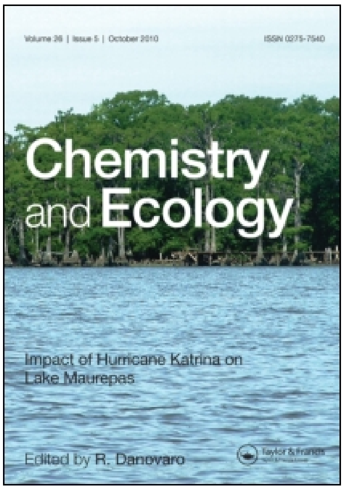

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Aquatic Chemistry and the Human Environment

R. JOHNSTON
(present address, 24 Hilton Drive, Aberdeen, Scotland).

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The evident physical continuity in the cycles of water in air, soil, lake, river, estuary and sea is difficult to describe accurately; there is also a chemical continuity that is impossibly complex in detail but has unifying principles that need to be explored. Amid current somewhat myopic concern about the effects of certain toxic metals in the environment specifically in relation to man it is appropriate to reflect on the wider issues of aquatic chemistry that affect the human environment. These issues embrace the aquatic chemistry of the countryside and the health of the population and reciprocally the impingement of human activities on the aquatic realm. If one can demonstrate a coherent core of chemical principles there may also be an implied need for more enlightened co-ordination in the study of aquatic chemistry, its applications and developments. At present, fundamental chemistry, water and wastewater technologies, environmental chemistry and epidemiology are discrete provinces of aquatic science. Insularity is even more serious in professional affiliations and consequently job qualifications; also among the central, local and industrial bodies who establish legislation and set and administer standards for water.

Benefits of greater collaboration and co-ordination would reach not only scientists, learned institutions, managers and the general public here but would also lead to much more effective understanding and practical help in other lands where water supply and water-related problems are enormously more acute.

INTRODUCTION

Since the first half of this century scientists have striven to establish a sound general understanding of the cycles of the chemical elements in air, precipitation, soil, lakes, rivers, estuaries and the sea. Recently under increasing governmental pressure, many of these scientists of every calling have been re-directed to work on selected *ad hoc* problems related to pollution which have been promoted to the general community as of greater and more immediate concern. Weakened support for major programmes of fundamental value to the general public is seldom mentioned.

Given the chemical principles which govern the fate of elements and compounds in the aquatic environment how far are these basic principles applicable to less generalised realms of water, aquatic pollution and to pollution control and regulation. Moreover are these principles helpful regarding aspects of the aquatic environment germaine to human welfare?

Two lines of approach might be considered (a) the orderly study and development of specific chemical processes in the various water systems and (b) the discussion of these processes as they dominate in waters from upland catchment area to the ocean. Stumm and Morgan (1981) developed the first approach in their book but not specifically in relation to mankind, the second option has been attempted here on a much more tentative and exploratory scale for some of the major interrelationships.

CORE ISSUES IN AQUATIC CHEMISTRY

Water in upland catchment areas

In relatively undisturbed upland areas, water characteristics are determined primarily by geological criteria modulated by biological factors, in particular the dominant herbage or tree cover. For specific cases powerful local geological features can make generalisations unrealistic but, for the major continental areas, the major chemical elements in water (Si, Ca, Mg, Na, K, Fe, Al, S, Cl and C in inorganic form) are all determined by the mineral composition of the rocks in at least 95% of the world's river flow (Meybeck, 1981). The relative proportions of these elements are primarily associated with the content of Si and K which are always present in rocks and sediments. These major ion characteristics are subsequently modified, sometimes substantially, by contact with calcium-rich minerals which are of common occurrence. Much less common are the soluble evaporite minerals (halite, gypsum, anhydrite) which when present can contribute major ions in substantial concentrations.

By comparison with these geological factors natural vegetation (itself subject to these governing forces) has little effect on the major ions.

However, major changes in vegetation, for example caused by afforestation or clearance, can greatly affect the influx of suspended particulate matter and thereby elements readily mobilised by this process. Additionally, suspended solids affect the course of river systems, their flora and fauna in a great many ways. Vegetation generates much organic matter which significantly modifies the mode of occurrence of trace metals and nutrients.

In developed countries the original river systems have long since been replaced by successive imposed biotic and abiotic regimes. Elsewhere, intensive land and forest exploitation over large virgin areas is currently creating an alarming scale of disturbance of land and of pristine lake and river systems. Among the causes of important changes of natural flow of rivers, lakes, waterways and wetlands over many years are diversions, control of flow, dredging, abstraction of water supplies for domestic or industrial purposes, improvement of access, and provisions for water transport. These changes in turn affect the residence time of water, sediment distribution, sediment quality and locally alter flora and fauna. Where irrigation is practised, increased amounts of salts and nutrients are passed on to the river system. In developed countries such changes are so familiar that they are often not noticed and it is only introduced treated or untreated polluting discharges that register any disturbing awareness in most people.

While man might hope to rehabilitate freshwater and estuary it would be foolhardy to manage pollution in hope of hereafter rejuvenating the sea.

Rain water chemistry

Precipitation provides an input of a great many substances in gaseous, soluble or particulate form to the land and the sea. Atmospheric input is much higher in some areas than others; its quality reflecting such factors as industrial and domestic emissions, sea spray, volcanoes, and dust from vast areas of sparsely vegetated desert. Broadly speaking the "crustal elements" (Al, Fe, Mn and the major elements) are associated with coarser dust particles which are subject to on-going natural processes of recycling and slow redistribution. Disturbances such as dust storms from agricultural unbalance can be locally important. The "volatile elements" such as Cd, Pb, Zn, Hg are borne on or are much smaller particles and have association with high temperature origins such as volcanoes and to an increasing extent industrial and domestic inputs.

Industrial transport of metals and minerals, their processing and use, add novel forces to their natural redistribution or recycling processes by air and water. Major repercussions affecting the human environment are the creation of incomparably higher local concentrations of normally trace elements in the domestic habitat, in work areas, in waters and in discharges to them.

The feature described as "acid rain" is alas widely distributed and is becoming more and more strongly linked with extensive damage to or destruction of forests, freshwater fishes, lichens and possibly other members of the biosphere. The suspected dominant cause of acid rain is SO_2 and other acid gases primarily from electricity generating plant fuelled by coal or oil (and to a small extent peat, wood and similar fuels) and to a lesser extent refinery gases, the burning of crop residues, the incineration of town wastes, for example. Excessively high levels of SO_2 in the air, especially when enhanced by climatic conditions, causes severe, sometimes fatal, respiratory problems among humans or at least vulnerable individuals.

It has been estimated that approximately 40% of the total sulphur content of the average river water in developed countries is attributable to the combustion of fossil fuels, exposure of mining wastes, irrigation, agriculture and other activities to a lesser degree. Virtual total removal of sulphur from fuels is technically possible but is only seriously practised in a few countries with sensitive upland areas.

Those who would contend that coniferous trees are to blame for "acid rain conditions" might ponder on the findings of Malaspino College, Nanaimo, B.C. (Hartman, 1982) which demonstrate a highly favourable effect on biomass and fishes of large coniferous debris (up to the size of a whole tree) which has fallen into streams and rivers.

Sensitivity to acid rain is less due to the presence of sulphur acids and nitrogen acids than it is to the increased hydrogen ion concentration which vulnerable hard rock terrains and acid catchments do not have the capacity to neutralise. Lowered pH leads to the mobilisation of aluminium hydrous oxides and the release of metallic ions.

Changes in the soil matrix lead to the reduction or expunging of cation exchange capacity and the disturbance of the intricate hydration processes in complex silicates and secondary minerals. At the same time there is progressive inhibition of plant growth and the accelerating trend is marked by serious damage to lichens, wild flowers and forest trees.

In the aquatic realm, similar chemical events take place in water and sediment leading to reduction in phytoplankton, normal fauna and, in turn, fish species. A sore point of dispute arises when excessive acid emission in one country or continent has its repercussions in another which possesses a less resilient geological and biological environment.

The chemistry of soil-water

There are many intricate and interrelated abiotic and biotic processes in soil. These processes control and modulate the nature of the surficial inorganic substrate, soil-water composition, water flow, microbial, plant and animal populations and their demands, activities and products.

Among readily quantifiable characteristics of soils and thus of soil-water is the capacity for exchange of cations which for sandy soils, loam and clay is typically about 2, 12 and 30 milli-equivalents per 100g respectively. Soil and sediment matrices can be very heterogeneous and ion exchange capacities are derived both from inorganic and organic components. Frequently these components are amphoteric covering a wide range of negative and positive charges and possessing from very low to very significant exchange capacity. Anion exchange capacity relates primarily to PO_4^{3-}, SO_4^{2-} and NO_3^-. This is less than cation exchange capacity and has negligible effect when the pH falls below about 6. In addition, there is specific adsorption of polyvalent anions including PO_4^{3-} on clay minerals, hydrated oxides of iron, manganese and other metals. The net surface charge on soil particles, the balance of components and of adsorbed substances and the stability of organic chelates can all be greatly altered by change of pH. Some degree of seasonal pH change arises from cycles of rainfall and growth, for example, but much greater fluctuations and significant permanent change, follows seasonal cropping, tilling, change of land cover and rock exposure, use of total herbicides for example. Change as it affects living organisms is mediated through water.

In greater chemical detail the hydrous oxides of Si, Al and Fe on the inter-lamellae and surfaces of layer silicates (e.g. vermiculite) and mixed hydrous oxide coatings or co-gels bear negative charges that are not only dependent on soil-water pH but also reflect soil condition. It is thought that organic matter bearing carboxyl, phenolic carboxyl, enolic hydroxyl and some kinds of alcohol hydroxyl groups go to make up the predominant organic groupings associated with cation exchange. The groupings may be dominated by Al and Fe hydroxy ions carrying a considerable negative charge.

Positive charges are attributed to other hydrous oxides and hydroxides of Al, Fe and Mn, to exposed crystal edges of clay minerals and to organic matter bearing N-groups especially in very acid soils. Adsorption of weak inorganic acids and to some extent SO_4^{2-} and F^- is also reported.

Natural and accelerated weathering processes give rise to enhanced levels of Na^+, K^+, Ca^{2+}, Mg^{2+} and HCO_3^- as the dominant ions passing into soil-water, with carbonic acid another major factor. Where anaerobic conditions exist or are created, a number of very important changes ensue, in particular the conversion of NO_3^- to NH_3^+ and SO_4^{2-} to S° and H_2S caused by soil bacteria in presence of biologically available organic matter. In turn Fe^{3+} and Mn^{4+} are reduced or, along with many other metals, converted to insoluble sulphides.

Agriculture and aquatic chemistry

Everything said about the upland areas applies also to areas in regular cultivation. Plant cover and crops have less effect on soil structure and associated water chemistry than mechanical cultivation and irrigation, application of soil conditioners, fertilizers and biocides, harvesting and drainage. The overall extent of change is best understood for common cereal and root crops. Calcium and forms of nitrogen (mainly NO_3) are often enhanced in drainage water. Usually inorganic and complex organic phosphates are strongly held in the soil though a small proportion of simpler organic phosphates may escape. Farming of livestock on open pastures accelerates turnover and loss of N and P especially when the animals are housed at night. Notable losses occur during storage and disposal of manure and slurry. Nutrients are also lost in uncontrolled discharges of silage liquids.

Typical annual rates of loss of nitrate for established British farm areas are 5 $kgha^{-1}N$ for grass, 30 $kgha^{-1}N$ for clover and between 20 and 80 $kgha^{-1}N$ for pasture carrying dairy cattle, high values go with increased grazing density, (Gasser, 1980). As a rough guide, loss of phosphate is in the region of 1/100 of these rates but varies greatly with soil type. With good agricultural housekeeping, a large proportion of the increased fertility is retained in the soil since almost all animal waste matter, silage liquor (if any), straw and other vegetable litter is recycled.

Very large experimental application of fertilizer to grass generated as much as 60 $mgl^{-1}NO_3$—N in drainage water and much higher concentrations from excessive treatments with slurry or sewage sludge. The WHO drinking water upper limit is 11.3 $mg\,l^{-1}$ NO_3—N. Luxurious vegetation in drainage ditches and streams, buffers but does not prevent the transfer of these nutrients to rivers and lakes.

Minor and trace elements in water

In the sense of quantifying and predicting the progress of minor and trace metals from rock, sediment and soil into drainage water and thence to the sea, it is honest to confess as Edmond (1981) does that "Almost nothing is known about this topic". Minor and trace elements in this context are those whose crustal abundance is on average less than 100 $\mu g\,g^{-1}$.

Some general guidelines can be assembled for the expected occurrence of minor and trace elements above atomic number 26 (Fe) in various useful groupings. Hard and soft waters are readily recognisable in everyday life and these display different chemical features (Hamilton, 1979):

hard waters are rich in Ba, Br, B, Ca, F, I, Mg, Ni, Si, Hg, Sr
soft waters are rich in Al, As, Cu, Fe, Mn, Pb, K, Rb, Sc, Sn

These features imparted by the upland mineralogy are passed on to the raw waters of the catchment areas and to some extent to the drinking waters derived from them.

Waters affected by massive metalliferous ore bodies, by exploitation of these and by acid mine waters are regarded as atypical of the general issues; sometimes the evident environmental damage affecting aquatic life and man can be severe.

Freshwater and the sea

The nominal residence time of many elements has been derived from concentrations in river water and in the sea; overall these times provide some broad indications of the extent of conservative behaviour. Seawater composition does not directly reflect global river-water composition.

Major constituents have a remarkably consistent occurrence in sea salt and this is reflected in their long residence time (Stumm and Morgan, 1981; Brewer, 1975). Minor and trace elements limited by freshwater × sea-water interactions and by biological utilisation and cycling are marked by much shorter residence times. As yet these chemical equilibria (primarily located in estuaries), water × sediment interactions and seasonal and biological cycles governing for example utilisation, settlement, mineralisation and mixing are not adequately quantified for useful modelling. Residence times are therefore a gross overall measure of these processes and do not by themselves identify metals that are "toxic but largely removed from water by sedimentation processes" and those that are "toxic and biologically cycled".

The aquatic chemistry of metals and its relevance to man

Financial pressures and research curbs have assigned to a small group of metallic elements almost exclusive importance in research on food crops, herbage, cattle, fish and man.

Very recently Bryan (1984) has written a major chapter on marine pollution due to heavy metals and their compounds. This includes quantitative assessments of sources and inputs and an outline of the fate and the effects of heavy metals on man and marine life. Acknowledging that the major elements are not enhanced or enhanced to only a modest degree in living tissues, some 70 minor and trace elements are markedly or impressively enhanced and in this group essential elements greatly outnumber those exclusively toxic. Less study is made of intake of demonstrably useful elements than of the few potentially noxious ones.

Minor element deficiencies are important factors affecting common crop plants (e.g. Fe, Cr, P, Zn, Mo); cattle, sheep and other farm animals (e.g. Co, Se, Zn) and man (e.g. Fe, Ca, I, Zn) ranging from minor to serious and even fatal effect. In the same way these and all other elements can have deleterious effects of varying degree when taken up at high concentrations. It is difficult to produce hard and fast rulings on essentiality to man (Table I) or place these elements within narrow chemical classifications on this basis alone. Whether "essential" or not the human body contains a great number of elements, for example the list (Table II) of elements (plus H, C, O, N, Na, Mg, P, Cl, Ca) detected or measured in the enamel of healthy teeth from individuals selected from 32 zones of 17 states of America (Losee *et al.*, 1973). This list is deemed capable of expansion as analytical methods become more sensitive. Apart from Pb no element of Atomic Number greater than 60 was detected.

Whereas dental enamel is a durable tissue, blood represents tissue with a rapid turnover. The important elements in blood include some with remarkable enrichment (Fe, K, S) and others show little or no

TABLE I
Groups of chemical elements and current assessment of essentiality to the human body

	Essential	Probable	Possible	Suspect	Toxic (No known need)
Classification	1	2	3	4	5
Group I	H				
	Na			Li	Li
	K = Rb*				
	Cs			Ag	Ag
Group II					Be
	Mg				
	Ca = Sr*				Ba
					Heavy radionuclides
					Transuranium series
	Zn = Cd*		Cd		Hg, Cd
Group III	B			B	Tl
Group IV	C				
	Si = Ge*	Si			
	Sn		Sn		Pb
Group V	N		As		As
	P				Sb
	V	V			Bi
Group VI	O				
	S = Se				
	Cr				
	Mo				
Group VII	F				
	Cl				Br
	Mn				
	I				
Transition Group	Fe				
	Co = Ni	Ni			Ni

1. Based on Hamilton 1979, (Fe added); Hopps, 1980.
2,3,4. Based on Hopps, 1980.
5. Toxic elements (Hamilton, 1979).
e.g. K = Rb* associated transport into the body, minor element not essential.
e.g. S = Se associated transport into the body, both elements essential.
(Elements of uncertain essentiality or toxicity or not appraised include the inert gases, Cs, Au, Pt group, Al = Sc, Y = La = rare earths, Ga, In, Tl, Ti, Zr = Hf, Th, Nb = Ta, Pa, W, U, Te, Po, Tc, Re, At)

enhancement (Ba, Cd, Mo, Sr, Nb, Al, Li), (Table II).

Physical chemists have classified the chemical elements as "hard" and "soft" *in relation to their fundamental characteristics in the aquatic realm*; in broad terms, elements that occur predominantly as free ions and those that are completely hydrated. Further, cations are termed

TABLE II

Chemical elements in U.K. examples of hard and soft freshwater; blood in associated human populations; tooth enamel (U.S.A. states); arranged in groups according to speciation in freshwater (pH 6) after Whitfield *et al.* (1981); also EEC raw and drinking water standards

Form of element (a) cation	Hard* water $\mu g\,l^{-1}$	Soft* water $\mu g\,l^{-1}$	Blood* (H.W.) $\mu g\,ml^{-1}$	Blood* (S.W.) $\mu g\,ml^{-1}$	Tooth enamel $\mu g\,g^{-1}$	All $\mu g\,l^{-1}$	DMAC $\mu g\,l^{-1}$
Al^{3+}	700	31000	0.2	0.2	14.0		200
Ba^{2+}	1700	67	0.07	0.1	5.6		(100)
Be^{2+}					0.090		
Ca^{2+}	154000	15000	54	54	high		(100000)
Cr^{3+}	17	21	0.2	0.2	2.30	50	50
Cs	0.1		0.03	0.03	0.040		
$Fe^{3+}(+Fe^{2+})$	540	210	497	501	8.0	300	200
Ga^{3+}	0.05	0.2			<0.02		
Hf^{4+}					<0.08		
In^{3+}					n.det		
K^{+}	2620	6720	1900	1900	458		12000
La^{3+}	0.1				0.004		
Li^{+}	21	0.9	0.006	0.002	1.60		
Lu^{3+}					<0.02		
Mg^{2+}	5000	500	59	98	major		50000
Na^{+}	7000	5000	major	major	0.31		175000
Rb^{+}	3	2	2.7	2.8	0.41		
Sc^{3+}					<0.10		
Sr^{2+}	1450	120	0.02	0.12	121		
Th^{4+}					<0.03		
U^{4+}	1	<1			<0.03		
UO_2^{2+}							
Y^{3+}	0.04		0.001	0.003	0.007		
Zr^{4+}					0.53		

Form of element borderline (a) cations	Hard* water $\mu g\,l^{-1}$	Soft* water $\mu g\,l^{-1}$	Blood* (H.W.) $\mu g\,ml^{-1}$	Blood* (S.W.) $\mu g\,ml^{-1}$	Tooth enamel $\mu g\,g^{-1}$	All $\mu g\,l^{-1}$	DMAC $\mu g\,l^{-1}$
Co^{2+}					0.006		
$Cu^{2+}(Cu^{+})$					6.80	50^5	$100^2/3000^1$
Mn^{2+}	0.8	13	0.07	0.04	0.32	(50)	50
Ni^{2+}					0.64		50
Pb^{2+}	2	4			3.1	50	$50^3/100^4$
Zn	100	50	7.0	7.0	203	3000	$100^2/5000^1$
borderline (b) cations							
Bi^{3+}					0.006		
Cd^{2+}	0.4	0.6	0.004	0.005	0.99	5	5
$Tl^{+}(Tl^{3+})$					<0.04		
(b) cations							
Ag^{+}			0.009	0.009	0.06		10
Au^{+}					<0.02		
Hg					<0.11	1	1

TABLE II (Contd.)

Form of element anion (oxy/ hydroxy)	Hard* water $\mu g\,l^{-1}$	Soft* water $\mu g\,l^{-1}$	Blood* (H.W.) $\mu g\,ml^{-1}$	Blood* (S.W.) $\mu g\,ml^{-1}$	Tooth enamel $\mu g\,g^{-1}$	AII $\mu g\,l^{-1}$	DMAC $\mu g\,l^{-1}$
$Sb^{III\,\&\,V}$	0.2	0.02	0.02	0.13		10	
$As^{III\,\&\,V}$			0.001	0.001		50	50
Sn	0.7	2	0.02	0.1	0.53		
Ti^{IV}							
Sc^{IV}						10	10
Nb			0.006	0.006	0.31		
Ta							
Si	8000	160	13	12	243		
V	3	0.4			0.033		
Mo	1	1	0.001	0.001	5.5		
W							
B	6	2	2	0.3	18.2	(1000)	(1000)
Re							

Form of element mixed organic and inorganic forms	Hard* water $\mu g\,l^{-1}$	Soft* water $\mu g\,l^{-1}$	Blood* (H.W.) $\mu g\,ml^{-1}$	Blood* (S.W.) $\mu g\,ml^{-1}$	Tooth enamel $\mu g\,g^{-1}$	AII $\mu g\,l^{-1}$	DMAC $\mu g\,l^{-1}$
C, H, O (except H_2O)	diverse forms		major	major	major	diverse forms	
P (T.P.)	2800	700	major	major	major	400 (P_2O_5)	5000
N (NO_3^-)			major	major	major	50000	50000
S (SO_4^{2-})	3000	3000	1700	1800 TS.	294	250000	250000
free anions							
F^-						8–12°C 25–30°C	1500 700
Cl^-	66000	11000	2700	2600	major	(200000)	(25000)
Br^-	71	18	4.3	4.7	1.09		50000
I^-	2	1	0.03	0.03	0.036		

* Data from Hamilton, 1979. H.W. hardwater areas S.W. softwater areas. Tooth enamel data from Losee *et al.*, 1973.

AII Mandatory maximum admissible concentrations in raw water meeting EEC Category AI, employing simple physical treatment and disinfection in preparation of drinking water. Values in brackets are Guide Level concentrations.

DMAC EEC mandatory maximum admissible concentrations in drinking water; values in brackets are Guide Level concentrations.

1 eg Cu 3000[1] above 3000 $\mu g\ l^{-1}$ there is perceptible taste, discoloration and corrosion risk.

2 eg Cu 100[2] maximum concentration in drinking water supply sampled at works outlet valve.

3 concentration in running domestic supply.

4 concentration signalling need to undertake reduction in consumer's exposure to lead.

5 values subject to waivers due to exceptional climatic or geographical conditions.

hard (a)—type if they form mainly ionic bonds and interact preferentially with hard donors such as N, O, F. Cations are soft (b)—type if they are not fully hydrolysed, are highly polarisable, tend to form mainly co-valent bonds and interact preferentially with soft electron donors such as P, S, Cl. The categories tend to merge and are not rigid. In natural waters most of the prospective donors co-ordinate via hard oxyatoms; the halide ions (except F^-) are the only soft ligands in oxic waters together with S^{2-} and HS^- ions in anoxic waters. The affinity of organic ligands acting through bonds incorporating —COOH (carboxylic) and —OH (phenolic) groups is regarded as hard by analogy with CO_3^{2-} (carbonate) and OH^- (hydroxyl), (Whitfield, Turner and Dickson, 1981). In estuarine waters affinities of cations are classified in relation to F^- and Cl^-.

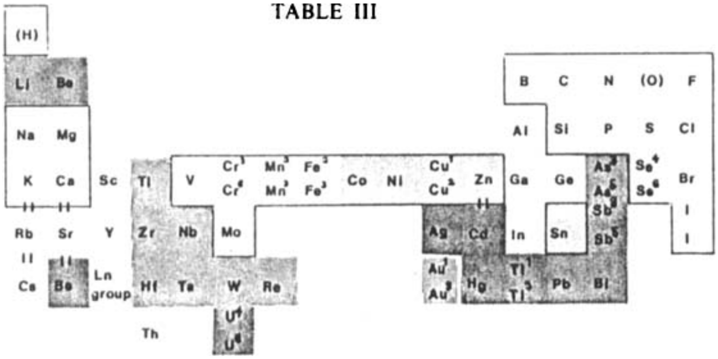
Borderline (a)—type cations include the toxic element Pb^{2+} and metabolically important Co^{2+}, Cu^{2+}, Fe^{2+}, Mn^{2+}, Ni^{2+}, Zn^{2+} which exhibit complex speciation patterns. Such elements undergo marked change in speciation in passage from clean freshwater through estuarine transitions to the ocean largely through the involvement of OH^-, CO_3^{2-}, HPO_4^{2-} and to an important extent humic compounds and other natural ligands which are stable over this time scale. The speciations of (b)—type cations (e.g. Bi^{3+}, Cd^{2+} and Tl^+) are of minor significance in freshwater but on transfer to sea-water Bi^{3+} is predominantly hydrated, Cd^{2+} and Tl^+ form relatively strong chloro-complexes.

The numerical comparison of element concentrations in water, blood and tooth enamel is interesting with many puzzling details; the fate of (a)—type cations and strong anions in blood and enamel with the above exceptions is generally closely controlled by biological mechanisms and it is the borderline elements that tend to display marked enrichment.

To put chemical characteristics in the Periodic Table into relationships with man (and animal and plant life to a considerable extent), for example as defined by the broad categories of "essential" and "toxic", all three presentations are shown side by side in Table III. This identifies clearly the special situation of the important cations of the metastable (oxic/anoxic) environment namely Cr^{3+}, Mn^{2+}, Fe^{2+}, Cu^{2+} and the ambivalent function of Cu^{2+}, Zn^{2+}, Se which are essential elements that are highly toxic in modestly enhanced concentration.

Yet another chemical-biological association exists for As and Hg which can be reduced in nature from ionic forms into stable organic (e.g. methyl) metal compounds by certain microbial species given suitable conditions. Wood (1975) predicts that Sn, Pt, Au and Tl may also

TABLE III



Essential elements (Hamilton, 1979; Hopps, 1980; Wood, 1975).
Essential elements, toxic at elevated concentrations.
▨ *Toxic elements whose damage is limited by availability in natural waters.*
▨ Toxic elements, relatively accessible.
(H) and (O) abundant elements of water, not included in Whitfield *et al.* (1981).
K = Rb an example of elements with linked biological pathways. The arrangement of elements is derived from Whitfield *et al.* (1981).

be detectable in methylated form in the aquatic environment, but regards the alkyl forms of Pb, Cd, Zn as probably unstable in water. There are claims however (Chau and Wong, 1981) that alkyl-Pb can be formed *in vitro* under conditions similar to those in some natural sediments. From *in vitro* studies, bacterial reductions are claimed for As^{5+}, Fe^{3+}, Hg^{+}, Hg^{2+}, Mn^{4+}, Te^{4+} and oxidations for As^{3+}, Fe, Fe^{2+}, Mn^{2+}, Sb^{3+}, and some forms of Mo, Cu, U are oxidatively solubilised.

Alkyl metals are regarded as potentially serious toxicants, and polluting conditions or natural processes which favour their production attract close attention. In addition to their toxicity, alkyl metals are notable for their high degree of retention and localisation in tissues. The half-life for protein-bound $MeHg^{+}$ in man is about 70 to 76 days, but fatty and nervous tissues have higher accumulations and longer retentions. Natural organo-arsenic compounds have lowered toxicity.

With regard to toxic metals in general, the half-lives of Zn, Pb, Cd and Cu introduced into soil are long (typical ranges for sparse and dense vegetative cover being Zn 1.4–5.5; Cd 2–11; Pb 1.2–15; Cu 8–23 years (Roberts and Goodman, 1973), but the retention time is prolonged if the additions are low level and gradual. Corresponding half-lives in man vary, for example Pb in soft tissues is only about 27 days but is 20–90 years in bone which normally carries about 90% of the total body burden.

Without delving into the deeper intricacies of specific elements in the environment and living tissues generally, it is clear that there is a profound and logical coupling between chemistry and biology (Chemistry in Ecology) in which water is the enabling factor.

Aquatic chemistry and human welfare

Setting aside the very important role of bacteria and water-borne disease organisms, many complex associations and proven relationships linking human welfare, male and female, from gametes to old age, with the environment are mediated by some defined or ill-defined characteristics of air/water vapour, water, and food under diverse conditions of voluntary and involuntary exposure. In relation to man, one immediately thinks of the epidemiology of drinking water but indirect pathways through plant and animal foodstuffs (in turn subject to water quality to an important degree) are usually more important routes.

Public health authorities in Britain recognise Ca, Fe and I as the only representatives of essential elements possibly worthy of attention for residents eating a normal diet. Recommended intakes of these nutrients in organic and mineral forms have been set out by the Department of Health and Social Security (1973). These recommendations particularly stress the highly variable efficiency of uptake and availability to the body of these elements in free, combined and mineral forms in appropriate components of the diet. Very many similar studies have been made in countries all round the world which demonstrate characteristic national and geographical dietary deficiencies.

Excesses and deficiencies of chemical elements and compounds in human welfare strongly relate to cultural and sociological factors; a topic which has acquired a vast literature. Single and multiple denial or introduction of elements and compounds at all stages of human development have been variously measured and interpreted for widely ranging conditions of exposure, intensity and duration. Recent monographs are available in public health literature on most toxic metals, radioactive elements, natural and synthetic drugs, alcohol, household chemicals, oil and many substances encountered in industry. Many of these contain information relevant to the aquatic environment and aquatic chemistry.

Man's need for water

All life is absolutely dependent on water and the form and activities of organisms must abide within the limits of this dependency.

The average human contains about 26.5 l water distributed as 12 l flowing between cells, 3.5 l in blood and the remainder associated with tissues within which there is slower turnover. The body processes water in highly complex ways and although water input closely matches water output in between lies much of human biochemistry. On average 1.3 l water daily comes from drinks, 1.2 l in foods of which 0.85 l is debatably classified as "free water" as distinct from water held in the macromolecules of food constituents. On average, 0.4 l is expired from the lungs and 0.5 l (in temperate climates) from the body surface, this water having passed through cell systems. The remainder (1.5 l in urine, 0.1 l in faeces) has passed through the gut or is returned there from inner organs.

As in almost all organisms a very sensitive and selective osmotic balance and pattern of throughput must be maintained. For man palatability of safe fresh water is important. While the expert chemical analyst may seek to learn its detailed chemical speciation, once inside the body internal processing largely overwhelms such natural properties within fairly generous limits. Accommodation within characteristically different and variable limits can be demonstrated for estuarine aquatic species. The human although sensitive of palate is not a feasible assay organism for determining sub-lethal water toxicity.

The scale of necessary water intake by family units, discussed above, contrasts sharply with the water usage in the home (approaching 200 l per day^{-1}) and total consumption (domestic, industrial, agricultural etc.) in excess of 630 l d^{-1} per head of population in developed countries. Dry luxury items such as motor cars and television sets consume directly (materials and manufacture) and indirectly (through use of hydrocarbons and electricity for example) many hundreds of times their weight of water and such less obvious usage of water can be extended to most familiar things. No figures are available quantifying this luxury use of water but the proportion is very high.

MAN AND THE CHEMISTRY OF POTABLE WATER

The status of drinking water

Consideration of the impact and control of microbial contamination and water-borne disease must be set aside as a separate topic. That apart, the chemistry of drinking water and its links with human health is a profoundly important topic (see for example the review by Hamilton, 1980). Also paramount to any practical demonstration of the value of aquatic chemistry, are the factors of climate, geography, politics and proprietorial claims which dictate the ultimate availability of potable water and the right to a supply.

Instinctively a modern chemical analyst or industrial chemist feels he or she could do miracles in (a) describing every detailed feature of raw water and drinking water in precise terms and (b) radically transforming established water processing; but under the present central government cash restraints both realms seem to emerge slowly, if at all, from the alchemy of past centuries.

Consequently, despite the earnestness with which medical studies on health and the environment are being pursued the absence of good hard data is a severe handicap; also, except for a fortunate few, improvement in drinking water quality means patching up the same old traditional treatment plants.

It is only fair to emphasise one over-riding factor, namely the status of public drinking water supplies in Britain. Today's domestic water supplies are used for health-related purposes to an extent of 25%, or frequently much less, of total consumption. The major uses range from street cleansing, toilet flushing and firefighting to a wide range of service and industrial demands. World resources of potable water are declining and, in a growing number of countries, water for drinking and other critical domestic uses is purchased in bottles. Although this practice may, and potentially could, ensure high quality potable water it may also encourage if it does not already highlight, inadequate standards of management of lakes, streams and rivers. Since customary water treatment practices cannot economically restore foul water to pristine quality, the need to sustain a minimum quality for down-stream abstraction for public potable supply compels some effort at maintaining the quality of surface and ground waters. This powerful constraint is inapplicable as an argument for protection of estuaries and seas.

Water, disease and mortality

"Mortality is a late health effect, a final and objective phenomenon" (Sauer *et al.*, 1973). Interpretation of the causes of death is complicated and incapable of high precision since the causes are seldom single and have not been reported in orderly fashion, at least until recently. For successful computer analysis clear-cut categories of the causes of death, along with details of social, occupational and geographical factors must be organised in a consistent, orderly manner using uniform scales for each parameter. Coronary heart disease and cancer dominate the search for links between human mortality and the environment. Frequently statistical analysis identifies some mortality association between say cancer and geographic (geochemical) factors, degree of industrial pollution, smoker–non-smoker, social class, extreme dietary anomaly and nutritional features. Very often chemical environmental factors appear out-weighed in such analyses by the other factors but they are also the least well observed and measured.

Bølviken, Ottesen and Glattre (1979) attempted greater chemical definition of environmental factors by comparing the chemistry of 60 sets of stream sediments in a region of Norway in relation to cancer mortality rates ascribable to specific organs and also to pernicious anaemia, multiple sclerosis and Parkinsons disease. Chemically the area covered by the sediment sampling split into 2 areas one characterised by Al, As, Ba, Bi, Co, Cu, Fe, Li, Mn, Mo, Ni, Pb, Se, Sr, V, U and Zn and the other with a different pattern of Ca, Cr, F, K, Mg, Na, Sb and Ti.

From a comparison with page 7 it would appear that the former has numerous soft water features with a wide range of heavy metals present, the latter shows predominantly hardwater tendencies and is less notable for its heavy metal content. Best single element correlations were found between Cu and cancer of digestive organs ($p < 0.005$, $r = -0.47$) and similar correlations for Cu, F and Sr with total cancers. Correlations were also found for Mn and Sb and cancer of respiratory organs. Positive correlations were found for Zn and cancer of the throat and mouth, skin, bone and connective tissue. Yet further correlations were found for Be, Mo and Zn with other types of cancer and Ca, F and Sr with multiple sclerosis. Various correlations using geochemical groupings of elements were found for some cancers, some only for males. Stream sediments for this region of Norway are derived from relatively homogeneous geological sources and these detailed analyses suggest complicated mechanisms of element dispersion locally and interactions in the sediments.

In the eastern part of U.S.A., Kutina (1979) found (i) a belt of high "all causes" mortality associated with a monazite belt which might transport Th and other radioactive elements into water supplies *via* placer deposits and (ii) U associated with deep-seated fracture zones of this belt.

For very many studies however, unless geographical features are very strongly marked, epidemiological studies emphasise occupational and social factors more strongly than loosely specific chemistry of the environment.

Perhaps the most puzzling health studies relate to unusual exposures experienced over many generations. For example, Pima Indians drink about 1.6 l day^{-1} of extremely hard water containing Na and Cl above MRC (U.S.A.) standards, Fe maximum, and Ca, Mg, SO_4, F, Sr near maximum. Despite this high F level the incidence of skeletal and dental fluorosis is low and also the incidence of atherosclerosis and hypertension. Sievers and Cannon (1973) believe that accompanying high Li levels strengthen the cell membranes thus reducing atherosclerosis and hypertension and controlling high serum uric acid, type A hypomanic behaviour and elevated serum lipid. The water has high alkalinity and is low in heavy metals except Mo and has only moderate Cr enhancement.

In Great Britain, Cornwall and Devon are very heavily contaminated with mineral debris from former Sn and Cu mines and as a result As, Zn, Cu and other metals reach high concentrations in river sediments. Locally there are deficiencies of Mg, Mn, Co and B in root and green fodder crops attributed by Thoresby and Thornton (1979) to the nature of the bedrock. For humans none of the usual evident patterns in morbidity linked with very high As are found despite values in sediment as high as several thousand mg kg^{-1}. However in some areas where soil Cd is high, high Cd in various human organs is found but without evidence of associated ill-health.

In relation to foodstuffs and fodder, barley grain in the metalliferous mining areas variously reflects only a small part of the enhanced soil metals anomalies in As, Cu, Cd, Pb and Zn. In one extreme example for a range of winter vegetables grown in garden soil containing Cd up to 800 mg kg^{-1} and Zn up to 70000 mg kg^{-1}, the average concentrations for these metals was 19 times normal with a peak of 120 times. For summer vegetables which need a shorter growth period the peak and average concentrations were only twice U.K. normal values. Such produce is potentially a more serious hazard if, as tends to happen, much of it is consumed locally without recourse to supplies from outside the area.

The cattle of the metalliferous area also reflect higher toxic metal levels in their various organs but do not appear to suffer evident ill-health. Cattle, in addition to acquiring metals from feed barley and pasture, also take in about a further equal amount on fine soil particles. Countless other examples might have been used.

In the realms of for example epidemiology, health, plant and animal nutrition (with some notable exceptions), the anions have attracted much less attention.

Some aspects of effects of NO_3^-, F^- and more recently Se as tetravalent and hexavalent anions have been studied in cattle and man. The healthy human has a generous tolerance of Cl^- and SO_4^{2-} and of course both chlorine and sulphur are important essential elements significantly supplied in drinking water. Phosphate, virtually 100% from food, has many important functions in man. Anions such as OH^-, CO_3^{2-}, HCO_3^- are important in drinking water potability but body secretions dominate any contribution from these sources in overall metabolism. The balance between cations and anions in water is maintained notably by SO_4^{2-}, Cl^-, SiO_3^{2-}, PO_4^{3-} and NO_3^-.

A striking correlation between death rate from apoplexy (stroke) and the cation–anion balance in water and diet is claimed by Kobayshi and Morii (1978). Alkalinity of river water correlated negatively with mortality rate, excess sulphate gave a positive correlation, and $\frac{\text{sulphate}}{\text{alkalinity}}$ ratio yielded a strikingly positive correlation; calcium showed a less significant negative correlation. The authors stress that conventional analyses do not adequately describe anion : cation balance.

Kobayashi *et al.* (1980) extended the concept to foodstuffs. An index for the base-forming components of foodstuffs was related to the recommended Japanese daily cation intake of 600 mgCa, 200 mgMg in association with 600 mgP. Diets rich in alkali metals, especially Ca, show a large positive ion anomaly; diets rich in anions or deficient in Ca, Mg yield a large negative correlation and are linked to communities where apoplexy is high. Diets containing kale and seaweeds, which have high positive indexes, were introduced in some areas to prevent and cure arteriosclerosis and hypertension.

Numerous studies relate specific elements or groups of elements to conditions of ill-health or disease in babies, children and adults during specific periods of life. Occupational health research is specifically aimed at exceptional conditions in factories and other work areas. These also demonstrate broad links between chemistry, (sometimes including aquatic chemistry) and human welfare.

Drinking water treatment processes

Except on the scale of remote rural supplies, public drinking water in the U.K. usually originates from multiple upland catchments which usually merge in a natural or artificial reservoir. This has the practical advantage of providing storage which combats usual variations in supply and demand. Storage has a number of important chemical functions, some of which depend on the residence time of the system. Incompatible raw waters can react and stabilise at least with regard to the more active fractions. The settling out of larger particulate fractions brought in by turbulent streams takes place rapidly. Longer storage promotes greater natural clarification. Storage promotes more uniform quality in the raw water which would otherwise reflect the extreme effects of drought, flood and season.

Primary processes used in preparing drinking water are similar in principle world-wide and differ mainly in the size of installation. The number and complexity of advanced processes required thereafter depend on the quality of the raw water. Full treatment might comprise some or all of screening, micro-straining, bed filtration, flocculation, sedimentation, chemical treatment and disinfection by any of a number of processes. For specific applications, chemical treatment may be required to promote removal of high BOD, colour, taste or excessive softness or hardness. Because of the high costs of further treatments these are available only to major conurbations; most plants are simple.

Filtration

It is important to emphasize the differences that exist between filtration in the laboratory sense and filtration practices in water treatment. Filtration has complications enough in the laboratory, especially when the element(s) being analysed is/are in micro concentration but it is a totally different concept for raw water passing through a sand filter bed, for example. Performance data are available for media and bed structures with regard to relatively gross particles but little is published on the associated chemical changes. One can extrapolate from familiar natural situations. The processes that take place between raw water and the sand, gravel, anthracite or other medium for the initial state of a fresh bed are principally the containment of particles of suitably large dimension and geometry simultaneously with exchange processes dependent on the state of the raw water and the mineralogy of the medium. High purity in the bed material(s) is desirable to prevent the introduction of additional elements especially Fe. Initially one might expect at least partial reactions affecting (a)—type and borderline (a)—type cations. Only the traces of hydrous oxides of Fe and Al offer any significant scope for ion exchange on clean sand. Soon the accumulation of particulate matter and build-up of bacterial and other communities alters the flow rate and converts the media into something more resembling river sediment. As in a river bed the most active changes affect the upper 5–10 cm layer at least until anaerobic conditions become established. Periodic removal of the upper layer of medium extends the period of efficient filtration until the bed depth is so reduced that renewal is necessary. Normally the build-up would never reach the stage when percolating waters become anaerobic with consequent major changes in the ion regime. Just as important as particle removal, the activities of the biological layer break down degradable organic matter. There is release of inorganic P and N, and soluble organic P and N fractions. A proportion of the organic and inorganic matter escapes as colloidal or finely particulate fractions. Some of the organic matter is in the form of stable assemblages (e.g. humic compounds) and metabolites. Sporadic growths of moulds and microscopic algae can give rise to stale odours and off-flavours in the water supply.

To overcome the practical disadvantages of periodic bed renewal, more elaborate structured filter beds and beds which can be flushed by counter-flow have been devised. These developments control the biological layer and preclude the formation of anoxic conditions. In practice, high flow filter beds are best suited to raw waters that do not require much BOD removal; if BOD reduction is needed, slow sand bed treatment is better and this also retains a higher proportion of incoming, perhaps undesirable, micro-organisms.

Clearly, bed filtration is a process which must modify the chemical composition of raw water but while the function of a bed filter may be describable for a given period of operation it may be difficult to assess the overall changes that emerge in practice when a series of filter beds of different age, and perhaps structure, are variously employed in parallel use. Presumably the major ions are least affected, exchangeable ions and biologically important elements may undergo changes which may result in removal but the fate of most elements is unpredictable and perhaps extremely variable.

Flocculation

The primary objective of flocculation treatments is the removal of perceptible and often coloured colloidal matter which escapes filtration processes. Flocculation has an essentially physico-chemical basis but, like filtration, also introduces chemical effects. The aluminium salts commonly used are hydrates of aluminium sulphate (mainly $Al_2(SO_4)_3 14H_2O$) which have a neutral or slightly acid action in solution and $Na_2OAl_2O_3$ which is alkaline. Alternatively ferrous sulphate has long been used in conjunction with lime, but "chlorinated copperas" a mixture of about 40% $Fe_2(SO_4)_3$ and 60% $FeCl_3$ or more rarely acidic $FeCl_3$ or $Fe_2(SO_4)_3$ solutions alone can be used.

By laboratory standards the pH ranges for water treatment are fairly wide ranging. For alum treatment pH 5.5 is used on natural waters with very low dissolved solids content and 5.7 to 7.8 more generally. For iron coagulants pH 8.4 is a working lower limit and above 9.0 is commonly used, the alkaline additions being generated by addition of hydrated lime ($Ca(OH)_2$), soda ash (Na_2CO_3) or caustic soda (NaOH). The archaic nomenclature may reflect the status of the chemistry practised.

The theory of flocculation and coagulation is complex. Hydrous oxides and hydroxides of Al and/or Fe specifically adsorb alkaline earth metals (Ba, Ca, Sr, Mg) and heavy metals (Pb, Cu, Zu, Cr, Ni, V, Cd, Co). In addition phosphate, selenite, selenate, molybdate, silicate, arsenite and arsenate can be adsorbed and certain organic acids, peptides and other natural compounds. The degree of acidity or alkalinity will affect the efficiency of adsorption. Presence of organic chelates can enhance or suppress the adsorption of individual metal complexes depending on detailed characteristics. There are demonstrable limits to the efficiency of ordinary flocculants as they are used in the water industry for the removal of toxic metals and therefore corresponding limits to water quality improvement attainable.

There are few comprehensive descriptions of the performance of typical flocculation treatments either for plant operations or pilot scale models. The literature makes frequent reference to the purity of the chemicals used as a major factor governing the quality of water produced. Since the quantities involved are large, pure (e.g. analytical grade) chemicals are seldom used and the choice usually lies between various proprietary preparations for this specific use and selected trade-wastes that are a convenient source of the principal reactants. Cost and availability may well be the deciding factors. Significant amounts of toxic elements have been encountered in sources of both types.

Other less common drinking water treatment processes are reviewed later in the context of industrial water treatment. Usually flocculation is succeeded is succeeded by sedimentation and rapid sand or mixed bed filtration. Recycling of some used floc may be practised.

Disinfection

Chlorination is the customary final drinking water treatment process designed to kill or suppress microbial populations. A slight excess of chlorine is administered to combat growth within the distribution network.

Chlorination is a biocidic process alien to the natural environment. The destruction or suppression of bacteria proceeds by various pathways such as the oxidation of sulphydryl-containing enzymes and direct reaction with cell substances and metabolites. Deactivation of viruses by normal chlorination cannot be relied on. Many metals (such as Fe, Mn, Cu, Hg, Cr, As, Sb) are oxidised and ammonia, bromides and iodides react. There are possible side effects on man. It is suspected that chlorination may affect normal intake of essential bromide and iodide from water. Many organic substances react to form predominantly organochlorine derivatives including alkylhalogens, at variable rates. Few of these compounds are devoid of proven toxic properties to plants, animals and man but if the raw water has a low TOC content, the residues present at very low concentrations are considered harmless.

Up to 1982, the total number of organic contaminating compounds detected in the aquatic environment was 2221 on a world-wide basis of which 765 have been identified in drinking waters (Bedding, *et al.*, 1982). The trihalomethanes are the most ubiquitous and abundant contaminants almost invariably more concentrated in drinking waters than in the source waters. Clean source waters are characterised by ketones, alcohols and aldehydes. These are oxidised on chlorination but some common amino acids are chlorinated e.g. chlorotyrosine and dichlorotyrosine. The group known as humic acids may also yield trihalomethanes.

Ozonisation and ultraviolet irradiation are alternative disinfection processes somewhat akin to natural photo-oxidation at a very high intensity. These produce mainly less harmful oxidised organic residues but some unstable organic peroxides may be formed which might be toxic in high concentration.

Associated issues

Water treatment processing yields appreciable amounts of litter, dirty and clogged filtration media, and possibly used flocs and spent treatment chemicals (charcoal, resins). The heavy, less wet materials may be buried in refuse tips but the disposal of bulky used flocs is difficult on land and the creation of high turbidity and glutinous slime precludes disposal to small streams and rivers. A common practice which utilises the residual properties of the floc is controlled introduction into a sewerage system where it assists the coagulation of the large amounts of finely dispersed material.

Many water treatment works in Britain have little or no reserve capacity and in periods of heavy rainfall, at the end of the growing season, at snow-melt, and under other extreme conditions such as massive algal growth, the quality, if not the safety, of the water supply may be drastically changed. Except in new towns much of the plant is very old and replacement is slow because of very high capital costs and high land occupancy.

Consequently, there is very slow emergence of alternative treatment technology. In the main, treatment is aimed primarily at the removal of suspended solids, bacteria and excessive degradable organic matter and, sometimes, colour and taste. Deliberate additions of lime and fluoride may be made but otherwise the manipulation of most elements is incidental or accidental with little accurate control of final composition.

Interpretation of the representative performance of current treatment practices is uncertain other than the broad generalisations relative to suspended solids and BOD. Many environmental chemists face much greater perplexities in studying natural bodies of fresh- and sea-water and would jump at the opportunity of studying filter beds as macro-experimental ecosystems. It is for them particularly disappointing that so few data exist on typical performance of such units with respect to the biologically important elements. Seemingly the efficient performance of water treatment plants merits little attention from the public who pay for them or the politicians who tend to make so much play about cost effectiveness in less vital matters.

As a result of EEC, EPA and WHO programmes, for example, the growing committment of many countries to target water quality standards has been declared openly for the first time for a very wide range of new parameters. This may have a catalytic effect on the accepted static condition.

Quality standards for drinking water

The recent challenging proposed standards for drinking water provide not only an interim target for bacteriological and chemical quality but also enable water and health authorities to advise governments regarding regional requirements for the provision and the protection of raw water sources and also regarding the treatments required for the supply of potable water to the whole community. Nevertheless at this time in many countries countless people have only uncertain and unsafe water for drinking.

Over this century in a period of greatly increasing demands for water supplies in major development areas, standards have slowly progressed in the direction of safe water for all and simultaneously a more quantified statement of safe and potable water quality has emerged. Unlike other beverages whose quality and desirability stem from freshness, bouquet, flavour and provenance, the prosaic characteristics of drinking water prescribe that it should not be toxic or unhygenic.

Sets of standards have been suggested or laid down by the World Health Organisation, the Environment Protection Agency (in U.S.A.), and the European Economic Council and there must be others. In addition, the EEC has laid down standards for raw water abstracted for the preparation of drinking water possibly in recognition of the limitations of economically-practical methods of water purification to potable quality. Whatever the standard of drinking water quality at the treatment plant, deterioration in quality, which can amount to serious contamination, takes place within the service and domestic distribution systems.

Some of the raw water "guideline" criteria appropriate for Category A1 treatment given in the EEC Directive have been summarised in Table IVa. The idea behind Categories A1, A2 and A3 Table IVb is that the additional treatment processes will compensate for poorer raw water quality to produce equal final products. It has not been possible to trace data adequate to illustrate before and after water characteristics for a range of different raw water types and treatments but data on

TABLE IV

(a) Characteristics pertaining to surface water for abstraction

1. Specific	Temperature*, NO_3*, F, Fe, Mn, Cu, Zn, B, As, Cd, Cr, Pb, Se, Hg, Ba, CN, SO_4*, Cl, P_2O_5, O_2 saturation, Kjeldahl N, NH_4*.
2. Broad categories	pH, coloration*, total suspended solids, conductivity, surfactants, phenols, polycyclic aromatic hydrocarbons (PCAH), total pesticides, COD, BOD.
3. Arbitrary parameters	odour, dissolved or emulsified hydrocarbons, substances extractable by chloroform.
4. No ascribed limits	total extractable organochlorines, Be, Co, Ni, V, TOC, residual TOC after flocculation and membrane filtration.

* standard subject to waivers for exceptional climatic or geographical conditions

(b) Quality standards for abstracted raw waters are related to Categories of subsequent treatment methods:—

Category A 1	Simple physical treatment and disinfection e.g. rapid filtration and disinfection.
Category A 2	Normal physical treatment, chemical treatment and disinfection e.g. pre-chlorination, coagulation, flocculation, decantation, filtration, disinfection (final chlorination).
Category A 3	Intensive physical and chemical treatment, extended treatment and disinfection e.g. chlorination to break-point, coagulation, flocculation, decantation, filtration, adsorption (activated carbon), disinfection (ozone, final chlorination).

(Extracted from Council Directive of 16 June, 1975–75/440/EEC (EEC, 1975).

TABLE V

Characteristics pertaining to drinking water

1. Specific	temperature, Cl^-, $SO_4^=$, Ca, Mg, Na, K, Al, O_2, NO_3^-, NO_2^-, NH_4^+, Kjeldahl N, B, Fe, Mn, Cu, Zn, P_2O_5, F, Ba, Ag, As, Cd, CN, total Cr, Hg, Ni, Pb, Sb, Se.
2. Broad categories	colour, turbidity, pH, conductivity, total hardness, oxidisability, chloroform extractable substances, surfactants, other organohalogens, suspended solids, specific and total pesticides and related products, PCAH.
3. Arbitrary parameters	odour, taste, dry residues, H_2S, dissolved or emulsified hydrocarbons, phenols.
4. No ascribed limits	silicates, CO_2 forms, TOC, Co, residual Cl, Be, V.
Waivers	There are many exceptions for specific parameters provided no hazard exists to human health. Certain general relaxations apply to supplies to geographically defined populations allowing a longer period to attain these standards.

(Condensed from Council Directive of 15 July, 1980–80/778/EEC; (EEC, 1980).

suspended solids, BOD and bacterial parameters are abundant and invariably substantiate beneficial effects. The enquiring chemist will find it difficult to gauge the exact outcome of water treatment processes on the parameters listed (Tables II, IVa,b) since representative observations are so hard to find.

Table II shows a very limited number of values for chemical elements in average U.K. hard and soft natural waters alongside EEC standards which probably does not depict the wide regional differences in the composition of natural waters. The criteria used in assessing drinking water quality are summarised in Table V.

It is particularly disturbing that there are hierarchical drinking water standards in the U.S.A. and the EEC (possibly also elsewhere). The terms of these standards in effect are directed at securing best possible services, quality and quality control for major urban centres and inferior services, quality and quality control for provincial and in turn rural districts as if these communities were less civilised. Perhaps the well-known extreme longevity of isolated high mountain communities in Russia, India and South America and indeed in isolated rural communities here and there in other countries has been argued in support of these graded standards, but it would be more politically honest to produce on-the-spot epidemiological evidence to support these lowered standards. Equally disturbing is that least effort at quality control is offered where least treatment and supervision is proposed; if quality fluctuates nobody wants to find out or provide a cure.

There are many who criticise the grounds on which these water quality standards are based. The figures are derived from a rag-bag of miscellaneous and heterogeneous observations. All sorts of cell cultures, bacteria, unicellular plants, insects, birds, eggs, fish, plankton, polychaetes, small mammals and sundry human organs from autopsies are listed as the sources in the "Review of the EPA Red Book: Quality Criteria for Water" produced in April 1979 by the American Fisheries Society, Water Quality Section (Thurston *et al.*, 1979). The assessment of toxicity in relation to man is difficult enough for pure single substances and is enormously complex for the natural and unnatural blends of inorganic and organic compounds found in raw, drinking, domestic, trade and other waters. In recent years more direct and meaningful criteria have been investigated for possible adoption. The evolution of a new set of standards will take many years to validate, build up an adequate body of observations and be linked into epidemiological studies. In the meantime, here, as in aquatic toxicology related to waste waters, streams, lakes, estuaries and the sea, such uncertain toxicity criteria must serve for the foreseeable future. Possible future bases for the chemical element standards and probable new and more controversial parameters (e.g. carcinogens, viruses) has aroused no small political interest, apprehension and concern as regards their statutory, financial and legal repercussions.

It would be wrong to conclude that currently or in the immediate future proposed drinking water standards will be fully met everywhere in countries signifying their adoption. There is much dispute about the relevance of even the simplest standard, e.g. total dissolved solids (DS) and concern about the costs of implementation, (Nace, 1976).

The generally quoted upper limit for dissolved solids (DS) in geological samples of freshwater is about 100 mgl^{-1}; that for drinking water is 500 mgl^{-1}; brackish waters may be many times higher. In the U.S., millions of people drink water with above 500 mgl^{-1} DS and more than 100 public supplies exceed 2000 mgl^{-1}, a level of salts not tolerated by sheep and other animals. Yet, intake of common salt is currently a lively matter of public health concern mainly because of rising intake in convenience foods and as an additive and component of flavour and sauce mixes.

In arid areas of other countries public and rural water supplies may range up to 3000 mgl^{-1} DS. Generally above 1000 mgl^{-1} DS is regarded by water authorities as undesirable and higher values are only tolerated because of severely adverse local water resource factors.

The use of desalination can provide more acceptable water but the process generates highly saline wastes which can be difficult to dispose of. Large-scale desalination for industrial use can present a major environmental problem (Nace, 1976).

The problem of excess dissolved solids is only one of many prevalent in rural and recycled water sources. Treatment is expensive, labour and energy-consuming and not without its own environmental problems.

Harmonised programmes of water analysis

Most countries compile a manual of standard analytical procedures for the analysis of raw and drinking waters or adopt a widely used reference book such as the U.S. "Standard Methods for the Examination of Water and Waste water". As Gurnham *et al.* (1976) point out "Some of the methods are controversial especially for the very low concentrations that exist in some samples; in general the analyst should conform to the methods that are employed by the cognizant authority. Some methods of analysis are very arbitrary (the test for oil and grease is a good example) and the recommended procedures must be followed exactly." (p. 528).

The EEC Council Directive of 16 June, 1976 (75/440/EEC) lists 42 physical and chemical and 4 bacteriological characteristics for surface water intended for the abstraction of drinking water. Of the first group 22 are reasonably specific, 10 are broad categories, 3 are arbitrary, no less than 7 have no specified guideline or mandatory upper limits (Table IVa), and 5 have elastic limits for exceptional climatic or geographic conditions. Further waivers relate to conditions of flood or disaster, locations undergoing natural enrichment and for shallow lakes or stagnant water with a slow turnover. No exceptions may disregard the requirements of ensuring the immediate health of the public.

The corresponding categories for drinking-water parameters are 31 specific, 12 broad categories, 6 arbitrary measures, 7 no ascribed limits (Table V). There are many exceptions to compliance for specific characteristics related to treatment procedures and local conditions and general interim waivers for defined geographical population groups. There are no mandatory minimum concentrations for numerous elements generally accepted as essential for health.

In time, one outcome of the EEC Directives could be the generation of an extremely valuable set of compatible data on raw waters and drinking waters over a large part of Europe provided that the analytical basis is sound. Provision of a scheme for validating and intercalibrating these analyses would be highly desirable. These future data will (a) add a new dimension in epidemiology and (b) with associated costings will greatly contribute to appraising the performance and value for money of current water treatment methodology. It is essential that actual measured values be made accessible to scientists, not merely overall compliance percentages. One looks forward to the incorporation also of standards for radioactive contamination, the incidence of viruses, carcinogens and substances that cause common allergic responses.

Since the Directive (or any other guideline such as WHO or U.S. Water Quality Act and its extensions) lays down maximum acceptable desirable concentrations (except for oxygen saturation), any water supply just meeting all the criteria would be of worse than usual minimal quality since most waters would normally be limiting in only a few characteristics.

ORGANIC MATTER AND HUMAN ECOLOGY

The human element and the organic chemistry of waste water

It is commonly accepted that the 1882 Royal Commission on Metropolitan Sewage Discharge under Lord Bramwell was the first direct move to "enquire and report upon the system under which sewage is discharged, whether any evil effects result therefrom .... and measures for remedying or preventing the same", but the whole unpleasant history of the Thames documented from as early as 1357, provides a sensational record (Wheeler, 1979) of disease, contact experience, evil smells and revolting sights, much of it related to "The Human Element". Between 1882 and 1883 intensive research identified the marked "oxygen sag curve" in the intermediate estuarine reaches linked with foul odour and scarcity of fish as the key environmental factors caused by liquid and solid sewage and trade wastes. This set the rules for wastewater treatment that have dominated ever since, namely, separation of the solid phase to be disposed elsewhere and adequate treatment or dilution of the liquid phase to secure a minimum oxygen saturation in the receiving water. As early as 1884 precipitation of solid matter was attempted using lime and ferrous sulphate and later between 1884 and 1887 deodorising with bleaching powder and sodium permanganate was attempted. Sewage treatment works using lime and ferrous sulphate were started up in 1889 and 1891 and the resulting sludge was shipped to the outer estuary for dumping.

Elsewhere similar wastewater disposal processes have evolved and gradually many thousands of public wastewater treatment plants were built over the next century and look like having to serve for much of the next fifty or one hundred years. The total capital and maintenance outlay has been colossal.

The establishment of a public wastewater treatment plant is neither a final nor a complete solution. Population migration and growth can greatly increase wastewater loading, as in London, where it became necessary to undertake massive additional sewerage schemes to relieve the mid-tidal reaches and build large secondary and full treatment plants initially to restore the estuary to a minimum acceptable level and within recent years to a standard which would encourage the return of migratory fish (salmonids) and the earlier wealth of estuarine species.

"Regular passage of migrating salmon would represent the crowning achievement in purifying the river which at that time (1964) was in danger of posing a threat to public health" (ibid). (Can one conclude that to preclude risk to public health all rivers should afford free passage to migratory species?). The Thames story is not typical in Britain and in many counties a sizeable proportion of heavily populated and industrialised streams, rivers and elongated estuaries have no migratory fish species and, even worse, a significant proportion are fishless.

Setting aside important aesthetic aspects, poorly managed wastewaters relate directly and indirectly to human ill-health, disease and morbidity caused by viruses, bacteria and other water-borne organisms. Particular instances affecting the sea are seasonally populous seaside resorts where at peak times the normal modest services are swamped.

Other general issues are (a) eutrophication, (b) disposal of sewage and industrial sludges, (c) disinfection of wastewater with chlorine and (d) use of recycled waters for drinking water preparation, among others. The consequences for man of incomplete BOD and nutrients removal can be loss of migratory and river fish. Failure to treat or loss of control at treatment works can result in massive fish kills (EPA, 1970).

Toxic metals are removed by processing, the more extended treatments tending to remove a larger proportion though published figures are possibly too few and representative at best of the exceptionally good plants. Paradoxically if there are no local fisheries there is no threat to humans from high metals concentrations but if there are fish there is a possible threat of metal toxicity to man especially for Hg and MeHg. Over the long-term, naturally occurring metals migrate seawards and together with a large proportion of the introduced metals in freshwater tend to accumulate in estuaries (Windom, 1981).

The hazards of some means of sludge disposal are potentially a greater threat to man. There is the important aspect of disease, particularly if contaminated water or sludge is applied to crops near the point of harvesting. Also, enhanced levels of toxic metals (Cu, Hg, Pb, Cd, Zn, As) working along with the associated organic matter may raise the existing soil concentrations of these metals to levels harmful for herbage, cattle and man. Additions are cumulative. The degree of hazard is related first to the overall availability of the total toxic metals to plants. Then metals in fodder and in attached soil particles are passed to cattle. Hence metals are transmitted directly from crop to man or *via* meat. Accumulative recycling may also occur through cattle manure.

There is particular concern about Cd, Pb and Hg in sewage sludge added regularly to crop soil over an extended period. Cadmium which is usually present in very low concentration is freely available to plants, is freely translocated and generally increases in plants in relation to soil concentration. Different crops such as grain, potatoes and leaf vegetables show different degrees of Cd accumulation. Some cultivars (of lettuce) concentrate Cd to widely varying degrees which may indicate that strains might be evolved that are safe to grow on sludge-enriched soil. Lead is significantly increased in soils by atmospheric input and sludge additions. Uptake by crops is usally very limited but transfer as Pb-enriched particles on forage can be a hazard to animals. This transfer is only a serious hazard where exposures are very high or where there is a high native Pb content in the soil. The Hg content of most sewage sludges is low and after application losses occur to the atmosphere (perhaps to return in rain) and uptake by plants is limited.

Molybdenum in sewage sludge can cause problems for cattle by suppressing essential uptake of copper especially if the soil pH is 7 or above. Chromium transfer from sludge is virtually non-existent. Depending on the crop Zn, Cu and Ni are variably toxic and at heavy rates of application can cause crop failure. Of these Ni is usually the most toxic but the combined effects of all three metals vary in a complex manner with soil characteristics.

These comments relate to sludges not unduly contaminated by industrial metals whose presence can greatly reduce any nutrient benefits from sludge application to crops. Similar considerations relate to the disposal of pig, cattle and poultry manures derived from intensive rearing with special problems where Zn, Cu and As are used as dietary supplements. In all cases, contamination of water for abstraction as drinking water may occur through surface run-off and by penetration of more mobile metals (perhaps as their organic compounds) into ground water.

Compared to sea water whose low bacterial, toxic metals, SS and BOD levels appear useful qualities, the removal of the very large amounts of salts (35 gl^{-1}) is a much more daunting task than the upgrading of recycled wastewater (0.5 gl^{-1}). The refractory problems of recycling used fresh water are the increased major inorganic salts (about 200 mgl^{-1}), greater need to control nutrients, and enhanced levels of organochlorines, minor and trace elements. Viral concentrations are also increased. The uncertainties regarding the efficacy of treatment plants to restore used water to a pristine condition have already been discussed. Certainly, recycled water while better than none never tastes remotely like pure fresh water.

Chlorination of waste waters is seldom practised in Britain. Analyses of chlorinated waste waters in U.S.A. have revealed a large number of chlorinated or halogenated by-products, potentially of considerable toxicity, persistence and objectionable organoleptic properties (Jolley, 1975, Jolley *et al.*, 1977) but in the absence of notable industrial contaminants, such as phenols, are not likely to be obviously harmful or obtrusive for man.

Indeed as regards human welfare the increasing need to use recycled water for drinking water preparation demands close study. In practical terms recycling leads to increased costs and difficulties in preparation of potable water due to clogging of filters; interference with flocculation and precipitation; persistent unpleasant odour, taste and colour; abnormally high levels of NH_4^+, Mn, Fe adding to processing difficulties; greater risks of post-treatment growth of bacteria and fouling organisms, and increased quality loss due to organochlorines.

Eutrophication and associated knock-on effects in sludge dumping areas essentially reflect large additional energy inputs or the squandering of valuable nutrients in the production of energy-rich but useless weeds. On a global scale the wasted energy from human excretions is of the order of $5 - 50 \times 10^{11}$ W day^{-1} (compared to photosynthesis at 10^{14} W day^{-1}); cattle manure which is to a useful extent employed as a soil improver would be equivalent to many times this number. Methods exist for biogas (methane) production from animal manures and a few plants are in operation using domestic sewage. Such developments would diminish the problem of organic-C removal, perhaps achieve some NH_4^+ recovery but would require P-removal to control eutrophication if residues were discharged to fresh water; hence using waste water sludge as an energy source would not eliminate all pollution problems.

Industrial discharges

Human fatalities in manufacture and use of products (weapons, vehicles, ladders, drugs, etc.) greatly outnumber those dying through causes linked to industrial effluents. Modern technologies generate novel waste recovery and effluent disposal problems. Progressively, treatment processes are being introduced which are novel, superior to preceding arrangements and more cost effective. The chemical challenge of devising suitable methods for treating single or multiple process streams is frequently much better defined and quite differently motivated from that for public mixed industrial and sewage discharges. The components for removal from new product manufacture are usually, but not always, few in number, reasonably constant, identifiable and quantifiable and offer predictable behaviour in response to treatment and possibly recovery of valuable product.

Many products e.g. petroleum, hazardous chemicals, poisonous wastes can be directly harmful to man by exposure, explosion, spillage, or accidental entry to water. Single acute doses can damage plants, animals or humans but these are uncommon and atypical of prevalent widespread, low level chronic types of exposure (Johnston, 1984). The aquatic pollutants with proven health risk to man are Hg, Cd, Pb to which might be added carcinogens, allergens, irritants and objectional tastes and odours. The special case of radioactive contamination is mentioned but not pursued. The pathways for some pollutants (PCB's, pesticides etc.) into humans, identifiable in various organs and tissues also include first-hand contact.

The massive and continuing discharge of Hg from the combustion of coal, mainly in power stations, is equivalent to 86% of natural mobilisation (3.5×10^3tHg yr^{-1}) (Bertine and Goldberg, 1971, Joensuu, 1971) and results in ubiquitous contamination of plants, animals, soil, water and sea. However Hg is bound on soils and any river-borne input eventually joins millions of years of natural input in estuaries and the sea. Mercury is usually poorly assimilated by plants but is almost the most toxic metal for bacteria. The main hazard to man comes from industrial discharges to fresh water, estuaries and coastal waters. The major source has been chloralkali plants but significant inputs arise also from some petrochemical plants, other electrochemical operations, uses in bactericides, herbicides, insecticides and fungicides, seed treatment and in anti-fouling preparations. The tragic incidents at Minamata and Nūgata are well-known; MeHg being the main toxic agent. Organomercury can also be transmitted to man from treated grain fed to pigs whose pork is later consumed; also a pathway *via* herbage and herbivore to man may exist in nature if there is bacterial methylation in soil and uptake by plants. The pathway through the aquatic food chain to edible species of fish has been demonstrated (Westöö, 1966).

Skerfving *et al.* (1974) found evidence of an increase in the frequency of human chromosome breakage in persons consuming fish containing MeHg.

In the open sea there is natural bioaccumulation through the food chain to fish, particularly large, fish-eating fish resulting in exceptionally high concentrations in the livers of some species (Topping and Graham, 1966).

The ever present organic matter

Organic matter is present in live or inanimate form on all rock surfaces and in all soils and fresh waters at concentrations much higher than in the oceans. The largest part of organic matter produced is transient and is in a biological flux with CO_2 or its dissolved forms. These in turn largely control the dissolution of SiO_2 and simultaneously dominate the major ion status of surface and groundwaters and in a more complex manner, the distribution of minor and trace elements.

The organic chemistry of soils is most familiar in broad descriptive terms such as organic acids, humic and fulvic acids but conceals a great wealth of highly complex, often unstable, organic macromolecules and a great galaxy of less abundant molecules often containing N, P and S. Almost certainly more is known about the entry, fate and impact of synthetic herbicides, pesticides etc. in soil systems than about any single class of equally abundant natural substances present. Similarly, in fresh waters and drinking waters a great deal more is known about man-made introductions than about the ever present natural organic matter that gives flavour, odour, metal-binding and surface properties to the water and profoundly conditions the availability of trace elements both essential and noxious.

Organic matter therefore has a very fundamental action in soil with profound effects on the crops that can be grown and on their elementary composition at least and perhaps also their subtle organic characteristics made evident in "quality", odour and taste. To some extent repetitive crop-growing can become a recycling, reinforcing and conditioning process that alters both the inorganic and organic features of the soil.

One suspects that natural drinking water sources reflect the contrasting situations of upland catchments and the year-by-year changes in agricultural usage. Were water wine, the cognoscenti would proclaim the virtues of the products of successive fermentations.

One can only guess at the effect of water treatment on this blend of organic matter. Perhaps the elusive homeostatic properties that confer longevity to remote communities are removed or inverted by the time the same source waters reach urban populations. Certainly protracted treatment and chlorination would effectively transform active molecules leaving behind unresponsive and biologically xenobic residues.

A recent epidemiological review (Frerichs, 1984) reached the following conclusion:—

"Given the general negative results of our ecologic and household survey analyses and the suggestion raised by our computer simulation model that population-based studies theoretically may not be sufficiently sensitive to identify low levels of increased risk, what advice should be given to the public officials who must in turn decide if the reclaimed water practice should be expanded? When we issued the final report to our funding agency, our point of view was summarized as follows:

> While we can never ensure complete safety, it is reasonable to assume that the disease risk attributed to the consumption of reclaimed water has been minimal for persons residing in the high and low recycled water areas in eastern Los Angeles County. This does not mean that there is no risk. Nor does it mean that there will be no risk in the future. Rather, available epidemiologic evidence provides no indication that the reuse of water has had a noticeable harmful effect. If findings in the on-going water characterization study are also negative, the combined investigations should provide strong evidence to both the public and to the responsible governmental officials as to the relative safety of water reuse."

The epidemiology of drinking water is a vast subject but the chemical support data are short-sighted and colour-blind having no detailed reference to organic matter and its many functions. The evaluation of drinking water quality has scarcely begun.

If the primary organic burden of the streams, rivers and lakes is drawn from sources reminiscent of the compost heap, that of ordinary urban sewers is more like that of the midden. In terms of plant nutrition, animal manure (or processed sewage sludge) contributes only nitrogen and phosphorus and to a minor extent accessory and unnecessary other elements. Liebig showed that plants acquire carbon entirely from the atmosphere and the function of the added and endogenous organic matter is predominantly to condition the soil and sustain its living battalions of degraders that mobilise some and immobilise other elements. While plant extracts and fermented products are found in drinks worldwide, there are few drinks in everyday use that overtly contain degraded residues from animal excretion. Essentially contact with or incorporation of plant-derived residues is acceptable and any hint of excretory products is wholly repugnant. Nevertheless much effort has gone into seeking outlets for urea in the feeding of crops, plants, flowers etc. and also as a nitrogen supplement to cattle feeds for animals whose digestion affords scope for its incorporation into proteins. The recycling of faeces has also been attempted as a feed supplement. The conversion of waste waters into potable water even if it contains a small element of recycling of excretory residues is unlikely to pose any health threat providing disease parameters are eliminated. The organic substances and their chlorinated derivatives thus contributed will be different from those from pristine water.

The province of public wastewater treatment is highly political. Probably in no country are effluent standards uniformly laid down and monitored and even where modest achievable discharge limitations are set these are often violated. For example, the U.S. Water Pollution Control Federation President Mr. C. F. Guarino (1981, page 1358) declares, "Our industry has been under considerable attack this year" ... "The General Accounting Office released a report on the failure of treatment plants to perform because of operation and maintenance problems"... "87% of the plants surveyed were in violation of their discharge permits and 31% were in serious violation" ..."many treatment plants were elaborate hulks of expensive and failing machinery littering the American landscape". Similar accounts emerge in the river board annual reports in other countries. Regarding the aging water and sewer distribution systems, frequent traffic disruption is caused by burst pipes and collapsed sewers as all road users are aware.

There are however successful modern systems with impressive performance usually involving multistage treatments to reduce soluble nutrients, toxic metals, excessive salts and exotic organic contaminants as may be necessary.

In many ways the treatment of industrial wastewater or single effluents can be more logically and economically designed to employ selected unit processes often with cost effective recycling and/or product recovery. Sewage contains energy-rich matter but this is greatly diluted in water thus at the same time making the energy expensive and difficult to recover and creating a large amount of foul water. Many alternative systems have been proposed but, while these could be introduced into new towns, general adoption would be enormously expensive for a general public that can scarcely afford the present system.

The organic components of rainwaters, soilwaters, lakes and rivers, arguably have little in common and it is probably true that there is very little constancy in any of these or in drinking water, wastewaters and treated wastewaters derived from them.

Estuarine chemistry and the human environment

Estuaries are frequently foci of urban and industrial developments and, in turn, pollution. Round the world, many estuaries have been constrained by reclamation, confined by docklands and concrete, dredged beyond historic depth, and swollen by every conceivable type of accidental and deliberate discharge. Popular beach resorts and water sports areas do not always enhance the attractive environments which they have "developed".

Manipulation of estuaries has gone on for many centuries and there is a record of these changes in the sediments and in the flora and fauna. It would not be hard to show equally dramatic effects on the welfare of the generations of mankind that imposed these changes. There are strong historic links between unrestrained pollution, disease. social squalor and ecological decay. The faint marks of lost communities whose livelihood was seaweeds, shellfish, salmonids and sea fishes often persists in overgrown townships. Expressions of the nostalgic charm of long-past fishing communities are their thanks for lives of hardship serving the wider community.

The mixing of river and sea generates a whole repertoire of chemical and biological change whose long-term record is laid down according to the degree of retardation of sediment transport characteristic of the brackish-water zone. In a most useful recent review, Postma (1981) summarises the main physical and chemical features and his group of writers develop the principle themes of flushing times, sediment accumulation and retention, and geochronology. Schink's team (1981) review chemical forces and speciation, the elucidation of chemical dynamics and chemical reactions in general and with respect to certain specific elements.

In lands where the meeting of river and sea generates extensive wet land areas there is concern and controversy about the ecological value of these areas and the degree of damage done to them by eutrophication and accumulation of metals (Lasserre and Postma, 1982). A great deal of this aquatic chemistry has already been touched on and is familiar to marine chemists. In Great Britain all the major estuaries have been studied in depth and many minor ones; in other countries there have been equivalent appraisals.

Apart from very local incidents involving particularly large and toxic specific discharges (e.g. mercury in Japan, Sweden, Canada) and disastrous oil spills virtually worldwide (Johnston, 1984) serious repercussions affecting man have been related to microbial contamination or "Red Tide" toxins (which may or may not be pollution-related). Abnormally high levels of Pb, Cd, Hg and Cu have been recorded in estuarine fish and shellfish; also notable levels of various organochlorine compounds such as PCB's and pesticide residues. Similarly there are enhanced levels of radioactivity in seaweeds, fish and shellfish around outfalls from atomic power stations and nuclear fuel reprocessing plants. Mistakes and accidental discharges happen and the enhanced contamination may at times approach or exceed recommended contact and intake levels but when all goes well the risks even for the people at the end of the extreme critical pathway are extremely slight.

The broad environmental signals given by losses of flora and fauna, enhanced contamination of food species and specific anomalies highlighted in "Mussel Watch" are symptoms of environmental sickness not, or only exceptionally, contagious to humans.

The marine environment in relation to man

In recent years marine pollution has received much attention largely because of enormous oil spills, losses of hazardous cargoes, serious incidents (e.g. Minamata) in estuaries and coastal seas, and the mistaken interpretation of Hg in tuna and swordfish.

Several features of marine life indicate need for caution. The propensity of odd plant and animal species to achieve and survive remarkable accumulation and concentration of any of a wide range of elements and compounds illustrates wide diversities in their metabolisms and potential for dangerous levels. The unexpected and sensational discovery of the ability of commonly-eaten large fish species to acquire threateningly-high concentrations of mercury, mainly in its more toxic methyl form, demonstrates the immediacy of aquatic ecology acting on man. Equally threatening was the discovery of high levels of organochlorines in fish remote from land and even higher concentrations in birds and mammals preying on them. Some fish contain high concentrations of arsenic; some crabs large amounts of cadmium but are these discoveries meaningful for man? The direct adverse impact of enhanced levels of pollutants on developmental stages and diminished, damaged or altered food chains may reduce yields of valuable food species. These responses may be demonstrable only in estuaries, or inshore waters or at dumping sites where marked pollutant gradients are found but some at least may have wider influence which would be very difficult to measure.

The ocean is the final repository of much, perhaps eventually all, of the persistent materials, polluting or not, from terrestrial or urban or industrial sources. A few elements are recycled but the entry of most elements, compounds and particulates is permanent, similarly there is little prospect of removing from the seas and ocean materials introduced by man.

Maynard (1976) claims to recognise a variety of mechanisms for the conversion of river-born major constituents into oceanic carbonate minerals, amorphous silica, altered deep-sea basalts, pyrite formation, Mg–Fe exchange, authigenic silicate mineral formation, cation exchange with clays, evaporate deposition and basalt weathering, all of which might be described as "reverse weathering", but other experts contest these interpretations or regard the processes as insignificant.

According to the recent review of Mackenzie *et al.* (1981) the complex mass balances involving the sea, interstitial water, soils, stream waters and sediments are insufficiently known for these major elements to resolve the issue. How much more uncertain must be the mineralogy and balances for the trace metals and in turn pollutants.

Possibly assisted by a remote and less variable regime, quantitative chemical and biological studies on oceans, open seas and unpolluted estuaries add up to produce a clearer picture of processes linked with human welfare than has emerged for fresh water or drinking water.

Quantitative studies on inputs (Bryan, 1984) and sea-water enrichment (Topping, 1976) are approaching the stage when modelling becomes meaningful. In this context the marine chemists have exhibited an exemplary attitude towards demonstrating the validity and reliability of their oceanographic, chemical and biochemical data, nationally and internationally. This is particularly laudable when the difficulties of collecting, storing and analysing the pertinent range of samples are appreciated and contrasted with the many much less demanding circumstances for achieving similarly valid results for freshwater or drinking water.

Aquatic chemistry and the human environment—conclusions

Although the wider problem of the whole man in the total environment is vast, emotive and unruly, the thread of aquatic chemistry can be shown to offer a measure of rationality and provide at least rudimentary guidelines.

Awareness of contributory processes affecting from rainfall to abyssal ocean waters has attracted sincere attempts to quantify and model the fate of water and key aquatic elements on a global scale. Also other models stem from immediate practical necessity to understand the dynamic processes affecting sediments, water circulation, biological systems and hence budgets for non-conservative elements within individual water bodies.

Experimental large scale ecosystem enclosures have been used, especially by marine scientists, to quantify productivity and ecosystem interrelationships which are so difficult to study at sea. These same units are also useful in determining ecosystem response to stress of pollutants.

Much has been learned about predicting biological response to marine pollution by cooperative ventures such as "Mussel Watch" (National Academy of Sciences, 1980). With the benefit of hindsight one realises that a timely "Mussel Watch" in Minamata Bay could well have warned of impending tragedy.

In recent years the principle findings of on-going research have added a valuable dimension to popular television viewing especially when the research demonstrates a continuous, simplifying concept. Such programmes help to offset the often idiosyncratic interpretations of environmental issues promoted by "movements" and "parties". There are severe limitations to isolated *ad hoc* studies on individual pollution problems as a foundation for environmental understanding. Pressures of immediacy overrule long-term considerations. Concern for scoring legal points outweighs balanced assessment; money limits define the scope of time allotted to sampling, coverage and scientific interpretation. There is little or no recourse either to comparisons with contingent areas and sciences.

Aquatic chemistry is a fundamental element of public health but it seldom emerges as such unless there is a Love Canal, Servaso or Three Mile Islands incident.

Modern technologies are revolutionising traditional heavy industries and introducing many new ones but innovations in man's use of water resources lag a century or more behind. One cause is the extraordinary magnitude of existing works for handling drinking water, sewage and waste water and the excuse is always lack of money. "The technological miracles in certain aspects of water supply and quality standards set in the 1960's and 1970's are at an end and present imposed 'short-term' strictures in the name of economy and efficiency may be expecting too much continued miracle working by staff in all sectors' (Speight, 1982 referring to major plant sites in the U.K.). Continually reinforced financial hurdles preclude any implementation of scientific and technological advances for example in alternatives to water transportation of sewage, alternative chemistry to improve drinking water quality, alternative chemistry to exploit, recycle and treat wastes, alternative energy from large continuing waste inputs.

National and international bodies advocate improved standards but is it the best option to pursue new water quality standards in many parts of the world on the basis of archaic and crumbling methodologies and treatment plants? How valid in chemical and medical terms are the quality objectives being proposed and has established treatment technology even been adequately proven? Here is a very relevant challenge to waterworks chemists and those expert in the physical chemistry of natural waters.

Not all aquatic chemists are particularly conscious of their close commitment to the human environment.

Worldwide, safe drinking water supplies are decreasing. The Director of the World Health Organisation estimated that 13 million children died in 1980 from causes related to contaminated water (World Environmental Report, 5 January, 1981). In relation to the UNE Programmes on the wider environment, U.S. has cut its monetary support by 33% with particular effect on water pollution and many leading countries are decreasing support to national programmes for the maintenance and local improvement of the environment, including the aquatic environment. In this light the current WHO Decade Programme "Clean water and adequate sanitation for all by the year 1990" is a "frighteningly ambitious target" which if not substantially fulfilled has fatal consequences for many millions of the less fortunate in this world.

Superpowers might rate 13 million primary casualties resulting from a nuclear conflict as a fair return for their enormous technological effort and expenses over many years. Over the same period, ordinary technologies and a tiny fraction of the expenses could substantially remove for ever the causes of diseases related to contaminated water throughout the world. This is the sad upsetting aspect.

In our much more comfortable domestic scene much can be done. There are many gaps to fill in present knowledge of the chemistry of water and plenty of scope regarding water and wastewater technologies. Basic tools such as experimental techniques and analytical methods could be greatly improved by coordination and cooperation among chemists working on water.

Aquatic chemistry is taught as pure science in universities, as applied courses for water and wastewater students in trade institutes and as environmental chemistry elsewhere, all with no formal links between courses, lectures, projects or the emerging trained personnel. Integration would be helpful for students from lands with acute water and sanitation problems. Insularity is no less in the acceptability of the various qualifications for entry into employment, also within related academic and trade affiliations. Responsibilities for water in all its aspects are segregated among widely unrelated government departments which avoids the serious disadvantages of one grand scale super department but interdepartmental scientific links are virtually absent.

Although many other cases could be mentioned it would be an overstatement to claim that aquatic chemistry was the only catalyst needed but surely there is enough of common interest to bring together all the scientists if only to begin by forming local groups.

Much is attempted in toxicology, epidemiology, setting water quality criteria, environmental monitoring and even in analytical effort that would greatly benefit by relaxing formal exclusiveness.

Promotion of wider relationships is vital to the development of more direct and practical relationships abroad. It is necessary to breathe life into well-intentioned international programmes on water, sanitation and environmental protection and to provide the broad scientific basis necessary for their success.

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