98: Water Quality

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Water quality is the term used to describe the chemical, physical, and biological characteristics of water. Furthermore, the physical, chemical, and biological characteristics of a water body, "its water quality", determine the suitability of that water for a particular value, for example, potability, ecosystem status, agriculture, industry, recreation. Water-quality issues have become a rapidly evolving component of the environmental sciences primarily due to the increasing demand on water resources and amenity value and the intricate linkage between water-quality use and ecosystem health. Water quality varies markedly in time and space. Episodic temporal water-quality variations can occur in minutes whereas, periodic variations can occur on short timescales from diurnal, associated with variations in light and temperature, to seasonal and longer associated with climatic variations. Spatial variations also vary markedly from millimeters and centimeters in soil profiles to very large-scale variations (>1000 km), for example, associated with water residence times, lithology, landscape position, land use, and bioclimatic zone. In the absence of the effects of human activities, water quality is primarily controlled by climate (precipitation and temperature) and geology (lithology, geomorphology, soil). The water quality of a given volume of water is derived from the sum of effects of mixing and interactions from all upstream sources including atmospheric deposition (precipitation and dry deposition), soil water (matrix and macropore), groundwater, springs, wetlands, irrigation ditches and canals, streams, ponds, lakes, reservoirs, rivers, and estuaries. In most parts of the world, human activities have now caused multiple and complex changes in background water quality.

INTRODUCTION

Water quality is a rapidly evolving environmental science discipline that began more than 150 years ago with a few basic physical (e.g. temperature), chemical (e.g. ammonia, dissolved oxygen), and microbiological (e.g. fecal coliform) variables. Now, water quality integrates dozens of analyses, *in situ* or in the laboratory, on water, particulates, and aquatic organisms and has evolved towards a global understanding of the aquatic environment including the description of habitat and biotic communities. Water-quality studies are conducted by all types of hydroscientists and on all types of continental waters including precipitation, soil water (matrix and macropore), groundwater, springs, wetlands, irrigation ditches and canals, streams, ponds, lakes, reservoirs, rivers, and estuaries. •The currently rapid evolution of the water-quality discipline is attributed to the intricate relation among humans and the ecosystem or environmental needs and wants for water (short and long-term), the associated water-quality requirements for the prescribed use and the availability of water with an appropriate quality, and the decreasing availability of water having acceptable water quality. Q2

Water-quality research and development has been driven for many years by the need for (i) scientific understanding of the aquatic environment, (ii) qualification of water for human uses, and (iii) management of land, water, and biological resources. More recently, a fourth objective also has driven water-quality research and development: the fluxes of dissolved and particulate material, through rivers and groundwater, including organic and inorganic

components to lakes and reservoirs (Vollenweider, 1968) and from the land to the oceans as part of the Earth System functioning (Livingstone, 1963; Garrels *et al.*, 1973; Berner and Berner, 1987; Vörösmarty and Meybeck, 2004), and is responsible for the degradation of the highly productive and recreationally attractive estuarine and coastal zone (Rabalais and Turner, 2001).

Water quality varies in time and space and its assessment largely depends on the state of scientific knowledge, the financial and technical means available to support the assessment, and the level of "water-literacy" of the community/society. Despite natural linkages between water quality and the lithosphere, water-quality characteristics are increasingly dependent on effects of human activities. Human activities create multiple and competing pressures on land and water resources through agriculture, urbanization, mining, industry, energy production, tourism, water supply, and transportation (water and land). These activities generally degrade water quality while being very demanding for specific water-quality criteria.

This article focuses primarily on surface water chemistry, and river chemistry in particular. Characteristics of water quality are presented in the first section ("Introduction"). General origins, pathways, and controls of water-quality variables are presented in the Section "Water-quality characteristics" and the lithological controls on river chemistry are presented in the Section "Natural river water quality: origins, pathways, and controls of river chemistry". The spatial and temporal distributions of water quality in river basins are the foci for Sections "Spatial variability of major ion concentrations in streams and rivers" and "Temporal variations of river water quality" respectively. Finally, the Section on "Riverine fluxes" focuses on riverine fluxes.

For additional information about water quality, read the articles on monitoring (**Chapter 99, Water Quality Monitoring, Volume 1**), acidification (**Chapter 100, Acid Deposition: Sources and Effects, Volume 1**), effects of human activities on water quality (**Chapter 101, Affects of Human Activities On Water Quantity and Quality, Volume 1**), point and nonpoint sources of pollution (**Chapter 102, Point and NonPoint Source Pollution, Volume 1**), nutrient cycling (**Chapter 103, Nutrient Cycling, Volume 1**), urbanization (**Chapter 104, Urban Water Quality, Volume 1**), pathogens (**Chapter 105, Pathogens, Volume 1**), trace elements (**Chapter 106, Trace Elements, Volume 1**), salinization (**Chapter 203, Integrated Land and Water Resources Management, Volume 1**), and modeling (**Chapter 108, Water Quality Modeling, Volume 1**). Also, please see Hem (1989), Hem *et al.* (1990), Berner and Berner (1996), and Drever (1988, 2003) for surface water geochemistry; Chapman (1996), Neal *et al.* (2000) and Meybeck (2002) for multiple approaches for local water-quality assessment; Meade (1995), Chapman (1996), Hooper and Kelly (2001),

and Kimstach *et al.* (1998) for regional water-quality monitoring and assessments; Meybeck *et al.* (1989, •2003) for global assessment; Livingstone (1963), Meybeck and Ragu (1996), and Global Environmental Monitoring System GEMS Water Program (GEMS, 2004) for global databases including hundreds of references on water-quality variables; Chapman (1996), Zhulidov *et al.* (2000), Timmerman *et al.* (2004), and MHSPE (1995) for water-quality surveys and their critics; Phillips *et al.* (1999) for river-flux calculations loads; Helsel and Hirsch (1993) for statistical methods for analyzing water-quality data; Peters (1996) for trend analysis; and Horowitz (1995) for the chemistry of suspended material.

WATER-QUALITY CHARACTERISTICS

Water quality incorporates information primarily from three scientific disciplines (physics, chemistry, and biology) to provide a holistic characterization of a freshwater body.

Physical and Chemical Aspects of Water Quality

The physical component consists of physical measurements that describe the aquatic habitat and its time and space variability. Some physical characteristics that effect biota and chemistry include, but are not limited to, the distribution and characteristics (scattering) of light in a water body, usually below the air-water interface; the color of the water; the water temperature (T°) and its distribution temporally and spatially in the water body; specific conductance (K_{SC}), the ability of the water to transmit an electrical current at $25\,^\circ C$ that is primarily determined by the total concentration of charged solutes dissolved in the water; the amount and distribution of particle sizes of suspended material and bed material; the density of the water; the hydrologic characteristics including water discharge and the circulation or hydrodynamics; the slope of the water surface, the spatial interrelation of water flow, and characteristics of the bed material, biota, and geomorphology.

The chemical data comprises analyses of water either filtered or raw (unfiltered), particulates, biota tissues or whole organisms; for organic and inorganic components, elemental isotope content, metals, and radionuclides. For solids, the chemical contents are usually expressed as mass per mass (e.g. $g\,kg^{-1}$, $\mu g\,g^{-1}$), and for "dissolved" (i.e. conventionally after filtration on $0.45\,\mu m$, which may still include part of the colloidal fraction) or suspended components, the contents typically are reported as mass per unit volume of water (e.g. $mg\,l^{-1}$ or ppm, $\mu g\,l^{-1}$ or ppb), or for solutes, as moles of solute per unit volume of water ($mol\,l^{-1}$, $\mu mol\,l^{-1}$) or equivalents of charge per unit volume of water ($eq\,l^{-1}$, $meq\,l^{-1}$, $\mu eq\,l^{-1}$). Most natural freshwaters, in the absence of human impacts, have a relatively narrow range of few characteristics that either

reflect the chemistry, such as specific conductance (K_{SC}), or control the chemistry, such as the acid–base status as measured by pH (minus the logarithm of the hydrogen ion concentration) and alkalinity (capacity of water to neutralize acid), and the oxidation and reduction conditions or redox as typically measured by ion pairs and the dissolved oxygen (DO) concentration. In addition, biogeochemical cycles are affected by the affinity of the elements and compounds to adsorb or bind to each other and to other compounds and solids, and by their ability to dissolve in water.

For natural or background conditions, the chemical composition of waters and waterborne particulates is characterized by dozens of elements and compounds including:

Major dissolved ions: cations: Ca^{2+}, Mg^{2+}, Na^+, and K^+; anions: Cl^-, SO_4^{2-}, HCO_3^-, and CO_3^{2-}; generally reported in $mg\,l^{-1}$ in ion or elementary form (e.g. $mg\,NO_3\,l^{-1}$ or $mg\,NO_3\text{-}N\,l^{-1}$)

Minor dissolved elements: Fe, Al, Mn, Ba, and Sr, reported in $\mu g\,l^{-1}$;

Trace dissolved elements: As, B, Cd, Cr, Cu, Hg, Pb, Se, Sn, Sb, Zn, and many others that generally are reported as $\mu g\,l^{-1}$ or $ng\,l^{-1}$;

Natural organic compounds: amino-acids, lipids, humic and fulvic acids, and natural hydrocarbons, generally in trace amounts and dissolved organic carbon (DOC in $mg\,l^{-1}$);

Synthetic organic compounds: several hundreds of man-made products (*xenobiotics*), generally toxic, must be controlled particularly for drinking waters including herbicides, pesticides, solvents, plasticizers, fire retardants, hydrocarbons, and polyaromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs). Some of them are very persistent (●POPs) and can be transported in aerosols over long distance, or attached to suspended matter.

Nutrients: used by aquatic plants, including nitrogen (N) species (NO_3^-; NO_2^-; NH_4^+); dissolved and particulate organic N (DON and PON); Kjeldahl N (N_K); total N (TN); phosphorus (P) species (PO_4^{3-}); dissolved organic P (DOP); particulate P (PP); total P (TP), and dissolved silica (H_4SiO_4, generally reported as SiO_2).

Miscellaneous: total dissolved solids (TDS); sum of cations $\sum^+$ and anions $\sum^-$ (expressed in $meq\,l^{-1}$; they should be equal in balanced analyses); suspended solids (SS), typically expressed as total suspended solids concentration (TSS), and deposited sediments in lakes, reservoirs, floodplain, and sometimes river beds. SS are often considered as a key media for the monitoring of nutrients (N, P), particulate organic carbon (POC; carbon linked to carbonate minerals or PIC both expressed in % of particulate matter), minor and trace particulate elements (Al, Fe, Mn, Si, As, Cd, Cu, Hg, Pb, Sb, Zn) and these are commonly analyzed and reported as content per dry weight ($\mu g\,g^{-1}$, $ng\,g^{-1}$); chlorophyll A and total pigments ($\mu g\,l^{-1}$) as a measure of active and total phytoplankton biomass.

Biological and Microbiological Aspects of Water Quality

All aquatic organisms, whether bacteria, invertebrates, vertebrates, vascular plants, or planktonic algae, have preferred environmental conditions in which they thrive. Many, however, can also be found within certain tolerance limits of these conditions. The basic parameters to which biota are sensitive are physical (e.g. light, $T°$, DO, turbulence, sediment grain size) and chemical (e.g. acidity, nutrients, toxic chemicals). Aquatic organisms need a source of energy – for photosynthetic organisms this means adequate light and nutrients and for others it means a source of suitable food, ranging from organic detritus to plant material to other invertebrates or vertebrates. Thus, directly, or indirectly through the food chain, aquatic organisms are dependent on the physical and chemical aspects of water quality.

In turn, the presence of aquatic organisms influences water quality – photosynthesis by planktonic algae and macrophytes can increase oxygen concentrations to levels of supersaturation at times of high light intensity, and the respiratory action of bacteria decomposing dead and dying plankton or macrophytes can use up the oxygen in the water thus resulting in a daily O_2 cycle whose intensity is a measure of the aquatic production. A living plankton is a component of the total suspended matter, and decaying plants and plankton contribute organic matter particles to both suspended and deposited sediments with a ratio algal organic carbon/total pigments between 30 and $40\,g\,g^{-1}$ for plankton. During photosynthesis (or production P), phytoplankton uptakes dissolve inorganic nitrogen, NO_3^- and NH_4^+, and phosphorus (PO_4^{3-}) according to the Redfield molar ratio $C_{106}:N_{16}:P_1$. As organisms decay, they also release nutrients back into solution and the seasonal cycles of phytoplankton species and/or macrophytes can greatly influence the seasonal fluctuations in lake nutrient concentrations. Under less productive conditions, the oligotrophic state, diatom algae are generally dominant particularly in spring blooms of the temperate and cold regions. In addition to N and P nutrients, these algae also use dissolved silica. As a result of seasonal algal uptakes marked cycles of H_4SiO_4, NO_3^-, NH_4^+, and PO_4^{3-} are observed in lakes and reservoirs and in some highly productive (eutrophic) rivers. The bacterial decomposition (or respiration, R) of the organic matter produced in the aquatic system leads to oxygen depletion. When the P/R ratio <1 there is a net O_2 depletion, as in lake bottom waters in the absence of vertical mixing, or in turbid macrotidal estuaries. This depletion may also be caused by the decomposition of organic wastes, for example, from urban sewage, thus resulting in an oxygen sag-curve downstream of untreated and partially treated effluents. Thus the traditional perception of water quality cannot be separated from the aquatic organisms present in the water body and this has led, in

recent decades, to a more holistic approach to the study of water quality to include some, or all, biological components of aquatic systems.

The interaction between suitable habitats, that is, environmental conditions, and suitable food supplies leads to communities of organisms that typically thrive together in natural water bodies. These communities include bacteria using dissolved organic carbon, primary producers (plants and plankton), herbivorous invertebrates, detritivores, fish, and even mammals (the tropic pyramid). Any impact on one of these groups can cause effects on the dependent groups, for example, through loss of food supply, alteration of environmental conditions (physical or chemical), and altered predator–prey relationships. Ultimately, the natural balance of the whole aquatic system may be altered, and with it the physical, chemical, and biological water quality.

Aquatic organisms are more and more used to describe the water quality in its wider definition (Chapman, 1996). Certain individuals or combinations of organisms can be associated with narrow ranges of water quality, particularly the extremes of clean and polluted water. Thus, the organisms themselves provide a monitoring tool, whereby their presence or absence can be indicative of certain classes of water quality (*see* **Chapter 99, Water Quality Monitoring, Volume 1**). Some of those aquatic organisms are chosen for their limited mobility (e.g. benthos); they integrate at one given station the effects of human influences on their environment (chemical and physical) over the period of their lifetime that can vary from months to decades. Other organisms have a great mobility, such as fish, or may even travel along an entire aquatic system from headwaters to ocean, and are chosen for their overall integration of both physical and chemical degradation (e.g. salmon). Some aquatic organisms also accumulate toxic compounds and can serve as indicators of contamination through biomagnification of the signal. Organisms also demonstrate physiological or morphological effects caused by the presence of anthropogenic emissions (*see* **Chapter 99, Water Quality Monitoring, Volume 1** and MHSPE (1995, vol 32))

Historical interest in water quality has been largely based on potential human health impacts and, even today, the presence of pathogenic organisms in water, including some bacteria, enteric viruses, and parasites, is a major concern. In many developing parts of the world, it is the only aspect of water quality to which resources are directed for monitoring and management. *Escherichia coli* (E. coli, a primary indicator of fecal contamination) and fecal coliform are usually found in low concentrations (10^0 to 10^3 counts per 100 ml) in the absence of human impacts, and therefore, are the most common indicators of fecal contamination. Fecal pathogens can cause a wide variety of intestinal diseases, many of which result in diarrhea; the

World Health Organization (WHO) considers them as the most important water-quality issue globally, particularly in the developing world. Once added to water by disposal of human excreta, particularly (by one to two orders of magnitude within 24 h) domestic sewage, coliform decay very rapidly at ambient temperature. In highly contaminated water, total coliform may exceed 10^5 or 10^6 coli 100 ml^{-1}. WHO recommends that water containing any *E. coli* should not be used for drinking (WHO, •2004). Also, a monthly geometric mean for *E. coli* of <130 coli 100 ml^{-1} is recommended for contact recreation, such as swimming and boating.

More recent human health concerns relate to the presence of naturally occurring planktonic organisms known as *cyanobacteria* or blue–green algae. These organisms thrive in highly eutrophic water bodies with limited water circulation, such as ditches, shallow lakes, and ponds and the surface layers of stratified lakes in the summer months. Some species produce toxins and release them into the water as the cells decay during the end-of-season collapse of the population. The toxins are hard to detect, but the presence of the species themselves can be used to signal caution that the water may not be of "good quality" for human as for domestic animals (Chorus and Bartram, 1999).

Water-quality issues can be assessed by specific variables (Table 1). Depending on the availability of human and financial resources, their monitoring can focus on first order variables or include also the second order variables. Simple to complex combinations of water-quality variables referred to as a *water-quality index*, are used to indicate the status of a freshwater body with respect to some particular problem or issue. For example, pH and alkalinity, a measure of the capacity of a water body to neutralize acid, are used to indicate the susceptibility of a water body to acidification, and various nutrient species and chlorophyll A concentrations are used to determine the tropic status of a water body. •Sodium and calcium are combined in a Sodium Adsorption Ratio, which is used in irrigation to assess the risk of salinization.

NATURAL RIVER WATER QUALITY: ORIGINS, PATHWAYS, AND CONTROLS OF RIVER CHEMISTRY

The natural origins and pathways of riverine materials are multiple and vary from headwaters to estuaries and are controlled by many physical, chemical, and biochemical processes (Figure 1). The fate of river-borne material eventually depends on the chemical composition of the dissolved or particulate phases, the source of the component, the hydrologic pathways, the transformation of the component or other interactions or reactions with materials

Table 1 Major water quality issues. Physical and chemical monitoring variables, their relevance to aquatic biota (0 to $+++$ scale), the origin of pressures, and limitations of uses (**bold**: very important)

Issues	1st priority variables	2nd priority variables	Aquatic Biota	Origins of stresses	Use limitations
Thermal pollution	Temperature[a]		$++$	**D, F, G_1, G_2**, Z	G, I
Salinization	Electrical conductivity[a]	Major ions	$++$	**B_3**, D, **K, X**, Z	A, **B_3**, C, D, I
Acidification	pH[a], Alkalinity	Major ions; DOC	$++$	**D, E, K**, G_2	C, **D, I**
Oxygen balance	Dissolved oxygen[a]	BOD, COD; DOC, POC	$+++$	**B_2, J, D**	**C**, D, H, **I**
Chemical contamination					**A**, B, **C**, D, H, **I**
NH_4^+	NH_4^+		$+$	**B_2, J**	
NO_3^-	NO_3^-			**B_3, J**	
Metals	Cd, Cu, Hg, Pb, Zn; Al	As, Cr, Ni, Se, Sb...	$++$	**D**, E, J, **K**	
POPs	total PCBs; total PAH	Individual compounds	$+$	**D, J**	
Pesticides	total pesticides	Individual compounds	$+$	**B**, J	
Endocrine disrupters		Individual compounds	$+$	**B_2, D, J**	
Microbial contamination	Total coli; *E. coli*	Streptococci...	0?	**B_2, J**	**A, B, C**, D, H, **I**
Eutrophication	Total P and N; chloro A	C, N, P, Si species, algal counts	$++$	**B, B_2**, D, I, **J**, W	C, E, G, **H, I**
Water-related diseases	Specific surveys (parasites, insects larvae...)			**B_2, J**, X, Y, W, Z	**A, C**, D, **H**
Habitat destruction	Specific surveys		$+++$	B, **E, F, G_3, J**, X	
Radionuclide contamination	Total α, β, γ activity	Individual radionuclides		**D, G**, J	**A, B, C**, D, **H, I**

[a]possible *in situ* and continuous measurement
Human activities: A = traditional agriculture and rural settlement, B = Intensive agriculture (B_1 = fertilized crops, B_2 = cattle feedlots, B_3 = irrigated agriculture), C = Drinking water, D = Industries (D_1 = nuclear industries), E = Transportation (ground, air, fluvial), F = Damming, G = Energy production (G_1 = nuclear power plant, G_2 = coal and fuel power plant, G_3 = hydropower), H = Recreation, I = Fisheries, J = Urbanization, K = Mining.
Global change: W = Biodiversity alteration, X = Hydrological balance, Y = Sea level rise, Z = Global warming.

during transport, the residence time and interaction of the various hydrological pathways resulting in mixing, and biogeochemical processes. Atmospheric deposition (Figure 1, #4) is an important source of Na^+, Cl^-, and SO_4^{2-}, originating from ocean aerosols (Figure 1, #1), with the highest deposition occurring closest to the source, and somewhat important sources of Ca^{2+}, Mg^{2+}, and SO_4^{2-}. Dust originates from Aeolian erosion (Figure 1, #3) and volcanism and terrestrial vegetation (Figure 1, #2). Decaying terrestrial and aquatic vegetation (Figure 1, #2), which previously fixed atmospheric CO_2 and N_2, are the main source of C and N species in surface waters. Soil leaching provides DOC and DON. Soil mechanical erosion delivers POC, PON, PP, and SS. Mineral weathering provides major ions and silica (Figure 1, #10) through different water pathways including groundwater inputs (Figure 1, #11); the highest streamwater concentrations are associated with the highest groundwater proportion in surface waters during the dry season. Saline deep aquifers and hydrothermal water can yield high concentrations of SO_4^{2-}, Cl^-, and K^+ in some volcanic and/or tectonically active regions, as in the East African Rift or in New Zealand (Figure 1, #12). Erosion or resuspension of particulates resulting from stream and riverbed incision also may be important.

The fate of SS in aquatic systems is characterized by a succession of deposition and remobilization within a river channel dependent on variations in the velocity of streamflow and through different filters that characterize the river system. The filters include hillslopes and wetlands located in headwaters (Figure 1, #5), lakes (Figure 1, #6), alluvial plains and related wetlands (Figure 1, #9), and estuaries. Each filter retains particulate matter and associated chemicals (PIC, POC, PN, PN, PP, and POPs), except during major floods when some of these materials may be remobilized. The in-stream/channel retention (erosion and deposition) of SS varies markedly between high and low flows and is highly variable during individual hydrological events. However, riverbed storage generally is not permanent on medium timescales ($2-10$ years), unless cementation occurs in the channel sediment (e.g. the Huang He river channel in China).

Several chemical and biochemical processes occurring in terrestrial vegetation, soils, and waterscape filters, such as wetlands, lakes, and reservoirs control major ions,
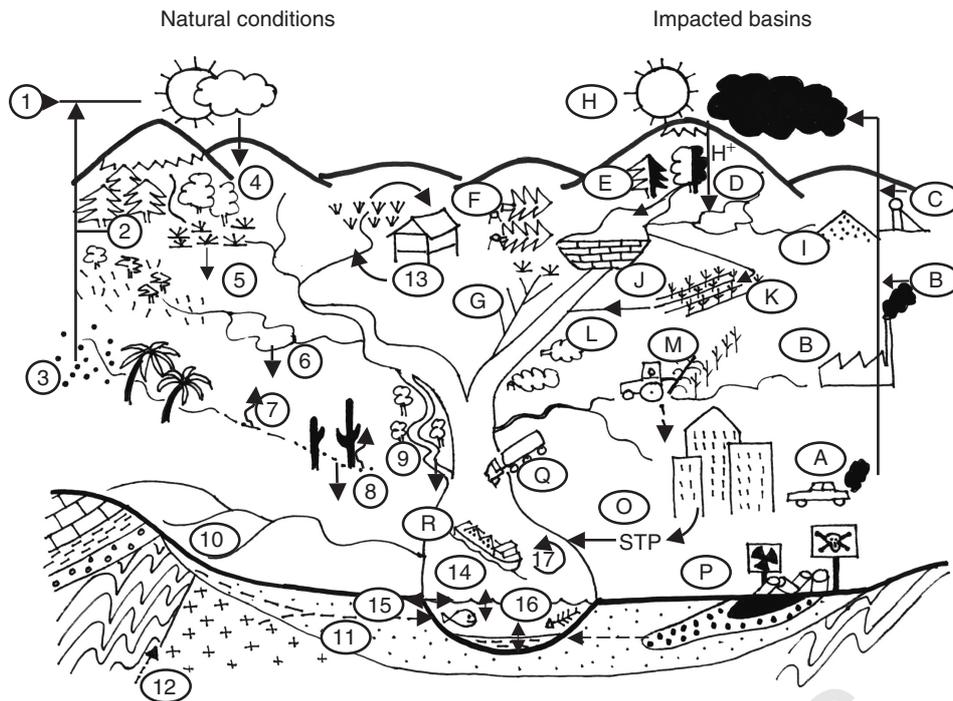
Figure 1 Sources, pathways, and main processes regulating water quality in natural conditions and impacted basins. Atmospheric fallout (4) originating from oceanic inputs (1), vegetation emissions (2), and Aeolian erosion (3); retention and transformation in wetlands (5) and lakes (6); evaporation leading to salinization (7) and precipitation in soils and endorheic basins (8); retention and exchange with floodplain (9); chemical weathering and mechanical erosion of various rock types (10); direct inputs of groundwater (11); hypothermal inputs (12); closed N, P cycles in traditional agriculture (13); exchange between surface waters and atmosphere (14), groundwater (15), and sediments (16); internal cycling of carbon and nutrients in aquatic food webs (17). Contaminated and/or acidified atmospheric deposition (D) due to urban and traffic (A); industrial sources and mining/smelting sources (C); forest die back (E) and forest cutting (F); wetland draining (G); climate change (H); mining (I) and industrial (B) wastewaters; river fragmentation through damming (J); enhanced evaporation after irrigation (K); use of fertilizers and pesticides in agriculture (K, M); river course channelization and floodplain isolation (L); release of treated and untreated urban sewage (O); leak of dangerous chemicals from waste dumps (P); accidental spills (Q) and chronic leaks (R); enhanced eutrophication (17)

nutrients, organic carbon, and particulates (Table 2). For a more detailed discussion of nutrient cycling in freshwater, see **Chapter 103, Nutrient Cycling, Volume 1**.

Evaporation concentrate solutes in surface waters (Figure 1, #7) and ultimately in dry and semiarid regions (e.g.Central Asia, Altiplans, Great Basin, and Lake Eyre Basin) causes the water to become saturated with respect to various minerals that precipitate typically in the order of calcite, magnesium calcite, gypsum, and anhydrite. The precipitated minerals occur in soils, floodplains, and depressions where water ponds after floods (Figure 1, #8).

Figure 1 In impacted basins, new sources and pathways of materials occur leading to accelerated fluxes and/or increased retention (e.g. in impoundments). Physical changes due to climate change and land use change are also important for water quality. These impacts are schematically described in Figure 1 (right part) and in Table 2, and fully developed in **Chapter 100, Acid Deposition: Sources and Effects, Volume 1**, **Chapter 101, Affects of Human Activities On Water Quantity and Quality, Volume 1** and **Chapter 102, Point and NonPoint Source Pollution, Volume 1**.

SPATIAL VARIABILITY OF MAJOR ION CONCENTRATIONS IN STREAMS AND RIVERS

Global Scale Variability of Water Chemistry

At the global scale under natural conditions, major ion concentrations of streams are regulated by chemical weathering for more than 90% of river basin area and for more than 90% of river water flow followed by atmospheric deposition and evaporation (Gibbs, 1970). In some highly dilute waters and for some constituents, the storage and cycling of elements by vegetation may be another important control on streamwater chemistry (Meybeck, 2003).

Table 2 Principal sources, sinks, and controls of main chemical descriptors of rivers under natural conditions. For an explanation of the numbers in column 1, see Figure 2

Figure 2 Schematic	Processes	SS	POC	H_4SiO_4	Ca^{2+} Mg^{2+}	Na^+	K^+	Cl^-	SO_4^{2-}	HCO_3^- (DIC)	TN	PO_4^{3-}	DOC	O_2
					Sources									
4	Atmospheric inputs	+			+	++	+	++	+		+			
2	Terrestrial vegetation uptake		+++							++	+++		+++	
5, 10	Soil (erosion, weathering, leaching)	+++	+++	+++	+++	++	++	+	++	+++	+++	+++	+++	
11	Groundwaters			++	+++	++	+		+	++		+		
12	Hydrothermal (1)			+		+	+	+	+					
18	River bed incision	++												
					Controls									
2, 5, 6, 9, 17	Biogeochemical cycles (2)	+	++	++	+				+	++	++	++	++	
8	Chemical precipitation			++	+++				++	+++				
16, 17	P/R balance in aquatic systems		+++										+++	+++
					Sinks									
5, 6, 8, 9	Particulate retention (permanent)	+++	+++									+		
16	River bed retention (short term)	+			+					+				
2	Terrestrial vegetation storage		+				+		+		+			
8	Soil storage (3)	+	+	+	+	+	+	+	+	+	+			

+ + +: essential process; ++ important in some occasions; + may occur. SS: suspended solids; POC and DOC: particulate and dissolved organic carbon.

Chemical weathering is controlled by soil mineralogy, rainfall amount, and partitioning into groundwater recharge and surface runoff, temperature, and terrestrial vegetation (Drever, 2003). The relative abundance of minerals in the soil and surficial rocks and their sensitivity to weathering are major factors controlling the composition of a basin's surface water.

Surface water can be further classified into nearly a dozen of principal chemical types on the basis of major ion concentrations (Meybeck, 2003). These include a few classes that are dominated by atmospheric deposition and evaporation/precipitation (Table 3).

Atmospheric deposition may affect river water quality. In the first 100 km of coastlines where rainfall is an important contributor to surface water, the ocean inputs of Na^+, Cl^-, Mg^{2+}, K^+, and SO_4^{2-} may be important and may even dominate relative to the contribution of chemical weathering. These constituents are present not only in rainfall, but in oceanic aerosols that accumulate on vegetation and land surfaces and are washed off by the rainfall. For some of these constituents (Na^+, Cl^-, Mg^{2+}), the primary source is almost always atmospheric deposition, particularly if the content in local rock types is negligible or low and, consequently, the concentration ratios among these constituents are similar to that of seawater (Table 3(b), The Cusson River).

Except in evaporitic sedimentary rocks, chlorine is generally very rare at the Earth's surface. Chloride ion (Cl^-), the dominant form of chlorine in surface water, is generally attributed to ocean-derived atmospheric deposition in the absence of human activity. In turn, the related ions can be determined on the basis of ionic ratios of the solute to Cl^-, as occurs in seawater (e.g. $Na^+/Cl^- = 0.88 \, eq \, eq^{-1}$). However, Cl^- is concentrated and contributed by many human activities and natural levels of Cl^- are often exceeded by anthropogenic inputs, as for Na^+, K^+, and SO_4^{2-}.

Table 3 Natural stream water chemistry. (A) common variations associated with bedrock type of moderately undisturbed basins in France, (B) uncommon controls from around the World (full references in Meybeck, 2003)

Basin bedrock type	H_4SiO_4 (mg l^{-1})	Σ^+ (μeq L^{-1})	Ca^{2+} (mg l^{-1})	Mg^{2+} (mg l^{-1})	Na^+ (mg l^{-1})	K^+ (mg l^{-1})	Cl^- (mg l^{-1})	SO_4^{2-} (mg l^{-1})	HCO_3^- (mg l^{-1})	Chemical type (eq L^{-1})
(a) Weathering dominance: examples on monolithologic basins										
Alkaline granites, gneiss, micaschists	8.4	130	0.4	0.2	1.9	0.3	0.0	1.9	5.5	Na^+–HCO_3^-
Quartz sands & sandstones	10.2	170	1.0	0.4	1.8	0.3	0.0	3.3	6.2	Na^+–HCO_3^-
Trachy-andesites	11.4	220	3.2	1.5	4.0	1.6	0.0	0.5	29.9	Na^+–Ca^{2+}–HCO_3^-
Calco-alkaline granites, gneiss, micaschists	6.0	300	3.2	0.9	1.2	0.5	0.0	2.2	15.5	Ca^{2+}–HCO_3^-
Arkose sands	12.0	400	3.8	1.7	1.1	0.8	0.0	3.8	19.5	Ca^{2+}–HCO_3^-
Shales	5.4	500	6.0	1.8	0.9	0.3	0.0	6.0	22.9	Ca^{2+}–HCO_3^-
Basalts	12.0	500	4.2	2.3	2.0	0.5	0.0	0.5	29.9	Ca^{2+}–Mg^{2+}–HCO_3^-
Serpentinite	13.6	1500	11.4	10.9	2.4	0.6	0.0	5.0	85.1	Mg^{2+}–HCO_3^-
Flyshs	3.0	2200	34.8	5.1	0.8	0.4	0.0	2.1	131.	Ca^{2+}–HCO_3^-
Marls	5.4	3000	49.9	5.1	1.7	0.6	0.0	2.9	179.	Ca^{2+}–HCO_3^-
Limestones	3.6	4500	85.7	1.6	0.6	0.7	0.0	5.4	267.	Ca^{2+}–HCO_3^-
Chalks	12.0	4500	85.7	1.4	2.3	0.9	0.0	5.4	267.	Ca^{2+}–HCO_3^-
Coal shists	9.0	5000	30.1	33.4	16.1	2.0	0.0	132.	137.	Mg^{2+}–SO_4^{2-}
Dolomite	4.0	5900	63.8	33.0	0.1	2.3	0.0	24.1	329.	Ca^{2+}–Mg^{2+}–HCO_3^-
Gypsum marl	9.6	22000	339.	58.8	1.0	1.7	0.0	878.	228.	Ca^{2+}–SO_4^{2-}
(b) Other chemical controls: atmospheric inputs, vegetation storage, evaporation, hydrothermalism										
Rio Negro tributary (1)	4.5	18.1	0.0	0.0	0.2	0.1	–	–	–	Na^+–DOC
Rivière de l'est (2)	22.4	1255	6.1	5.8	9.1	3.1	3.2	1.6	68.7	Mg^{2+}–HCO_3^-
Cusson (3)	15.1	1463	4.0	3.8	20.7	2.0	35.8	8.7	16.7	Na^+–Cl^-
Lufira (4)	18.6	3830	38.5	17.6	10.2	0.8	10.3	18.1	198.	Ca^{2+}–HCO_3^-
Semliki (5)	12.8	8736	11.2	38.4	79.5	60.0	45.2	97.9	330.	Na^+–HCO_3^-
Tedzhen (10)		13240	79.2	41.1	131.	6.7	144	223.	243.	Ca^{2+}–SO_4^{2-}
Saoura (6)	–	26150	122.	53.4	356.	7.2	582	348.	153.	Na^+–Cl^-
Redwater (7)	7.0	40700	87.	121.2	599.	9.6	14.4	1410.	663.	Na^+–SO_4^{2-}
Tokaanu (8)	286.	41600	120.	15.2	760.	50.6	1336	116.	88.8	Na^+–Cl^-
Salt (9)	1.2	312,000	606.	68.2	6340.	12.2	9924	1390.	190.	Na^+–Cl^-

(a) analyses corrected for rain inputs assuming Cl^- to be of oceanic fallout origin. (b) uncorrected analyses from various climatic zones and lithology: (1) pure quartz sand, Brasil; (2) basalt (La Réunion); (3) arkose sand with important oceanic fallout (Landes, France); (4) with limestone outcrops Congo basin; (5) outlet of Lake Edward, hydrothermal inputs (Uganda); (6) evaporated endorheic river (Morocco); (7) pyritic shales (Montana); (8) hydrothermal stream (New. Zealand); (9) draining salt deposits (N.W.T., Canada); and (10) Central Asia.

In basins where chemical weathering is very low (see Rio Negro tributaries, Table 3(b)), terrestrial vegetation is a major store and regulates the release of elements derived from atmospheric deposition, including Ca^{2+}, K^+, SO_4^{2-}, NO_3^-, NH_4^+, and Cl^-.

Examples of average chemical concentrations of streams draining monolithologic basins are given in Table 3(a) for 15 rock types from a set of 200 small temperate and relatively undisturbed basins in France. A second set of analyses is from heterogeneous lithologic basins (Table 3(b)). Differences in the solute concentrations among these rivers are primarily due to the bedrock composition except for H_4SiO_4, which increases with average annual temperature for a given rock type. Note that except for H_4SiO_4, the solute concentrations for the wet tropics such (e.g. Rivière de l'Est, basalt, La Réunion or Lufira, limestone, Congo basin) are very similar to those in the temperate regions for

the same rock type. For the Cusson River in the coastal French Landes (quartz and feldspar sand deposits), more than 80% of major ions are derived from the atmospheric deposition of ocean aerosols, and consequently, the Na^+ to Cl^- ratio (0.87 eq eq^{-1}) is approximately that of seawater (0.88). If the atmospheric deposition of marine-derived constituents (i.e. all Na^+, all Cl^-, most Mg^{2+}, and most SO_4^{2-}) were subtracted from the Cusson River analyses, the cation sum would decrease from 1463 μeq l^{-1} to 250–300 μeq l^{-1}.

Waters draining basins containing evaporite minerals, particularly halite (NaCl), are difficult to differentiate from waters subjected to high evaporation in arid and semiarid regions. Both can be extremely mineralized. For example, where rainfall greatly exceeds potential evaporation, the Salt River in northern Canada ($\Sigma^+ = 312$ meq l^{-1}) (Table 3(b), #9) and where evaporation exceeds rainfall

by about 10 times ($q = 14\,\mathrm{mm\,y^{-1}}$), the Saoura River (South Morocco, $\Sigma^+ = 26.1\,\mathrm{meq\,l^{-1}}$, Table 3(b), #6) and the Tedzhen, a river in Central Asia ($\Sigma^+ = 13.2\,\mathrm{meq\,l^{-1}}$, Table 3(b), #10).

The hydrothermal and/or deep-water discharge to surface water can effect surface water solute concentrations in some volcanic regions (e.g. Iceland, New Zealand, Japan, Kamchatka), active mountain building regions (e.g. Himalayas, Caucasus), and in rift zones (e.g., Semliki River of East Africa, Table 3(b), #5). H_4SiO_4 concentrations also can be very high (e.g. the Tokaanu in New Zealand, Table 3(b), #8).

Spatial Distribution of Water Chemistry within River Basins

The statistical analysis of mean chemistry at stations that are implicitly assumed to be independent from each other is a first step in many spatial analyses. Mapping of water chemistry is common for groundwater, but is more difficult for surface water within river basins because: (i) river water quality integrates the water quality of contributing waters upstream, that is, from the entire drainage basin, (ii) differences in the drainage area of each station reflects, to some extent, the residence time of water in the basin that,

in turn, a effects weathering-derived solute concentrations, and (iii) the upstream–downstream interdependency of nested stations.

For river basins with many water-quality monitoring stations, concentration distributions can be represented and compared using a probability scale. *Very common* concentrations are represented by concentrations between C_{25} and C_{75} percentiles, *common* concentrations between C_{10}–C_{25} and C_{75}–C_{90}, *uncommon* concentrations C_1–C_{10} and C_{90}–C_{99}, and *rare* concentrations between $C_{0.1}$–C_1 and C_{99}–$C_{99.9}$ (Meybeck, 1996). These qualifications apply to any basin scale and are useful for comparing results among regions. Examples of within-basin spatial distributions are shown in Figure 2 for SO_4^{2-} and pH for some regions in relatively undisturbed basins, from the very dilute central Amazon waters to the mineralized Mackenzie River basin.

Longitudinal and Transversal Profiles of River Chemistry

Most mapping is realized on major stream orders through longitudinal profiles by simple interpolation between stations, particularly on the river main stem, such as for the Mississippi River (Meade, 1995). In river basins that are heterogeneous with respect to climate or lithology, water
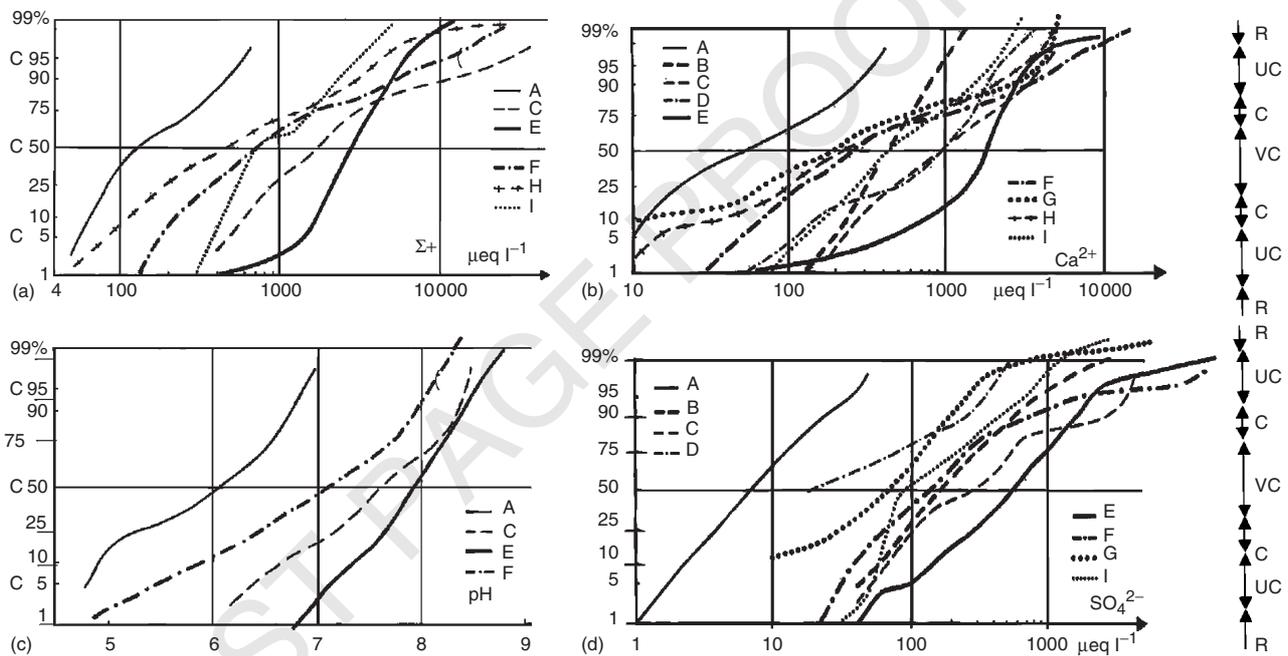

Figure 2 Cumulative distribution of ion chemistry in rivers from selected relatively undisturbed regions. (a) cation sum Σ^+ (μeq L^{-1}); (b) Ca^{2+} (μeq L^{-1}); (c) pH; (d) SO_4^{2-} (μeqL^{-1}). A: central and lower Amazon ($n = 40$); B: Japan ($n = 225$); C: Andean tributaries of Amazon ($n = 42$); D: Thailand ($n = 31$); E Mackenzie river basin ($n = 100$); F monolithologic French streams ($n = 250$); G "temperate" stream model; H: Monolithologic miscellaneous streams ($n = 75$); I: major world rivers ($n = 60$). For distributions of K^+, Na^+, HCO_3^-, and SiO_2: see Meybeck (1994). For more detailed information about the individual data series, see Meybeck, 2003 and Meybeck and Ragu, 1996 and references therein. VC = "Very common" concentrations: between 25% and 75% of distributions; C = "common": 10 to 25% and 75 to 90%; UC = "uncommon": 1 to 10 % and 90% to 99%; R = "rare": 0.1 to 1% and 99% to 99.9%

quality can vary longitudinally, and, occasionally, across the river section as a result of poor mixing of tributary flow into the river.

For example, the TDS of the Arkansas River, a major tributary of the Mississippi River varies longitudinally (Stoner, 1984). The river headwaters in Colorado are somewhat mineralized with an average TDS of $273 \, \text{mg} \, \text{l}^{-1}$. Downstream in Kansas, TDS increases to $3670 \, \text{mg} \, \text{l}^{-1}$, then decreases to $880–1100 \, \text{mg} \, \text{l}^{-1}$ in Oklahoma and increases again to $3000 \, \text{mg} \, \text{l}^{-1}$ in Arkansas. During low flow at some stations, TDS and Cl^- may exceed $35\,000$ and $250 \, \text{mg} \, \text{l}^{-1}$ (the drinking water limit) respectively. The cause of the salinity variations is mostly natural due to drainage of underlying Permian salt deposits, common in this basin but rarely found at the global scale, but evaporation in reservoirs also may be important.

Under certain conditions, river water quality varies laterally across the river section, such as downstream of confluences where the water quality of each stream differs markedly. Two examples have been particularly well described: (i) in Brazil, the confluence of the Rio Negro "Black water" (organic rich, extremely dilute; Table 3(b), #1) with the Rio Solimoes "White waters" (sediment rich, dilute) that forms the Amazon River downstream of Manaus; (ii) in Canada, the triple confluence of the Upper St Lawrence River (i.e. the Lake Ontario outlet) that is depleted in DOC and is medium dilute, the Ottawa River that is organic rich and dilute, streams draining the southern Laurentian Mountains, that have high SS and are medium dilute (Centre Saint Laurent, 1996). In each case, complete mixing does not occur until hundreds of kilometers downstream of the confluence despite very high-stream velocity ($>1 \, \text{m} \, \text{s}^{-1}$).

In basins impacted by human activities, the spatial distribution of water quality is generally more variable and is often affected by stepwise degradation of the aquatic habitat, downstream of point discharges of pollutants, downstream of nonpoint or diffuse sources of pollutants atmospheric deposition, and mobilization of the agrochemicals applied to fields, or as a result of water engineering (e.g. dams, diversions, irrigation returns).

TEMPORAL VARIATIONS OF RIVER WATER QUALITY

Temporal variations in river systems are specific for each water-quality variable and provide important information on the origins, pathways, and controls of that variable, particularly when evaluated with respect to changes in climate, hydrology, and land use or human activities in the basin. The variations range from sub-daily to secular. Although some patterns are associated with major changes either due to climate or human activities, frequently periodic patterns occur within each year associated with seasonality for

which the cycles are called "*regimes*", and daily, called *diurnal* (24 h) and *nychtemeral* cycles; *nychtemeral* cycles are more specifically linked to the alternating light conditions from day and night that controls aquatic primary production. In most rivers, important water-quality variations are observed during floods due to the mixing of surface runoff, subsurface runoff, and groundwater discharge – for streams – and/or, for the large and heterogeneous basins, due to the mixing of major tributaries. In impacted basins during high water stages, point sources of contaminants are diluted, whereas soil erosion (e.g. TP) and leaching (e.g. NO_3^-) may result in higher concentrations. Initial steps in analyzing streamwater concentration variations include assessing the concentration relation with discharge and evaluating concentrations patterns during individual floods.

Long-term (>10 years), fixed-interval (weekly to bimonthly) monitoring provides information for assessing seasonal variations of river water quality. Several types of seasonal chemical regimes have been described from these data including (i) the influence of seasonal river flow regime; (ii) seasonal biogeochemical cycles; and (iii) seasonal anthropogenic affects from various types of human activities, such as reservoir operation, agriculture, forestry, mining, industry, and tourism. At least 10 years of water-quality indicators are needed to detect trends from interannual variations by appropriate statistical tests (Peters, 1996 and Hooper and Kelly, 2001). The trends of riverine concentrations are generally linked to the magnitude of human activities and related implementation of waste management and pollution abatements.

Concentrations Variations with River Discharge

Constituent concentrations (C_i) typically vary with water discharge (Q). The use of specific discharge q ($\text{l s}^{-1} \, \text{km}^{-2}$) also allows for the easy comparisons of stations with very different basin size; normalizing q to long-term average q and concentrations C to median values C_{50} aids the comparison of different chemical variables from trace elements to major constituents (Figure 3). Most major ions and dissolved silica concentrations are higher in groundwater than in soil water or surface water due to a longer residence time of the groundwater that provides more time for concentrations to increase as a result of weathering. For streams where the source of these constituents is primarily groundwater, concentrations moderately decrease (partial dilution) with increasing discharge (Figure 3, #A). Near-perfect dilution (i.e. a quasi-constant flux) (Figure 3, #B) occurs downstream of point sources, such as saline springs and wastewater outfalls (e.g. NH_4^+, PO_4^{3-}). Clockwise hysteresis (concentrations increase more rapidly with increasing discharge on the rising limb of a storm hydrograph than decrease during recession) often occurs for DOC concentrations (Figure 3, #C1) because of rapid leaching or flushing and subsequent depletion of the DOC from the

upper soil layers during stormflow. SS concentrations in lowland basins typically show the same pattern because of the scouring of previously deposited channel sediment (Figure 3, #C_2). In contrast, in mountainous regions on a double logarithmic scale, the SS concentration is often linearly related to discharge (Figure 3, #D). Most particulate nutrients, pollutants, and metals, follow patterns of C_2 or D. POC, expressed in percent of SS, typically decreases with increasing SS in most rivers, but the concentrations as mg l^{-1} increase moderately (Figure 3, #E) with regards to the SS pattern.

A few other patterns occur including: (i) apparent plateau at high flows (Figure 3, #F) resulting from seasonal nutrient uptake at lake outlets or stream denitrification of NO_3^- at summer low flows, a common pattern in some western European rivers; (ii) a dilution/resuspension pattern (Figure 3, #G) occurs for TP concentrations downstream of urban wastewater outfalls; the dilution of urban sewage PO_4^{3-} is followed by a resuspension of P-rich sediment, an example of the inverted behavior for two chemical species that are often analyzed together in unfiltered samples; (iii) a dilution/hysteresis pattern (Figure 3, #H), either clockwise or counterclockwise occurs in heterogeneous basins because of the different timing of tributary discharges to a river; they are often associated with variable concentrations because of basin heterogeneity, some combination of processes, or processes yet to be identified; (iv) near constant concentrations (Figure 3, #I) can be observed in groundwater dominated streams and are also observed for Cl$^-$ when derived primarily from atmospheric deposition; and (v) temporally, sometimes seasonally, variable rare patterns with maximum or minimum concentrations ●lagging some main climatic or hydrologic event.

Q7

Common and Rare Events

Water quality can change rapidly under natural conditions. Some variations are systematic and may occur each year. For example, during snow melt in the northeastern United States and in Scandinavia, acid anions (NO_3^-, SO_4^{2-}) and H$^+$ ion increase in streamwater resulting in episodic stream acidification, which has adverse affects on biota, such as macroinvertebrates and fish (*see* **Chapter 100, Acid Deposition: Sources and Effects, Volume 1**). Other natural accidental events, including extreme droughts, hurricanes, monsoons, landslides, forest fires, and volcanic eruptions can result in major changes in water quality, with concentration variations at least one order of magnitude higher than under normal conditions. These events typically are rare on the human timescale (>100 year return period), and are generally not captured during routine surveys. The duration of rare events may be short, but their impact on water quality may be enormous and last for (forest fires)hundreds of years. After the mount St Helen eruption (Oregon, USA), the local river TSS concentrations and yields increased by two orders of magnitude and the sediment discharged by the Columbia River increased from 10 to 40 Mt y^{-1} in the years after the eruption, although most of the sediment (140 Mt) remained in the Cowlitz River, a Columbia River tributary (Meade and Parker, 1985).
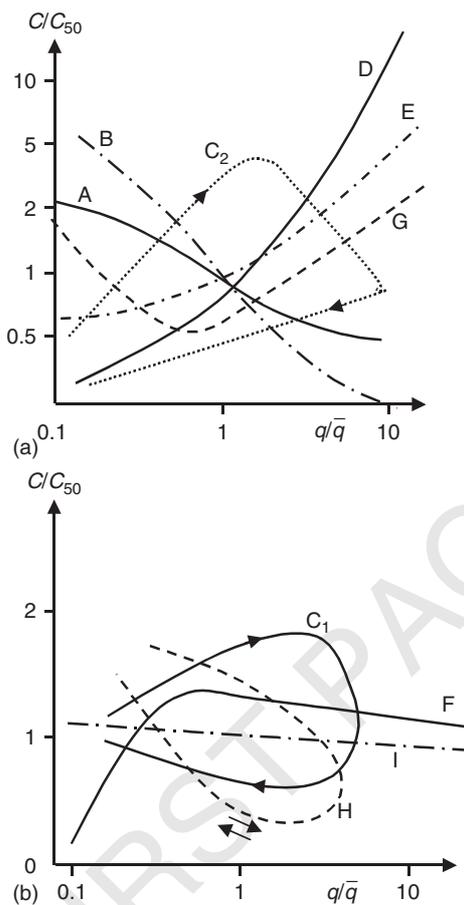
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Water-quality Trends and Interannual Variations

Year-to-year or interannual variations of water quality are caused by climatic and related hydrological variations (e.g. water discharge for rivers) and by changes of human activities in river basins. During wet years, material derived from point sources are diluted more than during dry years, and major ions, NH_4^+ or PO_4^{3-} concentrations are generally lower (Figure 3, dilution patterns #A, B, H). In contrast, average concentrations of particulate-bound components (Figure 3, patterns #C_1, C_2, D, E, and G) are much higher than during dry years. Particulate-bound components include POPs and total (unfiltered water) metal

Figure 3 Concentration patterns (C. normalized to median concentrations, C_{50}) with respect to specific discharges (q, normalized to the annual average q). A, B: dilution; C_2, D, E: soil erosion and leaching; F, G: complex variations; C_1, C_2, H: hysteresis cycles; and I: constant

concentrations, POC, and TP. Interannual variations of eutrophication indicators such as total pigment, chlorophyll A, and daily cycles of pH and DO are caused by insulation and water temperature variations.

RIVERINE FLUXES

The mass output (or flux) from a given upstream basin is used to evaluate material balances (outputs minus inputs), and more recently, to assess the status of degradation or improvement of stream reaches to assist land and water resources managers. For example, water-quality standards in the United States have targeted the total maximum daily load (TMDL) of contaminants for stream reaches (US EPA, 2004).

A mass flux (F, mass per time) combines concentration (C, mass per volume) of a solute, solid, or compound with discharge or streamflow (Q, volume per time). The mass flux is commonly determined for major ions, suspended matter (SPM), toxic substances, nutrients, carbon species, and organic matter, and several commonly used synthetic organic compounds, such as PAHs, PCBs, herbicides, and pesticides. The flux typically is determined at stream-gauging stations at which streamflow is continuously monitored because the computation requires discharge, and sometimes the use of specific sampling instrumentation and at higher frequencies than available from synoptic or routine manual sampling. Theoretically, F should be derived from the continuous measurements between t_1 and t_2 of both Q and C of the targeted dissolved or particulate constituent (i):

$$F_i(t) = \int_{t_1}^{t_2} C_i(t) Q(t) \, dt \qquad (1)$$

Because C_i is rarely continuously measured or estimated (e.g. through a relation with a surrogate variable that is continuously measured like electrical conductivity), it is necessary to rely on a set of discrete water-quality (chemistry) analyses obtained from n fixed samples taken at time t_j coupled with continuous Q data, sometimes only with discrete Q_j measured during the water-quality sampling. Different approaches to flux calculation can be used and many of them incorporate concentration–discharge relationships (Phillips *et al.*, 1999).

CONCLUSION

During the last 150 years, measurement of water quality has evolved from few physical and chemical determinations to the analysis of the concentrations of hundreds of chemical compounds conducted in many types of media from dissolved to various particulate phases and to the consideration of aquatic biota and habitat. Also, while water quality

is still considered a "subjective standard for human usage" for drinking water and multiple other uses, such as agriculture and industry, it is increasingly complemented by *aquatic environmental quality* that aims to be an "objective attribute for classification" (Boon and Howell, ●1997).   Q8

Under natural conditions, water quality can vary markedly in time and space with most chemical descriptors varying by more than 1–2 orders of magnitude. In addition, human activities can markedly affect spatial and temporal variations of water quality, that is, chemical concentrations, the nature of the habitat, and modification of the aquatic communities. Metrics of water quality and reference scales also are evolving rapidly reflecting human and water relations at a given location and time for a given culture, even if some water-quality criteria (e.g. drinking water) are now universally used.

The continuous developments of our scientific and technical knowledge on water quality and of new issues and the growing linkage between water quality and social sciences (e.g. predictive models of carbon and nutrients for the twenty-first century combining Global Change and local pressures scenarios) have transformed water-quality studies into an autonomous multidisciplinary hydroscience.

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Q10

Q11

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Q2. We have rephrased "is attributed to the intricate relation among the human and ecosystem" as "is attributed to the intricate relation among humans and the ecosystem". Please clarify if it retains the intended meaning.

Q3. This reference has not been listed in the reference list. Please provide the reference details.

Q4. Please confirm if this abbreviation needs to be spelt out. If yes, please provide the expansion.

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Q7. There seems to be some text missing after "lagging". Please clarify.

Q8. This reference has not been listed in the reference list. Please provide the reference details.

Q9. This reference has been moved to Further Reading as it has not been cited in text. Please confirm if this is fine.

Q10. Please provide the editors' name for this reference.

Q11. Please list out the all editors' name for this reference.