

James W. Moore

Inorganic Contaminants of Surface Water

Research and
Monitoring Priorities

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Series Preface

This series is dedicated to serving the growing community of scholars and practitioners concerned with the principles and applications of environmental management. Each volume is a thorough treatment of a specific topic of importance for proper management practices. A fundamental objective of these books is to help the reader discern and implement man's stewardship of our environment and the world's renewable resources. For we must strive to understand the relationship between man and nature, act to bring harmony to it, and nurture an environment that is both stable and productive.

These objectives have often eluded us because the pursuit of other individual and societal goals has diverted us from a course of living in balance with the environment. At times, therefore, the environmental manager may have to exert restrictive control, which is usually best applied to man, not nature. Attempts to alter or harness nature have often failed or backfired, as exemplified by the results of imprudent use of herbicides, fertilizers, water, and other agents.

Each book in this series will shed light on the fundamental and applied aspects of environmental management. It is hoped that each will help solve a practical and serious environmental problem.

Robert S. DeSanto
East Lyme, Connecticut

Preface

Environmental cycles can be split into two broad categories: those induced by natural processes and those induced by Humankind. Until recently, nature-induced environmental cycles overwhelmingly dominated anything created or caused by humans. However, in a time when the world's population expands at an unparalleled rate, the corresponding burdens placed on the environment and on the process of environmental protection have intensified as well. Today, the impact of Humankind on the environment has overcome certain natural cycles and now demands complex and far-reaching responses.

Over the last twenty years, improvements in environmental protection and modifications in policy have yielded cleaner water, fresher air, an abundance of fish and wildlife, and a higher quality of life in many western nations. Jobs have blossomed as a result of these trends, and entire industries, such as hazardous waste management, have grown dramatically since 1970. Yet for every force in the direction of positive environmental change, a complementary force has labored to oppose it.

As the environment undergoes progressively greater strains, the process of environmental protection must be designed to meet the challenge. Trends in the positive direction should include the diversion of more money to the protection of water and air, the management of hazardous wastes, and the control of nonpoint sources of pollution. But instead we seem to migrate in the opposite direction, toward an era of heightened indifference and lessened control. Conditions in many countries may very well deteriorate in the 1990's as populations grow and money for the environment is compromised.

Only a determined effort by all those concerned about the world they live in, from laymen, educators, and scientists to policy makers and heads of state, will rescue the cycle and reverse the decline in environmental protection. As an important step toward a reversal of these trends, the effective management of inorganic contaminants of surface water has long been the goal of professionals in public health and the environment. Although the greatest progress has been made in controlling some of the sources of these contaminants, the sheer weight of population and economic growth during the 1990's will likely offset many of these gains. The purpose of this book therefore is to provide an information base for the management of inorganic contaminants in an era of reduced environmental commitment. The reader will initially find a prognosis of environmental change during the 1990's, followed by a technical review of current data on inorganic agents, and concluded by recommendations for research and monitoring.

I would like to thank all those who helped with the preparation of this book and, in particular, Greg, Jill, and Inge.

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1

Introduction

The process of environmental protection will come under staggering pressure during the 1990s and for the foreseeable future. It took all of human history to develop an economy of \$600 billion by the year 1900. Eighty-five years later, the world economy was expanding by more than that amount every 2 years. In the year 2050, the global economy is expected to reach \$13 trillion, more than five times what it is today (Speth, 1988). Resource use will expand enormously, as will the production of waste, the formation of chemical by-products, and the deposition of contaminants into surface waters.

The other staggering inevitability for environmental protection is growth in the world's population: from 3 billion in 1960 to 5.1 billion in 1989 to 10 billion in 2050 (World Resources Institute, 1988; Speth, 1988). All of these people will produce, either directly or indirectly, more waste in an attempt to maintain or increase their standard of living. This will in turn force much of the Western world to use water that does not comply with current quality guidelines, simply because better water will not be available. The same will apply to direct users of surface water, such as fish and aquaculturalists.

Despite the oncoming crush, most Western nations have progressively reduced their expenditures in environmental protection. In the United States, for example, the total amount of money dedicated to research and development by the Environmental Protection Agency has declined from a maximum of \$219 million in 1975 to only \$90 million in 1985. The most recent budgets have featured a small increase in funding, roughly equivalent to the change in GNP (Livernash, 1988). In Canada, total expendi-

tures by the federal government on the environment have declined by more than 25% since 1980 (Environment Canada, 1980–1988). No country in continental Europe has augmented its environmental budget to keep pace with economic development and population expansion. In the United Kingdom, regulatory agencies are underfunded to the point where their effectiveness is diminished (O’Riordan, 1988).

The relatively low priority placed on environmental protection by many technologically advanced nations is manifest in the adulteration of numerous water supplies as well as drinking water. Some of the best examples come from densely populated nations with an expanding industrial economy. Numerous examples can be cited from Europe, including:

North Sea—titanium, chromium, and PCB (polychlorinated biphenyl) contamination

Mediterranean Sea—mercury, oil, microbial pathogens, eutrophication

Rhine River—copper, zinc, lead, chromium, nickel, organochlorine compounds

Elbe River—heavy metals, low dissolved oxygen levels

Wadden Sea—heavy metals, chlorinated organics (Dethlefsen, 1988; Beukema et al., 1986).

There are numerous other similar examples from other heavily industrialized countries such as Japan (Kimura, 1988) and the Soviet Union (Thompson, 1989), where the multiple use of water has been greatly curtailed by untoward control of anthropogenically derived wastes.

One of the major draws on the water pollution control budget of many nations is the need to replace old sewer systems and other related waterworks. Many billions of dollars need to be spent in Canada, the United States, Europe, and elsewhere on decaying systems that may be 50–80 or more years old (Livernash, 1988). In one sense, then, huge sums of money are being spent by many nations on water pollution control, but this refurbishing activity greatly reduces the budget for research, monitoring, development of pollution control technologies, and other activities.

Objectives

The presence of inorganic contaminants in surface water continues to be one of the most pervasive environmental issues of our time. Although control technologies have been applied to many industrial and municipal sources, the total quantity of these agents released to the environment remains staggering (Table 1.1). Such discharges will, in the 1990s, limit the multiple use of water in many regions of the world, and potentially increase the frequency of chronic disease in the human population (Nriagu, 1988). In fact the annual total toxicity of all the metals mobilized

Table 1.1. Global discharges of trace metals (in 1,000 metric tons/yr).

Metal	Water	Air	Soil
Arsenic	41	19	82
Cadmium	9.4	7.6	22
Chromium	142	30	896
Copper	112	35	954
Lead	138	332	796
Mercury	4.6	3.6	8.3
Nickel	113	56	325
Selenium	41	3.8	41
Tin	ND ^a	6.4	ND
Zinc	226	132	1,372

Sources: Nriagu (1988), Nriagu and Pacyna (1988).

^aNo data.

worldwide exceeds the total activity of all organic wastes generated each year (Nriagu and Pacyna, 1988). What effect this will have on the health of future generations is not known.

The management of inorganic contaminants will become progressively more difficult in future years. Scientists, engineers, technologists, and bureaucrats will need to improve both their effectiveness despite diminishing resources and their ability to identify timely and relevant issues. This then leads to the purpose of this book: to help environmentalists control or otherwise manage inorganic contaminants in surface water during an era of fiscal restraint. The reader will find an initial review of the sources, chemistry, and toxicology of many major pollutants of water, followed by a series of recommendations for research and monitoring. The agents selected for review fall into at least one of the following categories: (1) highly toxic and/or persistent; (2) instrumental in regulating the concentration or hazard posed by more toxic agents, or (3) poorly studied but potentially hazardous. The book concludes with a series of overall recommendations and conclusions.

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2

Aluminum

Aluminum is the third most abundant element in the earth's crust, with an average concentration of approximately 8%. It is chemically reactive, occurring principally as the halide or oxide, usually in complex silicates. Although aluminum is found in essentially all plant and animal species, it is not essential for survival. The environmental significance of aluminum has waxed enormously in recent years for two reasons: (1) increased mobilization due to acidification of surface waters, and (2) potential agent in the genesis of Alzheimer's and related diseases.

Production, Sources, and Residues

Production

Aluminum is produced and consumed in enormous amounts in many nations of the world, including both developed and developing countries. Total world production in recent years has exceeded 15×10^6 metric tons annually (Table 2.1). The United States is the world's largest producer, followed by the USSR, Canada, and Australia. The USA and the USSR also lead the way in consumption, closely followed by Japan and the Federal Republic of Germany (FRG).

Sources and Residues

Water. Because aluminum is abundant in the earth's crust and is produced and consumed in huge amounts, it is inevitable that relatively high

Table 2.1. The world's major producers and consumers of aluminum (1986).

Producing nation	Quantity (1,000 metric tons/yr)	Consuming nation	Quantity (1,000 metric tons/yr)
USA	3,037	USA	4,268
USSR	2,300	USSR	1,885
Canada	1,360	Japan	1,624
Australia	882	China	750
Brazil	762	France	593
Norway	712	Italy	510
Venezuela	424	Brazil	424
China	410	Canada	405
Spain	375	UK	389
All other nations	4,287	All other nations	4,363
World total	15,314	World total	16,396

Sources: World Resources Institute (1988); World Bureau of Metal Statistics (1989).

residues will be found in surface water. Furthermore, the decreasing pH of many surface waters and soils, a result of acid deposition, mobilizes aluminum into dissolved species (see Chemistry section) which are easily transported and are biologically available.

One of the major sources of aluminum in freshwater, surpassing industrial users, is the discharge of alum sludge from municipal water treatment plants. Alum sludges are produced when alum or aluminum sulfate ($\text{Al}_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$) is used for coagulation and flocculation of raw water supplies to remove turbidity and/or color. The aluminum content of commercial alum is typically $>50,000$ mg/L (Cornwell et al., 1987). The floc particles are removed mainly during the sedimentation process in which the flocs slowly settle and form a sludge blanket referred to as alum sludge. This blanket consists mainly of aluminum hydroxide [$\text{Al}(\text{OH})_3$], other particles, and flocculated materials. Although the discharge of sludge inevitably increases aluminum residues in surface water, the extent of change does not appear to be great. Cornwell et al. (1987), for example, reported that total Al in the water of the Ohio River rose by a maximum of 0.0008 mg Al/L following the discharge of alum sludge from municipalities.

Aluminum-bearing solid wastes may be dumped in offshore areas, resulting in high but transient aqueous aluminum residues. The North Sea off the coast of Belgium periodically receives 1,000–2,000 metric tons of such waste, causing an initial increase in aluminum to 120 mg/L and pH to 8.5 (Vandelannoote et al., 1987). These can be compared to background levels of 0.007 mg/L and 8.1 pH units, respectively. A hydroxalite-manasseite-like precipitate ($\text{Mg}_6\text{Al}_2\text{CO}_3(\text{OH})_{16} \cdot 4\text{H}_2\text{O}$) is formed on contact with water, which is then highly dispersed.

Evaporation of water is a key factor in controlling aluminum in the water of bogs, ponds, and, to a lesser degree, lakes. As the water evaporates during the summer, aluminum also increases, sometimes to high levels. Urban et al. (1987), working on a series of bogs in eastern North America, found residues of up to 0.5 mg/L in midsummer. The same authors suggested that pH and organic complexation did not control aluminum concentrations in bog water.

Sediment. Relatively high concentrations of Al_2O_3 and related species are found naturally in sediment. Mudroch and Duncan (1986), for example, reported that Al_2O_3 comprised 5.5–16.2% of the dry weight of sediments in the Niagara River (Canada). Similarly elemental Al in the Ganges delta (India) averaged 56,500 mg/kg dry weight of sediment (Subramanian et al., 1988). Such quantities from natural sources are likely to mask most anthropogenic inputs. In fact, Johnson et al. (1986) reported that precipitation loadings to a series of lakes in central Canada accounted for only 2–8% of background loadings. In that study, the concentration of total Al in sediments ranged from 31,000 to 49,500 mg/kg dry weight.

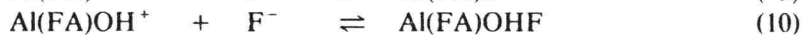
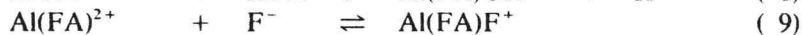
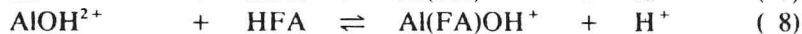
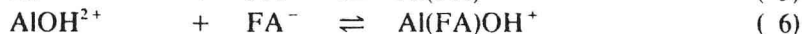
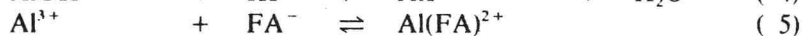
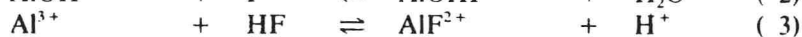
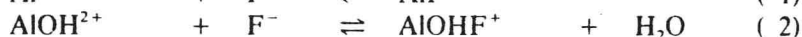
Aluminum from sediments may significantly contaminate surface water if there is turbulence or a decline in pH. Bull and Hall (1986), working on two rivers in the United Kingdom, found that total Al ranged from 0.005 to 0.065 mg/L during periods of low flow but, during moderate flow conditions, the range increased to 0.025 to 0.36 mg/L. The same authors found that, at low pH (<5.5), inorganic Al increased from <0.02 mg/L to a maximum of approximately 0.5 mg/L. Similar findings were reported by Tipping and Hopwood (1988) for monomeric Al and by Sprenger et al. (1987) for total Al in six acidic lakes in New Jersey.

Chemistry

The chemistry of aluminum in water is complex and influenced by pH and the presence of fluoride, sulfate, organic matter, and other ligands. Dissociation of aluminum salts in pure water yields $\text{Al}(\text{OH})_6^{3+}$ and other hydrated aluminum ions. Progressive hydrolysis of the aluminum ion produces $\text{Al}(\text{OH})_2^+$ and ultimately $\text{Al}(\text{OH})_3$, a colloid. If the pH is above neutrality, $\text{Al}(\text{OH})_3$ is converted to $\text{Al}(\text{OH})_4^-$, the aluminate ion. At extremely low pH (<4), aluminum exists mainly as the trivalent cation; at pH 4.5–6.5, the major species are $\text{Al}(\text{OH})^{3+}$, $\text{Al}(\text{OH})_2^+$, and $\text{Al}(\text{OH})_3$; and at pH >6.5, the main species is $\text{Al}(\text{OH})_4^-$. Aluminum solubility is lowest at pH 5.5 to 6.0 (Burrows, 1977).

Aluminum may form relatively stable complexes with fluorides, fulvic acids, and other agents (Plankey and Patterson, 1987, 1988). In addition, monomeric, dimeric, and polymeric Al hydrates may be formed in surface waters, which greatly affect the environmental toxicity of aluminum. The

rates of complexation are apparently dependent not only on pH but also on temperature. An example of the mechanism of complexation with fluorine (F) in the presence of fulvic acid (FA) is given below (Plankey and Patterson, 1988):



where HFA is a fully protonated aluminum binding site and FA^- is a deprotonated site. Reactions 1–3 and 5–8 are important for the complexation of fluoride alone and fulvic acid alone, respectively. The final two reactions (9 and 10) involve fluoride and fulvic acid.

In an experimental watershed in New Hampshire, the speciation of aluminum was determined before and after logging (Lawrence and Driscoll, 1988). The logging operations resulted in an increase in the concentration of nitrates, inorganic Al, and basic cations in the stream, whereas sulfate declined after logging. Precut conditions yielded a predominance of Al-F at the head of the stream followed by Al(OH)_2^+ and AlOH^{2+} (Table 2.2). After cutting, the main species was Al^{2+} followed by AlOH^{2+} and Al-F.

Goenaga and Williams (1988) similarly evaluated the impact of changing water chemistry on aluminum species in a Welsh river, particularly in relation to storm episodes. Organic Al complexes increased significantly during high water, reflecting the increase in total organic carbon and ionic Al. Adsorbed Al also increased during floods to the point where it was second in concentration only to Al^{3+} . This means that suspended solids

Table 2.2. Distribution of inorganic Al complexes in a stream" in New Hampshire before and after logging.

Precut		Postcut	
Species	Percentage	Species	Percentage
Al-F	46.1	Al^{3+}	39.0
AlOH^+	20.1	AlOH^{2+}	25.0
AlOH^{2+}	19.0	Al-F	22.6
Al^{3+}	14.8	Al(OH)^+	13.4

"Stream pH approximately 7.

Source: Lawrence and Driscoll (1988).

could act as a sink for inorganic monomeric Al released during storm events.

Another key aspect of aluminum chemistry is the dissolution of aluminum in soil to neutralize acid inputs such as acid rain. Dissolved Al is highly toxic to crop roots and forests, and may wash into surface waters. Mulder et al. (1989) showed that the most soluble fraction is mainly non-silicate organic Al, formed during the course of soil development. The process of dissolution is relatively rapid and may eventually result in reduced soil acid neutralization.

It is important to note that the toxicity of different aluminum species is poorly understood at the present time. Increased mobilization of aluminum due to acid rain, plus a rise in the frequency of cognitive disorders such as Alzheimer's disease, means that the importance of aluminum species in environmental toxicology and human health will increase. Elucidation of the formation of aluminum species is an important step in managing these conditions.

Bioaccumulation

Plants

Total Al in aquatic and marine plants is often elevated near industrial/municipal waste outfalls. Soderlund et al. (1988) reported residues ranging from 17 to 246 mg/kg dry weight in the growing tips of the macrophyte *Fucus vesiculosus*. These samples were collected in the Baltic Sea near Stockholm. Mason and Macdonald (1988) similarly noted that metal mine drainage resulted in total Al residues of up to 54,000 mg/kg dry weight in aquatic mosses (*Fontinalis squamosa*) in a Welsh river. Less contaminated reaches yielded residues in the 2,000–7,000 mg/kg range. In a study of six acidic lakes (pH 3.6–5.8) in New Jersey, Sprenger and McIntosh (1989) determined total Al in water, sediments, and aquatic plants. The resulting concentration factors (plant concentration/water concentration or sediment concentration) for floating-leafed plants were much lower than for submerged rooted plants, indicating that the primary source of total Al was lake sediment (Table 2.3).

Table 2.3. Summary of concentration factors of total Al in plants from six lakes in New Jersey.

Plant type	Concentration factors	
	Plant/sediment	Plant/water
Submerged-rooted	0.02–0.41	7,100–89,000
Submerged-nonrooted	0.28–0.41	21,600–54,800
Emergent	<0.01–0.17	3,700–11,500
Floating-leafed	<0.01–0.04	180–4,100

Source: Sprenger and McIntosh (1989).