

# Speciation of aluminum in the stream waters from the Susquehanna River watershed, Chesapeake Bay

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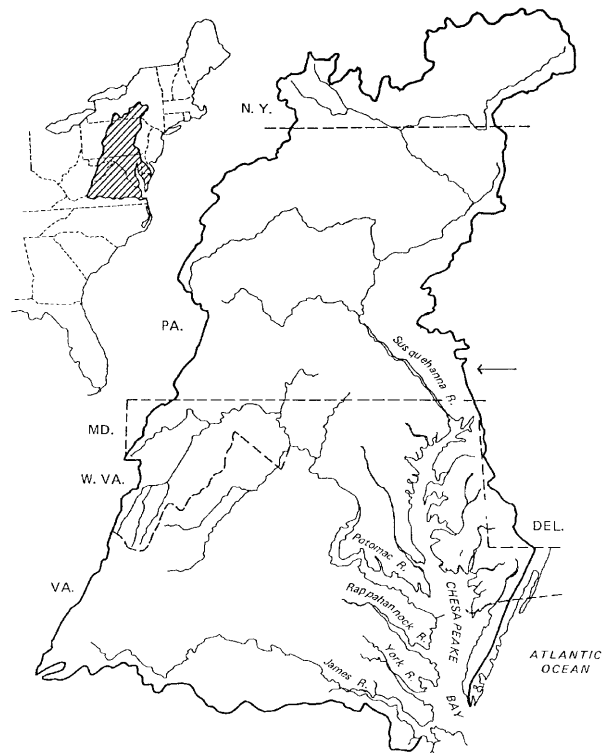
**Abstract** The aim of this paper was to analyze the processing and transport of aluminum speciation through the terrestrial and aquatic ecosystems of the Chesapeake Bay landscape. Stream waters were sampled in 14 different streams from the Susquehanna River watershed to the upper reach of Chesapeake Bay. The basic water quality data were documented and Al speciation was evaluated by modified MINEQL computer model. It was found that the increase in acidity in some of the stream waters near New York were closely linked with a marked decline in basic cation concentrations. In these areas, the sum of the toxic forms of  $\text{Al}^{3+}$  plus  $\text{AlOH}^{2+}$  and  $\text{Al}(\text{OH})_2^+$  concentrations exceeds the critical level of  $5 \mu\text{mol l}^{-1}$ . A potential threat from aluminum may occur.

**Keywords** Acid precipitation · Aluminum speciation · Chesapeake Bay · Stream water · Watershed

## Introduction

In the Chesapeake Bay region, acidic deposition has deleterious effects on watershed and freshwater ecosystem (Jordan and others 1995). One of the most serious problems is the mobilization of aluminum from the soil into drainage and surface waters. Elevated aluminum concentrations are toxic to plant roots and aquatic organisms (Sposito 1995; Astrom 1998). It has been documented that surges in acidity and dissolved total Al concentration reached extremes of pH 3.2 and  $300 \mu\text{g/l}$  Al in the stream waters from the Rhode River watershed, resulting in a decline of anadromous fish populations throughout the Chesapeake Bay (Correll 1986; Correll and others 1987).

The toxicity of Al depends on the forms present in the water, rather than its total concentration only. Free  $\text{Al}^{3+}$ , aluminum hydroxide Al-OH complexes (including  $\text{AlOH}^{2+}$  and  $\text{Al}(\text{OH})_2^+$ ) are thought to be the most toxic species, whereas Al fluoride complexes (Al-F) may mitigate toxicity and organically complexing Al (Al-org) are non-toxic. It has been reported that fish mortality occurs at aqueous plus OH-complexed Al concentrations as low as  $5 \mu\text{mol l}^{-1}$  (Baker and Schofield 1982). The Susquehanna River is the upper reach of the Chesapeake Bay. Many economically important anadromous fish species enter the streams to spawn. The author selected the Susquehanna River watershed as representative to investigate the distribution of aluminum speciation in stream waters in order to better understand the effects of acidification on the ecosystems of the Chesapeake Bay. The purposes of this paper are:



**Fig. 1** Location of the Susquehanna River on the upper reach of Chesapeake Bay

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**Table 1**

Characteristics of the sampling stations

No.	Station	Description	Location
1	412	Small unnamed wooded tributary, at private drive off Wilson Road, first-order stream, 2.5 km <sup>2</sup> , 80–100% forest	Lat. 39.607 N, long. 76.620 W
2	525	Seglock Run at Hopeland Road bridge, third-order stream, 7.2 km <sup>2</sup> , 80–100% forest	Lat. 40.232 N, long. 76.278 W
3	531.1	Walnut Run at Pumping Station Road bridge, second-order stream, 3.4 km <sup>2</sup> , 80–100% forest	Lat. 40.243 N, long. 76.335 W
4	531.5	Kettle Run just above juncture with Hammer Creek at Speedwell Forge Road bridge, second-order stream, 3.2 km <sup>2</sup> , 80–100% forest	Lat. 40.236 N, long. 76.335 W
5	604	Main branch of Buffalo Creek at Aikey Road bridge north of Hartleton, second-order stream, 14 km <sup>2</sup> , 80–100% forest	Lat. 40.920 N, long. 77.158 W
6	606	Upper main branch of Buffalo Creek at Buffalo Flat Road bridge, second-order stream, 4.0 km <sup>2</sup> , 80–100% forest	Lat. 40.940 N, long. 77.227 W
7	608	Upper north branch of Buffalo Creek at Brandon Road bridge, third-order stream, 24 km <sup>2</sup> , 80–100% forest	Lat 40.960 N Long 77.124 W
8	609	Rapid Run at Hwy 192 bridge just west of Jones Mountain Road intersection, fourth-order stream, 38 km <sup>2</sup> , 80–100% forest	Lat. 40.987 N, long. 77.074 W
9	610	Lower Spruce Run south of Mazeppa at old bridge off Johnson Mill Road, fourth-order stream, 57 km <sup>2</sup> , 80–100% forest	Lat. 40.978 N, long. 76.981 W
10	710	Lower West Branch Owego Creek at Creek Road bridge, 1.2 miles north of Flemington, sixth-order stream, 140 km <sup>2</sup> , 40–60% forest	Lat. 42.186 N, long. 76.248 W
11	720	Michigan Creek at Signor Road bridge, ~0.1 mile east of Michigan Hollow Road just south of Tompkins/Tioga County line, third-order stream, 16 km <sup>2</sup> , 80–100% forest	Lat. 42.279 N, long. 76.492 W
12	726	Upper Willseyville Creek at Ridgeway Road bridge just west of White Church, third-order stream, 6.0 km <sup>2</sup> , 40–60% forest	Lat. 42.342 N, long. 76.390 W
13	727	Lower unnamed eastern branch of Willseyville Creek at Hwy 96a bridge, 1.8 miles north of Candor just south of Shindagin Hollow Road, fourth-order stream, 33 km <sup>2</sup> , 80–100% forest	Lat. 42.262 N, long. 76.376 W
14	735	Miller Creek at Fisher Settlement Road bridge just above junction with Michigan Creek, fourth-order stream, 27 km <sup>2</sup> , 80–100% forest	Lat. 42.234 N, long. 76.488 W

**Table 2**

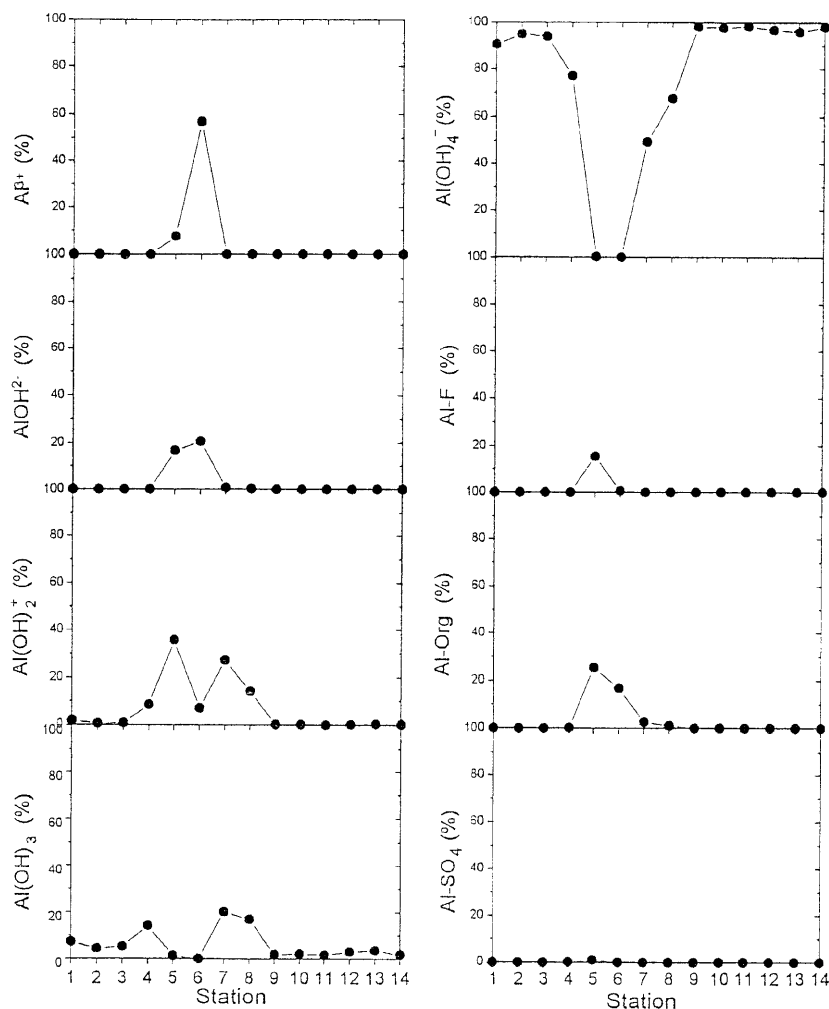
Basic stream water quality. DIC Dissolved inorganic carbon

No.	Cl	NO <sub>3</sub>	SO <sub>4</sub>	Na (mg/l)	K	Mg	Ca	Fe (μg/l)	Mn	DIC (mg/l)	Cond. (s <sup>-1</sup> )
1	10.890	0.732	2.733	4.675	1.954	3.128	6.874	13	4	3.949	94.5
2	7.007	1.909	3.054	4.103	1.048	2.731	12.521	25	14	6.838	114.6
3	6.804	0.201	2.206	4.126	0.865	3.078	7.497	54	7	6.019	86.4
4	2.755	0.411	1.970	1.868	0.748	1.509	3.085	17	9	1.634	41.3
5	0.760	0.053	1.824	0.549	0.599	0.594	1.185	25	62	0.312	22.1
6	0.693	0.000	1.645	0.470	0.254	0.245	0.459	38	83	0.395	26.4
7	0.613	0.066	1.242	0.508	0.653	0.786	2.023	22	0	2.533	23.0
8	2.180	0.078	1.160	1.394	0.543	0.989	2.624	59	0	1.162	29.7
9	3.426	1.439	2.557	1.530	0.857	4.986	19.702	50	2	13.45	150.6
10	11.014	0.851	3.555	5.923	1.032	4.544	24.061	17	0	15.87	191.4
11	4.453	0.083	2.421	3.769	0.562	4.409	21.418	250	9	15.26	155.7
12	2.855	0.034	2.095	2.639	0.496	4.513	19.500	588	64	14.77	142.7
13	5.238	0.146	3.227	3.937	0.911	3.011	10.862	67	21	7.682	104.0
14	4.877	0.336	3.624	3.746	0.783	4.218	18.878	50	7	13.26	149.0

1. to document the basic stream water quality data in the Susquehanna River watershed; and
2. to inspect the distribution of Al speciation in stream waters in this area and to evaluate its possible ecological effects.

## Study site and method

The Susquehanna River is located in south-east Pennsylvania. It accounts for ~15% of the total watershed flow and originates almost entirely in the Appalachians. This



**Fig. 2**  
Distribution of aluminum speciation

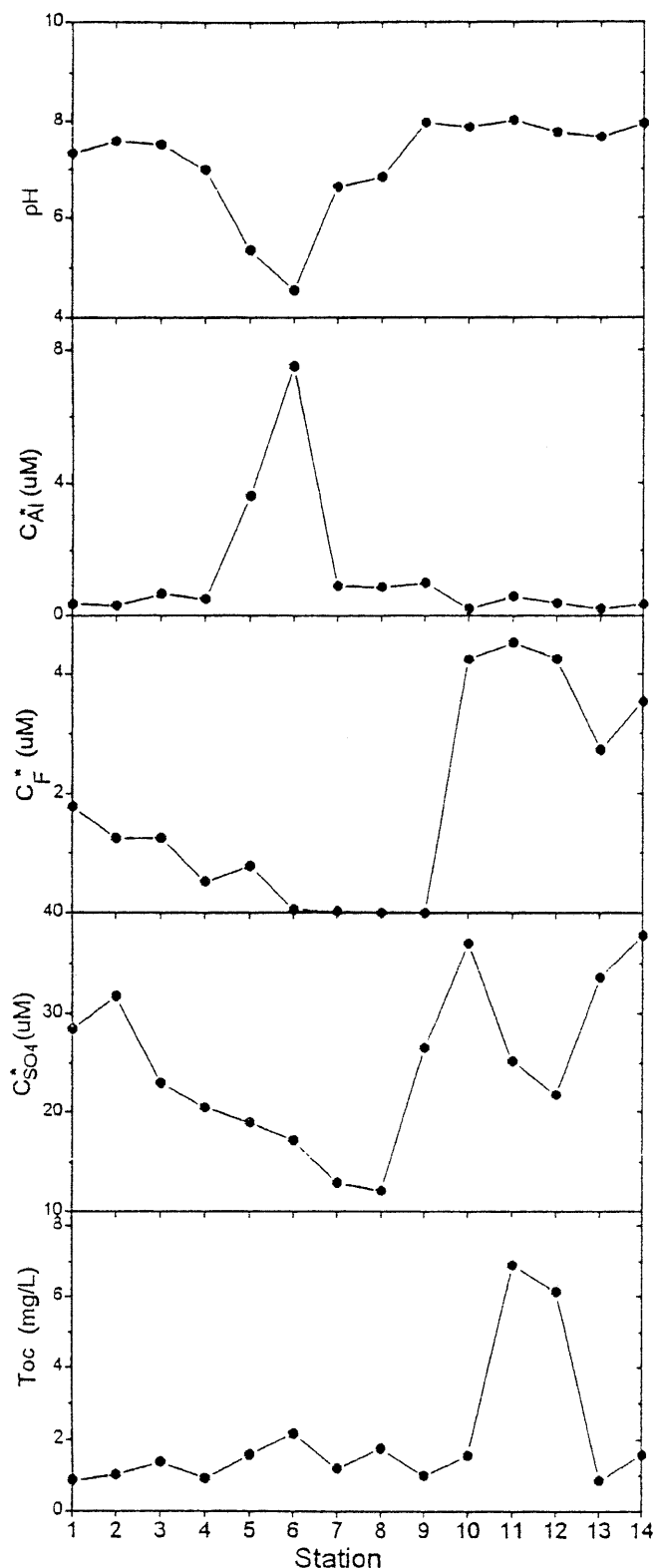
system is located on the parts of the Appalachian and Piedmont (see Fig. 1). Sampling stations include the main stream or streams that drain this basin area. They were selected to avoid urbanized areas, but included forest, cropland, pastureland and residential areas. The characteristics of these stations are described in Table 1. The date of sampling was 12 August 1996. Samples were taken in polyethylene bottles that were pre-rinsed in the stream several times, and immediately filtered through a Millipore HA filter (0.4- $\mu\text{m}$  pore size) that had been pre-washed with distilled water, then immediately placed on ice until analysis 2 weeks later. Detailed information on analytical methods is available elsewhere (Bricker 1984). Aluminum speciation was calculated by the modified MINEQL computer model based on the chemical equilibrium:  $C_{\text{Al}}^* = [\text{Al}^{3+}] + [\text{Al-OH}] + [\text{Al-F}] + [\text{Al-SO}_4] + [\text{Al-Org}]$  (Bi and others 1997).

## Results and discussion

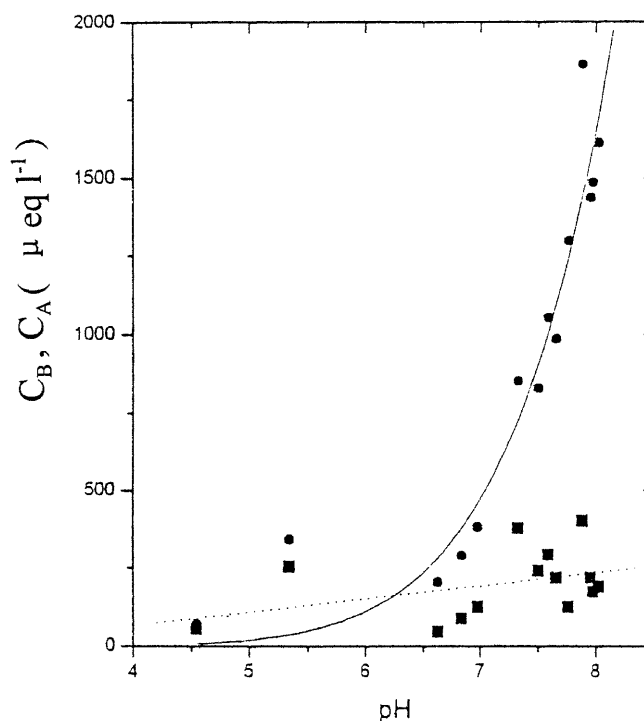
Distribution of Al speciation and water chemical parameters of  $C_{\text{Al}}^*$ ,  $C_{\text{SO}_4}^*$ ,  $C_{\text{F}}^*$ , total organic carbon (TOC) and pH

are given in Figs. 2 and 3. They indicate that for most stream waters with circumneutral values,  $C_{\text{Al}}^*$  concentrations are low ( $< 25 \mu\text{g/l}$ ) and that  $\text{Al(OH)}_4^-$  is the dominant form. These sites appear non-toxic. At site 604 (no. 5), the stream water is slightly acidified with a pH of 5.34, which results in increased concentrations of  $C_{\text{Al}}^*$  (98  $\mu\text{g/l}$ ) and concentrations of inorganic and organic Al complexes. At site 606 (no. 6), which is located in the upper north branch of Buffalo Creek, near New York, the stream water experienced large acidic inputs. The pH value declined to 4.55 and  $C_{\text{Al}}^*$  had the highest concentration of up to 202  $\mu\text{g/l}$ . The sum of the toxic forms  $\text{Al}^{3+}$  plus  $\text{AlOH}^{2+}$  and  $\text{Al(OH)}^{2+}$  concentrations exceeds the critical level of  $5 \mu\text{mol l}^{-1}$ . A potential threat from aluminum may occur in this area.

The increase in concentrations of  $\text{H}^+$  in the streams was associated with a marked decrease in concentrations of basic cations. After inspecting the relationship between basic water quality data (Table 2) and pH, the author found that both  $C_{\text{B}}$  and  $C_{\text{A}}$  are functions of pH. Here,  $C_{\text{B}}$  is the sum of basic cation equivalence ( $C_{\text{B}} = [\text{Na}^+] + [\text{K}^+] + 2[\text{Ca}^{2+}] + 2[\text{Mg}^{2+}]$  in  $\mu\text{eq l}^{-1}$ ) and  $C_{\text{A}}$  the sum of the acidic anions



**Fig. 3**  $C_{Ai}$ ,  $C_{SO_4}$ ,  $C_F$ , TOC and pH values in different sampling stations



**Fig. 4**  $C_B$  and  $C_A$  change as functions of pH. Circle  $C_B$ ; square  $C_A$

( $C_A = [Cl^-] + 2[SO_4^{2-}] + [NO_3^-]$  in  $\mu eq l^{-1}$ ). The pH of receiving waters is governed by a series of processes that either produce or consume the acid neutralization capacity (ANC), which can be defined as:  $ANC = C_B - C_A$  (Schecher and Driscoll 1988). Figure 4 indicates that in the Susquehanna River watershed,  $C_A$  is almost linearly declined with the decreasing pH ( $C_A = -101 + 42.0 pH$  in  $\mu eq l^{-1}$ ,  $r = 0.4010$ ), whereas  $C_B$  declines exponentially much more than  $C_A$  ( $C_B = 84.8 + 0.00659 \exp \{1.55 pH\}$  in  $\mu eq l^{-1}$ ). At site 606,  $C_B - C_A$  value declined below  $20 \mu eq l^{-1}$ , suggesting a slight excess of cations over anions in stream water. This indicates that, in this area, the acidified mechanism is mainly caused from the dilution of basic cations because of the displacement of  $Ca^{2+}$ ,  $Mg^{2+}$  and  $K^+$  by  $H^+$ , rather than the increase in acidic anions  $SO_4^{2-}$  and  $NO_3^-$ . This general decrease in cations is consistent with the reports on an acid-sensitive Massachusetts catchment (McAvoy 1989).

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