

Use of Bromide:Chloride Ratios to Differentiate Potential Sources of Chloride in a Shallow, Unconfined Aquifer Affected by Brackish-Water Intrusion

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Abstract: Brackish water from Chesapeake Bay and its tributaries has entered the Aquia aquifer in east-central Anne Arundel County, Maryland, USA. This determination was made based on chloride analyses of water samples collected in wells screened in the Aquia aquifer between October 1988 and May 1989. The Aquia aquifer, which is composed of fine- to medium-grained sand, is a shallow, unconfined aquifer in this area. Land use is primarily urban, consisting of a mixture of residential and light commercial areas. Associated with the urban setting is the potential for chloride contamination to enter the Aquia aquifer from anthropogenic sources, such as residential septic-tank effluent, leaky public sewer lines, road-deicing salt, stormwater infiltration basins, and domestic water-conditioning recharge effluent.

In order to map the distribution of bay-water intrusion in the Aquia aquifer, chloride derived from Chesapeake Bay was differentiated from chloride derived from anthropogenic sources by comparing the ratio of dissolved bromide to dissolved chloride (bromide:chloride) in groundwater to the distinctive ratio in Chesapeake Bay water. Two additional factors considered in determining the source of the chloride were nitrogen concentrations and well-screen positions of sampled wells in relation to the estimated depth of the fresh-water/brackish-water interface.

Of 36 Aquia-aquifer water samples with chloride concentrations greater than 30 mg/L, 22 had bromide:chloride ratios similar to the ratio in Chesapeake Bay water, an indication that bay water is the primary source of the chloride. Of the other 14 samples with bromide:chloride ratios dissimilar to the ratio in Chesapeake Bay water, seven were from wells where screen positions were substantially above the estimated fresh-water/brackish-water interface. Three of these samples had nitrogen concentrations (as nitrite plus nitrate) greater than 3.0 mg/L, an indication that chloride in these groundwater samples comes from anthropogenic sources, at least in part.

Résumé: Les eaux saumâtres de la baie de Chesapeake et de ses affluents ont pénétré dans l'aquifère d'Aquia, dans la partie centre - est du comté d'Anne Arundel (Maryland, Etats-Unis). Ce fait a été révélé par des analyses d'échantillons d'eau prélevés dans des puits crépinés dans l'aquifère d'Aquia, entre octobre 1988 et mai 1989. L'aquifère d'Aquia, constitué de sable fin à moyen, est dans cette région peu profond et libre. Cette région est essentiellement occupée par un tissu urbain constitué de zones résidentielles et commerciales. Une contamination de l'aquifère d'Aquia par les chlorures est possible à partir des zones résidentielles, du fait de sources anthropiques, comme les effluents des fosses septiques, les fuites des collecteurs d'eaux usées, le salage hivernal des routes, les bassins d'infiltration d'eaux pluviales et les eaux usées domestiques.

Afin d'établir une carte de la répartition de l'intrusion de l'eau de la baie dans l'aquifère d'Aquia, les chlorures provenant de la baie de Chesapeake ont été distingués de ceux fournis par les sources anthropiques par une comparaison du rapport brome/chlore dissous de l'eau souterraine à celui constant de l'eau de la baie. Deux facteurs supplémentaires ont été pris en compte pour définir l'origine des chlorures : les concentrations en azote et la position des crépines des puits échantillonnés en relation avec la profondeur estimée de l'interface eau douce - eau salée.

Sur les 36 échantillons d'eau de l'aquifère d'Aquia dont les teneurs en chlorures sont supérieures à 30 mg/l, 22 présentent un rapport brome/chlore identique à celui de l'eau de la baie, ce qui signifie que l'eau de la baie est la source principale de chlorure. Sur les 14 autres échantillons dont le rapport brome/chlore est différent de celui de l'eau de la baie, 7 proviennent de puits dont la crépine est nettement au-dessus de l'interface eau douce - eau salée. Trois de ces échantillons présentent des teneurs en azote (nitrates et nitrites) supérieures à 3 mg/l, ce qui indique que les chlorures de ces échantillons d'eau souterraine proviennent au moins en partie de sources anthropiques.

Resumen: Agua salobre de la Bahía de Chesapeake y sus tributarios ha penetrado en el acuífero de Aquia, en la parte centro-oriental del Condado de Anne Arundel, Maryland, Estados Unidos. Este dato se basa en el análisis de cloro de muestras de agua recogidas en pozos ranurados en el acuífero de Aquia entre octubre de 1988 y mayo de 1989. El acuífero de Aquia, que está compuesto por arenas de grano fino a medio, es un acuífero superficial y no confinado. El uso del suelo es fundamentalmente urbano, consistente en una mezcla de zona residencial y áreas comerciales. Asociado al asentamiento urbano existe el riesgo potencial de contaminación del acuífero por causas antropogénicas, como

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efluentes de fosas sépticas, filtraciones de la red de saneamiento pública, sales utilizadas para el deshielo de carreteras, cuencas de infiltración de aguas de tormenta y efluentes de acondicionadores de agua domésticos.

Para poder dibujar la distribución de la intrusión de agua de la bahía en el acuífero, se diferenció el cloruro procedente de la Bahía de Chesapeake del procedente de causas antropogénicas, mediante la comparación de la relación entre cloruro y bromuro disueltos en el agua subterránea y su relación con el valor constante en el agua de la bahía. Otros dos factores adicionales que se consideraron para la determinación de la procedencia de los cloruros fueron la concentración de nitrógeno y la profundidad de las muestras en relación con la profundidad estimada de la interfaz agua dulce-agua salobre.

De las 36 muestras del acuífero de Aquia con concentraciones de cloruro superiores a 30 mg/L, 22 tenían una relación bromuro/cloruro similar a la del agua de la Bahía de Chesapeake, indicación que el agua de la bahía es la fuente principal de cloruros. De las otras 14 muestras, con relaciones bromuro/cloruro distintas a la del agua de la Bahía de Chesapeake, siete correspondían a pozos donde la posición de las ranuras estaba sustancialmente por encima de la interfaz agua dulce-agua salobre. Tres de estas muestras tenían concentraciones de nitrógeno (nitrito más nitrato) superiores a 3.0 mg/L, indicación que el cloruro en estas muestras procede de fuentes antropogénicas, al menos en parte.

Introduction

Brackish water from Chesapeake Bay and its tributaries has entered the Aquia aquifer in east-central Anne Arundel County, Maryland, USA. Location of the study area is shown in *Figures 1* and *2*. The area is densely populated, consisting of single-family homes serviced by individual shallow wells tapping the Aquia aquifer. Chloride concentrations in areas affected by the intrusion may exceed the U.S. Environmental Protection Agency (1986) Secondary Maximum Contaminant Level of 250 mg/L. Chloride concentrations as high as 6,500 mg/L have been observed in water samples collected from wells in areas along the shoreline. To determine the current extent of the brackish-water intrusion and to help evaluate the effect that future groundwater development would have on brackish-water distribution and rate of movement, the Maryland Geological Survey and the U.S. Geological Survey studied the Aquia aquifer between October 1987 and June 1992. Results of the study are expected to aid in the development of a water-management plan for the areas affected by brackish-water intrusion.

Groundwater samples were collected and analyzed for dissolved chloride to identify the areas affected by brackish-water intrusion and to map the maximum extent of the fresh-water/brackish-water interface. In this report, brackish water is defined as water with dissolved-solids concentration of 1,000-20,000 mg/L (Drever, 1982, p. 12). Samples from several wells thought to be landward of the brackish-water zone contained chloride concentrations greater than the maximum background level of 10 mg/L. Brackish-water intrusion as the source of the chloride could be easily ruled out in some of the wells; these include, for example, wells that are screened at depths above sea level and with water levels several feet above sea level. In other wells, however, the source of the elevated chloride could be brackish-water intrusion, surficial contamination, or a combination of the two. The Aquia aquifer is unconfined in this area and thus is susceptible to surficial contamination in addition to brackish-water intrusion.

In order to produce a reliable map of the brackish-water distribution in the aquifer, the investigators differentiated chloride derived from Chesapeake Bay from chloride derived

from other sources by examining the ratio between the dissolved species of bromide and chloride. The objective of this report is to describe the means by which the chloride sources were differentiated. Previous studies have shown that bromide:chloride (Br:Cl) ratios in groundwater intruded with seawater are similar to those in seawater (Richter and Kreitler, 1993). This method for identifying chloride sources has also been used in groundwater studies to differentiate between chloride originating from road salt and seawater intrusion (Snow et al., 1990) and between chloride originating from road salt, natural saline groundwater, and formation brines placed in surface pits during drilling of gas wells (Knuth et al., 1990).

Nitrogen concentrations and well-screen positions in sampled wells were examined in relation to an estimated depth to the brackish-water interface to further aid in determining chloride sources. The presence of nitrogen in groundwater indicates possible contamination by sewage effluent, of which chloride is an accessory constituent (Bashar et al., 1990).

Background

The study area is in the Coastal Plain Physiographic Province of Maryland in east-central Anne Arundel County (*Figs. 1* and *2*). The area encompasses parts of three peninsulas that border Chesapeake Bay and two tidal tributaries to the bay. The irregular shoreline forms numerous small inlets and peninsulas. The area, once mostly farmland, is now highly urbanized. Land use is a mixture of residential and light commercial areas. The State Capital, Annapolis, is within the study area.

Beneath the study area are coastal-plain deposits that consist of interbedded gravel, sand, silt, and clay that range in age from Cretaceous to Holocene. The deposits dip gently toward the southeast at about 40 ft/mi (12 m/km). The Aquia aquifer occurs within the Aquia and Severn Formations, which are hydraulically interconnected by an intervening silty clay layer (Brightseat Formation) 10-15 ft (3-4.6 m) thick. The Aquia Formation, a marine deposit of late Paleocene age, crops out within the study area and consists of fine- to medium-grained quartzose and glauconitic sand. The Aquia Formation sub-crops Chesapeake Bay and its tidal tributaries within the study area. The maximum thickness of the Aquia

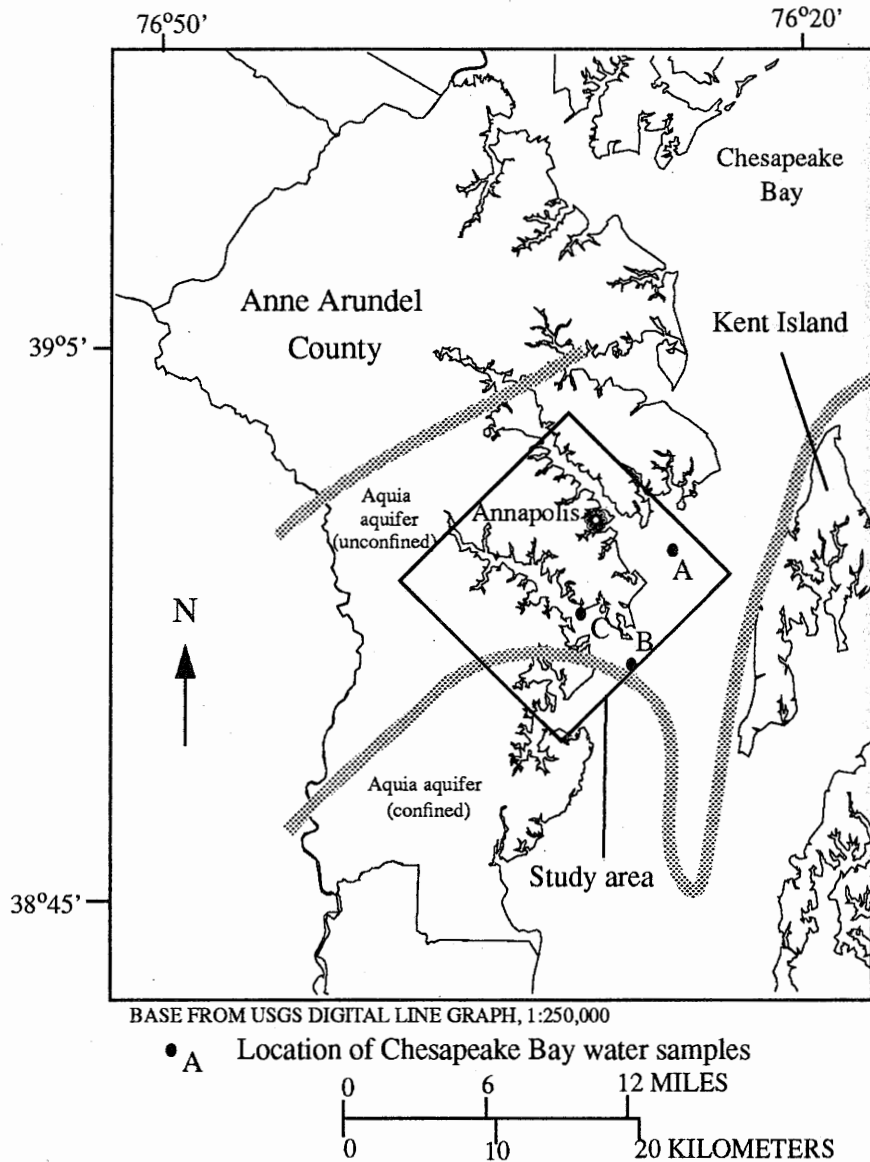
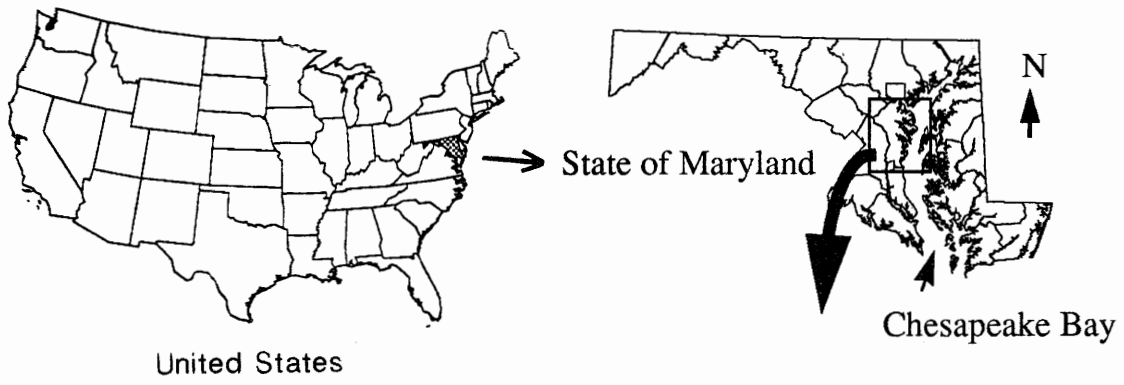
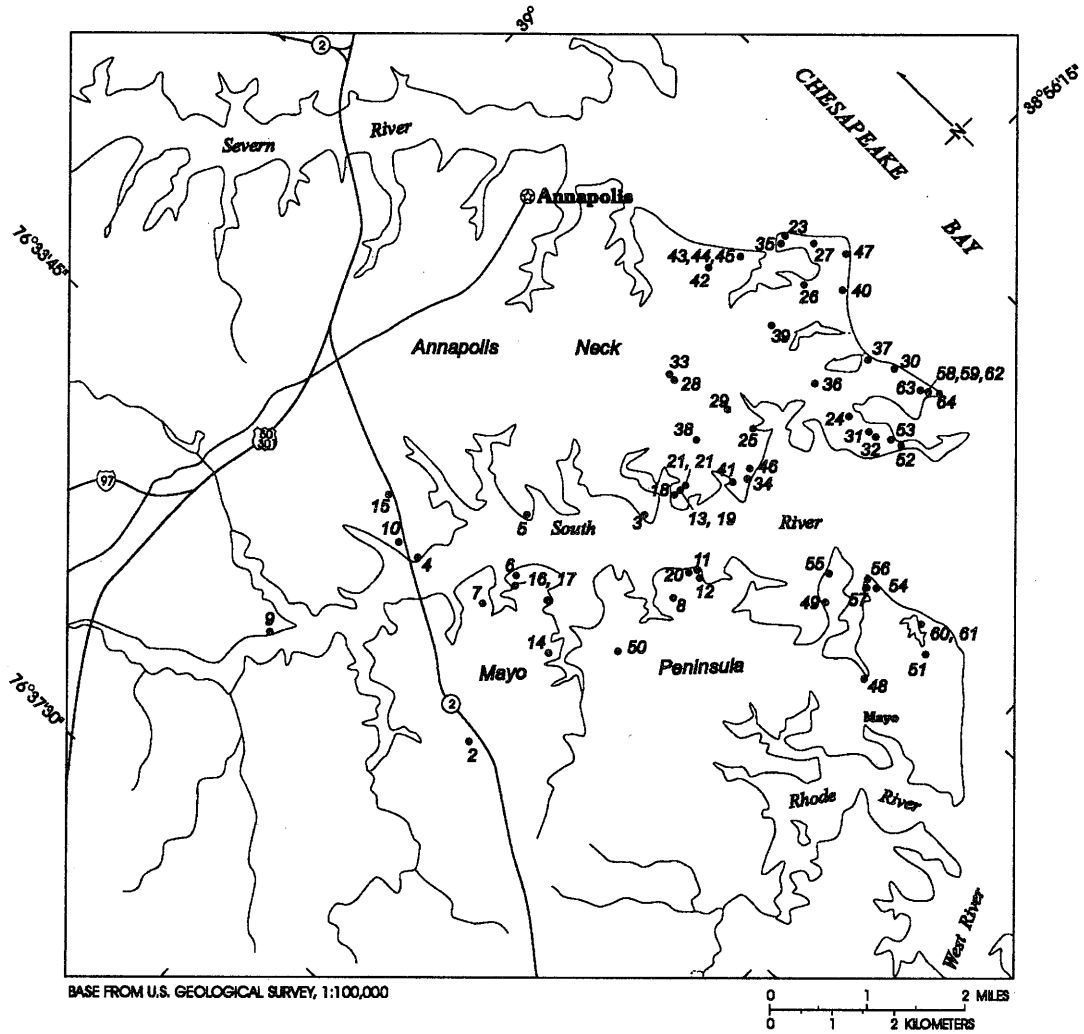


Figure 1. Location of study area.



EXPLANATION

2. Well sampled during study. Number refers to the plot number used in figure 4 and table 1. Well AA Cg 25 (plot no. 1) is located approximately 1 mi (1.6 km) north of study area.

Figure 2. Locations of wells sampled.

Formation within the study area is approximately 120 ft (36 m). Weathered shell beds and calcite-cemented sand are common throughout the formation. In places, irregular weathering has altered the glauconite to goethite or limonite, which forms locally indurated beds of sandstone. The Severn Formation, a marine deposit of late Cretaceous age that is 30-40 ft (9-12 m) thick, is predominantly a fine-grained glauconitic, silty sand. Maximum total thickness of the Aquia aquifer is approximately 160 ft (49 m). The Aquia aquifer is under water-table conditions within the study area and is moderately productive, capable of supplying sufficient quantities of water for domestic use. The horizontal hydraulic conductivity of the Aquia aquifer ranges from 4-43 ft/d (1-13 m/d) (Fleck et al., in press).

Most water use in the Aquia aquifer within the study area is domestic, supplied by individual wells. In 1990, an average of approximately 2.0 Mgal/d (8,000 m³/d) of water was pumped from the Aquia aquifer within the study area (Fleck et al., in press). In 1988, water levels in the Aquia aquifer within the study area ranged from near sea level to 20 ft (6 m) above sea level. In general, the highest water levels are in topographically high areas. Groundwater flows from these areas to discharge areas near the shoreline. Pumpage from the aquifer has caused water levels to decline slightly – approximately 3 ft (1 m) during 1970-94. The lower water levels are thought to have caused a landward migration of brackish water from Chesapeake Bay and its tidal tributaries.

As of 1988, the wedged-shaped interface extended about 300 ft (91 m) inland along the shoreline.

Wells screened in the fresh-water part of the aquifer near the interface may pump brackish water by locally lowering the head, causing upconing of the brackish water into the wells. Upconing near pumped wells was described by Dagan and Bear (1968). The process of upconing of brackish water tends to occur slowly over many years of pumping. Once the chloride concentrations in water pumped from these wells reaches the taste threshold (typically at chloride concentrations of 250 mg/L), well owners in this area commonly switch to bottled water for drinking and cooking or install new wells into a shallower part of the Aquia aquifer or into the deeper Magothy aquifer (Fleck et al., in press).

Methods

Ratios of bromide to chloride in water from the Aquia aquifer were compared to Br⁻:Cl⁻ ratios in brackish Chesapeake Bay water and to the Br⁻:Cl⁻ ratio in seawater. Water from Chesapeake Bay has a distinctive Br⁻:Cl⁻ ratio that can be used as an indicator for brackish-water intrusion. Bromide and chloride are particularly good indicators because both ions are chemically conservative in natural aqueous environments: they do not participate in redox reactions, they are not sorbed onto mineral or organic surfaces, and they do not form insoluble precipitates (Fetter, 1993). Both ions also move freely in the subsurface. Similar Br⁻:Cl⁻ ratios in groundwater and bay water would indicate that bay water is the source of the chloride. Dissimilar ratios in groundwater and bay water would indicate that the chloride is derived, at least in part, from another chloride source.

Nitrogen (as nitrite plus nitrate) concentrations were determined in order to indicate the possible presence of sewage effluent, another source of chloride in the groundwater. Nitrogen in shallow groundwater is typically in the nitrate form. Nitrate and chloride commonly occur together in groundwater contaminated by sewage effluent. Potential sources of sewage contamination to groundwater in the study area include residential septic systems and public sewer lines. Contamination of groundwater by nitrate from fertilizer may also result in elevated chloride concentrations (Richter and Kreitler, 1993).

The fact that some sampled well screens occur above the estimated depth of the fresh-water/brackish-water interface indicates that the source of some chlorides is not likely Chesapeake Bay. The theoretical depth to the fresh-water/brackish-water interface at each well sampled was estimated by use of the Ghyben-Herzberg relation. According to this relation, the depth to the fresh-water/salt-water interface is approximately 40 times the height of the water level above sea level. However, if the density of Chesapeake Bay water in the study area is assumed to be intermediate between that of fresh water and seawater, then the depth to the interface is about 80 times the water-level altitude. Implicit in this relation is the assumption of a sharp interface and hydrostatic conditions. The interface between fresh water and bay water

determined by geophysical logging of test wells indicates that the interface is relatively sharp, about 30 ft (9 m) across; therefore, the sharp-interface assumption is reasonable. Static water levels measured in each well were used in the computation. Where well-screen positions are at least 100 ft (30 m) above the interface, chloride in the groundwater is unlikely to originate from Chesapeake Bay.

Bromide:chloride ratios in water from the Aquia aquifer beneath Kent Island, Maryland, across Chesapeake Bay from the study area (Fig. 1), were determined. The Aquia aquifer at this location has been intruded by brackish water from Chesapeake Bay (Drummond, 1988). Here, the aquifer is overlain by a confining bed that effectively seals it off from surficial contamination. In Chesapeake Bay, adjacent to Kent Island, the confining bed is eroded by a paleochannel, thereby providing a conduit for movement of the brackish water into the aquifer. Therefore, these data reflect groundwater Br⁻:Cl⁻ ratios affected solely by brackish-water intrusion and serve as a contrast to the ratios in the water from the unconfined part of the aquifer that can be affected by surficial contamination.

Water samples were collected from 64 wells in the study area between October 1988 and May 1989 and were analyzed for dissolved chloride, bromide, and nitrogen (as nitrite plus nitrate) (Fig. 2 and Table 1). The water was discharged to an open bucket, where specific conductance, pH, and temperature were measured periodically. After these measurements stabilized, the water was passed through a 0.45-micrometer membrane filter and collected in polyethylene bottles. The water was tested onsite for chloride by use of a Hach³ test kit (mercuric nitrate titration). Water samples collected for nitrogen (as nitrite plus nitrate) analysis were preserved by treating with 1 mL of mercuric chloride. The samples were labeled, packed in ice, and sent to the U.S. Geological Survey's National Water Quality Laboratory in Arvada, Colorado, where they were analyzed for nitrogen, chloride, and bromide.

Error in the laboratory method used to determine chloride ranges from 2-4 percent. Error in the bromide analysis ranges from 8-17 percent for concentrations less than 0.25 mg/L and from 4-8 percent for concentrations greater than 0.25 mg/L (Gary Cottrell, U.S. Geological Survey, written commun., 1995). The reporting levels for chloride and bromide are 0.1 mg/L and 0.01 mg/L, respectively (Pritt and Jones, 1989). Chloride was determined by use of ion chromatography; bromide was determined by use of colorimetry.

Potential Sources of Chloride and Bromide Within the Study Area

Dissolved chloride is common in shallow groundwater, but concentrations resulting from natural sources are generally low (Hem, 1992). The unconfined Aquia aquifer in the Annapolis area is susceptible to chloride contamination not only from

³Use of trade names in this article is for identification purposes only and does not constitute endorsement by the Maryland Geological Survey or the U.S. Geological Survey.

Table 1. Chloride concentrations, bromide:chloride ratios, and nitrogen concentrations of groundwater in the Aquia aquifer. "Plot no." refers to points plotted in Figure 3; <, below reporting level.

Plot no.	Well no.	Cl (mg/L)	Br:Cl ratio	Nitrogen as NO ₂ + NO ₃ (mg/L)	Plot no.	Well no.	Cl (mg/L)	Br:Cl ratio	Nitrogen as NO ₂ + NO ₃ (mg/L)
1	AA Cg 25	6	0.022	0.1	33	AA Df 121	140	0.0011	0.2
2	AA De 64	100	.00062	3.9	34	AA Df 123	88	.0051	.9
3	AA De 165	41	.0020	1.5	35	AA Df 124	120	.0032	1.2
4	AA De 167	19	.0037	--	36	AA Df 126	4	.0056	<.1
5	AA De 168	120	.0030	--	37	AA Df 136	11	.0068	<.1
6	AA De 173	17	.0029	--	38	AA Df 139	14	.0051	1.3
7	AA De 174	10	.0080	--	39	AA Df 146	4	.0060	<.1
8	AA De 175	46	.0015	--	40	AA Df 147	19	.0028	15.0
9	AA De 176	4	.0080	--	41	AA Df 148	1,100	.0030	1.0
10	AA De 179	8	.0068	--	42	AA Df 150	300	.0003	.5
11	AA De 187	400	.0035	2.8	43	AA Df 151	51	.0037	<.1
12	AA De 188	9	.011	--	44	AA Df 152	6	.0011	.3
13	AA De 189	5	.0040	<.1	45	AA Df 153	46	.0018	7.8
14	AA De 190	37	.0022	<.1	46	AA Df 154	3	.014	<.1
15	AA De 191	24	.0011	.9	47	AA Df 155	6,500	.0040	<.1
16	AA De 193	5,900	.0034	<.1	48	AA Ee 71	11	.0027	--
17	AA De 194	310	.0042	<.1	49	AA Ee 77	15	.0053	--
18	AA De 196	3,400	.0035	<.1	50	AA Ee 78	11	.0023	--
19	AA De 197	3	.0071	<.1	51	AA Ef 17	48	.0014	--
20	AA De 198	4,600	.0037	.1	52	AA Ef 20	110	.0013	1.5
21	AA De 200	6,400	.0034	<.1	53	AA Ef 22	1,000	.0043	<.1
22	AA De 201	3,700	.0038	<.1	54	AA Ef 23	73	.0026	--
23	AA Df 32	1,700	.0028	.3	55	AA Ef 24	63	.0029	--
24	AA Df 86	190	.0043	1.4	56	AA Ef 27	190	.0030	--
25	AA Df 98	22	.0030	5.8	57	AA Ef 28	860	.0033	.4
26	AA Df 103	56	.0011	1.5	58	AA Ef 30	73	.0023	<.1
27	AA Df 105	22	.0027	3.5	59	AA Ef 31	6,000	.0032	<.1
28	AA Df 108	160	.0016	3.4	60	AA Ef 33	2,300	.0037	<.1
29	AA Df 112	28	.0036	2.6	61	AA Ef 34	12	.0058	<.1
30	AA Df 114	29	.0033	<.1	62	AA Ef 35	2,300	.0037	<.1
31	AA Df 118	26	.0058	--	63	AA Ef 36	480	.0038	--
32	AA Df 119	24	.0075	.1	64	AA Ef 37	190	.0038	--

Chesapeake Bay and the tidal parts of its tributaries, but also from surficial contamination from anthropogenic sources. Potential sources are identified in the diagram of *Figure 3*.

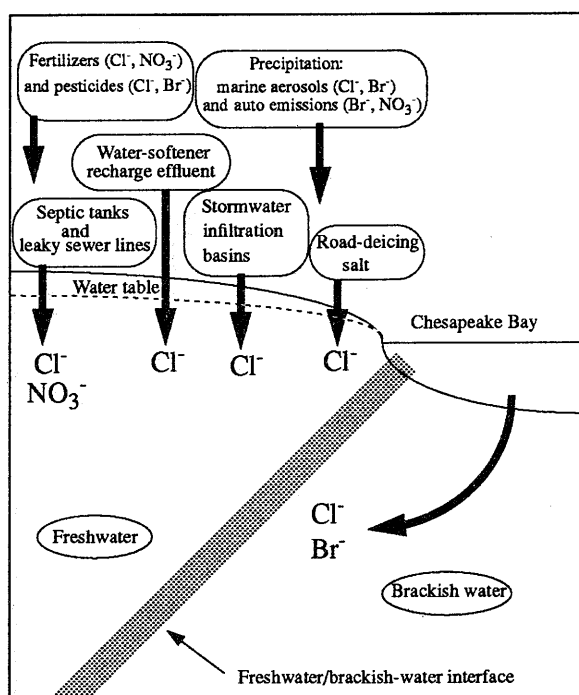


Figure 3. Potential sources of chloride, bromide, and nitrate contamination in the unconfined part of the Aquia aquifer.

The concentration of naturally occurring chloride in the confined part of the Aquia aquifer is as high as 3 mg/L and is derived primarily from precipitation (Chapelle and Drummond, 1983). Chloride concentrations determined in rainwater near Annapolis range from 0.81-2.1 mg/L (Wilde, 1994). Naturally occurring chloride concentrations in the unconfined part of the Aquia aquifer near Chesapeake Bay are probably higher (more than 3 mg/L). The higher concentration is probably a local effect caused by the entrainment in recharge water of wind-driven aerosols off Chesapeake Bay. The upper limit of ambient chloride concentrations in groundwater in the unconfined part of the Aquia aquifer is unknown. In this report, chloride concentrations less than 10 mg/L are considered background. The median chloride concentration was 5 mg/L in 11 water samples from the Aquia aquifer that had chloride concentrations less than 10 mg/L.

Surficial, anthropogenic sources of chloride within the study area that may contribute chloride to groundwater include septic-tank effluent, leaky public sewer lines, road-deicing salt, stormwater infiltration basins, and water-softener recharge effluent. These are only potential sources. In this study, no attempt was made to relate elevated chloride concentrations in the Aquia aquifer to specific anthropogenic sources.

Chloride concentrations in Chesapeake Bay water fluctuate seasonally and with depth in the water column. At two sample sites in Chesapeake Bay near Annapolis, chloride

concentrations measured at the bottom (depth approximately 24 ft, or 7 m) of the water column ranged from approximately 1,300-8,000 mg/L between 1989-95 (Deborah T. Everitt, Chesapeake Bay and Watershed Management Administration, written commun., 1995) (*Fig. 1*; sample sites A and B).

Median bromide concentration in the unconfined part of the Aquia aquifer is 0.032 mg/L, calculated from 11 water samples with chloride concentrations less than 10 mg/L. Bromide in these samples ranged from 0.0066-0.132 mg/L. The primary natural sources of bromide are precipitation and marine aerosols. Bromide analyzed in a rainfall sample taken at a site 30 mi (48 km) south of the study area at approximately the same distance to Chesapeake Bay was 0.03 mg/L (Wilde, 1994). Additional sources of bromide include auto emissions, fertilizers, stormwater infiltration basins and pesticides (Lundstrom and Olin, 1986; Wilde, 1994). These sources probably introduce only minor amounts of bromide into the groundwater system. Road salt is probably not a source of bromide in the study area. Bromide concentrations determined in road salt in Maine, for example, were below detection limits (Snow et al., 1990).

Bromide concentrations measured in bay water at three sites near the study area (*Fig. 1*) ranged from 24-29 mg/L. As with chloride, bromide concentrations in bay water fluctuate seasonally and with depth in the water column.

Bromide:Chloride Ratios in Chesapeake Bay Water

Water in Chesapeake Bay is a mixture of seawater from the Atlantic Ocean and fresh water from streams and groundwater discharge. The most abundant chemical constituent in seawater is dissolved chloride. Bromide, chemically similar to chloride, is also present in seawater but at much lower concentrations. The average chloride and bromide concentrations in seawater are 19,000 and 65 mg/L, respectively (Hem, 1992). Chloride and bromide concentrations analyzed in water taken from two locations in Chesapeake Bay and at one site in a tidal tributary to the Bay during October 1991 ranged from 6,200-6,400 mg/L and 24-29 mg/L, respectively, as shown in *Table 2*.

Table 2. Bromide concentrations, chloride concentrations, and bromide:chloride ratios in Chesapeake Bay water sampled October, 1991. "Plot no." refers to sites shown in *Figure 1*.

Plot no.	Bromide (mg/L)	Chloride (mg/L)	Br:Cl ratio
A	24	6,400	0.0038
B	24	6,200	.0039
C	29	6,300	.0046

Fresh streamwater and groundwater discharge contribute negligible quantities of chloride and bromide to the Bay. Chloride and bromide concentrations measured by the U.S. Geological Survey during 1990-91 at 39 fresh surface-water sites within Maryland's part of the Chesapeake Bay watershed were all less than 24 mg/L and 0.08 mg/L, respectively. Typical concentrations of chloride and bromide in natural groundwater are even lower, i.e., less than 10 mg/L for chloride and near or below reporting level for bromide.

Because bromide and chloride are chemically conservative in aqueous settings, they do not take part in the chemical reactions that typically occur in natural aqueous environments. As a result, the ratio between bromide and chloride is virtually constant with time and among locations. As seawater mixes with fresh water in Chesapeake Bay, the concentrations of chloride and bromide decrease with increasing distance from the mouth of the bay and depth in the water column, but the Br⁻:Cl⁻ ratio remains constant. Therefore, if dilution is the only process acting on dissolved chloride and bromide in Chesapeake Bay, then the Br⁻:Cl⁻ in bay water should equal the Br⁻:Cl⁻ in seawater. Based on the average concentrations of chloride and bromide given by Hem (1992), this ratio should equal 3.4×10^{-3} . This figure agrees with the ratio 3.5×10^{-3} determined by Morris and Riley (1966). The Br⁻:Cl⁻ ratios determined at the three sample sites (*Fig. 1*) ranged from 3.8×10^{-3} to 4.6×10^{-3} . Analytical error in the chemical analysis probably accounts for the difference between the ratios.

Results And Discussion

The Br⁻:Cl⁻ ratios and corresponding chloride concentrations are plotted in *Figure 4*. Two trend lines are included for comparison. One line is the theoretical Br⁻:Cl⁻ ratio in Chesapeake Bay, based on Hem (1992) (equivalent to the Br⁻:Cl⁻ in seawater); and the other characterizes groundwater with background bromide concentration affected by a chloride source not typically containing bromide, such as road-deicing salt, sewage effluent, or water-softener effluent. This trend line is meant to represent native groundwater affected by an anthropogenic chloride source. Also plotted on the graph are Br⁻:Cl⁻ ratios determined for Chesapeake Bay water at three locations. Water samples with nitrogen concentrations (as nitrite plus nitrate) greater than 3.0 mg/L are identified on the graph, as are samples from wells screened more than 100 ft (30 m) above the estimated fresh-water/brackish-water interface.

Bromide:chloride ratios are highly variable in the unconfined part of the Aquia aquifer where chloride concentration is less than 300 mg/L. The cause for variability in the data (mostly below the bay-water Br⁻:Cl⁻ level) between 10 and 300 mg/L is probably contamination from an anthropogenic chloride source. Below 10 mg/L, the chloride ratios are higher than the bay-water Br⁻:Cl⁻ ratio. The increase in the Br⁻:Cl⁻ ratio is probably attributed in part to bromide enrichment of recharge water in the soil zone caused by soil decomposition (Gerritse and George, 1988) or to an increase in bromide in precipitation from automobile emissions (Lundstrom and Olin, 1986). Bromide:chloride ratios in the

confined part of the Aquia aquifer at Kent Island under ambient conditions (low-chloride water) are also highly variable, as shown in *Figure 5*.

It is difficult to differentiate between chloride sources in samples from the unconfined part of the Aquia aquifer with chloride concentrations less than 30 mg/L, because groundwater affected by anthropogenic sources of chloride and bromide can have a Br⁻:Cl⁻ ratio similar to bay water at that low chloride concentration. Natural and anthropogenic sources of chloride and bromide can result in the same Br⁻:Cl⁻ ratio as bay water in this chloride-concentration range. In the Kent Island data, Br⁻:Cl⁻ ratios in water containing more than about 20 mg/L of chloride plot near the bay water Br⁻:Cl⁻ ratio trend line (*Fig. 5*); below 20 mg/L of chloride, however, the data points are scattered. The amount of scatter in the plotted Kent Island data below 20 mg/L is probably caused by variations in the concentrations of naturally occurring chloride and bromide in the aquifer. In the plotted Anne Arundel County data, the amount of scatter is probably caused by variations in naturally occurring chloride and bromide, as well as by input of bromide and chloride from anthropogenic sources.

The occurrence of Br⁻:Cl⁻ ratios that are similar to the bay-water ratio in samples from the unconfined and confined parts of the Aquia aquifer indicates that bay water is the primary source of the chloride. Thirty-six samples from the unconfined part of the Aquia aquifer had chloride concentrations greater than 30 mg/L. Of these 36 samples, 22 had Br⁻:Cl⁻ ratios similar to the bay-water ratios (*Fig. 4*). These samples, which did not have elevated nitrogen concentrations (as nitrite plus nitrate), were from wells whose screen positions were within the estimated fresh-water/brackish-water interface. The Br⁻:Cl⁻ ratios in these samples deviated from the theoretical bay-water ratio by a magnitude consistent with variations in the Br⁻:Cl⁻ ratios in bay-water samples and with the amount of possible analytical error. The scatter in the plotted data is similar to that shown for seawater-intrusion samples from California, Israel, Hawaii, Spain, and Texas (Richter and Kreidler, 1993).

In the unconfined part of the Aquia aquifer, 14 samples with chloride concentrations greater than 30 mg/L have Br⁻:Cl⁻ ratios dissimilar from that of bay water (*Fig. 4*). These samples are probably affected by surficial contamination or by a combination of surficial contamination and bay-water intrusion. Seven of these samples are from wells whose screen positions are more than 100 ft (30 m) above the estimated fresh-water/brackish-water interface. Three of the seven samples had nitrogen concentrations (as nitrite plus nitrate) greater than 3.0 mg/L, an indication of possible contamination from sewage effluent.

The occurrence of a Br⁻:Cl⁻ ratio that is different from the bay-water ratio does not eliminate bay water as a possible source of chloride; for instance, the Br⁻:Cl⁻ ratio in groundwater affected by a combination of bay water and sewage effluent may differ from the bay water Br⁻:Cl⁻ ratio if the amount of additional chloride from the sewage is great enough to affect the ratio. A Br⁻:Cl⁻ ratio similar to that in bay

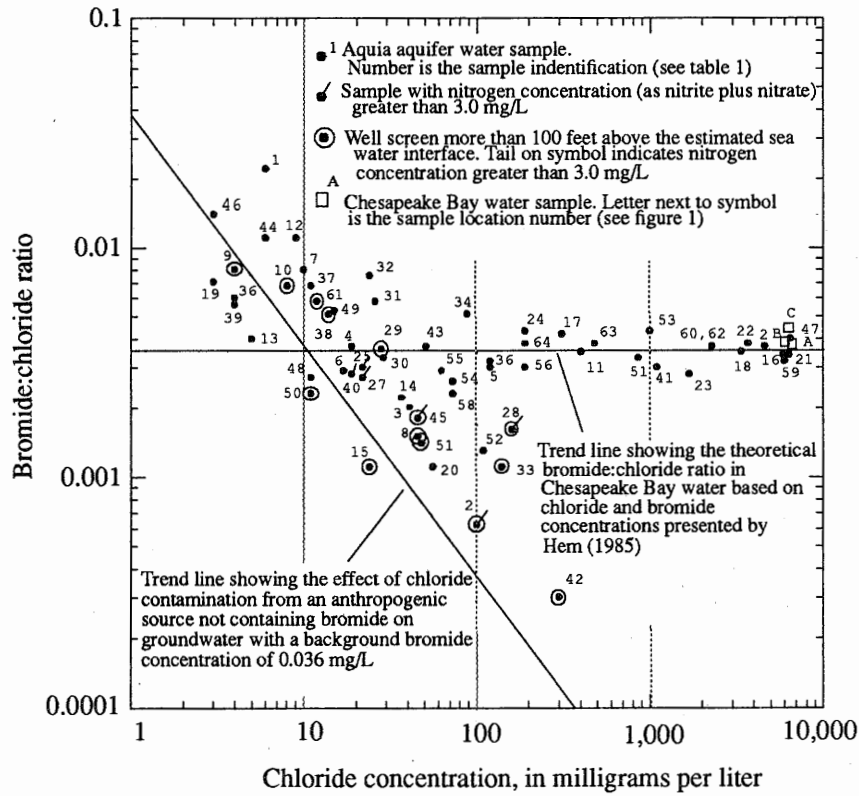


Figure 4. Bromide:chloride ratios related to chloride concentrations in water samples from Chesapeake Bay and the unconfined part of the Aquia aquifer.

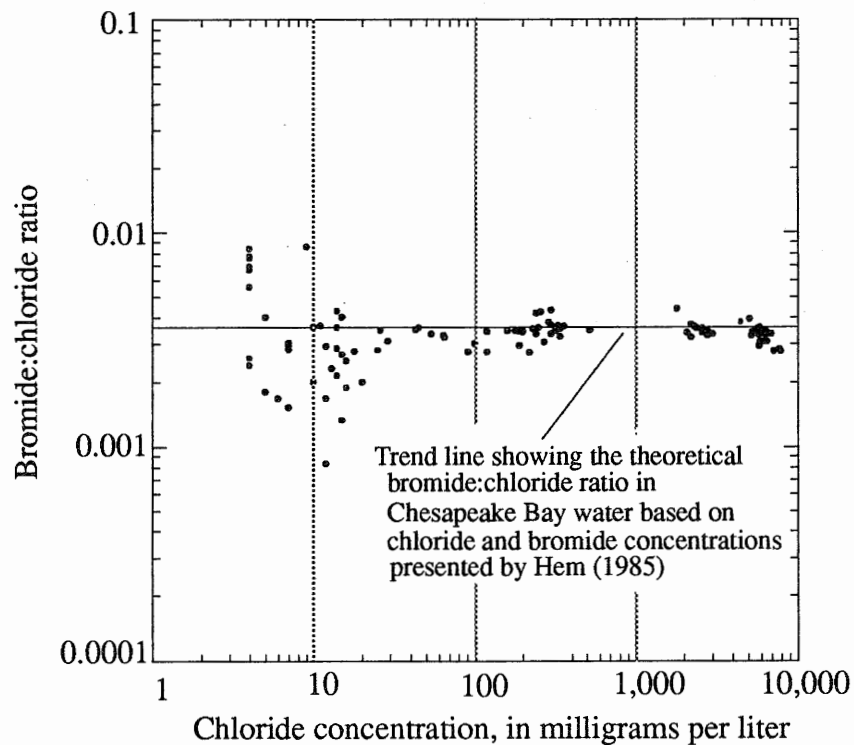


Figure 5. Bromide:chloride ratios related to chloride concentrations in water samples from the confined part of the Aquia aquifer.

water in groundwater with a chloride concentration greater than about 30 mg/L, however, indicates that bay water is a source of the chloride and likely the only source.

If samples that plot along the bay-water Br⁻:Cl⁻ trend line are disregarded, then the data show an inverse relation (decreasing Br⁻:Cl⁻ ratio with increasing chloride content). In *Figure 4*, this trend generally coincides with a line representing Aquia water affected by chloride sources not containing bromide. This trend line can be shifted to a parallel position by varying the values assigned as the background chloride and bromide concentrations.

In conclusion, chloride in groundwater from salt-water intrusion can be differentiated from chloride from anthropogenic sources by comparing the distinctive Br⁻:Cl⁻ ratio in seawater to Br⁻:Cl⁻ ratios in groundwater samples. Bromide:chloride ratios similar to the seawater ratio indicate that salt-water intrusion is the source of elevated chloride in groundwater suspected of being intruded by seawater. Dissimilar ratios indicate that chloride has entered the groundwater from anthropogenic sources or from a combination of seawater and anthropogenic sources. This method was effective for groundwater samples with chloride concentrations greater than about 30 mg/L, because anthropogenic sources of chloride and bromide can produce the same Br⁻:Cl⁻ ratio as seawater in samples with chloride concentrations less than about 30 mg/L. The presence of elevated nitrogen concentrations and the occurrence of well-screen positions above the estimated fresh-water/salt-water interface (calculated using the Ghyben-Herzberg relation) can also help to determine if the groundwater is affected by an anthropogenic chloride source. In the shallow, unconfined aquifer intruded by bay water considered in this report, water from 14 wells out of 36 sampled with chloride concentrations greater than 30 mg/L had Br⁻:Cl⁻ ratios different from the bay-water ratio. This indicates that chloride in these groundwater samples, at least in part, comes from anthropogenic sources. These samples were disregarded when mapping the extent of brackish-water intrusion in the aquifer.

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