The Dynamics of Aluminum Speciation in Ground Waters from Rhode River Watershed*

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Abstract: *In the Rhode River estuarine/watershed area, increased acidity of precipitation from atmospheric acidic deposition has deleterious effects on the freshwater ecosystems. One of the characteristics of an acidic watershed is the mobilization of aluminum from soils to aquatic environment. Increased concentrations of aluminum in surface waters are toxic to living organisms. Detection of long-term changes of acidity and elevated Al concentrations in surface and soil waters is a central issue. In this present paper, the dynamics of Al speciation in the shallow ground waters from Rhode River watershed 110 (1a) were investigated. This research provides a unique, regional analysis of important controls on the transport of Al speciation through the rural watershed of the Chesapeake Bay.*

Keywords: *Dynamics of aluminum speciation, Watershed, Ground water*

1. Introduction

Acid precipitation in northeastern North America has been shown to produce increased aluminum concentrations in both surface waters and soil waters. Elevated concentrations of dissolved aluminum on element cycling and potential toxicity to terrestial and aquatic biota, particularly to fish (Sullivan, *et al*). However, biotic impacts may be strongly influenced by the chemical speciation of aqueous Al. It has generally been found that the aqueous hydroxo-Al species, Al^{3+}, $AlOH^{2+}$ and $Al(OH)^{2+}$ are the most toxic forms of aluminum(Sposito, 1989). Therefore, an understanding of the speciation of Al is important when assessing geochemical control of aqueous concentrations and transport in surface waters or soil waters. The Rhode River estuarine/watershed system is a tributary of Chesapeake Bay located on the inner Atlantic Coastal Plain. The tidal Rhode River is a shallow, well-mixed, brackish tributary to Chesapeake Bay. Most of the watershed drains into the tidal headwaters through a single tidal creek system, the upper portion of which serves as a spawning ground for species such as yellow perch, white perch and chain pickeral. The most abundant land uses on the watershed are forest, cropland and pastureland.

The forest is composed of mixed deciduous, broadleaved species typical of the eastern U.S. deciduous forest. Since no calcareous minerals are found in the watershed soils, they are poorly buffered against acid rain inputs. (Correll, *et al.*, 1984, 1987). Past research on the Rhode River system has documented that the decline of pH and increased Al concentrations in soil and stream waters (Weller, *et al.*, 1987). Rhode River spawning runs of Perca Flavescens declined drastically during last two decades. Because acid deposition to acid-sensitive watersheds mobilizes Al within the mineral soil, causing elevated concentrations of Al in soil solutions and surface waters, therefore it is essential for us to understand the processes regulating the inputs of Al species to surface waters. In this paper, we would like to investigate how Al species in a shallow ground waters can change over the course of an acidic watershed as influenced by changes in major water quality parameters, particularly pH, concentrations of fluoride and dissolved organic carbon (DOC).
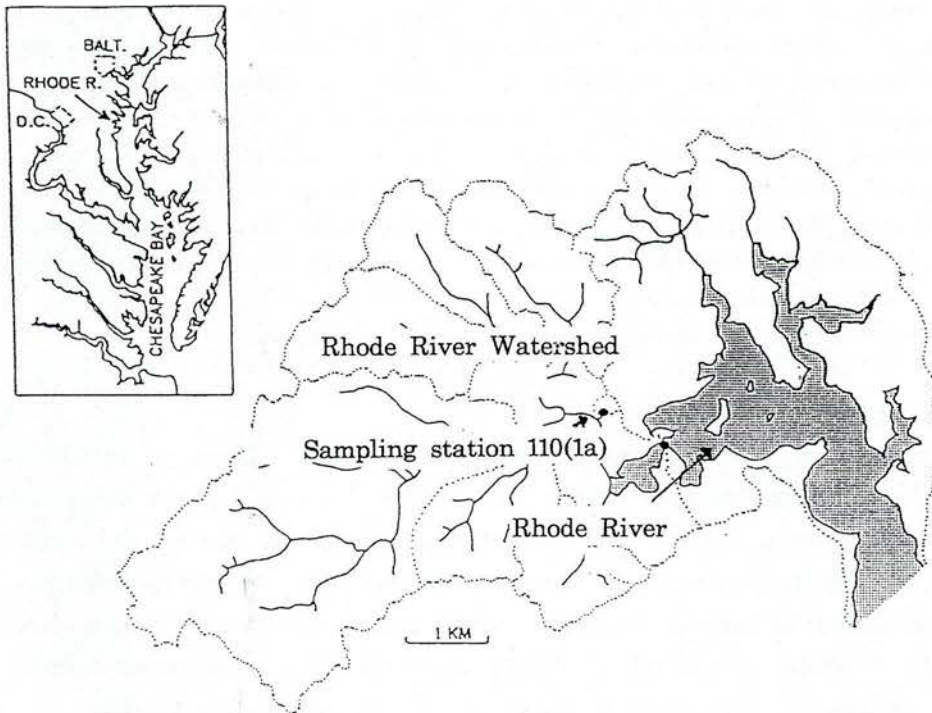

Fig.1 Map of the Rhode River Watershed (Left: Location of the Rhode River (arrow) in the Chesapeake Bay region near the cities of Baltimore and Washington, D. C. Right: The Rhode River watershed and estuary. Subwatershed boundies are indicated by dotted lines. Automated samplers are indicated by large dots.)

2. Study site

The Rhode River eatuary/watershed is located east of Washington, DC on the western shore of Chesapeake Bay, approximately 20 km south of Annapolis, MD (38°53'N, 76°35'W). A small

subwatershed 110 , entirely forested with deciduous hardwood species , was selected for study   to
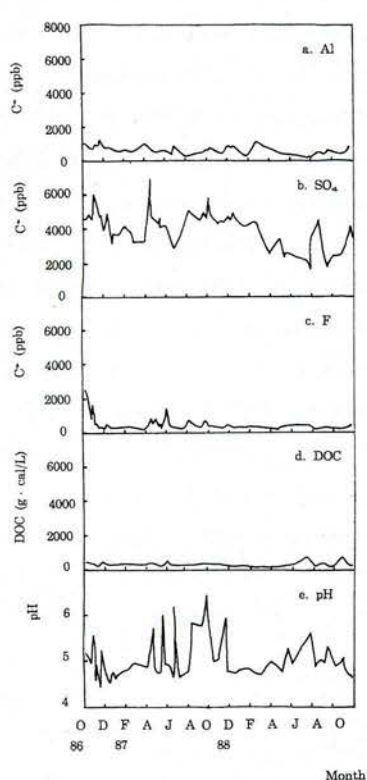

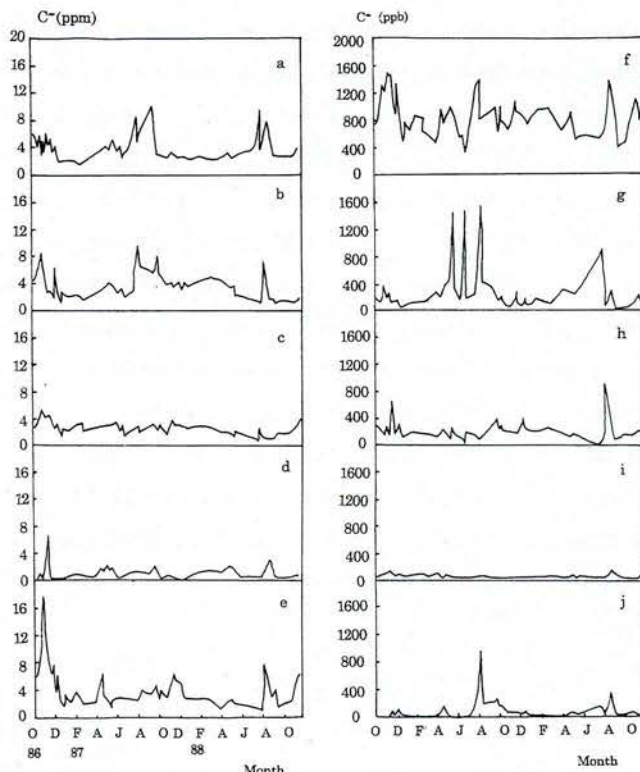**Fig. 2 Dynamics of the total con-
centrations of Al, SO4, F,
DOC and pH**

**Fig. 3 Dynamics of the total concentrations of
ionic composition;** a. K,   b. Na,   c. Ca
d. NO_3,   e. Cl,   f. Mg,   g. NH_4,   h. Fe,
i. Mn.   J. P

represent the most abundant land use on the watershed (Fig. 1). The average particle composition
of the watershed soils is 46 % sand, 39 % silt and 15 % clay. For 60 cm soil cores collected in all
seasons from different sites on watershed 110, the mean pH was 4.9 and soil organic matter
content was 4.2 %. Shallow groundwater was sampled from wells lined with PVC pipe. All of the
sampling and routine chemical analysis of water quality were conducted by the procedures
described by Correll, *et al.* (1987).   We use the data from Sept. 1986 to Oct. 1988 to illustrate
certain spatial trends in the aluminum chemistry of Rhode River watershed. The equilibrium
speciation of Al was calculated with the modified MINEQL computer model developed in our
laboratory (Shuping Bi *et al.*, 1997a,1997b,1997c).

3. Results and discussion

The data on the ionic composition of shallow groundwaters in Rhode River watershed 110 (1a)

are shown in Fig. 2 and 3. The total dissolved aluminum concentration increased when the water experienced episodically low pH values. The water was rich in DOC and the total fluoride concentrations were high relative Al. The combined effect of these trends was that the organically complexed and Al-F complex are the dominate forms in the water. Results for speciation of Al by computer Laboratory bioassays revealed that Al has its maximum toxicity to fish at about pH 5 (Driscoll *et al.*, 1979). The likely mechanism is the precipitation of Al hydroxide on gills or other surfaces. In addition Al has been known to kill fish in acidic soft waters at concentrations as low as $100\text{-}200\,\mu\,g\cdot L^{-1}$. However, complexing agents, such as organic acids and fluoride, can decrease greatly toxic monomeric aquo- and hydroxo-aluminum. Our study suggests that in the shallow groundwaters from Rhode River watershed, the aluminum toxicity is not very serious because of its presence in the forms of organic and fluoride bound complexes, even sometimes the pH values of the water are rather low. The reason responsible to the decline of fish population in Rhode River is mainly due to the increase of H+, rather than Al. This research provides essential knowledge for predicting aluminum speciation in Rhode River watershed and will continue to yield important practical information for national and international policy decisions on the controls of atmospheric acid deposition.
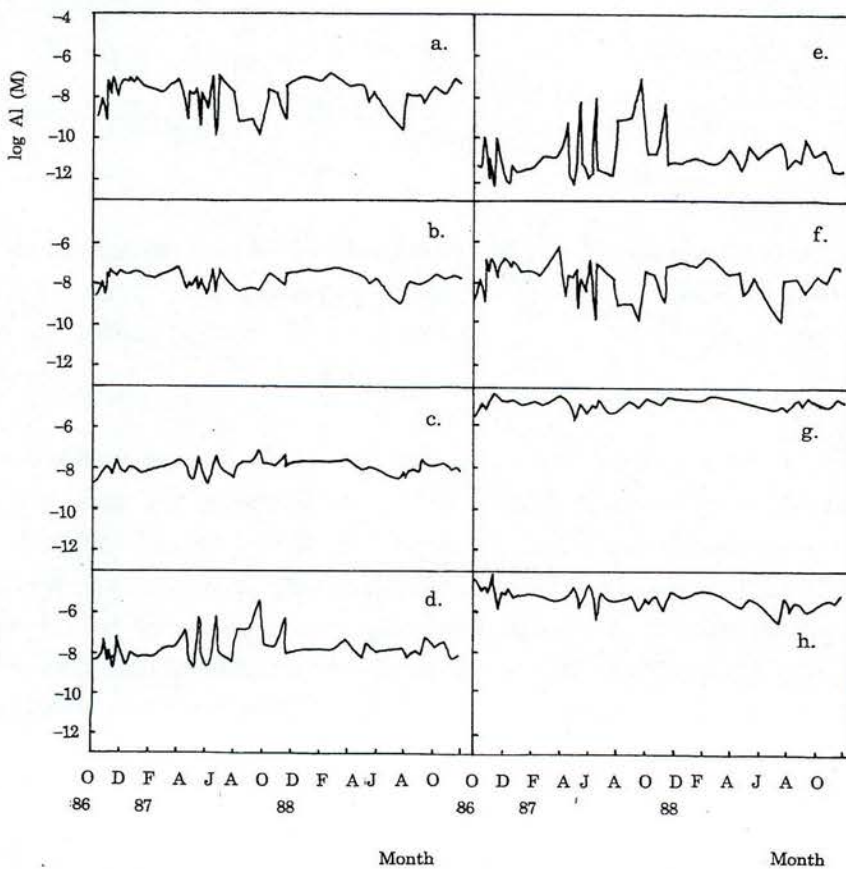

Fig. 4 Dynamics of the concentrations of aluminum species;   a. Al^{3+},   b. $Al(OH)^{2+}$,
   c. $Al(OH)_2^+$,   d. $Al(OH)_3$, $Al(OH)_4^-$,   f. $Al\text{-}SO_4$,   g. Al-Org,   h. Al-F
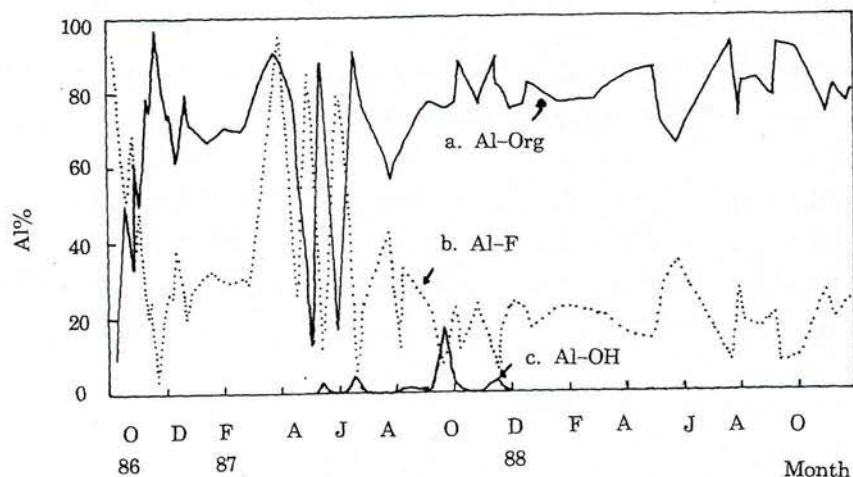
Fig. 5 Dynamics of the percentages of aluminum speciation

$(Al\text{-}OH = Al^{3+} + Al(OH)^{2+} + Al(OH)_2^{+} + Al(OH)_3 + Al(OH)_4^{-})$

Acknowledgements

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