CHEMICAL CHARACTERISTICS OF RIVERS

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Contents

1. Introduction

The chemical characteristics of waters are studied in aquatic ecosystems for multiple reasons: (i) in pristine conditions, they define the ambient quality in which aquatic biota has developed, as in rivers, lakes, wetlands, hyporheic waters, (ii) in conditions altered by human impacts they correspond to environmental pressures on aquatic species, (iii) riverine fluxes of organic carbon, nutrients and toxic substances to enclosed water bodies such as lakes and reservoirs and to the coastal zone, determine their state of oxygenation, eutrophication, and exposure to harmful substances. Also, the chemical characteristics of rivers are used in physical geography and in geochemistry to determine denudation and chemical weathering rates. Finally, most water uses are characterized by a set of water quality standards, such as for drinking water, irrigation, and industrial uses.

In natural conditions the controlling factors of surface water chemistry are multiple (e.g. lithology, climate, terrestrial vegetation, geological history, aquatic biota) and the spatial ranges of major ions, carbon species and nutrients under average concentrations are enormous, over 2 to 3 orders of magnitude depending on the location. The temporal variability at a given station does not exceed an order of magnitude for most water quality indicators. Comparing the river chemistry of a sample, a station or a reach to a world pristine average, makes therefore little sense: regional references should be used.

Over the last hundred years, and sometimes even more, water chemistry has gradually changed in rivers with major human activities and water uses. These impacts are dependent on the nature and relative importance of these activities and they affect differently the various chemical indicators.

The quality of an aquatic ecosystem is defined by (i) a set of concentrations, speciations and physical partitions of inorganic and organic substances and (ii) the composition and state of aquatic biota found in a water body. In addition one must also consider (iii) the hydrological regime that regulates water level, flow velocity and vertical mixing and (iv) the physical habitat conditions (e.g. grain size of deposited sediments, thermal regime).

The pollution of the aquatic environment means the introduction by man directly or indirectly (e.g. via the atmosphere), of substances or energy which result in such deleterious effects as (i) harm to living resources, (ii) hazard to human health, (iii) hindrance to aquatic activities including fishing, (iv) impairment of water quality with respect to its use in agricultural, industrial and often economic activities, and (v) reduction of amenities. Similar effects can be produced by multiple human impacts on the hydrological regime, sediment transport regime or by ecological modifications (e.g. species introduction and invasions) they will be termed here *degradation* of freshwater ecosystems with regard to natural conditions. The term *pollution* is here understood as an important chemical degradation of ecosystems; for minor impacts on ecosystems, the terms *alteration* or *contamination* are preferred.

2. Chemical characteristics and water quality

River chemistry can be defined on dissolved material (solutes, gases), on colloids, on suspended and on deposited particulate matter. We are focusing here on solute chemistry in rivers. Full developments can be found in Hem (1989) for water chemistry and in Chapman (1992) for water quality, including groundwaters, lakes and reservoirs. *The chemical characteristics of waters* are those determined by the analyst. They are generally performed within regular monitoring on discrete water samples taken at limited frequency (typically 12 per year) while ideally the sampling and/or the analysis should be continuous in space and time and performed on the hundreds of elements and compounds found in waters. Three types of analyses are performed: (i) on unfiltered waters as total phosphorus (tot P) and total organic carbon (TOC), (ii) on waters conventionally filtered at 0.45 or 0.5 µm defining "dissolved concentration" which actually may contain parts of the colloids, and (iii) on suspended particulates.

The water chemistry is then interpreted in terms of potential water uses and of capacity of the aquatic system to sustain a healthy aquatic biotic community, thus defining the

water quality, a further integrative step based on the discontinuous analyses, performed at some stations, of highly selected chemical variables, realized on different media. Although water quality may be defined at the individual sample level (e.g. for drinking water), it is generally determined for ecosystems at a station and throughout a full annual cycle. A further integrative step is made within water quality surveys when considering the spatial average quality for a whole water body, a river reach or a river basin combining several stations.

The physical descriptors are temperature $T°$, pH, color, electrical conductivity, turbidity, and total suspended solids or TSS. Major chemical descriptors of water chemistry classically include *major ions*, Ca^{2+}, Mg^{2+}, Na^+, K^+, Cl^-, SO_4^{2-}, HCO_3^- (CO_3^{2-} if $pH > 8.2$), which occur at levels exceeding 1 mg/L, *minor ions* such as F^- and borate, between 0.1 and 1 mg/L and seldom analysed, dissolved *trace elements* below 100 µg/L as common metals (Fe, Mn, Al) and potentially toxic metals (Cd, Cu, Hg, Pb, Zn…) or metalloids (As, Sb, Se, Sn…). In most common natural conditions ($6 < pH < 8.2$) metals and metalloids are found in or bound to the river particulates, from 80 to 99.9% if TSS exceed 50 mg/L. Dissolved trace elements are also difficult to sample and analyze due to high contamination risks: dissolved trace metals analyses routinely performed within water quality surveys in the 1970s and 1980s are rarely trustworthy. Total metal analyses on unfiltered samples are also commonly used particularly to check drinking water standards but they are much affected by TSS levels, therefore of limited information on the actual state of contamination of the aquatic ecosystems: now heavy metals are commonly analysed on suspended matter, on fine deposited sediments, on selected biota (fish, aquatic moss). Analyses on suspended matter also allow for the determination of riverine fluxes of metals, organic carbon and nutrients.

Dissolved oxygen (O_2 dis) is a key water chemistry and water quality indicator: it results from the redox balance, i.e. the occurrence of reduced (Mn^{2+}, Fe^{2+}, NH_4^+, As^{III}) or oxidised species (Mn^{4+}, Fe^{3+}, NO_3^-, As^V), which control the speciation of some of the metals and their solubility and toxicity, (ii) it also results from the balance between the production (P) of aquatic vegetation (algae, macrophytes) and the bacterial respiration (R) associated with dissolved and particulate organic matter, it is therefore a key indicator of the P/R balance in an ecosystem.

Nutrients which are necessary to algal uptake and therefore control the eutrophication process include nitrogen species (NO_3^-, NO_2^-, NH_4^+ and total organic nitrogen, usually analysed with NH_4^+ as Kjeldahl nitrogen N_K), the orthophosphates (PO_4^{3-}) and the total phosphorus. Dissolved silica (SiO_2) should be added for the diatoms, often the dominant algal group.

Riverine organic matter is now generally described by dissolved organic carbon (DOC), and particulate organic carbon (POC) or on total organic carbon (TOC, on unfiltered water). In the past it was approached by Biological Oxygen Demand, generally measured after 5 days (BOD_5) and compared to the Chemical Oxygen Demand (COD) which includes reduced inorganic species as dissolved H_2S, SO_3^{2-}, NO_2^- and NH_4^+ and the organic matter.

Hundreds of organic substances both natural and synthetic can now be analysed and found in fresh waters. A few of them may be found at very low levels in natural waters, such as phenols, hydrocarbons and some polyaromatic hydrocarbons. Most of them are not found in natural conditions (i.e. they are *xenobiotics*) derived from pesticides and solvents. In impacted river basins, phenols and hydrocarbon concentrations are much higher than natural background values.

Hundreds of important toxic organics have been listed (e.g. Chapman, 1992; WHO, 1994), particularly those that are bioaccumulated and/or biomagnified in aquatic biota and that are poorly or slowly degraded in the aquatic environment. These are termed *persistent organic pollutants* or POPs. They include polychlorinated biphenyls (PCBs) and polyaromatic hydrocarbons (PAHs) such as benzo-pyrene and anthracene. Other categories of harmful chemicals can also be monitored, if appropriate and if the analytical capacities are available: (i) the radio-nuclides which started to be surveyed in the 1960s, either as individual isotopes such as ^{137}Cs and ^{134}Cs, or as total alpha, beta and gamma emitters; these surveys are unfortunately decoupled from environmental surveys in most countries and/or kept classified; (ii) the œstrogen–like substances, such as medical products, likely to act on animal and human metabolism; after the pesticide and POPs surveys developed in the 1980s and 1990s, these could be a growing threat in the twenty-first century.

Many water quality criteria have been set up regarding various uses for all water chemistry variables. The most demanding criteria are found for drinking water, then for aquatic life. Agricultural use criteria concern mostly salinization (NaCl build-up in soils) and some elements affecting crops such as boron and selenium. Transports, cooling, hydropower and some industrial uses are the least demanding uses. A few industrial uses (electronics, textile, agroindustries) may require specific criteria, such as dissolved silica, DOC and nitrate.

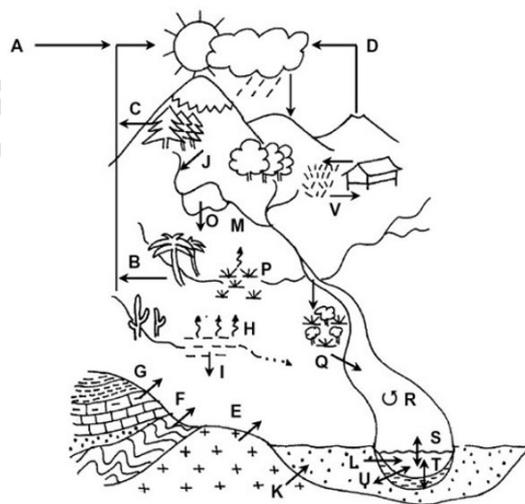## 3. Natural origin pathways and levels of river borne chemicals

Figure 1. Schematic sources, sinks and pathways of river dissolved material under natural conditions.

In natural conditions, river chemistry results from various origins: atmospheric inputs, soil leaching, weathering of minerals. These solutes and particulates can reach streams and rivers through various pathways and be controlled by multiple physical, chemical and biological processes (see Figure 1).

3.1. Atmospheric inputs

Atmospheric matter inputs originate (i) from oceanic aerosols (Figure 1, A), such as Na^+, Cl^- and SO_4^{2-}, (ii) from the dissolution of soil-derived particulates (B) such as Ca^{2+}, HCO_3^-, SO_4^{2-}, and (iii) plant emitted aerosols (C) as K^+ and SO_2, and from (iv) volcanic emissions (D) (such as SO_2).

In coastal streams and small rivers where the oceanic fallout may dominate over all other sources (e.g. islands) the most abundant ions are Na^+ and Cl^-, but at very low levels (NaCl < 100 mg/L).

The rain dominance may also be observed on rock types which are extremely resistant to weathering (quartz sands, sandstones, highly weathered soils), they correspond to the most dilute waters as in Central Amazon and Congo basins where the sum of cations TZ^+ does not exceed 0.2 meq/L.

3.2. Lithological control and cationic contents

The chemical weathering products found in surface and groundwaters greatly depend on local rock type (lithology). The plutonic and metamorphic rocks (see Figure 1) such as granite, gneiss (E) and micaschist (F) are characterized by very low mineralized waters with a low TZ^+ ($0.1 < TZ^+ < 1.0$ meq/L) (see Table 1).

Waters from volcanic rocks such as basalts and andesites are generally more mineralized than those of plutonic rocks ($0.3 < TZ^+ < 2.0$ meq/L). Weathering of sedimentary rocks (G) results in very variable cationic content ranging from very dilute waters for quartz sandstone ($TZ^+ < 0.5$ meq/L typically) to very saline waters for salt rock evaporite deposits (NaCl), found in salt domes or in arid regions (TZ^+ up to 50 meq/L).

In limestone-draining waters TZ^+ are typically between 3 and 6 meq/L and when gypsum layers ($CaSO_4$, H_2O) occur this content can be up to 10 meq/L. Other common sedimentary rocks such as shales and marl provide waters with TZ^+ typically between 0.5 and 3 meq/L depending on their contents of calcite minerals.

The minor occurrence (few percent) of calcite ($CaCO_3$), as cement of sedimentary rocks, or of pyrite (FeS), in some plutonic and metamorphic rocks or in some sedimentary rocks such as black shales, may results in important release of Ca^{2+} and HCO_3^- for calcite, and of SO_4^{2-} associated with Na^+, Mg^{2+} and Ca^{2+} for pyrite. Typical anlyses of streams draining a single rock type are presented in Table 1A.

	Elect. cond.	pH	TZ^+	SiO_2	Ca^{2+}	Mg^{2+}	Na^+	K^+	Cl^-	SO_4^{2-}	HCO_3^-	$N\text{-}NO_3^-$	$N\text{-}NH_4^+$	$P\text{-}PO_4^{3-}$	DOC
A. Streams draining specific rock types (analyses corrected for oceanic cyclic salts)															
granite/gneiss	35	6.6	190	8.4	1.0	0.5	1.9	0.35	0	2.1	8.0				
volcanic rocks	50	7.2	435	12	3.1	1.9	2.4	0.55	0	0.5	25.9				
sandstone	60	6.8	223	9.0	1.8	075	1.2	0.8	0	4.6	7.6				
shale			770	9.0	8.1	2.1	2.4	0.78	0.7	6.9	35.3				
carbonated rocks	400	7.9	3250	6.0	51.2	7.8	0.8	0.51	0	4.1	192				
rock-salt rich sediments	1700	8.0	18000	7.5	61.2	17.5	310	3.5	480	112	130				
gypsum rich sediments			20000	6.6	248	85	13.8	0.6	21	720	268				
B. Range and median for pristine rivers (Meybeck, 2003)															
minimum ($Q_{1\%}$)		5.5	128	0.2	0.64	0.12	0.4	0.15	0.13	0.24	2.9	0.01	0.005	0.001	<1
median ($Q_{50\%}$)				8.1	20	4.5	3.4	1.0	3.4	10.5	76.6	0.1	0.01	0.015	5
maximum ($Q_{99\%}$)		8.4	32000	41	186	72	337	19.8	600	700	363	0.5	0.07	0.03	43
C. Range for present-day rivers including Human impacts															
minimum (1%)												0.01	0.005	0.001	
maximum (99%)												6.0	1.4	0.5	

Table 1. Typical analyses of river waters from small monolithologic basins under temperate conditions (A). Global concentration ranges for pristine rivers (B) and for present-day rivers (C).

Differences in natural ionic chemistry resulting from basin lithology are greatest at the finest scale: in larger river basins the lithological composition, hence also the water chemistry, tends to be more homogeneous. In some regions of the world with very constant rock type such as the Canadian, Brazilian, and African shields, or for large sedimentary basins such as the central Congo or Amazon basins, stream chemistry can be relatively constant over 100 to 1000 km. In mountain streams that may drain very different rock types from one valley to another, the water chemistry is generally highly variable.

3.3. Climate influence and ionic types

The influence of climate on surface water chemistry is important at the global scale and is responsible for N-S or E-W gradients of stream chemistry, particularly in Asia. When the water balance is negative (precipitation < evapotranspiration), the products of chemical weathering and atmospheric inputs are gradually concentrated Figure 1, P, H). If evaporation is high enough concentrations reach saturation limits and some minerals may precipitate, in soil profiles or on river banks, as calcite ($CaCO_3$) then dolomite ($MgCO_3$) and even gypsum and anhydrite ($CaSO_4$, $n\,H_2O$) (Figure 1, I). This is particularly observed in enclosed basins (endorheism) such as those found in Central Asia, the Middle East, the American Great Basin, Bolivian Altiplano or Australia inland waters. Such waters are characterized by higher contents (TZ^+ typically > 6 meq/L) and dominant proportions of Na^+, Mg^{2+}, Cl^- and SO_4^{2-} and lower proportions of Ca^{2+} and HCO_3^-.

The combination of the three main ionic sources and control, ocean aerosols, rock weathering and evaporation, results in multiple ionic assemblages. The Na^+ - Cl^- dominance type can be observed either in wet coastal regions or in semi-arid, generally enclosed basins as in major parts of Central Asia. The Ca^{2+} - HCO_3^- type is by far the most widespread. It is found on many types of lithologies away from the direct coastal influence, such as for granites, some basalts, most detrital rock types with some amounts of carbonate minerals such as shales, and marls for limestones basins. The Ca^{2+} - SO_4^{2-} type is found in a few sedimentary basins with gypsum occurrence and/or in semi-arid regions. Other minor types may occur locally and even regionally, e.g. Mg^{2+} - HCO_3^- (some volcanic regions), Na^+ - SO_4^{2-} (pyritic shales, coal deposits). K^+ is generally the least abundant ion; in very dilute waters (Central Amazon and Congo) it is probably controlled by the terrestrial vegetation.

Extreme geological or climatic conditions may result in very odd water chemistry such as very acidic waters (pH < 3) in active volcanic regions or on sedimentary rocks rich in metal sulfide. Evaporated waters, particularly saline lakes, may have dozens of chemical types. These natural waters are commonly associated with an endemic fauna well adapted to these extreme conditions.

The global distribution of river ionic chemistry resulting from these natural controls is given in Table 1 together with the ranges of organic carbon and nutrients found in major rivers.

In traditional agriculture the fertilizer cycle between humans and animals and the field is nearly closed and very little N or P escape from cultivated or pastured fields (Figure, 1, V).

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Biographical Sketch

Michel Meybeck is working at University of Paris VI as a full time scientist within the French CNRS. Since 1976 he has been working on the present distribution of river chemistry at the global scale in pristine conditions and impacted basins for major ions, carbon, nutrients and particulate metals, in a perspective of river inputs to oceans and global scale controls of natural river water chemistry. He has been involved since 1978 in the international program on freshwater quality, the GEMS-Water program (UNEP/WHO/UNESCO) where he has directed several regional and global syntheses. He is also participating to the International Biosphere Geosphere Program concerning the riverine segment of biogeochemical cycles. He is currently focusing on the complexity of human/river relationships, particularly through a French program on the Seine River and an EU program on major Europe Catchments in which water policy issues are also addressed.