The total POC input from rivers to the oceans is around 180 $10^{12}$ g $yr^{-1}$. It originates mainly from highland rivers (35 percent) and mixed rivers (lowland-mountainous watershed, 36 percent). The rivers from the arid to semi-arid zone (Huang Ho included) only account for 21 percent of the POC load.

The weighted average $POC_s$ content in suspended matter is about 1.0 percent. However, due to the distribution of loads, 70 percent of rivers carry a suspended load with much higher values, between 1.6 and 6 percent. Similarly, the weighted POC concentration in waters is about 4.8 mg $l^{-1}$ with 70 percent of rivers having lower contents ranging between 4.8 and 1.8 mg $l^{-1}$.

This budget should be refined by establishing $POC_s$-$C_s$ relationships for given environmental conditions. For example, if the higher $POC_s$ values observed in the Amazon and Zaire rivers are confirmed, the total POC input to the sea could be somewhat higher than the above estimate.

The *particulate inorganic carbon* (PIC) in river suspended matter is seldom measured. It occurs mainly as residual carbonate material still not completely dissolved by chemical weathering. The average 0.9 percent value previously estimated (Meybeck, 1981) is confirmed by the PIC content in Nile River silt, which is 1 percent according to FAO-UNESCO (1973). The total PIC transport to the ocean is estimated to be 170 $10^{12}$ g C $yr^{-1}$, and this originates entirely from continental erosion.

The *particulate organic phosphorus and nitrogen* (POP and PON) are estimated assuming average POC/POP = 22 (wt ratio) and average POC/PON = 8.5 (table 4). The corresponding transports are 21 $10^{12}$ g N $yr^{-1}$ and 8 $10^{12}$ P $yr^{-1}$, and average contents in river suspended matter are $PON_s$ = 1200 $\mu$g/g and $POP_s$ = 450 $\mu$g/g. It must be remembered that these figures are weighted averages and are greatly influenced by the highly turbid waters which are poor in particulate organic material. Median values found in 50 percent of world rivers are likely to be twice as much as the weighted values.

*Total particulate phosphorus* has been estimated as 1150 $\mu$g/g (Martin and Meybeck, 1979). If the organic phosphorus is subtracted from this figure the remaining particulate inorganic phosphorus is around 700 $\mu$g/g.

The budget of *total organic carbon*, TOC, can be realized on much more data than those for DOC and POC. When considering all available data (Meybeck, 1981) the sample of rivers corresponds to 27 $10^6$ $km^2$ out of 99.9 $10^6$ $km^2$ but is clearly biased toward the colder regions due to the abundance of data on Siberian rivers (Tarasov, Maltseva, and Smirnov, 1977). Extrapolation to the remaining area (73 $10^6$ $km^2$) has been done on the basis of the average TOC export rates defined for six major climatic environments (table 2) according to method B. The total TOC transport by rivers is 380 $10^{12}$ g C $yr^{-1}$. This figure is in good agreement with the sum of the separate DOC (215 $10^{12}$ C $yr^{-1}$) and POC (180 $10^{12}$ C $yr^{-1}$) budgets. A similar TOC budget (410 $10^{12}$ g C $yr^{-1}$) is proposed by Schlesinger and Melack (1981). Their first method based on autocorrelations between TOC load, river discharge, and drainage area is question-

able. Their second one is very similar to the method used here (regional averages).

### *5.3. Summary*

World average concentrations and river loads of the various C, N, and P forms are given in table 6.

## 6. INFLUENCE OF MAN'S ACTIVITIES ON RIVER NUTRIENT TRANSPORT

The global result of man's activities at the Earth's surface is a marked increase of nutrient levels in rivers, particularly of nitrogen and phosphorus (Vollenweider, 1968; Stumm ,1973; van Bennekom and Salomons, 1981). According to Vollenweider, sources of P in surface waters are detergents, water softener, industrial wastes, urban wastes, and fertilizers; sources of N are mainly derived from agriculture (fertilizers and cattle) and from urban and industrial wastes. It is not the purpose of this paper to state the major origin of the nutrients but to estimate their overall increase and the resulting additional transport by rivers.

The influence of man on river chemistry has been studied by different approaches: (1) comparison of neighboring watersheds, where one is in a natural state and the other is influenced by man. (This kind of study is now widely developed as illustrated by work on the Hubbard Brook Experimental Forest, Likens and others, 1977, where logging and clear-cutting have produced a marked nutrient increase in surface waters) (2) evolution with time of nutrient level in representative rivers since the beginning of intensive agriculture and the industrial era, (3) direct measurements of various pollutant sources such as urban wastes, discharges, and agricultural runoff. This method has been considered by most authors such as Vollenweider (1968). The second method will be used here as it can better represent the real evolution of rivers exposed to various sources of pollution.

### *6.1. Evolution of Organic Carbon*

It is very difficult to state if the organic carbon levels in rivers have been increased by man's activities because of a lack of sufficiently long records for rivers. However they are indices of man's influence on organic carbon levels. The TOC content in treated waste waters (20 to 50 mg C $l^{-1}$, see Alberti, Adelt, and Nagel, 1977) is much higher than in natural rivers. As a result the TOC content in some major temperate rivers is much higher than the median value for such rivers (estimated to be 5 mg/l); for example 15 to 20 mg C/l are found in the Rhine, 15 mg/l in the Ems, 22 mg/l in the Danube (Rhine Commission; Tittizer, 1978). In United States rivers the TOC content remains surprisingly lower (Briggs and Ficke, 1977), and this may be an effect of self purification. In Switzerland, where present DOC levels are very low (DOC = 2.5 mg C/l), half of it is the result of man's activities according to Zobrist, Davies, and Hegi (1977). However, the study of the effect of a city sewage treatment plant on the quality of the river Vire in Normandy (Dulac and Laurenceau, personal commun.) has not revealed a significant increase of either DOC or POC downstream of the city of Vire, whereas important N and P in-

TABLE 6

Nutrient transport of rivers to the ocean (M in $10^{12}$g/yr) and average level in river waters (C in $\mu$g/l) and in river suspended particulate matter ([ ]pm in $10^{-6}$g/g). (ND = not determined)

| | Natural transport | | | | | | | Additional (pollutive) transport (1970) | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | Dissolved | | | | | Particulate | | | Dissolved | | | Particulate |
| | Organic | Inorganic | | | Total | Organic | Inorganic | Total | Organic | Inorganic | Total | |
| Carbon | | Atmospheric and soil origin | | Carbonate weathering origin | | | | | | | | |
| M | 215(B) | 217(C) | | 164(C) | 596(E) | 180(B) | 170(B) | 350 | ND | 19(C) | ND | ND |
| C | 5750 | 5800 | | 4400 | 15900 | 4800(H) | 4200 | 9000 | | 215 | | |
| [ ]pm | | | | | | 10000(H) | 10000 | 20000 | | | | |
| Nitrogen | | $N\text{-}NH_4$ | $N\text{-}NO_2$ | $N\text{-}NO_3$ | | | | | | | | |
| M | 10.0 | 0.5(D) | 0.05(D) | 4.0 | 14.5(E) | 21(F) | ? | ND | ND | | 7.0 | ND |
| C | 260 | 15 | 1 | 100 | 375 | 560(H) | | | | | 190 | |
| [ ]pm | | | | | | 1200(H) | | | | | | |
| Phosphorus | | $P\text{-}PO_4$ | | | | | | | | | | |
| M | ND | 0.4 | | | 1.0(G) | 8(F) | ND | 20 | ND | 0.4 | 1.0(G) | ND |
| C | | 10 | | | 25 | 210(H) | | 530 | | 10 | 25 | |
| [ ]pm | | | | | | 450(H) | | 1150(A) | | | | |

M = annual river transport in $10^{12}$ g $yr^{-1}$ (exoreic runoff only); C = avg river contents in river waters ($\mu$g $l^{-1}$) [ ]pm = avg particulate nutrient contents in river particulate material ($10^{-6}$ g $g^{-1}$), based on river water discharge to the ocean of 37400 $km^3/yr^{-1}$ and on river suspended material discharge to the ocean of 17500 $10^{12}$ g $yr^{-1}$ (see table 5).

(A) Martin and Meybeck (1979); (B) Meybeck (1981); (C) Meybeck (1979); (D) based on avg $N\text{-}NO_3$ assuming $N\text{-}NH_4$ = 0.1 DIN and $N\text{-}NO_2$ = 0.01 DIN; (E) sum of dissolved forms; (F) based on POC budget assuming that POC/PON = 8.5 and POC/POP = 22; (G) based on $P\text{-}PO_4$ budget assuming $TDP/P\text{-}PO_4$ = 2.5; (H) these contents are weighted world avgs much influenced by few very turbid rivers; median world contents are probably twice higher.

creases were noted. As a whole, some increase of organic carbon levels in rivers is likely, but it does not seem to affect significantly the world budget presented here, of which the accuracy is probably no better than 30 percent.

### *6.2. Nitrogen*

Examples of the increase in nitrogen levels of rivers are now numerous. In the Rhine a five-fold variation was observed between 1932 and 1969 (Van Bennekom, Gieskes, and Tijssen, 1975). It is probably due to several sources (agriculture, industries, cities). Evidence of the influence of agricultural practices on $N\text{-}NO_3$ content is now found in developing countries. According to Kobayashi and others (1974) the average $N\text{-}NO_3$ content in Java rivers is 370 $\mu$g N/l, while it is only 175 $\mu$g N/l in Sumatra and Borneo rivers which are still covered mostly with their original forest. Similar evolution is likely in other southeast Asian countries where the rice culture is intensive; for instance San (ms) found 500 $\mu$g $N\text{-}NO_3$ $l^{-1}$ in some Cambodian rivers around the Great Lake. Evidence of nitrate increase in some rivers draining densely populated areas in developing countries is now common (see Chao Phraya downstream of Bangkok, app. 2). Nitrate contents in the Chinese rivers, Changjiang (= Yangtze), Huang He (= Yellow river), and Zhujiang (Pearl river) (app. 2), reflect the influence of the very dense population and, perhaps, the effect of intensive rice culture. In Western Europe the $N\text{-}NO_3$ levels are now commonly 10 to 30 times higher, in major polluted streams and rivers, than the natural levels found in the temperate zone (see app. 1 and 2, and the British and French water quality yearbooks).

The ammonium proportion in polluted river waters may surpass 25 percent of the dissolved inorganic nitrogen (fig. 3). It reaches more than 80 percent in poorly oxygenated waters found for instance in the Sheldt river in Belgium (van Bennekom, Gieskes, and Tijssen, 1975) or in the Furan river downstream of the city of Saint-Etienne in France (Ministère de l'Environnement). Therefore the additional pollutive nitrogen load in rivers must be looked for not only in the nitrate fraction but also in the total dissolved nitrogen, including both inorganic and organic forms. When the latter form was missing in reported data it has been estimated to be at least equal to half the nitrate. This probably leads to an underestimate of total nitrogen.

Estimates of present day nitrogen levels are for the year 1970 and have been computed for 10 regions (see basic data in app. 2): Po for Northern Italy according to Fossato (1971 and 1973); Oder and Vistula for Poland (Andrulewicz, 1976); Rhône, Loire, Seine, and Garonne for France (Ministère de l'Environnement); Mississippi, Columbia, Susquehanna, Brazos, and 7 other rivers (Colorado excluded) for conterminous USA (Briggs and Ficke, 1977); Danube for the central European states (Acad. Romania, 1967); Rhine, Aare, Reuss and Rhône for Switzerland (Zobrist, Davies, and Hegi, 1977); Sweden (according to Ahl and Oden, 1972); 18 rivers for Java (Kobayashi and others, 1974); 16 rivers for Great Britain (Department of the Environment, 1978); and Rhine

and Meuse for Belgium and Western Germany (van Bennekom, Gieskes, and Tijssen, 1975). The natural levels were taken either directly from the authors, as for Sweden, obtained through comparison with unpolluted rivers, as for Java compared to Sumatra and Borneo, or supposed to be equal to the average total dissolved nitrogen levels found in the temperate zone (300 $\mu$g/l).

Additional pollutive inputs (additional contents multiplied by water discharge) are here computed and normalized to the estimated population of the watershed in 1970 (table 7). These *per capita* loadings are highly

TABLE 7

Additional nutrients loads carried by contaminated rivers in some regions (total dissolved nitrogen and orthophosphates)

| | | Additional content $\mu$g $l^{-1}$ | River discharge $km^3$ $yr^{-1}$ | Additional load $10^9$g $yr^{-1}$ | Population $10^6$ | Per capita loading kg $yr^{-1}$ | D.I. | Ref. |
|---|---|---|---|---|---|---|---|---|
| North Sea | TDN | 5600 | 90 | 500 | 48 | 10 | 60 | (A) |
| | $P\text{-}PO_4$ | 220 | 104 | 23 | 62 | 0.37 | 60 | (B) |
| Poland | TDN | 1000 | 50.5 | 50 | 32 | 1.5 | 37 | (C) |
| | $P\text{-}PO_4$ | 100 | 50.5 | 5.0 | 32 | 0.16 | 37 | (C) |
| Northern Italy | TDN | 1300 | 46.4 | 61 | 17 | 3.6 | 25 | (D) |
| | $P\text{-}PO_4$ | 37 | 46.4 | 1.7 | 17 | 0.10 | 25 | (D) |
| France | TDN | 1640 | 101 | 164 | 30 | 5.5 | 36 | (E) |
| | $P\text{-}PO_4$ | 127 | 101 | 13 | 30 | 0.44 | 36 | (E) |
| Switzerland | TDN | 1500 | 50 | 75 | 6 | 12.6 | 30 | (F) |
| | $P\text{-}PO_4$ | 45 | 50 | 2.3 | 6 | 0.37 | 30 | (F) |
| Sweden | TDN | — | — | — | 4 | 2.85 | 50 | (G) |
| | $P\text{-}PO_4$ | — | — | — | 4 | 0.15 | 50 | (G) |
| USA | TDN | 1190 | 825 | 980 | 125 | 7.8 | 97 | (H) |
| | $P\text{-}PO_4$ | 78 | 825 | 64 | 125 | 0.50 | 97 | (H) |
| Great Britain | TDN | 8000 | 7.4 | 59 | 15 | 4.0 | 47 | (I) |
| | $P\text{-}PO_4$ | 1400 | 7.4 | 10 | 15 | 0.67 | 47 | (I) |
| Java | TDN | 400 | 97 | 39 | 100 | 0.4 | 1 to 2 | (J) |
| | $P\text{-}PO_4$ | 16 | 97 | 1.5 | 100 | 0.015 | 1 to 2 | (J) |
| Central Europe | TDN | 1000 | 200 | 200 | 65 | 3.1 | 30 | (K) |
| Total | TDN | — | 1470 | 2076 | 442 | — | — | — |
| | $P\text{-}PO_4$ | — | 1280 | 120 | 391 | — | — | — |

DI = demophoric index (Vallentyne, 1978).

References of measured nutrient's contents: (A) Rhine and Meuse, van Bennekom, Gieskes, and Tijssen (1975); (B) Rhine, Meuse, Sheld, van Bennekom, Gieskes, and Tijssen (1975), plus Ems and Weser (see annex 2); (C) Andrulewicz (1976); (D) Fossato (1971 and 1973); (E) Ministère de l'Environnement; (F) Service Hydrographique National; (G) per capita loadings from Ahl and Oden (1972), assuming that half the Sweden population is connected with rivers; (H) Average of 1973/74 and 1974/75 from Unesco (1980) and Briggs and Ficke (1977), assuming $P\text{-}PO_4$ = 0.4 TDP; (I) Department of the environment; (J) Kobayashi and others (1974); (K) Acad. Romania (1967).

When TDN is not directly given it is assumed that DON was at least equal to 0.5 $N\text{-}NO_3$. Except for Java additional nutrients contents have been obtained from measured contents by subtracting natural values supposed to be 10 $\mu$g/l for $P\text{-}PO_4$ and 300 $\mu$g/l for TDN in temperate regions. The US rivers are: Mississippi, Apalachicola, Brazos, Columbia, Delaware, Hudson, Alabama, Potomac, Sacramento, San Joaquim, Savannah, Susquehanna.

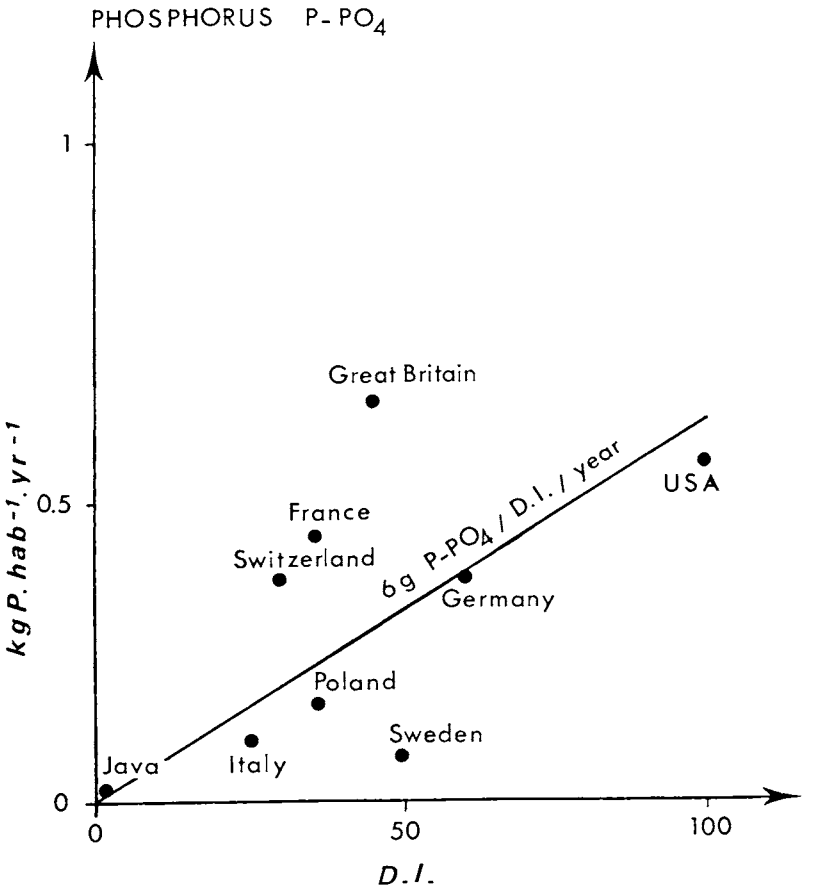
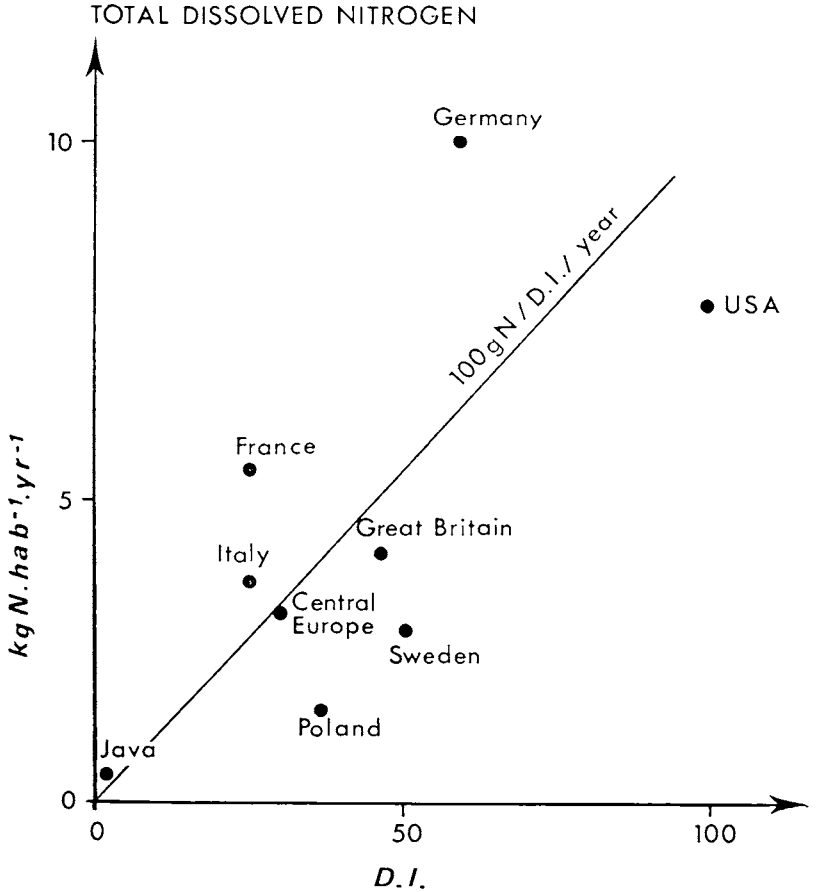



Fig. 5. Nitrogen and phosphorus additional loadings *per capita* in rivers of various

variable: from 0.4 kg N $yr^{-1}$ in Java up to more than 10 kg N $yr^{-1}$ in Swiss streams and somewhat reflect the state of development of each country and water uses in each watershed. It is of importance to note that many of these *per capita* loadings are below the quantity of nitrogen excreted by man (4.4 kg N per yr according to Vollenweider, 1968). This means that when human excreta are naturally recycled in the biogeochemical cycle they are certainly not a major source of additional nitrogen in rivers.

The *per capita* loadings may be compared with the Demophoric Index (DI) of (over?) development, defined by Vallentyne (1978) as the ratio between *per capita* energy consumption over a given period and the energy required to satisfy basic human needs (food, clothing, lodging). According to this author DI is up to 97 for the USA in 1970. It must be remarked that DI is below one for many African and Asian countries in




countries as a function of Vallentyne's demophoric index (DI). Straight line: weighted average of per capita loadings.

which people cannot satisfy their basic energy requirements. The per capita nitrogen loadings, computed in table 7, are effectively correlated with the demophoric index (fig. 5), except for Switzerland, where higher loadings values are found.

The total set of the 9 regions represents an area of $6.10^6$ km$^2$ and a population of the order of 440 $10^6$ inhabitants from countries of various DI (Switzerland is considered to be entirely taken into account in the Rhine River watershed). The total demophoric population of this sample is 20.7 $10^9$ demophoric unit (1 d u = 1 inhabitant x unit demophoric index). If a linear relationship between nitrogen loading and the demophoric index is retained as a first estimate, an average load per demophoric unit can be computed: it is here 0.10 kg N per demophoric unit per year. If this figure is extrapolated to the global demophoric population, estimated by Vallentyne to be 66.7 $10^9$ d.u. in 1970, then the total

additional nitrogen load to the ocean would be 7.0 $10^{12}$ kg $yr^{-1}$ of which 5.0 $10^{12}$ kg $yr^{-1}$ would originate from North America and Europe only. These values constitute a major fraction (30 percent) of total dissolved nitrogen delivered by rivers at the present time (table 6). They demonstrate the importance of man-made additions. (This budget includes the demophoric population of endoreic basins; it is however very small compared to the overall exoreic population.) It must be remarked that direct waste discharges in the estuarine and coastal zones are taken into account by this type of approach since the coastal demophoric population is included here. The influence of man on particulate nitrogen inputs is still unknown.

### *6.3. Phosphorus*

The phosphorus evolution in rivers presents the same pattern as for nitrogen. In Western Europe and in the USA the $P\text{-}PO_4$ contents have increased between 10 and 100 times. Much lower, but significant, increases are noted in some highly populated developing countries: in Java, where nearly 100 $10^6$ people are living, the average $P\text{-}PO_4$ in rivers in 23 $\mu$g P/l, whereas in Sumatra and Borneo it is only 7 $\mu$g P/l (Kobayashi and others, 1974). Other major world rivers in developing countries present higher phosphate levels than natural values (see Ganges, Magdalena, and Parana in app. 2). In the Chao Phraya River downstream of Bangkok the P level (500 $\mu$g/l for $PO_4\text{-}P$) is higher than in most European rivers (app. 2).

The additional phosphorus budget is determined by the method previously used for nitrogen (table 7). As phosphate is more commonly measured than total phosphorus, it will only be considered in the budget. Total phosphorus values are divided by 2.5 to be converted into $P\text{-}PO_4$, since the $P\text{-}PO_4$/TDP ratio was found to be of the same order in natural and polluted rivers. An average natural level of 10 $\mu$g $P\text{-}PO_4$ $l^{-1}$ is subtracted from all measured $P\text{-}PO_4$ levels to obtain the additional phosphate, except in Java rivers for which 7 $\mu$g P/l is taken. The *per capita* phosphate loadings vary between 15 g P $yr^{-1}$ for Java to more than 500 g P $yr^{-1}$ for highly developed countries. As for nitrogen the *per capita* loadings are related to the demophoric index (fig. 5), but a greater dispersion is observed. As for nitrogen it must be remarked that the physiological human excretion rate is very high compared to these values: 540 g P $yr^{-1}$ for total phosphorus (Vollenweider, 1968). Since in most non-industrialized countries the observed *per capita* loadings are an order of magnitude lower, it is believed here that physiological excreta are mostly reutilized by the biogeochemical cycle and do not cause important phosphorus increases in rivers.

The total sample of contaminated rivers used here represents an additional load of 120 $10^6$ kg P $yr^{-1}$ for 390 $10^6$ inhabitants and 19.5 $10^9$ demophoric units. The average phosphate load per demophoric unit is then around 6 g $yr^{-1}$. The global additional $P\text{-}PO_4$ input to the ocean is 0.4 $10^{12}$ g P $yr^{-1}$. If a $P\text{-}PO_4$/TDP ratio of 0.4 is taken, the corresponding total dissolved phosphorus input would be around 1.0 $10^{12}$ g P $yr^{-1}$,

keeping in mind all restrictions due to TDP measurements. This additional P load in rivers equals the natural load (table 6).

## 7. DISCUSSION

Rivers are a major link between continents and oceans; they can be considered on one hand as an output of terrestrial ecosystems and land erosion process, and on the other as an input to the ocean system. These two point of views will be examined together with the modification of the transfer rates resulting from man's activities.

### *7.1. Atmospheric Nutrient Inputs to Terrestrial Ecosystems*

Before considering the river output of terrestrial ecosystems it is essential to estimate the *atmospheric nutrient input.*

*Total organic carbon* content in precipitations is not well known. Schindler and others (1976) measured 3.75 mg/l in Western Ontario. According to Jordan and Likens (1975) TOC in rains over the Hubbard Brook Experimental Forest is between 0.6 and 12.4 mg/l. From various data quoted by these authors an average TOC around 2.5 mg C/l is likely. A similar value is proposed by Duce and Duursma (1977) for oceanic precipitations. The corresponding TOC atmospheric input would be of the order of 2 500 kg C $km^{-2}$ $yr^{-1}$, most of it being in the dissolved state.

Nitrogen and phosphorus in precipitations have been studied for a long time, and data are now available for all kinds of environments covering most climatic types (see table 8). Nitrogen seems to be determined more often than phosphorus, and organic forms are studied much less than mineral ones. As for rivers the influence of pollution on nutrient levels in precipitation is great, and a careful screening of data has been done to eliminate the most obviously contaminated stations. A few of them remain in table 8 as examples.

*Dissolved inorganic nitrogen* (DIN) content at uncontaminated stations is generally variable from 100 to 800 $\mu$g N/l (see fig. 3). Higher values are found near major cities or industrial settlements (see Ontario and Versailles) and may reach 2000 $\mu$g N/l (Paris and Hausen station in Switzerland). The lowest value (DIN = 15 $\mu$g/l) is found in British Columbia with an average rainfall of 4.5 m/yr (table 8). This value is exceptional. In Saigon and Addis Ababa the relatively higher value may be the result of some contamination. The median DIN content in non-polluted areas is around 450 $\mu$g N/l. In drier regions DIN is sometimes higher (710 $\mu$g/l in Chad) than in humid ones (280 $\mu$g/l in Lower Amazonia, 15 $\mu$g/l in the rainy part of British Columbia). As a result of this trend the DIN fallout is less variable. When considering 22 unpolluted stations DIN fallout is in between 300 and 600 kg $km^{-2}$ $yr^{-1}$; for 14 of them; the median is 450 kg N $km^{-2}$ $yr^{-1}$. It must be noted that the median amount of precipitation in these stations is of the order of 1 m/yr, which corresponds to the average rain over the exoreic part of the continents (Baumgartner and Reichel, 1975). This set of stations can be considered as representative. Higher inputs are measured in polluted stations. More than 950 kg N $km^{-2}$ $yr^{-1}$ is measured at Versailles, around the

TABLE 8

Nitrogen and phosphorus contents in atmospheric precipitations

| | $P\text{-}PO_4$ | TDP | $N\text{-}NO_2$ | $N\text{-}NH_4$ | DON | $N\text{-}NO_3$ | TDN | H | $\frac{N\text{-}NH_4}{DIN}$ | DIN | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | I. Stations supposed to be uncontaminated | | | | | | | |
| ELA (Ontario) | | 24 | | 293 | (90) | 259 | (642) | 0.81 | 0.53 | (550) | (A) |
| Thonon (France) | 9 | 18.5 | 2 | 215 | | 190 | | 1.08 | 0.53 | 407 | (B) |
| Norway | | | | 155 | | 114 | | 0.62 | 0.57 | (250) | (C) |
| Switzerland | | | | 310 | | 310 | | 2.0 | 0.50 | (620) | (D) |
| Mamai (New Zealand) | | 10 | | 220 | | 17 | | (2.6) | 0.9 | (240) | (E) |
| HBEF (New Hampshire) | 2.5 | 2.8 | | 170 | | 315 | | 1.25 | 0.34 | (490) | (F) |
| Walker Branch (Tennessee) | 40 | | | 130 | (195) | 250 | (575) | (1.9) | 0.34 | (380) | (G) |
| British Columbia | 2.9 | | | 9.7 | | 5.5 | | 4.5 | 0.64 | (15.5) | (I) |
| Colorado | 8.3 | | | 192 | | 273 | | 0.7 | 0.41 | (470) | (J) |
| Coweeta (North Carolina) | 4.5 | | | 99 | (195) | 141 | (435) | (2.2) | 0.41 | (240) | (K) |
| Victoriaville (Québec) | | | | 240 | 250 | 300 | 790 | | 0.44 | | (L) |
| Saigon | | | 11 | 458 | | 106 | | 2.2 | 0.80 | 575 | (M) |
| Addis Ababa | | | 14 | 554 | | 143 | | 1.33 | 0.77 | 711 | (N) |
| Rio Negro | 1.3 | 9.2 | | 125 | 73 | 111 | 310 | 2.0 | 0.53 | (240) | (O) |
| Delhi | | | | 218 | | 194 | | 0.72 | 0.53 | (420) | (P) |
| Calcutta | | | | | | 81 | | | | | (Q) |
| Manaus (Amazon) | 3 | 11 | 1.7 | 169 | 118 | 110 | (413) | 2.4 | 0.60 | 281 | (R) |
| Malaysia | 4 | | | 40 | | 80 | | 2.62 | 0.33 | (120) | (S) |
| Ivory Coast | | | | 260 | (1270) | 150 | 1680 | 1.08 | 0.63 | (410) | (T) |
| Chad | | | | 530 | | 180 | | 0.65 | 0.75 | (710) | (U) |
| Congo | | | | 206 | | 140 | | 1.55 | 0.59 | (350) | (V) |
| Ghana | 22 | | | 640 | | 135 | | 1.84 | 0.82 | (775) | (W) |

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| II. Stations probably contaminated | | | | | | | | | | | |
| South Central Ontario | | 21 | | 390 | 274 | 433 | 1100 | 0.76 | 0.47 | (830) | (AA) |
| Versailles (France) | | | | 1000 | | 680 | | 0.65 | 0.59 | (1700) | (BB) |
| Lake Maggiore (Italy) | 8 | 14 | 6 | 820 | | 510 | | 1.72 | 0.61 | 1336 | (CC) |
| Echallens (Switzerland) | 6 | 25 | 29 | 440 | | 430 | | 1.11 | 0.49 | 899 | (DD) |
| Dubendorf (Switzerland) | 1.9 | 14 | 110 | 760 | | 410 | | 1.20 | 0.59 | 1280 | (DD) |
| Altnau (Switzerland) | 33 | 66 | 56 | 1530 | | 530 | | 1.06 | 0.72 | 2116 | (DD) |
| Hausen (Switzerland) | 51 | 87 | 81 | 1660 | | 630 | | 1.27 | 0.70 | 2371 | (DD) |
| Paris (France) | | | 90 | 1390 | | 970 | | 0.58 | 0.57 | 2450 | (EE) |
| III. Averages | | | | | | | | | | | |
| Europe | | | | 410 | | 270 | | 0.60 | | 680 | (FF) |
| | | | | | | | | (1.0) | | (1200) | (FF) |
| | | | | 613 | | 220 | | 0.75 | | | (GG) |
| | | | | | | | | | | 395 | (HH) |
| World | | | | | | | | | | 530 | (II) |
| | | | | | | | | | | 250 | (JJ) |
| | | 70 | | | | | | (1.0) | | | (KK) |
| | | 27 | | | | | | (1.0) | | | (KK) |
| World (this paper) | 5 | 10 | 5 | 225 | 225 | 175 | 630 | 1.0 | 0.55 | 400 | (LL) |

TDP = total dissolved phosphorus; DON = dissolved organic nitrogen; TDN = total dissolved nitrogen; DIN = dissolved inorganic nitrogen (author's estimate when $NO_2^-$ is missing); H = annual precipitation in m; concentrations C are in $\mu g\ l^{-1}$; fallout rates I, in kg $km^{-2}\ yr^{-1}$ (or mg $m^{-2}\ yr^{-1}$) can be computed as I = C. H. Some other stations are taken into account in the world average but are not presented here as data are given in fallout rates only. Parentheses refer to author's estimates.

(A) Schindler and others (1976); (B) Average for 1979 according to B. J. Chassaing in Commission du Léman reports; (C) Låg (1976), average of 10 stations. Lista and Stend not included; (D) Keller (1978), Alpthal; (E) M. P. Mosley and L. K. Rowe, personal commun; (F) Likens and others (1977); (G) Swank and Waide (1980) and Swank and Henderson (1976); (I) Zeeman (1975); (J) Lewis and Grant (1979a); (K) Swank and Waide (1980) and Swank and Douglass (1977); (L) Campbell and others (1975); (M) Richard (1960); (N) Richard (1964); (O) Sioli (1969); (P) Kapoor, Khermani, and Ramana Marti (1972); (Q) Handa (1969); (R) Ungemach (1972); (S) Bishop (1973); (T) Villecourt and Roose (1978); (U) Lemoalle (1972) quoted in Villecourt and Roose; (V) Meyer and Pampfer (1959) quoted in Villecourt and Roose; (W) Nye (1961); (AA) Scheider, Snyder, and Clark (1979); (BB) Boniface, oral commun; (CC) Calderoni, Mosello, and Tartari (1978); (DD) Service Hydrologique National Suisse; (EE) Megnien (ms); (FF) Carroll (1970), table 26. World average is the median value of N fallout at 11 stations assuming H = 1 m. (GG) Vollenweider (1968); (HH) Stumm and Morgan (1970); (II) Delwiche and Likens (1977); (JJ) Garrels, Mackenzie, and Hunt (1971); (KK) Rigler (1974) and Oden and Ahl (1976), both quoted by Pierrou (1976), assuming H = 1 m; (LL) median of uncontaminated stations.

Lago Maggiore (Italy), and in all regular Swiss stations where a max 3000 kg N $km^{-2}$ $yr^{-1}$ was observed in 1978 at Hausen near Zurich.

*Nitrate* contents in precipitation are between 50 and 400 $\mu$g/l with a median of 175 $\mu$g/l. In 21 unpolluted stations its fallout is between 100 and 300 kg N $km^{-2}$ $yr^{-1}$.

*Ammonium* contents in precipitation are of the same order as nitrate: between 50 and 500 $\mu$g N/l with a median of 225 $\mu$g N/l. When considering 21 unpolluted stations the $N\text{-}NH_4$/DIN ratio is generally between 0.4 and 0.6 (10 stations) with a median ratio of 0.55. The highest ammonium contents are found at contaminated stations: 1000 $\mu$g N/l at Versailles, 1660 $\mu$g N/l at Hausen. At these stations the input rates are over 1000 kg N $km^{-2}$ $yr^{-1}$ while at non-contaminated stations rates range only from 100 to 400 kg N $km^{-2}$ $yr^{-1}$ (median 250 kg $km^{-2}$ $yr^{-1}$). The $N\text{-}NH_4$/DIN ratio is not different at contaminated stations: median is 0.6 for 8 stations.

*Nitrite* in precipitation is less studied. Its proportion is of the same order as in river water: $N\text{-}NO_2$/DIN is generally between 0.5 and 2 percent, except in polluted stations where a higher ratio — up to 9 percent — may be found.

*Organic nitrogen* has been measured at nine stations. The DON/total nitrogen ratio varies between 0.15 (Experimental Lakes Area in Ontario) to 0.75 in the Ivory Coast. A median value of 0.35 can be taken as a first estimate.

*The average nitrogen content in atmospheric precipitation* over the continents is ($\mu$g/l):

| $N\text{-}NO_3$ | $N\text{-}NH_4$ | $N\text{-}NO_2$ | DON | Total nitrogen |
|---|---|---|---|---|
| 175 | 225 | 5 | 225 | 630 |

In the more humid parts of the continents draining to the oceans, where the average precipitation is 1 m/yr, the corresponding fallout rates are 175, 225, 5, 225, and 630 kg N $km^{-2}$ $yr^{-1}$. This figure is of course not valid for the endoreic part of the continents (33.2 $10^6$ $km^2$) which is mostly desert.

*Phosphorus* contents in precipitation are not commonly reported in the literature. The median value of the data listed in table 8 (6 stations only) is around 5 $\mu$g $P\text{-}PO_4$/l. The $P\text{-}PO_4$/TDP ratio is generally of the order of 0.5. The total dissolved phosphorus was determined at nine stations with the median TDP value being 10 $\mu$g/l. As for nitrogen, higher contents are found at polluted stations: around 20 $\mu$g $P\text{-}PO_4$/l and 60 $\mu$g TDP/l. These figures must be considered with caution since more data are needed to confirm the levels. The corresponding atmospheric P inputs are 5 kg $km^{-2}$ $yr^{-1}$ for phosphate and 10 kg $km^{-2}$ $yr^{-1}$ for total phosphorus.

Previous values of atmospheric fallout found in the literature (see table 8) are similar to those given here. Dissolved inorganic nitrogen input is estimated to 395 kg $km^{-2}$ $yr^{-1}$ by Stumm and Morgan (1970), to 530 by Delwiche and Likens (1977), to 250 by Garrels, Mackenzie, and Hunt (1973). These authors have not taken into account the organic

nitrogen contribution which may represent around a third of the total nitrogen. Higher DIN inputs found in Vollenweider (1968), 630 kg N $km^{-2}$ $yr^{-1}$, or derived from Carroll's data (1970), 1200 kg $km^{-2}$ $yr^{-1}$ are probably most influenced by atmospheric pollution. Likens and others (1977) have presented a set of 17 stations located mainly in United States and Western Europe: their median inputs are 600 kg N $km^{-2}$ and 18 kg P $km^{-2}$ $yr^{-1}$, but it is not always stated which forms are included in these inputs.

### *7.2. Rivers and the Natural C, N, P Cycles on Land*

To what extent can rivers be considered as a minor output of the continental nutrient cycle? To answer this we have compared the river export rates with the quantities of global nutrients that are continuously recycled on land through the biological cycle. River-borne compounds can be considered to have derived from three origins: (1) direct land erosion products not involved in the biological cycle, that is all particulate inorganic forms and the dissolved bicarbonate originating from carbonate rocks weathering; (2) leaching and erosion of the inorganic soil components derived from the mineralization of terrestrial organic matter,

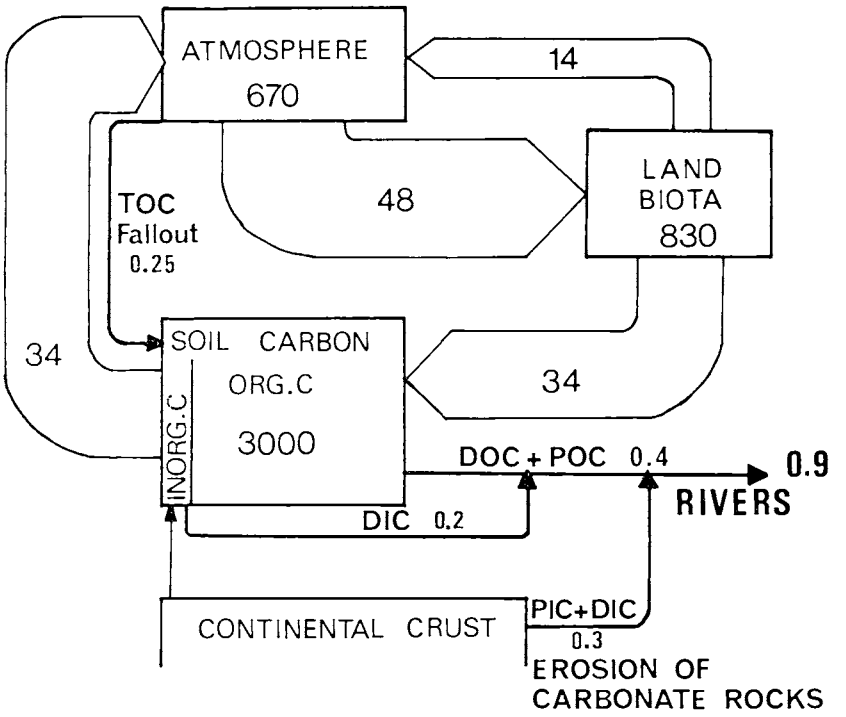



Fig. 6. Rivers and the natural continental carbon cycle. Annual fluxes and reservoirs are in $10^{15}$ g C (for the exoreic part of the continents). Atmospheric fallout and river transport data, from tables 7 and 8, are in boldfaced type. Other data are derived from Delwiche and Likens (1977). The ratio respiration/assimilation for land vegetation, taken as 0.3, is from Bolin (1970).

that is, dissolved inorganic nitrogen ($N\text{-}NH_4 + N\text{-}NO_2 + N\text{-}NO_3$), $P\text{-}PO_4$, part of $HCO_3^-$ derived from soil $CO_2$ picked up during rock weathering; (3) leaching and erosion of the organic soil components, that is, all dissolved and particulate organic nutrient compounds. This river output is compared to atmospheric fallout rates determined in table 8. The three schematic cycles are presented in figures 6, 7, and 8 in which all data derived from this paper have been underlined.

The terrestrial nutrient fluxes presented in these figures generally refer to the global continental surface including the glaciated area and the endoreic regions, whereas the river export data refer only to the exoreic regions. However it is believed that the exoreic area represents by far the major part of the vegetal production and of the recycled biomass over the continents with the exception of few endoreic non desertic basins (Caspian Sea, Chari) where biomass production is low.

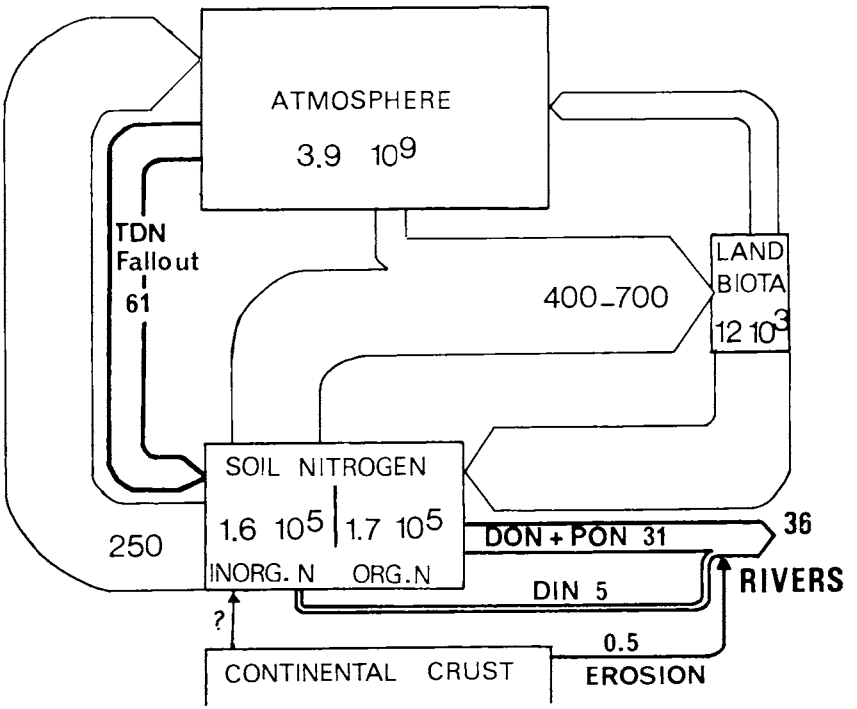



Fig. 7. Rivers and the natural continental nitrogen cycle. Annual fluxes and reservoirs are in $10^{12}$ g N (exoreic part of the continents). Data from tables 7 and 8 are in boldfaced type. Other data are author's estimates based on works of Delwiche (1970); Garrels, McKenzie, and Hunt (1973); Söderlund and Svensson (1975), quoted by Simpson (1977); and Rosswal (1981). The soil nitrogen data is from Delwiche and Likens (1977) and is consistent with the C/N ratio found in humus (C/N = 18 according to Likens, Bormann, and Johnson, 1981). The additional (pollutive) dissolved nitrogen load presently (1970) carried by rivers is estimated to be 7 $10^{12}$ g $yr^{-1}$. The industrial fixation is 40 $10^{12}$ g $yr^{-1}$. Total nitrogen assimilation by plants is estimated from the carbon assimilation (48000 $10^{12}$ g $yr^{-1}$) and C/N ratio in plants (table 9).

The influence of man on each component of the nutrient cycles has been considered recently (see Stumm, 1973; Simpson, 1977; Bolin and others, 1979) and will not be discussed here. A discussion of the nutrient increase in rivers and of speciation changes is presented.

The *carbon cycle* on land has been studied for some time and recent estimates can be found in Bolin (1970), Garrels, Mackenzie, and Hunt (1973), Delwiche and Likens (1977), and Bolin and others (1979). The simplified cycle presented in figure 6 is mainly derived from the Delwiche and Likens data. Both atmospheric TOC fallout and river export are minor fluxes, less than 1 percent of the atmospheric carbon uptake by terrestrial plants. This proportion has been noted for various types of environments (Meybeck, 1981). Erosion-derived inorganic carbon is also less than 1 percent of the recycled carbon. Carbon compounds derived from the biological cycle and found in rivers represent nearly two thirds of the carbon load, the remaining part originating from the erosion and dissolution of carbonate rocks.

The *nitrogen cycle* on land is still less known than the carbon cycle despite intensive studies: Rosswall (1981) reviewed 13 papers on the N cycle published during the last 20 yrs. The discrepancies between some

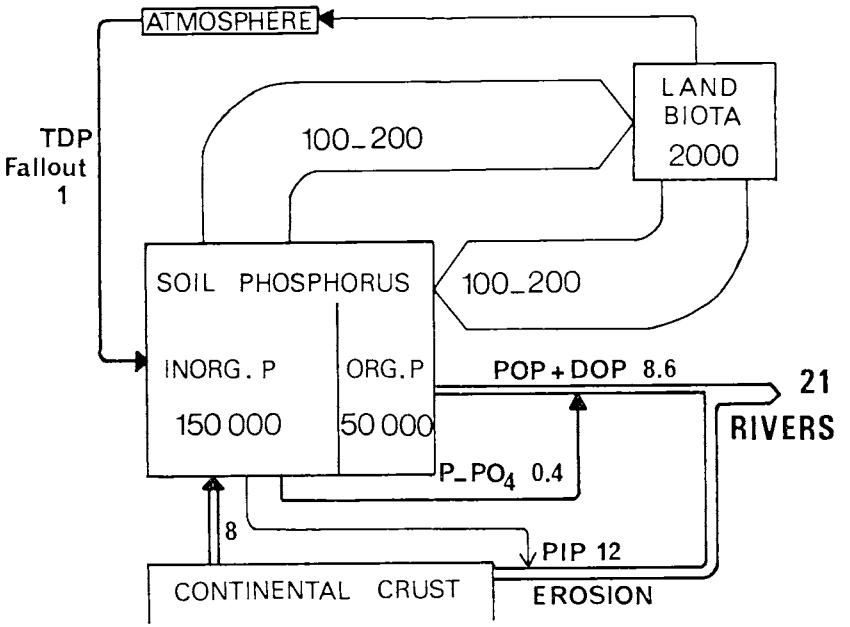



Fig. 8. Rivers and the natural continental phosphorus cycle. Annual fluxes and reservoirs are in $10^{12}$ g P (exoreic part of the continents). Data from tables 7 and 8 are in boldfaced type. Other data are author's estimates based on works of Garrels, McKenzie, and Hunt (1973), Stumm (1973), Pierrou (1976), Delwiche and Likens (1977), and Bowen (1979). The additional (pollutive) dissolved phosphorus load presently (1970) carried by rivers is estimated to be 0.4 $10^{12}$ g $yr^{-1}$. The P mining rate is about 13 $10^{12}$ g $yr^{-1}$.

fluxes (denitrification, ammonia volatilization, fires, et cetera) are sometimes very great, and the separation between continental and oceanic fluxes is not always done. As it is not the purpose of this paper to add one more cycle, we will only present in figure 7 a schematic cycle derived from various authors in which the global flux values are only suggestive. River transport represents about 5 percent of the amount of N annually recycled in the biosphere. The TDN fallout on land may account for 10 percent of the recycled nitrogen. Nearly all nitrogen compounds found in rivers originate from the biological nitrogen cycle, and about 85 percent are organic.

The erosion-derived nitrogen is very small (about 0.5 $10^{12}$ g $yr^{-1}$) and has been estimated as such: (1) nitrogen compounds in rocks are supposed to be entirely mobilized during weathering and carried in solution proportionally to the global amount of solution products from each rock type; (2) land denudation soluble products in rivers (exoreic runoff only) are estimated to be around 2400 $10^{12}$g $yr^{-1}$ of which 55 percent derive from carbonate rocks, 20 percent from evaporites, 14 percent from sandstones and shales, and 11 percent from cristalline rocks (Meybeck, 1979); (3) N content in these rocks is respectively: 150, 50, 580, and 20 $\mu$g N $g^{-1}$ (mostly from Wedepohl, 1968).

When comparing the atmospheric fallout of nitrogen on the world continental surface, 630 kg N $km^{-2}$ $yr^{-1}$, to the river output, 145 kg N $km^{-2}$ $yr^{-1}$, in the dissolved forms plus 210 kg N $km^{-2}$ $yr^{-1}$ in the particulate forms there is a major discrepancy: half the fallout is not found in river output. This is due to the other fluxes to and from the soil nitrogen reservoir such as denitrification and ammonia volatilization. This apparent retention of nitrogen by land ecosystems is widely found. Feller and Kimmings (1979) have reviewed 14 chemical budgets of undisturbed watersheds: N river output is lower than atmospheric input from precipitation in all cases. This "retention" is between 10 and 1970 kg N $km^{-2}$ $yr^{-1}$, with a median value of 450. However, consideration of particulate nitrogen export by rivers, generally omitted in these studies, would probably lower these "retention" rates by a factor of two.

The *phosphorus cycle* is completely different from the C and N cycle: the atmospheric fluxes are negligible here (about 0.5 percent of the cycle), whereas soil is the major reservoir of phosphorus. As for nitrogen, the P fluxes presented in figure 8 are the author's estimates derived from various sources. About 4 percent of the global mass of phosphorus cycling in the continental biosphere is exported by rivers as organic compounds and dissolved phosphates. As the atmospheric fallout cannot account for this export rate, it is supposed that 8 $10^{12}$ g P $yr^{-1}$ are mobilized from the surficial rocks and utilized by terrestrial plants. This is a peculiarity of the phosphorus cycle. According to a previous paper (Martin and Meybeck, 1979) the P budget in river particulate matter is not balanced: there is an enrichment factor (E.F.) of 1.5 with regards to aluminum. The latter element is poorly reactive, poorly soluble, and not affected by

pollution and therefore is used as a reference in land denudation studies. E.F. is defined as

$$\text{E.F.} = \frac{[\text{P}]\text{pm}/[\text{Al}]\text{pm}}{[\text{P}]\text{fr}/[\text{Al}]\text{fr}}$$

where [P]pm and [P]fr are the total phosphorus contents in the river particulate matter and in the average fresh rock. The average measured [P]pm is 1150 $\mu$g/g while the theoretical content should be around 800 $\mu$g/g. The average surficial content [P]fr is 610 $\mu$g $g^{-1}$, but there is a relative enrichment due to loss of the more soluble elements (Ca, Mg, Na, et cetera). As a matter of fact the inorganic particulate phosphorus corresponding to PIP (table 6) is 700 $\mu$g/g, a value close to the theoretical one. All the additional P load in river particulate matter can be accounted for by the POP (450 $\mu$g/g). If these data, which are still based on few results, particularly for POP, are confirmed, it would mean that terrestrial plants are an efficient phosphorus pump. The result of this process should be a relative increase of total P/Al ratio in the soil layer with regard to the parent rock; according to Bowen's data (1979) it is 0.0113 in the average soil compared to 0.0088 in the average fresh rock (Martin and Meybeck, 1979).

### *7.3. Specific Forms of Nutrients Exported by Rivers and C/N/P Ratios*

In nearly all previous nutrient budgets to the ocean *the particulate organic forms* of nutrients have been omitted most of the time because of a lack of data. (The only particulate nutrient sometimes considered is the inorganic phosphorus (PIP) which is poorly reactive). Based on the data of the present study, particulate organic nutrients, in terms of total reactive forms (dissolved plus particulate organic), represent 23 percent of total reactive carbon, 60 percent of total reactive nitrogen, and 89 percent of total reactive phosphorus. This is shown in table 6.

*The dissolved organic forms* of nitrogen and phosphorus have generally been omitted in previous budgets, although they represent 70 percent of the total dissolved nitrogen carried by rivers and probably more than 50 percent of the total dissolved phosphorus.

The ratio of dissolved content over total content in rivers (Soluble Transport Index) is the following:

| | C | N | P |
|---|---|---|---|
| organic forms | 0.55 | 0.32 | 0.06 |
| inorganic forms | 0.72 | ? | 0.03 |
| all forms | 0.64 | (0.40) | 0.05 |

It is of special interest to look at the variations of the C/N/P ratio in the organic matter from terrestrial plants to marine sediments (table 9). The C/N and C/P ratio continuously decreases from plant to humus and to river particulate material corresponding to higher loss of carbon to the atmosphere than nitrogen and phosphorus losses and to higher solubility in water of C and N compounds relatively to P compounds. As

a result the C/P and N/P ratio in river dissolved matter are much higher than in the particles.

The C/N weight ratio in river particulates (around 9) is similar to the ratio found in average soil (10 according to Bowen, 1979; from 8 to 12 in $B_2$ and $A_1$ horizons according to Stevenson, 1972). The typical C/N ratio of aquatic plants (5.7) according to Vallentyne, 1973, which is about 10 times lower than in terrestrial plants) is also close to the value for rivers. It is, therefore, likely that river organic matter is derived from both origins, aquatic and terrestrial. This ratio is not much different than values found in nearshore marine sediments (from 8 to 12, see table 9). Emery (1960) found that the C/N ratio increases up to 12 during burial. However Degens (1974) did not find any change with depth in a Black Sea core, and Bordovskiy (1965) does not report a marked trend in Bering Sea cores. In sedimentary rocks the C/N ratio would also be around 10 according to separate C and N data from Wedepohl (1968) and Ronov (1976). Although a great part of organic carbon and nitrogen found in river particulate material is lost by organic matter degradation, nitrogen and carbon behave similarly.

*The C/P weight ratio* (about 22) found in river organic detritus is also much closer to the value found in soil material (54) than in terrestrial plants (310-796) or in continental aquatic plants (40). Not much is known about the C/P ratio in marine sediments. Krom and Berner's data (1981) for Long Island sound sediments (C/P from 60-145) are much higher than for river detritus and are even higher than the Redfield ratio for marine plankton (41).

TABLE 9

C org/N org/P org weight ratio from plants to sediments

| | C/N | N/P | C/P | |
|---|---|---|---|---|
| Continental aquatic plants | 5.7 | 7 | 40 | Vallentyne (1973) |
| Terrestrial plants | 69 | 4.5 | 310 | Simpson (1977) |
| | 105 | 7.6 | 796 | Likens, Bormann, and Johnson (1981) |
| Soil humus | 18 | 2.5 | 54 | Likens, Bormann, and Johnson (1981) |
| River material | | | | |
| dissolved organic | 20 | 50 | 1000 | This paper |
| particulate organic | 8.8 | 2.5 | 22 | " |
| total organic | 12 | 4 | 46 | " |
| dissolved inorganic | 85 | 11 | 950 | " |
| Marine plankton | 5.7 | 7.2 | 41 | Redfield, Ketchum, and Richards (1963)* |
| Marine sediments | | | | |
| Long Island Sound (surficial) | 8.5 | 15 | 60-145 | Krom and Berner (1981) |
| Basin sediment (surficial) | 8-11 | | | Emery (1960) |
| Bering Sea (surficial) | 8.4 | | | Bordovskiy (1965) |
| Black Sea | 8-12 | | | Degens (1974) |
| Sedimentary rocks | 14.8 | | | quoted by Emery (1960) |
| | 10 | | | ** |

* quoted by Simpson (1977).

** assuming that N = 500 $\mu$g/g (Ronov, 1976) and organic C = 5000 $\mu$g/g (Wedepohl, 1968) in sedimentary rocks.

The net flux of nutrients to the oceans is difficult to estimate because of their high reactivity in the estuarine and coastal zones: phytoplankton uptake, change of chemical speciations from the soluble forms to the gaseous ones ($CO_2$, $N_2$, $N_2O$), and flocculation of particulate matter. These processes have been reviewed by many authors such as Aston (1978) and Wollast (1981). Most of the studies have concerned the more reactive nutrients, orthophosphates and nitrates. Moreover the estuaries that have been particularly studied are usually in the temperate zone, generally polluted, except for a few such as the Zaire (Van Bennekom and others, 1978). Sometimes the processes counterbalance one another; nitrogen can be lost to the atmosphere by denitrification but the green algae and photosynthetic bacteria may fix nitrogen (Wollast, 1981). For all these reasons it is not possible to state exactly the behavior of all nutrient speciations at the ocean-continent interface nor quantify the resulting fluxes. Therefore the loads presented on table 6 are only valid for the river transport upstream of the estuarine zone.

According to the present data rivers of the humid tropics, which drain about a fifth of the exoreic drainage area and carry about half of the river water to the ocean, transport about 55 percent of the dissolved organic carbon, total dissolved nitrogen, and total dissolved phosphorus.

### *7.4. Influence of Man on the Nutrient Cycle*

The nutrient cycle is now greatly modified by human activities and is no longer at steady state. The phosphorus mining rate during the year 1970, for which the budget of additional (pollutive) P has been computed, is of the order of 13 $10^{12}$ g P $yr^{-1}$ (Garrels, Mackenzie, and Hunt, 1973; Van Bennekom and Salomons, 1981). The industrial nitrogen fixation is generally estimated to be around 40 $10^{12}$ g N $yr^{-1}$ (Rosswall, 1981). The additional P and N loads in rivers estimated here (1 and 7 $10^{12}$ g $yr^{-1}$) would represent about 8 percent of production for P and 17 percent for N. Most nitrogen and phosphorus utilized by man is still stored at the Earth's surface (in waste dumping sites, as pollution of underground waters and lakes, as increase of organic matter in the surface waters, et cetera), although a part of the nitrogen may have reached the atmosphere.

The content of total dissolved phosphorus in river waters has already doubled. If it is assumed that most additional phosphorus occurs as orthophosphate and polyphosphate, the phosphate content has been increased globally by a factor of three. A similar evolution is noted for nitrogen: the total N has increased by 50 percent. If we assume that about 40 percent of additional N occurs as dissolved organic nitrogen (proportion most commonly found in polluted rivers), the dissolved inorganic nitrogen in rivers will have doubled.

These figures are slightly less alarming than those of van Bennekom and Salomons (1981) who stated that "man's activities have increased the P load of rivers by a factor of 5 and the N load 3 or 4 times" adding that the increases were "unevenly distributed over the world." Uneven distribution has also been clearly demonstrated in the present paper. In some rivers the N and P contents have increased by a factor 50 or even more.

This evolution is now a major environmental problem for it has induced a widespread eutrophication of surface waters (rivers, lakes, estuaries) resulting in overproduction of organic matter, oxygen consumption, metal release from sediment, and others consequences. In some regions the nitrate contents of waters, particularly of underground waters (such as in the French Bassin Parisien), have already exceeded the tolerance limit set by the World Health Organization for drinking waters.

Phosphorus is considered as being generally the limiting factor for production in surface waters. Globally the N/P ratio (TDN/TDP) has decreased with time due to man's activities. In natural waters representing the pre-man state it can be estimated to have been 15 (weight ratio), while it is now around 11. However this ratio is highly variable. When considering only $N\text{-}NO_3$ and $P\text{-}PO_4$ it varies between 5 and 25 in natural river waters and between 4 and 40 in polluted ones.

ACKNOWLEDGMENTS

I am very grateful to the following persons and administrations for oral and written communication of unpublished data and internal reports: M. Badruddin (Bandung), W. L. Bradford and S. Boniface (Versailles), A. Dessevre and F. Lelong (Orléans), C. Dulac and J-M. Laurenceau (Paris), J. Michalczewski (Warsaw), M. P. Mosley and L. K. Rowe (Christchurch), M. J. Orren (Rondesbosch), C. Praphorn (Bangkok), A. B. Viner (Taupo), J. Wartiovaara (Helsinki), and S. Whitlow (Ottawa); the Lower Sax Ministry of Agriculture, the Unesco Division of Water Sciences, and the Engineering Water Supply Department (Adelaïde), the WHO collaborating Centre (CCIW, Burlington). Helpful comments from G. Billen and R. Berner have been much appreciated.

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(references continued on p. 445)

APPENDIX 1

Dissolved nutrients ($\mu$g/l) in some small unpolluted streams (mainly in the temperate region)

| | $P\text{-}PO_4$ | TDP | $N\text{-}NO_2$ | $N\text{-}NH_4$ | DON | $N\text{-}NO_3$ | TDN | DOC | TOC | |
|---|---|---|---|---|---|---|---|---|---|---|
| **Temperate streams** | | | | | | | | | | |
| Nanaimo (British Columbia) | | 11 | | 11 | | 44 | | 6440 | | (A) |
| Jamesion (British Columbia) | 6.5 | | | 11.5 | | 5 | | | | (B) |
| Como (Colorado) | (1) | 3.5 | | (15) | 160 | (3) | | (2800) | | (C) |
| Hubbard Brook (New Hampshire) | 0.7 | | | 31 | | 440 | | 1000 | | (D) |
| Cascade streams (Oregon) | (5) | (15) | | (8) | (56) | (9) | | | | (E) |
| Washington streams | 7 | 69 | | | | | | | | (F) |
| Sweden streams | 15 | 43 | | 11 | | 18 | | | | (F) |
| Mamai (New Zealand) | 15 | 25 | | 15 | (61) | 31 | 107 | | | (G) |
| Lindaret (France) | 4 | 10 | 1.5 | 19 | 60 | 190 | (270) | | 470 | (H) |
| Brevon (France) | 5 | 15 | 1.5 | 15 | 60 | 185 | (300) | | 770 | (H) |
| Alpthal streams (Switzerland) | | | | 63 | | 195 | | | | (I) |
| Alberta streams | 15 | | | 140 | | 11 | | | | (J) |
| **Tropical streams** | | | | | | | | | | |
| Sungai Gombak (Malaysia) | 19 | | 3.3 | 60 | | 150 | | | | (K) |
| Maroni (Guyane) | 4.5 | | 1.4 | | | 98 | | | | (L) |
| **Arctic stream** | | | | | | | | | | |
| Char Lake inlet (Canada) | 2 | 4 | | 2 | (60) | 158 | 219 | | | (M) |

( ) Author's estimates.

(A) Naiman and Sibert (1978); (B) Zeman (1975); (C) Lewis and Grant (1979a and b), 3 yrs avg; (D) Likens and others (1977); (E) Stay and others (1978), median of 9 streams; (F) for P: quoted by Ryden, Syers and Harriss (1973), for N: Anderson-Calles and Eriksson (1979); (G) Neary and others (1978); (H) Serra-Bertral (1976); (I) Keller (1979), avg of 4 streams; (J) Singh and Kalra (1977), avg of 4 streams; (K) Bishop (1973) at station III; (L) van Bennekom and others (1978); (M) Schindler, Welch, and others (1974).

APPENDIX 2

Nitrogen and phosphorus dissolved contents ($\mu g\ l^{-1}$) of some major contaminated rivers

| | $P\text{-}PO_4$ | TDP | $N\text{-}NO_2$ | $N\text{-}NH_4$ | $N_K$ | DON | $N\text{-}NO_3$ | TDN | |
|---|---|---|---|---|---|---|---|---|---|
| **Europe** | | | | | | | | | |
| Rhine (Nederland) | 217 | 465 | | 1960 | | | 2450 | 5880 | (A) |
| Meuse (Belgium) | 235 | 487 | | 1820 | | | 3220 | 6160 | (A) |
| Sheldt (Belgium) | 1240 | 1860 | | 8400 | | | 0.0 | (11200) | (A) |
| Ems (West Germany) | | 800 | | 900 | | | | | (B) |
| Weser (West Germany) | | 620 | | 610 | | | | | (B) |

APPENDIX 2 (continued)

| | $P\text{-}PO_4$ | TDP | $N\text{-}NO_2$ | $N\text{-}NH_4$ | $N_K$ | DON | $N\text{-}NO_3$ | TDN | |
|---|---|---|---|---|---|---|---|---|---|
| **Europe (continued)** | | | | | | | | | |
| Po (Italy) | 47 | | 17 | 245 | | | 920 | | (C) |
| Rhône (France) | 137 | | | 80 | | | 880 | | (D) |
| Loire (France) | 48 | | | 80 | | | 1230 | | (D) |
| Seine (France) | 510 | | 100 | 1700 | | | 3950 | | (D) |
| Garonne (France) | 86 | | | <80 | | | 1100 | | (D) |
| Vire (France) | 189 | 208 | 26 | 450 | | 1490 | 4670 | 6636 | (E) |
| Danube (Rumania) | 15 | 50 | 7.4 | 70 | | (600) | 650 | 1325 | (F) |
| Poland | 107 | | 32 | 250 | | | 988 | | (G) |
| Black Sea (USSR) | | 80 | | 195 | | | 560 | | (H) |
| Aare (Switzerland) | 66 | 113 | 17 | 47 | | (578) | 1510 | 2152 | (I) |
| Reuss (Switzerland) | 32 | 85 | 8 | 36 | | (493) | 580 | 1153 | (I) |
| Rhine (Switzerland) | 61 | 112 | 13 | 40 | | (487) | 1340 | 1880 | (I) |
| Rhone (Switzerland) | 17 | 131 | 11 | 93 | | (478) | 500 | 1082 | (I) |
| Ticino (Switzerland) | 6 | 44 | 8 | 24 | | (416) | 510 | 958 | (I) |
| Thames (Great Britain) | 2475 | | | 991 | | | 9300 | | (J) |
| Severn (Great Britain) | 1001 | | | 247 | | | | | (J) |
| Tyne (Great Britain) | 36 | | 70 | 373 | | | 950 | | (J) |
| Trent (Great Britain) | 1335 | | 200 | 287 | | | 10100 | | (J) |
| **North America** | | | | | | | | | |
| Hudson (USA) | | 70 | | | 417 | | 669 | 1086 | (K) |
| Delaware (USA) | | 85 | | | 430 | | 860 | 1290 | (K) |
| Susquehanna (USA) | | 80 | | | 402 | | 920 | 1322 | (K) |
| Potomac (USA) | | 109 | | | 584 | | 857 | 1441 | (K) |
| Alabama (USA) | | 70 | | | 342 | | 192 | 534 | (K) |
| Mississippi (USA) | | 302 | | | 733 | | 1099 | 1832 | (K) |
| Brazos (USA) | | 375 | | | 921 | | 374 | 1295 | (K) |
| Sacramento (USA) | | 120 | | | 335 | | 82 | 417 | (K) |
| Columbia (USA) | | 45 | | | 280 | | 373 | 653 | (K) |
| Missouri (USA) | 59 | | | 210 | | 1070 | 700 | (2000) | (L) |

APPENDIX 2 (continued)

| | $P\text{-}PO_4$ | TDP | $N\text{-}NO_2$ | $N\text{-}NH_4$ | $N_K$ | DON | $N\text{-}NO_3$ | TDN | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | South America | | | | | |
| Magdalena (Columbia) | 64 | | | | | | 238 | | (M) |
| Parana (Argentina) | 67 | | 5 | 205 | | | 280 | | (N) |
| | | | | Asia | | | | | |
| Java (Indonesia) | 23 | | | | | | 370 | | (O) |
| Chao Phraya (Thailand) | 580 | | | | | | 630 | 1910 | (P) |
| Ganges (India) | 50 | 100 | | 150 | | | 200 | | (Q)(R) |
| | | | | Oceania | | | | | |
| Murray (Australia) | 140 | | | | | | 150 | | (S) |
| | | | | Asia | | | | | |
| Changjiang (Yangtze) | | | | 40 | | | 240 | | (T) |
| Huang He (Yellow River) | 11 | | | 10 | | | 1940 | | (U) |
| Zhujiang (Pearl River) | 4 | | | < 10 | | | 590 | | (V) |

(A) van Bennekom, Gieskes, and Tijssen (1975); (B) Specific German water quality year books, Hannover; (C) Fossato (1971 and 1973); (D) Ministère de l'Environnement 1971-74 median values except for Seine (1976-79 median value); (E) C. Dulac and J. M. Laurenceau, in preparation; (F) Acad. Romania (1967), avg 1961-63; (G) Andrulewicz (1976) based mainly on Oder and Vistula rivers; (H) Manheim and Chan (1974), Soviet Union rivers, Danube excluded; (I) Service Hydrologique National (1978) at the following stations: Brug, Mellingen, Rheinfeld, Scex, Riazino; (J) Department of the Environment, avg for 1976; (K) Briggs and Ficke (1977) $NO_3^-$ includes $NO_2^-$; (L) Delfino and Byrnes (1975); (M) Fanning and Maynard (1978); (N) Bonetto, Dioni and Pignalterri (1969); (O) Kobayashi and others (1974), avg of 19 rivers; (P) Reports of Thailand Ministry of Health (1978), downstream Bangkok; (Q) Van Bennekom and Salomons (1981); (R) Subramanian (1979); (S) Internal Rept. Eng. Water Supply Dept., Adelaide, avg for 1968-1978; (T) downstream of Wuhan, Changjiang bridge; mean for 1980 (24 analyses); (U) near the Luo Kou bridge; mean for 1980 (24 analyses); (V) downstream of Xijiang river bridge, mean for 1980 (24 analyses). For these three rivers, GEMS-WATER programme, WHO, CCIW, Burlington, the nitrate values include nitrite contents.

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