

BROMIDE IN LONG ISLAND GROUNDWATERS AND SURFACE WATERS

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INTRODUCTION

Bromine, Br, is a trace element in Long Island's groundwater and surface water. It is mostly present as bromide, Br⁻. Most bromide in the Long Island aquifer system is derived from precipitation originating over the ocean. Storm systems developing over the continent may also contain bromide. In continental storm systems, the bromide is probably principally derived from the combustion of fossil fuel. Non-atmospheric sources of bromide include agricultural chemicals and septic tank effluent. Once bromide is in the aquifer system it is largely unreactive and behaves conservatively. Hence, the bromide chemistry of the water may be used to identify different types of water (e.g., pre-development vs. post-development water). In this study, a large number of ponds in Suffolk County and 13 wells were analyzed for bromide, chloride, nitrate, and sulfate.

BROMIDE CHEMISTRY AND GEOCHEMISTRY

Bromine is a halogen (F, Cl, Br, I) with an atomic weight of 79.9 (g/mole). In natural waters, bromide, Br⁻, is the most abundant form of bromine. Methyl bromide, derived from pesticides, forest fires, and fossil fuel combustion (Manö and Meinrat, 1994), is also found in waters but its concentration in natural waters is largely unknown. It is likely, however, that methyl bromide becomes mineralized and leads to bromide. A second organic-Br compound that may have been important in the past is ethylene bromide. Before the introduction of unleaded gasoline, ethylene bromide was used as an additive to remove PbO from cylinder walls. Measurement by Lininger et al. (1966) showed a high correlation between lead and Br in aerosol samples taken near a bus stop in Boston. In the combustion of leaded gasoline a Pb-Br salt is apparently formed which subsequently releases bromine into the atmosphere (Lininger et al., 1966). Rain and snow would have removed most of the bromine (and Pb-Br salt) from the atmosphere. Once in surface or groundwater the bromine is likely to be reduced to bromide. Presumably, this source of Br is no longer important, but 20- to 50-year old groundwater near urban centers may still have elevated Br concentrations. Because methyl bromide and ethylene bromide are probably largely converted to bromide in the atmosphere, surface waters or shallow groundwater, the remainder of this paper will concentrate on bromide.

The ocean is the largest reservoir of Br in the hydrosphere. Average sea water contains about 67.3 ppm Br or 0.842 mM Br. In comparison, average sea water contains 19,354 ppm Cl or 546 mM Cl. Hence, the molar Br/Cl ratio in sea water is $1.542 \cdot 10^{-3}$. Earlier work by Duce et al. (1965) and Gerritse and George (1988) shows that rain water collected in coastal locations has typically a Br/Cl ratio equal or slightly higher than that for sea water. Because on Long Island most precipitation (dry and wet) is derived from the ocean, the Br/Cl ratio in wet and dry precipitation is expected to be close to that in sea water.

Bromide is also introduced in surface waters and aquifers as a result of agricultural, industrial and residential activity. Some herbicides and insecticides contain Br. Waste waters from food processing facilities are apparently enriched in Br compared to sea water, $\text{Br/Cl} = 8.9 \cdot 10^{-3}$ (Wilson et al., 1990). Septic tank effluent varies in Br/Cl ratio between $0.9 \cdot 10^{-3}$ to $3 \cdot 10^{-3}$ (Wilson et al., 1990). Halite, NaCl, which is the principle component of roadsalt on Long Island, excludes Br from the crystal lattice because Br^- is a much larger anion than Cl^- . This exclusion of Br leads to a molar Br/Cl ratio in halite that is a factor 20 to 30 lower than in sea water. Therefore, waters impacted by road runoff during the winter are expected to show a Br/Cl ratio below that of precipitation.

Bromide is taken up by plants (Gerritse and George, 1988) although it is not clear whether it is an essential nutrient. Soils and plant tissue often have considerable Br concentrations and their Br/Cl ratio is anywhere from a factor of 5 to 40 higher than that in sea water (Wedepohl, 1974; Gerritse and George, 1988). Hence, although Br is largely inert in the hydrosphere, some of it gets preferentially incorporated in organic material. Upon combustion of organic material, such as wood or coal, a significant fraction of the Br is released to the atmosphere (Manö and Meinrat, 1994, Krasnow and Palmer, 1988). Therefore, precipitation in areas where coal or wood is burned is expected to have higher Br/Cl ratios than in precipitation originating over the ocean.

RESEARCH STRATEGY AND METHODS

Because little is known about the Br chemistry in Long Island surface waters and groundwater, the first priority was to determine Br concentrations in these waters. A total of 58 samples from surface waters was taken during the spring of 1994. All of these ponds are located in Suffolk County, Long Island, with most of the ponds located in the Central Pine Barrens of LI. To evaluate the impact of road runoff, 38 ponds close to roads and developments were compared to 20 ponds in the most remote areas of the pine barrens. In addition to Br^- and Cl^- concentration, NO_3^- concentrations were also determined. This is particularly useful in determining whether a surface water is pristine (see Schoonen and Brown, 1994; Schoonen and Kovari, 1994). Besides ponds, we also analyzed over 100 samples from sample stations along the Peconic River. These records span a period of nearly three years and allow for a temporal analysis of Br and Br/Cl in the watershed. Finally, thirteen samples from selected wells were analyzed for Br^- , Cl^- , and NO_3^- . Three of the wells are located in the Peconic River watershed and are screened at depths from 27 to 100 feet. The remaining samples come from three sites along the Suffolk-Nassau border. Wells S95963, S95964, S95965 are located in West Hills County Park near the groundwater divide; N3355 is screened in the Lloyd aquifer south of the groundwater divide; S75033, S75034, S74587, S74586, S87041 make up a cluster of wells near Republic Airport. Because these wells represent both pre-development waters and post-development water, it is possible to evaluate if Br or Br/Cl can be used to "date" water.

Surface waters were collected using a teflon bailer. Groundwater samples were obtained as splits from samples collected by the US Geological Survey during the summer and fall of 1994. All samples were filtered over membrane filters with a nominal pore size of $0.45 \mu\text{m}$. Samples were stored in polyethylene containers and kept refrigerated until

analysis. Br^- , Cl^- , and NO_3^- concentrations were determined using ion chromatography. A Dionex 2000I with a AS4A-SC column and a standard carbonate eluant were used (see Choynowski and Schoonen, 1994). Conductivity was used as the detection method although Br^- and NO_3^- can also be detected with UV-vis spectroscopy. Dried sodium salts dissolved in deionized water were used as external standards. Samples were injected using plastic syringes. Latex gloves were worn throughout the analyses to avoid contamination of samples and syringes with salts present on human skin. The estimated detection limit for Br is 0.2 μM .

In addition to waters, the Br content of road salt was also determined. Road salt obtained from the salt storage facility along Rt 112 in Coram was dried, dissolved in water, and analyzed using the same procedure as for the waters.

RESULTS AND DISCUSSION

The results are summarized in Table 1 (surface waters), Table 2 (road salt), and Table 3 (groundwater).

Table 1. Br concentrations in Long Island surface waters

sample location	remote	[Cl] uM	[Br] nM	[NO3] uM	[SO4] uM	Br/Cl nM/uM
P1 FoX Pond North Shore	no	207	323	9.88	154.2	1.561
P2 Big Sandy west shore	yes	167	234	3.60	81.0	1.404
P3 Linus-Fox Connection	no	216	383	16.41	204.4	1.770
P4 Linus@Line Rd, South tip	no	117	167	1.00	104.0	1.434
P5 Fox South Drain	no	288	120	0.35	58.0	0.415
P6 Sandy Drain@Old River Rd	yes	170	239	3.60	84.1	1.406
P7 Sandy Drain at Sandy	yes	162	256	3.24	77.6	1.582
P8 Big Sandy East Shore	yes	163	263	3.12	77.5	1.613
P9 Grassy Pd	yes	117	191	2.01	47.4	1.637
P10 Wildwood North Shore	no	369	263	13.74	67.9	0.713
P11 Riverhead	no	334	275	9.97	85.2	0.823
P13 Fox Sandy Connection	no	212	299	1.65	132.0	1.407
P14 Artist Lake	no	864	167	9.25	148.7	0.194
P16 Preston at drain	no	192	239	3.77	55.4	1.244
P17 Forest	yes	139	215	0.57	77.2	1.547
P18 Preston beach	no	210	239	1.17	80.5	1.140
P19 Third	yes	129	215	0.15	80.5	1.674
P20 Linus East shore	no	210	263	0.15	68.5	1.251
P21 Linus @ bar	no	200	359	2.97	78.5	1.797
P22 Linus-Fox Culvert	no	209	406	13.13	233.9	1.944
P23 Fuch's Pd Northport	no	732	729	15.39	226.2	0.996
P24 Makamah Pd, Northport	no	662	591	19.77	247.5	0.892
P25 Lake Panamoka	no	325	176	482.49	290.3	0.541
P26 Tarkill Pond	no	129	101	169.30	149.6	0.782
P27 Randal Pond	no	359	113	28.19	88.0	0.315
P28 Horn Pond at Rt 25	no	1128	126	4.70	52.8	0.111
P29 Pond #2	yes	138	126	0.66	41.4	0.914

Table 1 Continued.

sample location	Remote	[Cl] uM	[Br] nM	[NO ₃] uM	[SO ₄] uM	Br/Cl nM/uM
P30 Dead Car Pond or Long Pond	yes	346	452	3.39	33.5	1.306
P31 Peasy's Pond	yes	259	302	5.16	94.1	1.165
P32 Duck Pond	yes	192	251	2.58	76.5	1.312
P33 Sandy Pond in Peasy	yes	195	226	1.20	67.7	1.162
P34 Grassy Pond in Peasy	yes	198	226	1.36	70.8	1.141
P35 Cranberry Bog	no	337	151	1.96	63.8	0.447
P36 Long Pond	no	307	490	2.06	61.6	1.596
P37 Crooked Pond	no	217	126	2.08	69.9	0.578
P38 Lily Pond	no	400	339	1.09	122.3	0.848
P39 Whaler's Drive	no	157	176	2.88	34.2	1.119
P40 Round Pond	no	356	402	4.53	81.2	1.128
P41 Bellows Pond	yes	266	377	1.92	45.6	1.420
P42 Grass Pond	yes	232	251	7.40	61.4	1.085
P43 House Pond	yes	210	277	0.74	71.7	1.319
P44 Division Pond	yes	130	176	1.25	57.0	1.353
P45 Wildwood	no	347	248	1.41	29.0	0.715
P46 Cranberry Bog	no	538	390	1.90	41.2	0.724
P47 Big Sandy Pond	yes	226	413	4.24	71.2	1.826
P48 Grassy Pond	yes	201	484	1.10	45.5	2.412
P49 Fox Pond	no	267	390	0.75	132.3	1.458
P51 Preston Pond	no	299	260	0.66	70.8	0.868
P52 Linus Culvert	no	257	402	3.23	254.9	1.560
P53 Forest Pond	yes	241	248	0.67	29.6	1.029
P54 Horn Pond	no	1588	425	1.07	78.8	0.268
P55 Lake Panamoka	no	356	189	6.42	262.9	0.531
P56 Randall Pond	no	431	71	0.84	80.1	0.165
P57 Makamah	no	597	614	0.78	76.1	1.029
P58 Fuch's Pond	no	728	697	20.51	94.7	0.957

Surface Waters

The surface water samples collected during the spring of 1994 show a distinct difference in Br/Cl ratio for those in remote areas compared to those near roads. This is illustrated in Fig. 1. The average Br(nM)/Cl(μ M) ratio for remote ponds is 1.415 (± 0.333) whereas for ponds near roads this ratio is 0.952 (± 0.501). This difference is significant at $\alpha < 0.2\%$ (based on two-sided *t*-test). As shown in Table 2, the Br/Cl ratio in road salt used on Long Island is a factor of 20 lower than that in sea water. Therefore, the lower Br/Cl ratio for the ponds near roads is consistent with an influence of road runoff. Of course, the winter of 1994 was exceptional in that the number of snow and ice storms was far higher than normal. Hence, variations in ratios due to road-salting during normal winters may be less pronounced.

Table 2. Br in roadsalt¹.

Sample	Br (nM)/Cl(μ M)
A	0.084
A	0.088
B	0.070
B	0.075
B	0.080
average	0.078

¹A and B are two different samples

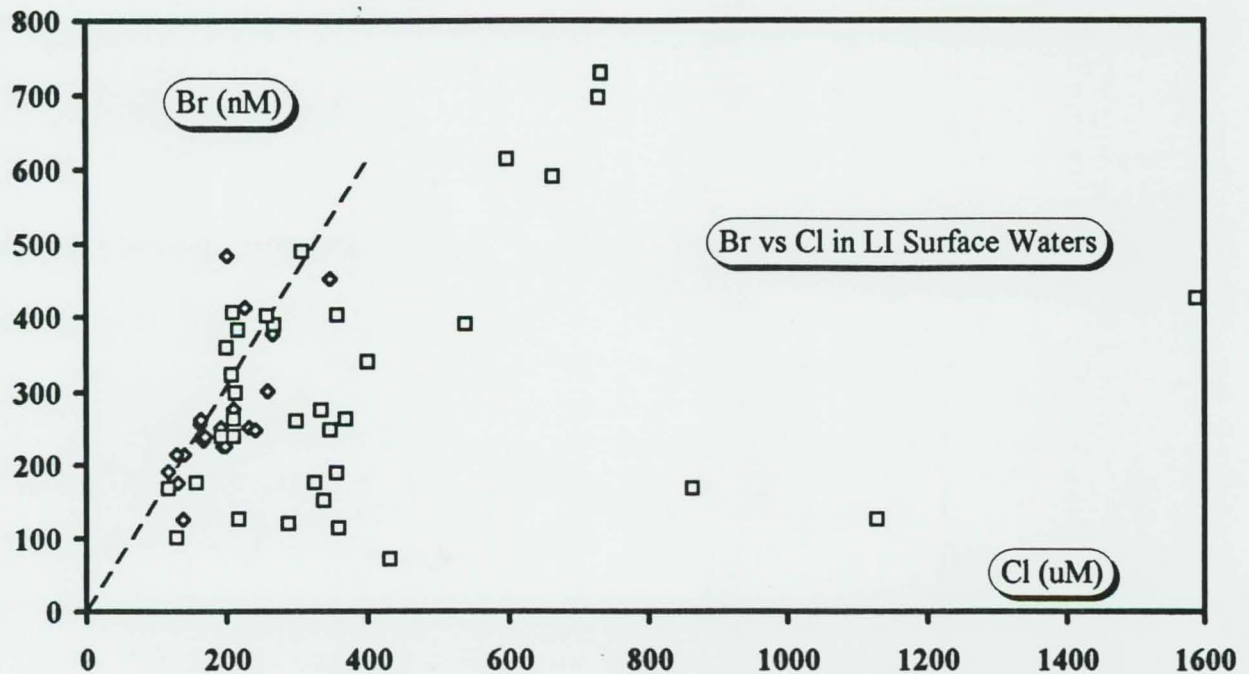


Fig. 1. Scattergram of Bromide vs. Chloride for 58 surface water samples collected in Suffolk County, NY. The diamonds represent remote sites, whereas the squares represent sites near roads and developments. The dashed line represent the molar Br/Cl ratio in seawater

The temporal variation of Br/Cl ratios is more difficult to interpret. Fig. 2 shows the Br vs. time curves for a number of sample locations along the Peconic River (see also Schoonen and Brown, 1994). The stations at River Road and Edwards Avenue show an increase in Br/Cl ratio during the summer. Overall, the average ratios for these stations is close to that expected for sea water but this may be fortuitous. It is possible (but also very speculative) that the increase in Br/Cl during the summer is related to a change in weather patterns. During the summer, local weather systems dominate and bring in rain water high in SO_4^{2-} and NO_3^- (Proios and Schoonen, 1994). The chemistry of this rain water is clearly affected by the atmospheric pollution resulting from the combustion of fossil fuel. Because organic matter (including coal) is enriched in Br over Cl, it is possible that summer rains have Br/Cl ratios higher than sea water. Alternatively (and equally speculative), the change in Br/Cl ratio may be due to biological activity. The temporal

variation in Br/Cl at the sampling station at the Swan Lake golf course shows a very different pattern. Throughout most of the year the Br/Cl ratio is well below the sea water ratio, but in the spring and fall of 1991, it was far higher than for any other water sample measured during this study. It is possible that these water samples were collected after the application of Br-containing turf chemicals. The temporal data for the USGS gaging station at Riverhead show a Br/Cl ratio that typically well below that for sea water, and the average Br/Cl ratio is close to that for the ponds near roads.

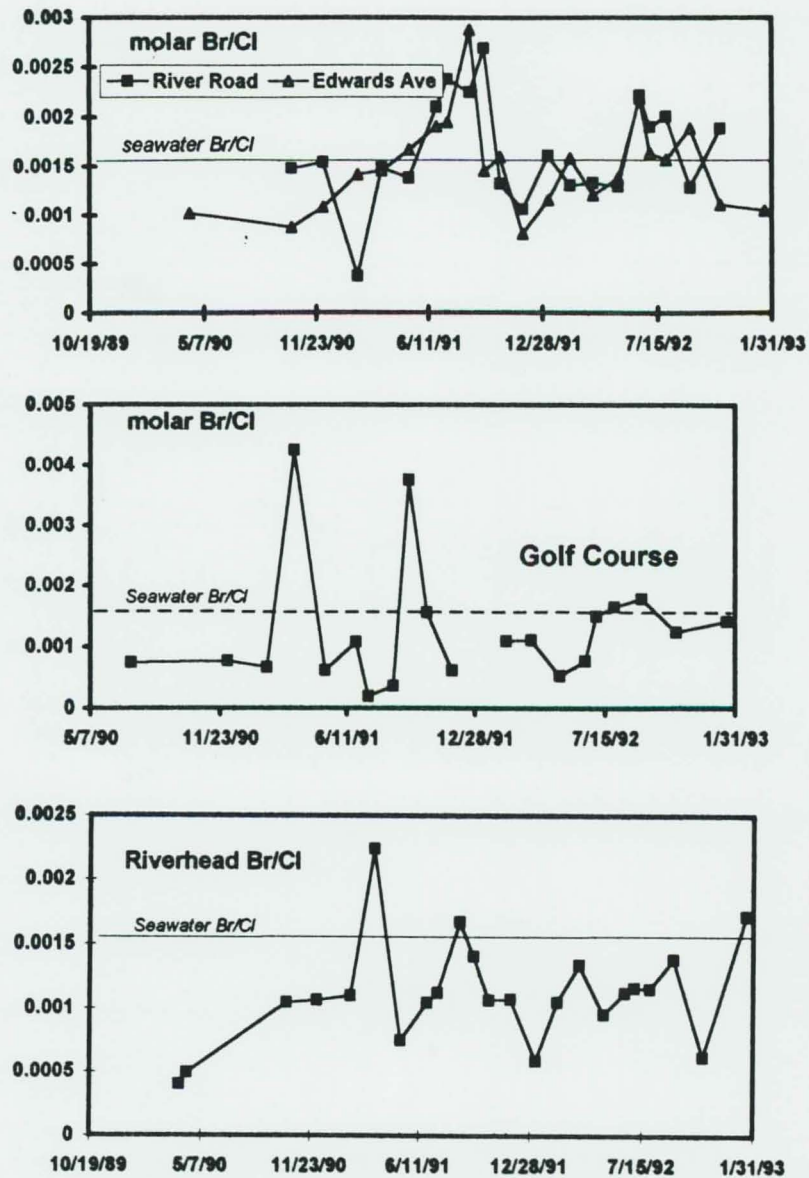


Fig. 2. Temporal record of molar Br/Cl ratio at three sites in the Peconic River watershed. For reference the molar Br/Cl ratio for seawater is shown in each panel. See text for details.

Groundwater

The Br concentrations in groundwater are summarized in Table 2 and illustrated in Fig. 3. Except for two shallow groundwater samples, all samples have a Br/Cl ratio around 1.5 or slightly higher. The shallow waters have exceedingly high Cl concentrations that are most likely due to roadsalt, hence their low Br/Cl ratio.

Well	Location	depth(ft)	Cl, uM	Br, nM	NO ₃ , uM	SO ₄ , uM	(Br/Cl)*1000
S95963	Nas-Suf	193.3	240	453	266.7	8.7	1888.931
S95964	Nas-Suf	411.3	120	453	19.2	8.2	3786.114
S95965X2	Nas-Suf	619	120	226	30.4	15.7	1893.057
S95965	Nas-Suf	619.3	118	302	27.5	14.2	2565.078
N3355	Nas-Suf	1090	95	151	0.3	14.6	1593.081
S75033	Nas-Suf	62.3	453	189	312.2	260.0	416.314
S74587	Nas-Suf	196	101	208	91.7	89.1	2045.995
S74586	Nas-Suf	441.3	80	179	12.8	15.0	2229.120
S75034	Nas-Suf	698	92	132	2.7	12.8	1437.452
S87041	Nas-Suf	983	74	202	1.5	30.8	2738.582
S47226	Peconic	27.2	142	255	0.6	32.7	1792.940
S51592	Peconic	41.1	794	377	17.9	102.9	475.171
S47227	Peconic	100.3	66	107	0.0	15.1	1618.203

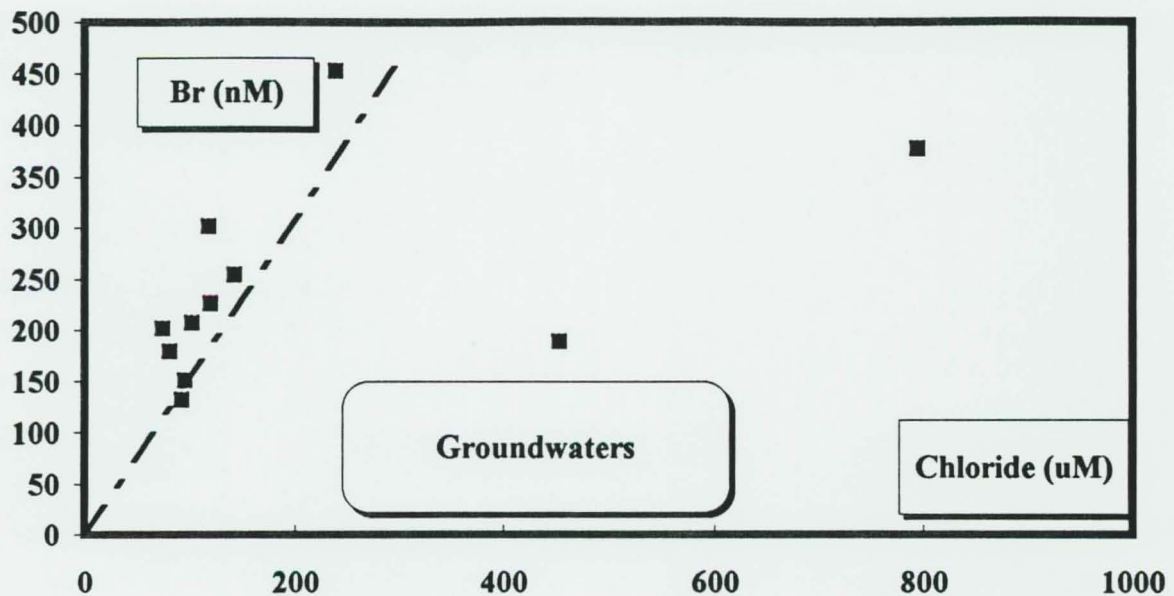


Fig. 3. Scattergram of Bromide vs. Chloride for 13 groundwater samples. The dashed line represent the molar Br/Cl ratio in seawater. The two samples with high Cl concentrations are shallow wells. See Table 3 and text for details.

It is not clear whether the Br/Cl ratios can be used to discriminate between pre-development and post-development waters. As seen in Table 3, waters that are clearly high in nitrate (a sign of development) do not necessarily have a low Br/Cl ratio. Perhaps the Br/Cl ratio tracks a different time scale than the nitrate pollution on Long Island. While parts of the island have been used as agricultural land for more than 200 years, the automobile did not appear in force until the 1940's or 1950's. Hence, the need to apply road salt did not arise until the automobiles were an important part of our society. Therefore, only waters that are less than about 40 years old are expected to show low Br/Cl ratios, whereas much older waters may show elevated nitrate concentrations.

APPLICATION OF BR GEOCHEMISTRY

Br geochemistry has not previously been applied to water-quality studies on Long Island. By contrast, Br geochemistry has been applied elsewhere to determine mixing between different aquifers (Gerritse and George, 1988), tracing of irrigation water (Goldowitz-Joshua et al., 1987), and tracing of different sources of salinity (Wilson et al., 1990). The results of this study show that Br/Cl ratios could possibly be used to "date" waters, i.e. determine if they are less than about 50 years. Of course, more work is needed to develop this application further. A second application may be to use Br as an early warning for salt-water intrusion.

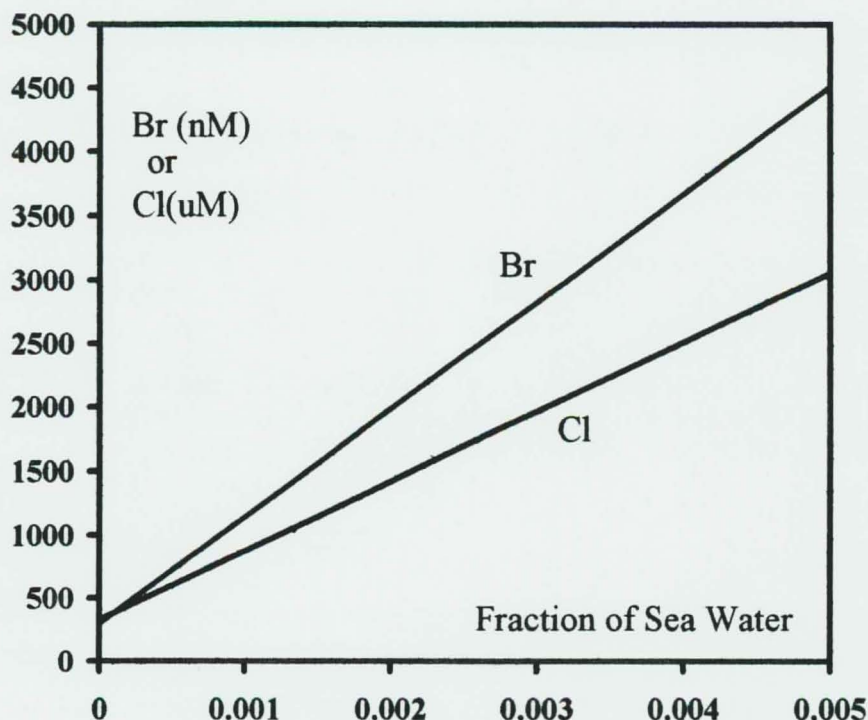


Fig. 4. Hypothetical Br⁻ and Cl⁻ concentrations upon mixing of for seawater and fresh water. Note that a seawater fraction of 0.001 is a mixture of 99.9% freshwater and 0.1% seawater. Also note that the slope of the Br⁻ mixing curve is steeper than that for Cl⁻, hence relative changes in Br⁻ concentration are more pronounced than for Cl⁻. These calculations are based on a Br concentration in freshwater of 0.3 μM (based on this study) and in seawater of 842 μM . For Cl⁻, it is assumed that freshwater has a concentration of 327 μM , while seawater contains 546 mM Cl.

Wells near the shores of Long Island are occasionally disabled by overpumping which draws in saltwater. Such shut downs are costly. Traditionally, chloride concentrations and conductance of the water have been used to monitor the onset of encroachment. These warning systems are based on the fact that sea water has a significantly higher chloride concentration (and salt concentration in general) than freshwater. Hence, when salt water encroaches into an aquifer the chloride concentrations and conductance of the water pumped into the well increase. Br may offer a more sensitive warning signal. As illustrated in Fig. 4., it is possible to determine the admixture of as little as 0.1% sea water. A pilot study to further develop this method is now being planned.

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