

## **Atmospheric inputs and river transport of dissolved substances**

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**ABSTRACT** Several different types of behaviour can be observed for elements between atmospheric input and river transport including very limited chemical or biological reactivity ( $\text{Cl}^-$ , in most cases), change of speciation (C, N, P), recycling to atmosphere (C, N, S, K), increase of dissolved contents through weathering (Si, Ca, Mg, Na), and build-up in soil or vegetation (C, N, P, Ca, Mg, K). Internal cycling within the soil and biosphere reservoirs is generally one or two orders of magnitude higher than wet and dry fallout rates or stream outputs. The influence of atmospheric input on river chemistry is exemplified by French streams, where it depends on the erodibility of basin rocks and on atmospheric inputs regulated by the distance to the Atlantic coast, wind-blown dust, vegetation aerosol release, and anthropic inputs. For any major element ( $X_i$ ), the atmospheric contribution to stream transport can be estimated on the basis of the stream  $\text{Cl}^-$  content, the rainfall/runoff ratio in the basin, and the regional  $X_i/\text{Cl}^-$  ratio in rainfall. For nutrients, the atmospheric influence can only be estimated from drainage basin budgets which include all organic material output by streams. New estimates of natural world average for rain and river composition are given for 10 elements and 18 specific forms, and from these are calculated the following contributions of natural wet and dry fallout to the global river transport to the ocean: Si, 4%; Ca, 6%; Mg, 19%; Na, 53%; K, 27%; Cl, 72%; S, 42%; P, 11%; N, 170%; org.C, 41%. Cyclic marine salts contribute to the average natural fallout rates over the exoreic part of the continents as follows: Ca, 40%; Mg, 76%; Na and Cl, 100%; K, 53% and S, 46%. The remaining part of this fallout is from natural continental origin.

*Les apports atmosphériques et leur transport par les rivières des matières dissoutes*

**RESUME** Le comportement des éléments depuis les apports atmosphériques jusqu'au transport par les rivières peut être classé ainsi: réactivité chimique ou biologique très limitée ( $\text{Cl}^-$  dans la plupart des cas), changement de formes spécifiques (C, N, P), recyclage vers l'atmosphère (C, N, S, K), augmentation des teneurs en solution due à l'altération des roches (Si, Ca, Mg, Na), rétention dans les sols ou la végétation (C, N, P, Ca, Mg, K). Les recyclages

internes dans les réservoirs sol et biosphère sont généralement d'un ordre de grandeur ou deux plus élevés que les retombées sèches et humides ou que les transports par les rivières. L'influence de l'atmosphère sur la composition chimique des rivières est illustrée par des exemples français: elle dépend de l'érodabilité des roches des bassins versants et des apports atmosphériques régulés par la distance à la côte atlantique, l'érosion éolienne, l'émission d'aérosols par la végétation, et les apports anthropiques. Pour un élément majeur donné ( $X_i$ ), la participation atmosphérique au transport des rivières peut être estimée sur la base des teneurs en  $Cl^-$  de la rivière, du rapport précipitation/écoulement sur le bassin, et du rapport  $X_i/Cl^-$  dans les pluies à l'échelle régionale. Pour les nutriments, l'influence atmosphérique ne peut être estimée que par des bilans de bassin versant incluant le transport des matériaux organiques par la rivière. De nouvelles estimations des compositions chimiques moyennes naturelles des pluies et des rivières sont présentées. Leur comparaison permet d'estimer la participation des retombées sèches et humides au transport mondial des rivières aux océans: Si, 4%; Ca, 6%; Mg, 19%; Na, 53%; K, 27%; Cl, 72%; S, 42%; P, 11%; N, 170%; C org., 41%. Les proportions des sels marins recyclés dans les retombées atmosphériques d'origines naturelles, sur la partie exoréique des continents, sont les suivantes: Ca, 40%; Mg, 76%; Na et Cl, 100%; K, 53%; S, 46%. Le restant est du aux sources continentales diverses.

## INTRODUCTION

The atmosphere has long been recognized by geochemists and agronomists as providing a major input of material to the earth's surface and a major source of elements carried by rivers (Anderson, 1941; Conway, 1942; Eriksson, 1960; Gorham, 1961). More recent studies on major elements (Douglas, 1968; Gibbs, 1970) and nutrients (Meybeck, 1982) confirm the importance of these inputs on global or local river chemistry. Increasing information on precipitation chemistry is now available through world or regional surveys such as the BAPMON programme or the Nordic Hydrological Programme and some individual scientific studies (Stallard & Edmond, 1981; Galloway *et al.*, 1982). Our knowledge of processes has also been improved by the evaluation of long-term and detailed chemical budgets for small basins or forested areas. The Hubbard Brook Experimental Forest programme (Likens *et al.*, 1977) was the first study of this kind, and many similar investigations are now going on in various countries (e.g. Schindler *et al.*, 1976; Balek *et al.*, 1978).

The purpose of the present paper is (a) to examine the position of atmospheric inputs within the external geochemical cycle, (b) to briefly review the various natural sources of atmospheric material, (c) to illustrate, mainly through French examples, the influence of these sources on river chemistry, and (d) to estimate the world budget of natural atmospheric inputs compared to the natural river transport for major elements and nutrients. The main problem in these

objectives arises from the influence of atmospheric pollution which has greatly modified the natural processes and fluxes (Galloway *et al.*, 1974, 1982), particularly in the Northern Hemisphere where 95% of the fieldwork is still undertaken. As far as possible, only natural water quality variations in rain and rivers are considered, and the effects of pollution will only be treated here through a few examples.

## THE PATHWAYS OF ATMOSPHERIC MATERIAL THROUGH THE EXTERNAL GEOCHEMICAL CYCLE

The external geochemical cycle on land can be characterized by the four major reservoirs of atmosphere, biosphere, soil and fresh rock. Inputs to the two reservoirs of the ecosystem, vegetation and soil, originate both from the atmosphere, through photosynthesis, N fixation, N and S impaction on vegetation, wet and dry fallout, and from soil, through weathering of fresh rock. Outputs occur mainly by river transport of particulate and dissolved material, but also to the atmosphere through gas emission from soil and vegetation ( $\text{CO}_2$ ,  $\text{NH}_3$ ,  $\text{H}_2\text{S}$ ), aerosol emission from vegetation ( $\text{K}$ ,  $\text{SO}_2$ ), and particulate emission (dust, forest fires, etc). In most cases, a given element will be present in this cycle in various specific forms, gases, ions, molecules, dissolved and particulate organic material and inorganic particulate matter.

The first process which modifies the amount of dissolved elements brought into the ecosystem by atmospheric fallout is the water cycle itself. If a given element is not enriched by soil weathering nor stored in the ecosystem, the total output should be equal to the total input. For a highly soluble element, such as chloride which is commonly not present in rocks, the stream content will simply be obtained from the fallout content by multiplication with the P/Q ratio, where P is the average rainfall over the drainage basin and Q is the runoff. (Anderson, 1941). This method has been developed by some hydrologists to estimate the water budget of drainage basins and even lysimeters (Schoeller, 1963). Some recent geochemical budgets have shown that  $\text{Cl}^-$  output is sometimes higher than atmospheric inputs (see review of these budgets by Feller & Kimmins, 1979), although  $\text{Cl}^-$  release from parent rock is unlikely. This most probably reflects the underestimation of atmospheric inputs of  $\text{Cl}^-$  in rain collectors, which do not take into account the higher uptake of  $\text{Cl}^-$  in forested areas through the impaction of aerosols.

For most elements, the cycle in the ecosystem is much more complex. First, they can be enriched by leaching of vegetation (throughfall). The counterpart of this cycle is the root uptake of nutrients, but in the litter, the water will be enriched again by the decay of organic material. Below the influence of roots, the dissolved contents can still be affected by various organic and inorganic processes, including mineral dissolution, neoformation of clay minerals, oxide precipitation and crust formation. The stream water quality, in turn, will reflect all the processes that regulate surface runoff chemistry, plus those (mainly dissolution) which affect the quality of deeper groundwater. The atmospheric signal will be greatly modified qualitatively, through a change of specific

forms, and quantitatively, by evapotranspiration, additional sources from rock weathering, and storage in soil and/or in living vegetation.

Evaluating the origins, pathways and reactions of a given element in the ecosystem cannot be achieved by simple comparison of rain and stream dissolved concentrations, but must be based on complex ecosystem budgets. These must include all specific forms of elements (gaseous, dissolved, particulate) and all fluxes in and out the ecosystem. In addition, the occurrence of a steady state within the system must be established, and total fluxes and reservoir quantities both must remain constant. Ecosystem budgets may exhibit natural trends, such as an increase in the standing crop of vegetation or in soil layers, or manmade trends, such as forest exploitation or change in atmospheric fallout. Nitrogen budgets provide many examples of an apparent non-steady state. Feller & Kimmins (1979) have reviewed a great number of budgets which indicate an apparent gain of N within the ecosystem, i.e. the stream output of  $\text{NH}_4^+$  and  $\text{NO}_3^-$  could not account for the atmospheric inputs of these elements. This discrepancy probably arises because other fluxes of nitrogen, including transport of particulate organic nitrogen in litter detritus carried by the stream, emission of  $\text{N}_2$ ,  $\text{NO}_x$ ,  $\text{NH}_3$  to the atmosphere, etc, are not considered. Particulate organic detritus are very seldom considered in geochemical budgets, although they usually represent between 1 and 20% of the suspended load (Meybeck, 1982) and carry some important elements originating from the atmosphere (C, N, K) or from rock weathering (Si, K, Ca). If this output is not considered, it may lead to underestimation of the actual erosion rate (Marchand, 1971) and/or the ecosystem output, as in the case of nitrogen.

When rock weathering is very low, the stream output is greatly influenced by atmospheric inputs. In some ecosystems and for some elements, the stream output may be less than these inputs from the atmosphere alone or from atmospheric and weathering sources together. This retention has been observed in the granitic Como basin, Colorado, where Lewis & Grant (1979) found that most elements (Ca, Na, K, N, P, S) were actually stored within the drainage basin in soil and vegetation. The same conclusion can be drawn from a study of Ca in central Amazonia (Furch *et al.*, 1982) on the simple basis of rain ( $3.6 \mu\text{eq l}^{-1}$ ) and stream ( $1.9 \mu\text{eq l}^{-1}$ ) concentrations, since another output of Ca, such as river particulates, is unlikely. This influence of plants on element accumulation in the ecosystem has been known since the work of Lovering (1959), and can affect elements originating from the atmosphere (C, N) or from rock weathering, such as silicon (Bartoli, 1981).

In many mass balances for stream basins, however, the atmospheric inputs are lower than those from rock weathering for most cations, and even for  $\text{HCO}_3^-$  and  $\text{SO}_4^{2-}$  when the underlying rock is sedimentary. Good examples of such budgets are now common (Feller & Kimmins, 1979; Lewis & Grant, 1979; Balek *et al.*, 1978; Zeman & Slaymaker, 1977; Henderson *et al.*, 1978). The most complete budget study undertaken to date is probably the one in the Hubbard Brook (HBEF) which began 15 years ago (Likens *et al.*, 1977). In this ecosystem, most fluxes and reservoirs have been measured and include precipitation, photosynthesis, N fixation, N and S aerosol impaction on vegetation, rock weathering, stream output and ecosystem storage. For some elements, the system is not at equilibrium and there is actually some storage

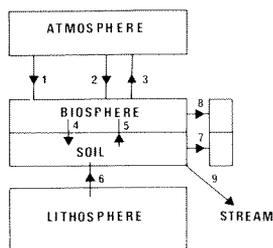


FIG.1 Schematic cycle of elements at the continental surface (1, atmospheric precipitation; 2, gaseous uptake and photosynthesis; 3, gaseous release; 4, throughfall leaching and litterfall; 5, vegetation uptake; 6, rock weathering; 7, increase of soil layer; 8, forest increment; 9, dissolved and particulate stream outputs).

in the living vegetation and in the newly-formed soil layer.

The external biogeochemical cycle is summarized in Fig.1 where groundwater storage has been omitted although it should be included in short-term budgets. Table 1 provides examples of the circulation of elements for two forest ecosystems on poorly weathered rock (metamorphic rock for the HBEF and quartz sandstone for Housseras). Moreover, these basins are relatively far from important atmospheric sources. Here, the internal cycle is clearly more dominant than atmospheric inputs and rock weathering for all the elements, and in this case, the forest ecosystem clearly regulates stream chemistry. The importance of storage (fluxes 7 and 8) is obvious for many elements in the Hubbard Brook. The chloride discrepancy is not

TABLE 1 Elemental fluxes within selected temperate forest ecosystems on weakly weathered rocks (fluxes 1 - 7 + 8 are standardized to the stream output (9) expressed as  $g\ m^{-2}\ year^{-1}$ )

Flux numbers (see Fig.1)						
	1	2-3	4	6	7+8	9
C*	2.5	126	370	?	127	1.23
N*	2.5	6.2	38	?	8.3	0.23
P*	5	0 ?	450	?	120	0.002
S*	0.78	0.38	1.9	0.05	0.13	1.62
Ca*	0.22	0 ?	5.7	1.9	1.13	1.17
Mg*	0.25	0 ?	3.7	1.25	0.52	0.28
Na*	0.22	0 ?	5.1	0.79	0.02	0.68
K*	0.65	<0 ?	40	4.0	3.7	0.17
Cl <sup>†</sup>	1.35	?	?	?	0 ?	5.0
Si <sup>§</sup>	0.50	0	7.7	0.83	?	0.3

\* Data from Whittaker et al. (1979), (HBEF).

† Data from Likens et al. (1977), (HBEF).

§ Data from Bartoli (1981), (Housseras).

significant. In these examples, the influence of the internal cycle is near to its maximum, but in most other basins (66% of the continental surface is underlain by sedimentary rock) weathering processes are dominant.

## SPATIAL VARIABILITY OF ATMOSPHERIC INPUTS

Atmospheric inputs are highly variable according to the relative influence of major sources, i.e. oceanic aerosols, continental dust, living and decaying vegetation, active volcanoes and anthropic inputs. Seasonal variations in atmospheric inputs will not be treated here, and the focus will mainly be on total fallout (wet and dry) as commonly measured in rainfall collectors. The influence of man on atmospheric constituents is now widespread, at least in the Northern Hemisphere where most measurements are made, and it is very difficult to separate the anthropic and natural sources. Furthermore, since the dilution effect greatly influences the concentration of fallout, the study of atmospheric inputs via fallout rates, expressed in  $\text{kg km}^{-2}\text{year}^{-1}$ , is preferred.

### *Major sources of atmospheric constituents*

For most elements, the oceans are the major source of atmospheric material. Since the first studies of atmospheric influence on river chemistry (Anderson, 1941; Eriksson, 1960; Gorham, 1961; Schoeller, 1963), Cl has been chosen as the reference element, i.e. the signature of the oceanic influence to which the other elements were compared. Some atmospheric physicists now prefer Na as an oceanic reference (Morelli, 1978; Delmas & Servant, 1974). However, the use of Cl should be maintained because in most river basins Cl is not released by rock weathering, which is not the case for Na. The composition of precipitation over the oceans and the coastal regions already differs from that of sea water when concentrations are normalized to  $\text{Cl}^-$ .  $\text{Ca}^{2+}$ ,  $\text{SO}_4^{2-}$ ,  $\text{K}^+$  and  $\text{HCO}_3^-$  are slightly enriched, whereas  $\text{Mg}^{2+}$  and  $\text{Na}^+$  are nearly in the proportion of sea water (Table 2). These enrichments are well known, and the typical value given here for the coastal zone (median of 16 stations in every continent) is very similar to the one reported by Savenko (1976) for oceanic precipitation. The  $\text{Cl}^-$  content at coastal stations varies with the rainfall total, but the  $\text{Cl}^-$  fallout rate is more constant at approximately  $20 \text{ t km}^{-2}\text{year}^{-1}$ , which corresponds to an average  $\text{Cl}^-$  content of  $18 \text{ mg l}^{-1}$  (minimum  $6 \text{ mg l}^{-1}$ , maximum  $30 \text{ mg l}^{-1}$ ).

When the distance to the coast exceeds 100 km, the oceanic influence is gradually superseded by continental inputs to the atmosphere from the dissolution of soil dust and forest fire material which provides  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  in calcareous regions, such as the French Prealps (Table 2), and  $\text{Ca}^{2+}$ ,  $\text{SO}_4^{2-}$  and even  $\text{Na}^+$  and  $\text{Cl}^-$  in arid regions, such as the central endoreic Soviet Union (Table 2). Forests can release K and S (Delmas *et al.*, 1978) while decaying organic matter produces  $\text{H}_2\text{S}$ ,  $\text{NH}_3$ ,  $\text{CO}_2$ , etc. At the centre of major continents, the  $\text{Cl}^-$  content, and probably the general oceanic influence, is very low as in central Amazonia, Alaska and Ontario. A recent study of uncontaminated precipitation (Galloway *et al.*, 1982) provides

TABLE 2 Typical composition of atmospheric precipitation for various influences

	$\text{Ca}^{2+}/\text{Cl}^-$ (eq eq <sup>-1</sup> )	$\text{Mg}^{2+}/\text{Cl}^-$ (eq eq <sup>-1</sup> )	$\text{Na}^+/\text{Cl}^-$ (eq eq <sup>-1</sup> )	$\text{K}^+/\text{Cl}^-$ (eq eq <sup>-1</sup> )	$\text{SO}_4^{2-}/\text{Cl}^-$ (eq eq <sup>-1</sup> )	$\text{HCO}_3^-/\text{Cl}^-$ (eq eq <sup>-1</sup> )	$\text{Cl}^-$ ( $\mu\text{eq l}^{-1}$ )	Annual rainfall (m)	Ref.
<b>OCEANIC INFLUENCE</b>									
Feroe (GB)	0.087	0.16	0.88	0.034	0.065	-	750	1.08	1
Oceanic precip.	0.16	0.24	0.86	0.021	0.30	0.05	113	-	2
Coastal precip.	0.085	0.22	0.88	0.025	0.18	-	525	-	3
Ocean water	0.037	0.19	0.85	0.018	0.10	0.0043	545x10 <sup>3</sup>	-	2
<b>CONTINENTAL INFLUENCE</b>									
Central Amazonia	0.16	0.17	0.90	0.073	0.74	-	13.7	(2.25)	4
Western Ontario	2.2	0.94	0.83	0.33	3.0	-	10	0.79	5
Prealps (France)	7.4	0.95	1.15	0.9	4.9	15	17	1.38	6
Alaska	0.038	0.077	0.38	0.23	2.75	-	2.6	0.28	7
Arid region (USSR)	1.1	0.24	(0.8)	-	0.68	0.79	1100	0.15	8
<b>VOLCANIC INFLUENCE</b>									
Kilauea station 3	-	-	-	-	2.1	-	9.5	-	9
Kilauea station 2	-	-	-	-	2.88	-	25	-	9
<b>ANTHROPIC INFLUENCE</b>									
Nemours (France)	0.88	0.18	1.07	0.19	2.2	1.1	41	0.71	10
Rouen (France)	-	-	0.74	0.13	13.7	-	141	0.45	11

<sup>1</sup>Nordic IHD.

<sup>2</sup>Savenko (1976), world average.

<sup>3</sup>Present study, world average.

<sup>4</sup>Stallard & Edmond (1981).

<sup>5</sup>Schindler et al. (1976).

<sup>6</sup>Haubert (1975).

<sup>7</sup>Galloway et al. (1982), Poker Flat.

<sup>8</sup>Zverev & Rubeikin (1973).

<sup>9</sup>Harding & Miller (1982).

<sup>10</sup>Average for 1981/1982, Meybeck & Papadopoulos, in preparation.

<sup>11</sup>Dessevre-Delepouille (1978), average for 1976.

reliable data for continental precipitation quality in Alaska, Australia and Amazonia, where levels of elements are very much lower than in most published data (Junge & Werby, 1958; Eriksson, 1960; Bapmon, 1981; Nordic IHD, 1971) and are thought to be much closer to natural background levels. It is interesting to note that in the Amazon basin the bulk of precipitation, although strongly diluted, is very similar in composition to coastal rain, with the exception of a slight enrichment in  $K^+$  and  $SO_4^{2-}$  (Stallard & Edmond, 1981). In Ontario, at the Experimental Lakes Area, rain water is much enriched in all elements except for Na, whereas in Alaska, it is only enriched in  $SO_4^{2-}$ .

The influence of pollution remains the major problem when investigating natural rain quality. In the Northern Hemisphere, at mid-latitudes, most of the stations present evidence of some pollution as in Nemours, 100 km south of Paris (Table 2), where  $SO_4^{2-}$  values appear suspect, or of acute pollution as in Rouen where refineries and fertilizer plants release enormous amounts of  $SO_2$ ,  $F^-$ , etc. (Table 2). In this case, the  $SO_4^{2-}/Cl^-$  ratio is about 30 times the natural value which is expected at 80 km from the sea.

Active volcanoes may locally alter rain quality by addition of  $SO_2$ ,  $HCl$  and  $NH_3$  from fumaroles. A rare example of this effect can be cited for the Kilauea volcano in Hawaii. At station 2, which is downwind of the summit, rain is enriched in many anions ( $Cl^-$ ,  $SO_4^{2-}$ ,  $F^-$ ,  $Br^-$ ,  $NO_3^-$ ) in comparison with station 3, which is located upwind. The enrichment of anions is balanced by a marked increase in acidity ( $13.9 \mu eq H^+ l^{-1}$  at station 2;  $36.4 \mu eq H^+ l^{-1}$  at station 3).

#### *Evolution of precipitation quality from coast to mainland*

The coastal zone is the most important localized source of atmospheric material, and there is a general decrease in the dissolved content of rain from the coast to the mainland (Conway, 1942; Eriksson, 1960). If the rainfall amount is constant,  $Cl^-$  content usually decreases exponentially in two or three steps, which correspond to the fallout firstly of larger sea-spray particles, and then of smaller salt nuclei (Delmas & Servant, 1974). If the rainfall amount is variable, these gradients are better studied using fallout rates, instead of concentrations, because of the dilution effect. This variation is presented in Fig.2 for France where distances are taken from the Atlantic coast, i.e. in the major direction of winds during rain events. In the Mediterranean regions, the  $Cl^-$  gradient is about 3 times higher, since sea winds do not provide much rain. The  $Cl^-$  input to land exhibits a 10-fold decrease in the first 100 km. A similar change is observed in the Amazon basin where the  $Cl^-$  fallout rates, based on the data of Stallard & Edmond (1981) and a constant rainfall of 2.2 m, are  $15 kg km^{-2} year^{-1}$  at the sea coast, 2.2 at 500 km, 1.6 at 1000 km and still 0.8 at 2000 km. The considerable dispersion of  $Cl^-$ , far from the coast, is probably due to other sources, namely pollution. This effect is also clear from the comparison of Magny-les-Hameaux (M), upwind of Paris, and Pargny (P), downwind of Paris, where  $Cl^-$  fallout rate is three times higher.

Evolution of other elements in continental precipitation will depend on distance to the sea, on rainfall amount, presence of various continental sources, etc. Since  $Cl^-$  is not very reactive

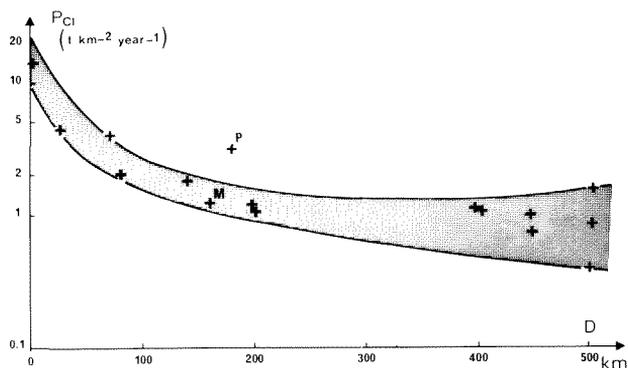


FIG.2 Decrease of  $\text{Cl}^-$  fallout rate ( $P_{\text{Cl}}$ ) at French stations with increasing distance ( $D$ ) from the Atlantic coast. M: Magny, P: Pargny (data mainly from French Bapmon network and from Delmas & Servant, 1974).

within the ecosystem and not usually released by rock weathering, it will be used as the reference element for the atmospheric input to river basins. Therefore, despite the possible atmospheric pollution of  $\text{Cl}^-$ , the variation of a given element  $X_i$  in rain will be studied through  $X_i/\text{Cl}^-$  ratios. The relationship  $X_i/\text{Cl}^-$  vs.  $\text{Cl}^-$  content is used here as a relative continentality index and has been constructed for the four elements of  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$  (Fig.3). Data include recent values from many stations located all over the world (Bapmon, 1981; Nordic IHD, 1971; Zverev & Rubeikin, 1973; Galloway *et al.*, 1982; Petrenchuk & Selezneva, 1970; Stallard & Edmond, 1981; and many others from basin budgets), although there is an emphasis on sites in the Northern Hemisphere.

Sodium behaviour is very much linked to  $\text{Cl}^-$  (Fig.3(a)) and in the Amazon basin as  $\text{Cl}^-$  decreases inland from 800 to less than  $10 \mu\text{eq l}^{-1}$ , the  $\text{Na}^+/\text{Cl}^-$  ratio remains relatively close to the ratio in coastal rain, which is 0.88 when expressed in  $\text{eq eq}^{-1}$ . In northern industrialized regions, the  $\text{Na}^+/\text{Cl}^-$  ratio is virtually constant for chloride values of 800 to  $100 \mu\text{eq l}^{-1}$  (i.e. up to 100 km from the coastline) and thereafter shows a scatter from 0.4 to  $1.4 \text{ eq eq}^{-1}$  due to other influences. Low  $\text{Na}^+/\text{Cl}^-$  ratios are most probably due to additional  $\text{Cl}^-$  from industrial sources. This variation confirms the observation of Delmas & Servant (1974) for northwestern Europe.

The variation of potassium in rainfall exhibits four trends (Fig.3(b)). The  $\text{K}^+/\text{Cl}^-$  ratio is constant at 0.025 for the Amazon basin and near to the coast for  $\text{Cl}^-$  values of 800 to  $150 \mu\text{eq l}^{-1}$ . A ten-fold enrichment of  $\text{K}^+$  occurs in temperate regions where the  $\text{K}^+/\text{Cl}^-$  ratio reaches 0.3 and further anthropic enrichment takes place due to contamination by fertilizers. The enrichment found outside of the Amazon basin at uncontaminated sites is probably due to natural processes since Alaskan and Venezuelan stations also have relatively high values of the  $\text{K}^+/\text{Cl}^-$  ratio at 0.23 and 0.32 (Galloway *et al.*, 1982).

The variation of calcium is very similar to that of potassium (Fig.3(c)). At stations assumed not to be contaminated, the  $\text{Ca}^{2+}/\text{Cl}^-$  ratio is enriched by about 20 times, from 0.085 up to 1.5.

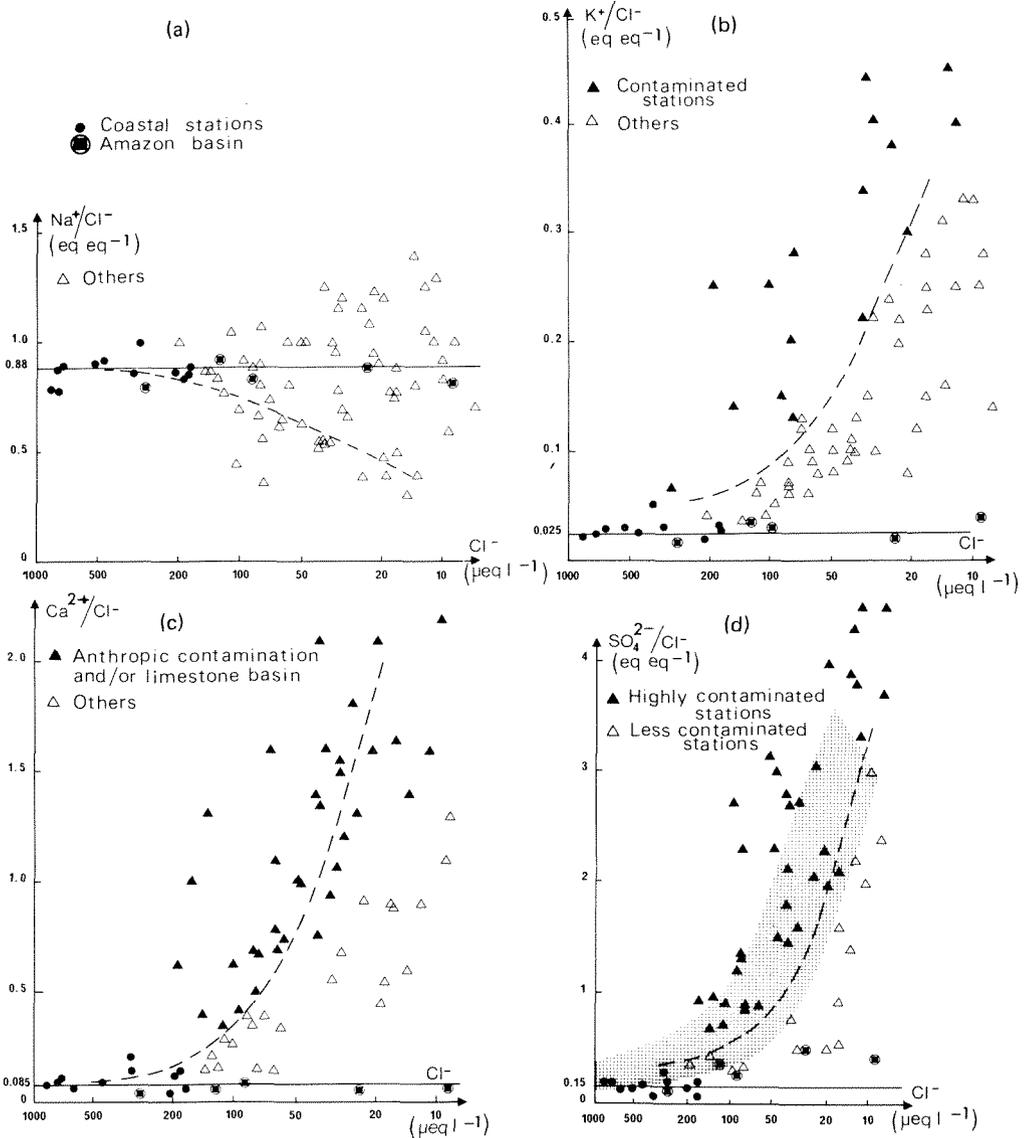


FIG. 3 World variation of  $\text{Na}^+/\text{Cl}^-$  (a), of  $\text{K}^+/\text{Cl}^-$  vs.  $\text{Cl}^-$  (b), of  $\text{Ca}^{2+}/\text{Cl}^-$  vs.  $\text{Cl}^-$  (c) and of  $\text{SO}_4^{2-}/\text{Cl}^-$  vs.  $\text{Cl}^-$  (d) in continental precipitation, dotted line represents standard variation for French stations and straight line represents average value for coastal rain. The shaded area is the range in unpolluted French streams draining non-sedimentary rocks.

At other stations, the  $\text{Ca}^{2+}/\text{Cl}^-$  ratio exceeds 2.0, probably due to the influence of pollution and to the dissolution of limestone dust. The  $\text{Ca}^{2+}/\text{Cl}^-$  ratio is constant for the Amazon basin, and in non-sedimentary regions, the ratio remains very low and assumes values of 0.038, 0.21 and 0.12 respectively in Alaska, Australia and Venezuela

(Galloway *et al.*, 1982).

Sulphate is even more enriched than calcium (Fig.3(d)), and for "less contaminated" stations of the Northern Hemisphere the enrichment factor is up to 3 times. At highly contaminated stations, the  $\text{SO}_4^{2-}/\text{Cl}^-$  exceeds 4, i.e. 20 times the value in coastal rain, and can be up to 13.5 at the Rouen station (see Table 2) where it should naturally be around 0.4. The Amazon rain is slightly enriched in sulphate (the  $\text{SO}_4^{2-}/\text{Cl}^-$  ratio is up to 0.45 at the centre of the basin). Even in the remote areas selected by Galloway *et al.* (1982), there is some enrichment of sulphate and the ratio is 2.75 in Alaska, 1.15 in Venezuela, 0.53 in Australia. These authors believe these values are mostly influenced by man.

Much more information is needed to separate natural and man-made enrichments. In Fig.3, the average variation in each  $X_i/\text{Cl}^-$  vs.  $\text{Cl}^-$  relationship, based on a dozen stations in France, has been added and will be used to correct river concentrations when local rain quality data are missing.

#### *Evolution of precipitation quality with altitude*

It is most likely that, at a given distance downwind from the ocean, the elemental concentrations in precipitation decrease at higher altitudes. This effect, however, is rarely observed since most precipitation quality stations are located at low altitude (<500 m). In the French Pyrénées (Bakalowicz, personal communication) and in the French Alps (Thomas, 1976), the  $\text{Cl}^-$  content in rain or snow exhibits a three-fold decrease between 500 and 1500 m. This is probably due to the combined effects of increasing precipitation and lesser atmospheric washout at higher altitudes.

### ATMOSPHERIC INFLUENCE ON RIVER QUALITY IN FRANCE

In order to avoid any terrestrial contamination of stream waters by direct and diffuse urban, industrial or agricultural sources, small stream basins generally between 5 and 50 km<sup>2</sup> in size, entirely located in forested areas, and with no human dwellings, industry or agriculture were selected for study. Moreover, the basins have been chosen so that the stream drains a single rock type.

#### *Coastal regions*

The composition of the small stream of Port Cros Island (Table 3) on the Mediterranean coast is essentially dilute sea water. This basin lies not more than 2 km away from the coast and the influence of rock weathering (micaschist) is negligible, with the exception of silica by the input of sea spray. The elemental ratios are quite similar to those of coastal precipitation (Table 2). In the Landes Forest, on the Atlantic coast, the water quality of the Larden stream, which drains only quartz sands, mainly reflects the oceanic influence (Table 3). This influence can still be observed as far as 100 km from the coastline, in the Céron stream which is underlain by the same geological formation. However, there are some modifications of elemental ratio, probably due to the internal cycling in forest and

TABLE 3 Elemental ratio (eq eq<sup>-1</sup>) in some coastal French rivers

	Ca <sup>2+</sup> / Cl	Mg <sup>2+</sup> / Cl <sup>-</sup>	Na <sup>+</sup> / Cl <sup>-</sup>	K <sup>+</sup> / Cl <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup> / Cl <sup>-</sup>	HCO <sub>3</sub> <sup>-</sup> / Cl <sup>-</sup>	Cl <sup>-</sup> (μeq l <sup>-1</sup> )	D (km)
Port Cros Island	0.17	0.26	0.82	0.016	0.14	0.08	9870	0.5
Larden stream (Landes)	0.17	0.26	0.87	0.045	0.25	0.31	688	13
Le Céron (Landes)	0.45	0.42	0.97	0.068	0.67	0.40	330	95
L'Avance (Landes)	4.0	0.45	1.07	0.070	0.80	3.7	333	105

D = distance from basin centre to the sea.

soil and to the weak chemical weathering of some feldspars. Nevertheless, these ratios are quite comparable to those observed in atmospheric precipitation at the same Cl<sup>-</sup> levels. In the L'Avance, a stream neighbouring the Céron, the influence of rock weathering is evident in the Ca<sup>2+</sup>/Cl<sup>-</sup> and HCO<sub>3</sub><sup>-</sup>/Cl<sup>-</sup> ratios due to the influence of limestone underlying sand.

In all the Landes streams, a Cl<sup>-</sup> decrease from the coast inland is observed (Fig.4(a)). This variation is quite parallel to the one observed in precipitation of this region (Schoeller, 1963), but the level of Cl<sup>-</sup> in streams is 3.5 times higher than the corresponding level in rain. This discrepancy is fully accounted for by the concentration of dissolved salts in water through evapotranspiration, since the precipitation/runoff ratio is between 3 and 3.5. In other coastal regions, the Cl<sup>-</sup> evolution can be somewhat different (Fig.4 (a)). In Brittany, the Cl<sup>-</sup> gradient is not well established due to the cape morphology which allows sea winds to go over 20 or 120 km of land depending on their direction. In Provence, the gradient is 3-5 times steeper than in the Landes since the sea winds rarely bear rain.

#### *Spatial variation of chloride in unpolluted French streams*

A few streams draining evaporitic rocks have been discounted here. The Cl<sup>-</sup> content in the others will essentially be derived from the atmospheric input and will depend on (a) distance to the Atlantic coast (b) water budget, i.e. precipitation/runoff ratio, and (c) altitude. When stations are grouped according to the average basin altitude (Fig.4(a)), the variation of Cl<sup>-</sup> with the distance to the Atlantic coast is parallel to the one observed for Cl<sup>-</sup> fallout (Fig.2). At a given distance from the sea (Fig.4(a)), there is an important scattering of data due to the other influences which cannot be separated at the present time. In lowland areas, the precipitation/runoff ratio is usually between 2.5 and 5 whereas above 1000 m it is mostly below 1.5. The combined effects of variation in water budget and variation of Cl<sup>-</sup> in precipitation at higher altitude is evident from Fig.4(b), which reveals a 10-fold decrease

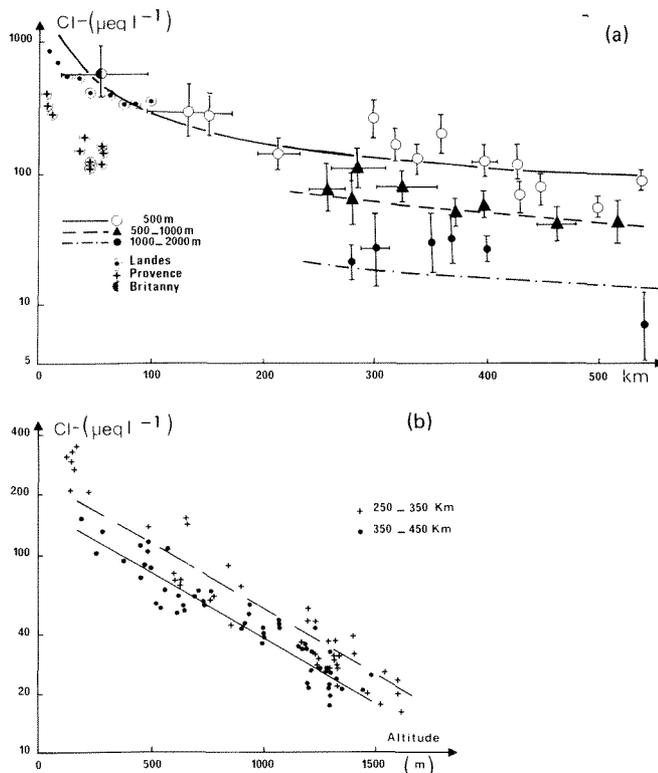


FIG.4 (a) Variation of  $\text{Cl}^-$  content with distance from the Atlantic coast in about 150 unpolluted French streams arranged according to their location and altitude, average variations are parallel to the  $\text{Cl}^-$  fallout pattern (see Fig.2); (b) variation of  $\text{Cl}^-$  content with average basin altitude in two sets of unpolluted French streams arranged according to their average distance from the sea.

in  $\text{Cl}^-$  concentration, at a given distance from the sea, between basins of 100 and 1500 m average altitude. A similar variation has been noted for some Scottish streams by Gorham (1961).

The variation of chloride is thought to be followed by most ions originating from atmospheric precipitation and poorly reactive within the ecosystem, such as  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{Na}^+$ . However, since these elements are also strongly released by rock weathering, this latter source will generally dominate the behaviour of these elements.

#### *Influence of atmospheric inputs with regards to basin lithology*

Gibbs (1970) has divided river waters into the three types of evaporation dominated, rock dominated and rain dominated. The latter type is defined by the  $\text{Na}^+/\text{Na}^+ + \text{Ca}^{2+}$  and  $\text{Cl}^-/\text{HCO}_3^- + \text{Cl}^-$  ratios. Some of his conclusions are biased by the fact that his data concerning the rain-dominated type were mostly based on crystalline or metamorphic basins. The French streams provide evidence, for each element under consideration, of greater variation in atmospheric

influence with regards to basin lithology. For each basin (Table 4), the measured water composition ( $C_i$ ) has been corrected from atmospheric inputs on the basis of stream  $Cl^-$  levels and corresponding  $X_i/Cl^-$  ratios in rain for each element as defined in Fig.3. All  $Cl^-$  is assumed to be of atmospheric origin. The  $X_i/Cl^-$  ratios have been fitted to ensure a proper ionic balance. Bicarbonate inputs through rainfall are thought to be negligible at the low pH (5-6) encountered in rain. The silica correction has been undertaken on the assumption of a constant content ( $0.3 \text{ mg SiO}_2 \text{ l}^{-1}$ ) in rain, taking into account an eventual concentration by evapotranspiration. For MD9, the  $X_i/Cl^-$  ratios are those of Nemours (Table 2), a nearby station.

The importance of correction for atmospheric inputs is evident for all ions in rivers draining weakly weathered rocks (sandstone, granite) whatever their distance to the coast may be. For limestone (MD190 and MD188), this correction mainly changes  $Na^+$ ,  $Cl^-$  and  $SO_4^{2-}$  contents, while for gypsum (MD18) it affects only  $Na^+$  and  $Cl^-$ . Some calculated atmospheric inputs exceed the stream output (MD9, MD111), especially for  $SO_4^{2-}$ . This is due to an overestimate of sulphate in rain. These discrepancies reveal the limitations of this method. It is much more desirable to make rain quality measurements for each drainage basin when possible. Finally, it must be pointed out the necessity of making atmospheric corrections when looking at cationic ratios ( $Ca^{2+}/Na^+$ ,  $Na^+/K^+$ , etc.), especially in crystalline basins where chemical equilibrium studies are so often undertaken. In 2- streams draining volcanic, crystalline and metamorphic rocks,  $SO_4^{2-}$  is probably mostly derived from the atmosphere, and the  $SO_4^{2-}/Cl^-$  range for 120 streams is very close to the one observed for the fallout rates (Fig.3(d)), taking into account the concentration factor of  $Cl^-$  by evapotranspiration ( $P/Q = 3$ ). For all cations, the  $X_i/Cl^-$  ratios in streams are usually much higher than those observed in precipitation, because of the addition of elements from rock weathering.

## GLOBAL ATMOSPHERIC INPUTS TO THE LAND AND THEIR EFFECT ON RIVER TRANSPORT TO THE OCEAN

### *Major elements*

The study of Eriksson (1960) was the first to specifically study the global influence of rain chemistry on river chemistry. More recent estimates of Garrels & Mackenzie (1971) and of Holland (1978) are still based on older data of Livingstone (1963) for rivers and of Wedepohl (1966) for rainfall quality. A previous study by the author (Meybeck, 1979), although based on more recent and carefully selected data, still retained a flaw in the analysis, in common with other studies, because the enormous coastal recycling of atmospheric inputs was not taken into account in the computation of average rain chemistry, nor in the calculation of river transport. The author's estimate of river water quality, in fact, was essentially based on stations upstream of the tidal reach, i.e. at a distance of more than 100 km from the coast for most of the world major rivers.

In order to make a proper comparison with river transport to the

TABLE 4 Influence of atmospheric precipitation in seven unpolluted French streams

		SiO <sub>2</sub>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Na <sup>+</sup>	K <sup>+</sup>	Cl <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	HCO <sub>3</sub> <sup>-</sup>	D (km)
<i>Quartzitic sandstone</i>										
MD9	Ci	138	250	98	319	63	327	222	219	150
	Cr	120	-40	38	-30	3	0.0	-495	219	
	% Pi	13	116	61	109	95	100	320	0.0	
MD128	Ci	117	194	101	100	51	91	188	80	400
	Cr	110	158	59	35	47	0.0	133	80	
	% Pi	6	18	41	65	8	100	29	0.0	
<i>Limestone</i>										
MD190	Ci	128	3 700	753	134	11	150	307	4380	35
	Cr	120	3 660	690	16	6	0.0	233	4380	
	% Pi	6	1	8	88	45	100	24	0.0	
MD188	Ci	50	2 470	139	18	2	11	75	2560	470
	Cr	45	2 430	130	11	0	0.0	35	2560	
	% Pi	10	1.6	6	39	100	100	53	0.0	
<i>Granite</i>										
MD111	Ci	293	117	42	237	13	117	79	200	380
	Cr	285	57	12	99	-10	0.0	-185	200	
	% Pi	3	51	71	58	230	100	330	0.0	
MD296	Ci	205	113	43	233	20	139	118	152	250
	Cr	195	74	-16	123	15	0.0	44	152	
	% Pi	5	35	137	47	25	100	63	0.0	
<i>Gypsum evaporites</i>										
MD18	Ci	115	15 384	5962	246	50	113	14 227	5519	450
	Cr	110	15 340	5920	172	45	0.0	14 180	5519	
	% Pi	4	0.3	0.7	30	10	100	0.3	0.0	

Ci = uncorrected contents ( $\mu\text{mole l}^{-1}$  for SiO<sub>2</sub>,  $\mu\text{eq l}^{-1}$  for ions).

Cr = contents after atmospheric inputs correction.

Pi = percentage of rain inputs in stream water.

D = distance from the Atlantic coast, except for MD190 (Mediterranean coast).

ocean, rainfall over the exoreic part of the continents is divided here into two groups:

(a) Along the 250 000 km coastline (Kossinna in Fairbridge, 1968), the average rainfall over a 100 km stretch is estimated to be  $1.5 \text{ m year}^{-1}$ ; its average Cl<sup>-</sup> content is supposed to be  $170 \mu\text{eq l}^{-1}$  (i.e.  $525 \mu\text{eq l}^{-1}$  at 0 km and  $50 \mu\text{eq l}^{-1}$  at 100 km from the coast), and X<sub>i</sub>/Cl<sup>-</sup> ratios are still those of the coastal rain (Table 2). The corresponding precipitation quality is given in Table 5.

(b) Inland, the remaining  $75 \times 10^6 \text{ km}^2$  of the exoreic drainage (see Baumgartner & Reichel world water balance in Meybeck, 1979) has been divided into eight major climatic zones for which standard elemental fallout rates have been chosen by combination of typical stations. This method is similar to the author's previous estimate, but the specific fallout rates have been more carefully selected in

TABLE 5 World average precipitation composition compared to world river quality (natural levels)

	SiO <sub>2</sub>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Na <sup>+</sup>	K <sup>+</sup>	Cl <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	DIC <sub>ero</sub> <sup>3-</sup>	P	POP	N	DON	N	N	PO <sub>4</sub> <sup>-</sup>	DIC	DOC	POC	H	Area
									(PO <sub>4</sub> <sup>3-</sup> )	(PO <sub>4</sub> <sup>3-</sup> )	(NH <sub>4</sub> <sup>+</sup> )	(NH <sub>4</sub> <sup>+</sup> )	(NO <sub>3</sub> <sup>-</sup> )	(NO <sub>3</sub> <sup>-</sup> )	(NO <sub>2</sub> <sup>-</sup> )	atm <sup>-1</sup>		(m)	(10 <sup>6</sup> km <sup>2</sup> )	
<b>AVERAGE PRECIPITATION QUALITY</b>																				
Coastal zone			0.29	0.45	3.45	0.17	6.0	1.45											1.5	25
Inland			0.43	0.19	0.37	0.15	0.75	1.73											0.625	75
World (exoreic) <sup>1</sup>	0.3	0.31	0.26	1.46	0.135	2.6	1.37		0.005	-	0.225	0.225	0.175	0.005	-	-	→2.5→	→1.0→	100	
Oceanic salts (%)	0	40	76	100	53	100	46													
<b>AVERAGE RIVER QUALITY</b>																				
World (exoreic) <sup>1,2</sup>	10.4	13.5	3.6	7.4	1.35	9.6	8.7	4.4	0.010	0.210	0.015	0.260	0.100	0.001	0.560	5.8	5.75	4.8	0.374	100
Total precipitation																				
input/river transport (%)									→11 <sup>5</sup> →	→	→	→	→170→	→	→	→	→	→	→	→41→
Marine atmospheric contribution/river transport (%)	4	6	19	53	27	72	42	0												
Mi	0	2.5	15	53	14	72	19	0												

Cd = dissolved and particulate contents in (mg l<sup>-1</sup>).  
 POP, PON, POC = particulate organic phosphorus, nitrogen and carbon.  
 DOC and DIC = dissolved organic and inorganic carbon.  
 H = average rainfall and runoff.  
<sup>1</sup>Nutrient data from Meybeck (1982).  
<sup>2</sup>Major elements from Meybeck (1979) corrected for additional inputs in coastal precipitation.  
<sup>3</sup>Dissolved inorganic carbon originating from rock weathering (Meybeck, 1982).  
<sup>4</sup>Dissolved inorganic carbon originating from the atmosphere.  
<sup>5</sup>Including organic P in rain.

order to minimize the anthropic influence. The resulting average continental fallout rate (Table 5) is effectively much lower than the previous estimate. Addition of the results for these two groups provides the estimate of global fallout of major elements over the continents. For  $\text{SiO}_2$ , the average content is simply the median value found from 16 stations in three continents (0.3 mg/l). After coastal inputs have been increased and inland inputs decreased, the new average values are not so different from previous ones, except for  $\text{Na}^+$  and  $\text{Cl}^-$  which have been tripled.

The new world river average composition given in Table 5 is based on a previous estimate (Meybeck, 1979) with the following correction. Only 30% of the 100 km coastal zone (i.e.  $8 \times 10^6 \text{ km}^2$ ) was taken into account in the previous work, and since data valid for  $63 \times 10^6 \text{ km}^2$  were extrapolated to the remaining area ( $37 \times 10^6 \text{ km}^2$ ) on the basis of a typology defined in inland stations, the atmospheric coastal contribution was greatly minimized. An additional transport by rivers has therefore been determined for the remaining unsampled coastal zone ( $17 \times 10^6 \text{ km}^2$ ) on the basis of the difference between coastal and inland fallout rates defined in Table 5.

The atmospheric inputs ( $P_i$ ) represent from 6% ( $\text{Ca}^{2+}$ ) to 72% ( $\text{Cl}^-$ ) of the river transport to the ocean, if a global steady-state is assumed. This contribution can be divided into the oceanic salts (see their proportion in rain ( $O_i$ ) and in rivers ( $M_i$ ) in Table 5) and continental salts which are originally derived from land erosion. These proportions are similar to those of Eriksson reviewed by Stallard & Edmond (1981). However, the proportions found by these authors for the Amazon River at Manaus are much lower than the present world estimate, due to the great distance between Manaus and the coast and to the importance of rock salt weathering in the upper Amazon basin.

### Nutrients

The nutrient content in rainfall is not dependent on proximity to the ocean, and its natural variations are not yet well understood. The estimated average contents (Table 5) were obtained on the basis of selected stations in the Northern Hemisphere (Meybeck, 1982). New measurements in very remote area (Galloway *et al.*, 1982) are similar to values in the present study, except for  $\text{N-NH}_4^+$  which is 4 times less. If these lower contents are confirmed, it would mean that either  $\text{NH}_4^+$  measurements in raincollectors are biased (possibly by transformation of organic nitrogen) or that the Northern Hemisphere is globally contaminated with regards to  $\text{NH}_4^+$ .

The average river quality given here is an estimate of the natural values, although present-day levels are much higher (Meybeck, 1982). Atmospheric contributions to river transport have been computed on the basis of total fluxes for each element, i.e. by considering all specific forms with the exception of the particulate inorganic forms which are believed to originate only from mechanical erosion. These contributions are very small for phosphorus but are important for carbon. It must be added that for carbon, about 99% of its land cycle is between the ecosystem and the atmosphere, and river transport represents only 1% of this enormous flux. In the case of nitrogen, the rainfall contribution far exceeds the river transport,

and this discrepancy probably reflects the gaseous release of nitrogen forms from the ecosystem to the atmosphere. This pattern, which is apparently opposite to the one observed in many stream basin budgets (Feller & Kimmins, 1979), is due to the consideration here of the river transport of particulate nitrogen. It must be added that erosion-derived nitrogen is probably negligible with regards to all other fluxes (Meybeck, 1982).

## CONCLUSIONS

The atmosphere is an essential component of the external geochemical cycle. For each element, its influence on river chemistry is highly variable according to the type of basin (lithology, vegetation, altitude, proximity to the coast). In the Northern Hemisphere temperate zone, natural processes are now very much affected by global atmospheric pollution and because of this trend and other human activities such as deforestation, the external cycle of elements is probably no longer in a steady state in this mid-latitude zone.

The stream basin budget approach, initiated in the Hubbard Brook and now widely used, has pushed forward our understanding of the coupling between atmospheric inputs, ecosystem cycling, rock weathering and stream output in the temperate forest. Similar studies should now be undertaken in less contaminated environments and in other climatic zones. More measurements of atmospheric inputs in the northern arctic and tropical zones and in all the Southern Hemisphere are eagerly needed to improve our global knowledge of atmospheric influence on surface water chemistry.

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