

Mobilization of Major and Trace Constituents of Highway Runoff in Groundwater Potentially Caused by Deicing Chemical Migration

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Mobilization of major and trace constituents of highway runoff in groundwater potentially caused by deicing-chemical migration is indicated by analyses of groundwater samples collected at test sites adjacent to Route 25 in southeastern Massachusetts during February and August 1991 and March, August, and November 1993. Analyses indicate that concentrations of major and trace chemical constituents of highway runoff in groundwater are substantially higher downgradient than upgradient from the highway. Highway runoff containing road salt and calcium-magnesium acetate seems to have the greatest effect on groundwater quality at one test site where highway runoff discharges locally to the land surface. This site has an open-drainage system typical of many highways. Analyses from these five sampling rounds are indicative but not conclusive because additional spatial and temporal data are needed. However, this information, when combined with 4 years of monthly groundwater-level measurements and water-quality analysis of groundwater and highway-runoff samples, show that potential mobilization processes include winter recharge, effects related to ion exchange, and acidification and mineral weathering caused by deicing-chemical migration. These processes are hypothesized because 75 percent of annual recharge occurred during the winter months, sodium was exchanged for calcium in infiltrating water, and pH decreased significantly in downgradient groundwater. None of the measured concentrations of the major and trace constituents in groundwater exceed national primary drinking-water standards. However, secondary standards were exceeded for chloride and manganese, and recommendations for surface-water criteria were exceeded for chloride, cadmium, and copper.

The quality of water in the unsaturated zone (1) and of groundwater (2,3) is affected by major ions in deicing chemicals applied to roads and highways. Assessment of the environmental effects of highway runoff requires investigations to determine whether other major and trace constituents are mobilized during deicing chemical migration through the unsaturated zone and in groundwater. To protect groundwater quality, the Massachusetts Highway Department (MHD) has taken steps to reduce salt contamination while maintaining highway safety (4). The U.S. Geological Survey (USGS), in cooperation with MHD, is currently investigating the relative effectiveness of four highway drainage designs in preventing contamination of groundwater by road salt (5) along Route 25 in southeastern Massachusetts (Figure 1).

Constituents commonly detected in highway runoff are sodium, calcium, chloride, aluminum, beryllium, bromide, cadmium,

chromium, copper, cyanide, iron, lead, magnesium, manganese, nickel, sulfate, and zinc, as well as organic chemicals and particulates (6-10). Although environmental issues related to highway runoff have been studied for more than 20 years, investigators generally have concluded that only the major salt ions—sodium, calcium, and chloride—affect the quality of groundwater (11-13). Many field studies have indicated that most metal species in runoff are effectively immobilized in the first 2 to 20 cm of the soil column (7,12,14-16). Similarly, an exponential decay pattern of attenuation has been observed in the first 20 cm of bottom sediments in retention and detention ponds (17). Studies of the mechanisms of immobilization have concluded that ionic constituents in highway runoff are not mobile because they preferentially occupy soil ion-exchange sites (18) and, more importantly, are incorporated into insoluble iron oxides, manganese oxides, metal carbonates, metal phosphates, and natural organic compounds (7,19,20).

Although most of the literature indicates that ionic constituents of highway runoff are effectively immobilized, some studies indicate that mobilization occurs under special conditions. Metals and other ionic species can be mobilized by ion exchange in conjunction with chloride and acetate complexation related to deicing chemicals (10,21-27). Sodium-related clay dispersion can cause mobilization of metal-colloid complexes (23,24,28,29). Metal solubility increases as pH decreases below 7 (12,18,30). Several studies have demonstrated ionic mobilization of highway-runoff constituents that can be associated with a decrease in pH (17,21,25,31,32).

PURPOSE AND SCOPE

This paper describes processes that require further study to determine if mobilization of major and trace constituents of highway runoff in groundwater is caused by deicing-chemical migration. Mobilization is indicated by analysis of groundwater samples for major and trace constituents collected in February and August 1991 and March, August, and November 1993 at a test site along Route 25. This site receives road salt and calcium-magnesium acetate (CMA) from local discharge of highway runoff (S. J. Pollock, Massachusetts Highway Department, personal communication, 1994). Discussion of mobilization processes is based on water-level measurements and water-quality analysis of groundwater samples collected monthly from December 1990 to May 1994 and water-quality analysis of highway-runoff samples collected since 1988.

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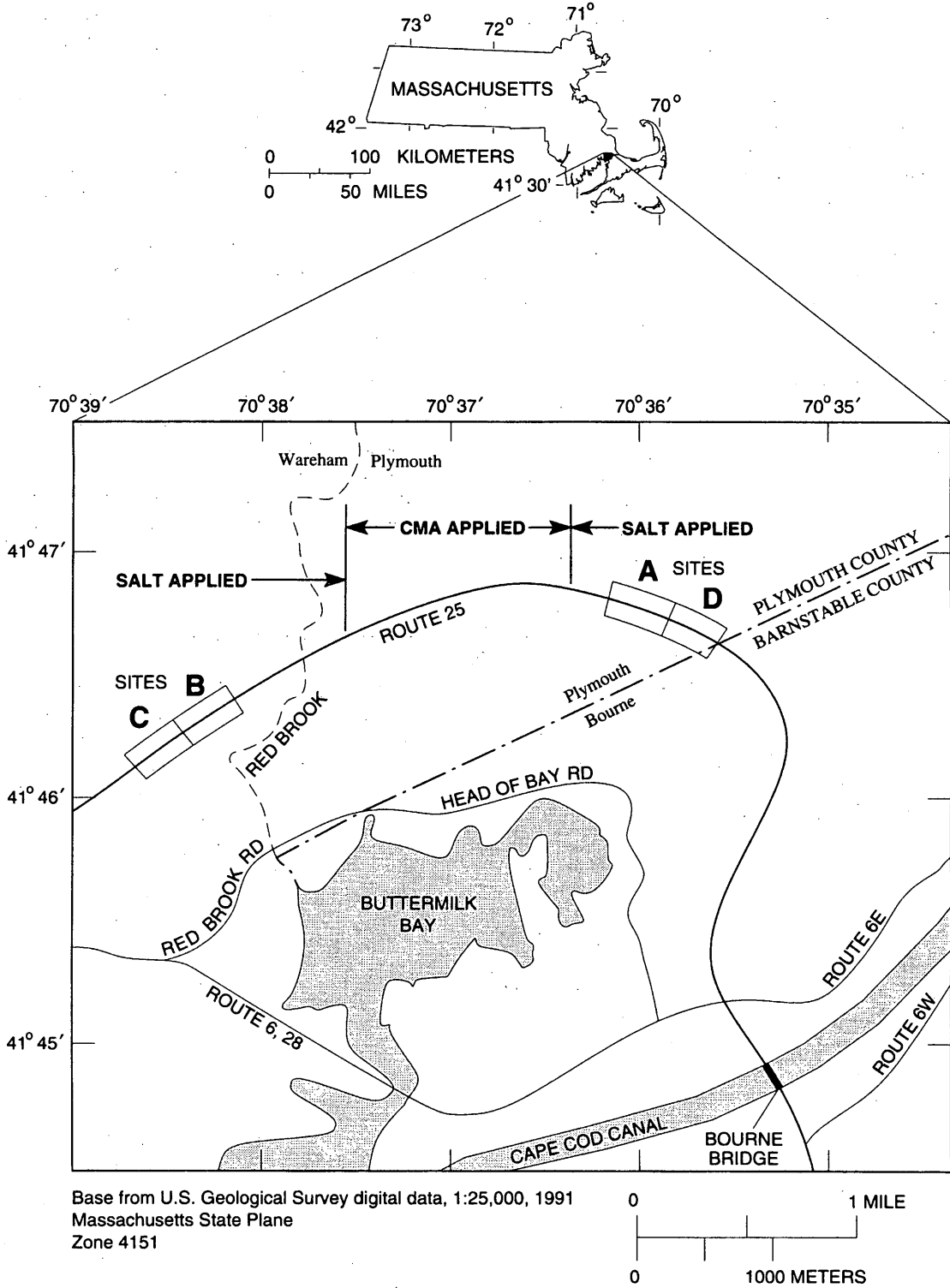


FIGURE 1 Location of study area and test sites A, B, C, and D along State Route 25 in southeastern Massachusetts.

ROUTE 25 RESEARCH SITE

The Route 25 research site is comprised of four test sites, each representing a different highway-drainage design, along a 5-km section of six-lane highway constructed in a forested area in southeastern Massachusetts (Figure 1). An average of 377,830 kg/year of sodium chloride, 7,830 kg/year of calcium chloride, and 106,450 kg/year of sand was applied to Route 25 at the research site for the three winters from December 1990 through March 1993 (S. J. Pollock, Massachusetts Highway Department, unpublished data). Traffic studies by the MHD in 1990 and 1993 indicate that the average daily traffic (ADT) was about 28,000 vehicles. Contaminant loading from deicing chemicals and vehicles was assumed to be equal at all four sites because the sites are between two interchanges.

The four sites (Figure 1) are designated A, B, C, and D in order of increasing highway-runoff control. Site A represents an open or "country" drainage system in which runoff is collected in catch basins on the pavement surface and drop inlets in the median strip and locally discharged to the land surface. Sites B, C, and D are closed-drainage systems where highway runoff is discharged to local surface-water bodies. Runoff control at sites C and D is enhanced by partial and full snow-berm drainage systems, respectively (5). Highway runoff is monitored at each site by an automated system that continuously measures stage, specific conductance, pH, and temperature of the runoff. The automated system collects runoff samples when thresholds of stage and specific conductance are exceeded.

Groundwater is monitored at each site using a network of observation wells, which includes clusters of short-screen wells installed in a line parallel to the direction of groundwater flow (Figure 2). In this report, the gradient is the slope of the water table in the direction of groundwater flow, and all groundwater data are referenced as either upgradient from Route 25 or downgradient from Route 25. Water levels were measured and water-quality samples were collected from water-table wells upgradient (designated as well 101 at each site) and downgradient (designated as well 201 at each site) from Route 25. These wells have 3-m-long screens centered on the mean water level. Water-quality samples also are routinely collected in one additional well upgradient (designated as well 102) and four additional wells downgradient from the highway (designated as wells 202 through 205). These wells have 1.5-m-long screens and were placed in a vertical array to screen the full depth of the deicing-chemical plume (fig. 2). Well clusters are about 60 m upgradient and about 60 m downgradient from the highway median strip. Borehole-induction logs were obtained from the deep wells (well 120 upgradient and wells 220 and 320 downgradient) to monitor the vertical distribution of the deicing-chemical plume at the well clusters (33).

HYDROGEOLOGY OF STUDY AREA

The study area is part of a coastal outwash plain bounded by till and bedrock hills to the north and west and by saltwater bays of the Atlantic Ocean to the south and east. Considerable small-scale vertical and lateral variation in grain-size distribution, typical of sand and gravel deposits, is present at all sites. In general, the sites are underlain by fine to coarse sand (75 to 95 percent), silt and clay (2 to 24 percent) and other sediments that range from pebbles to

boulders. Chemically, the soil has a pH from 5.1 to 5.5, a cation-exchange capacity of 110 to 140 meq/kg (milliequivalents per kilogram), and contains less than 1 percent calcium carbonate (23). Analysis of glacial sediments in the area indicates that sediments are about 40 to 55 percent quartz, 35 to 40 percent feldspar, 5 to 25 percent magnetic minerals, and less than 1 percent of other nonmagnetic minerals (34).

Depth to the water table below the highway ranges from 6 m at site B to 18 m at site A. Compared with land-surface topography, the water table is relatively flat with gradients less than 0.006. Groundwater flow generally is to the south, nearly perpendicular to the highway. Horizontal hydraulic conductivities were estimated from slug tests to be 67, 33.5, 30.5, and 33.5 m/day at sites A, B, C, and D, respectively. The estimated effective porosity was from 0.35 to 0.40 (33). Water-table fluctuations range from 0.5 to 1.5 m annually in response to recharge. The average annual precipitation is 131 cm for 1990 through 1993 (35). Few streams drain the area because precipitation infiltrates easily into the sandy soils.

The chemical effect of oceanic aerosols on precipitation is observed in the quality of natural groundwater in the research area. Background specific conductance and concentrations of sodium, calcium, and chloride in groundwater were monitored before construction and before operation and salting of Route 25. Background specific conductance ranged from 40 to 70 $\mu\text{S}/\text{cm}$, and concentrations of sodium typically ranged from 5 to 10 mg/L, calcium from 1 to 5 mg/L, and chloride from 5 to 20 mg/L at all sites.

SAMPLE COLLECTION

All water-quality samples from wells upgradient and downgradient from the highway were collected and processed using materials and methods designed to minimize potential contamination. Quality-assurance samples were collected at different stages in the sampling program to measure the potential contamination caused by materials and methods. Analysis of quality-assurance samples indicated negligible concentrations of contaminants introduced by materials and methods during sample collection and processing. Groundwater, highway-runoff, and quality-assurance samples were analyzed by the USGS National Water Quality Lab in Arvada, Colorado, according to standard methods (36).

RESULTS

Concentrations of chloride in groundwater samples collected monthly from December 1990 through May 1994 are shown in Figure 3 with chloride concentrations from groundwater samples collected for analysis of major and trace constituents during February and August 1991 and March, August, and November 1993. Monthly chloride concentrations at wells 101 and 102 upgradient from the highway vary little in comparison with chloride concentrations in the corresponding wells 201 and 202 downgradient from the highway. The temporal variations in chloride concentrations in Figure 3 indicate a pattern of annual road-salt plumes, presumably from the shoulders and median strip of the highway at each site. The magnitude and timing of the annual salt plumes at each site are affected by the hydraulic conductivity, hydraulic gradient, and unsaturated zone travel time, which are different at each site. There-

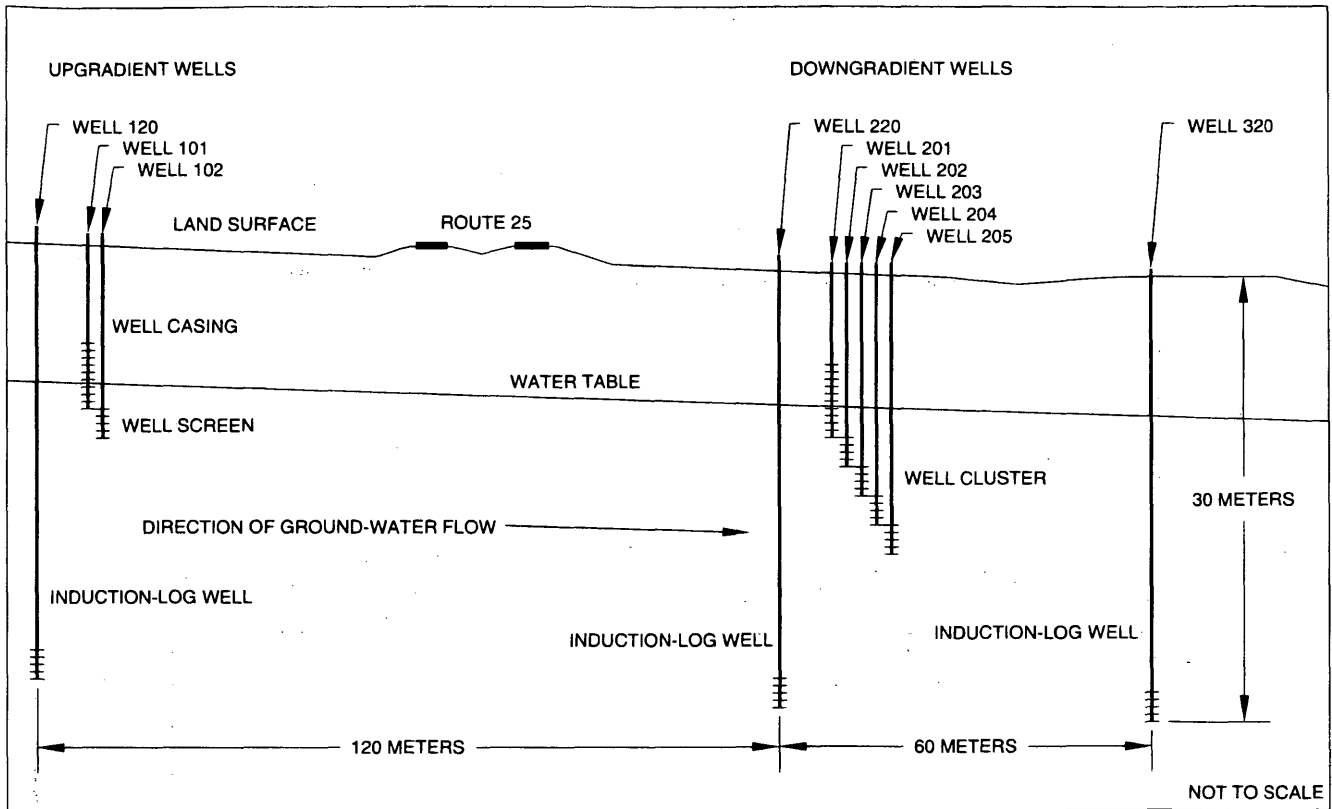


FIGURE 2 Vertical section of well network at test sites A, B, C, and D along State Route 25 in southeastern Massachusetts.

fore, the difference in arrival time of the maximum concentration at each site prevents a direct month-by-month comparison of concentrations among sites. However, when comparing sites, peak chloride concentrations in wells downgradient from the highway (Figure 3) generally decrease with increasing runoff control showing the relative effectiveness of the highway drainage systems in preventing road-salt contamination of groundwater (5).

Site A is geochemically the most interesting of the four sites. This site has an open-drainage system typical of many highways, and has the least drainage control among the four sites. This drainage system discharges highway runoff to the land surface just downgradient from the highway, resulting in the highest salt concentrations measured in the study area (Figure 3). Also, site A receives CMA tracking because it is adjacent to an area where CMA is applied (Figure 1). The analyses of major and trace constituents from samples collected during February and August 1991, and March, August, and November 1993 at site A show the greatest differences between upgradient and downgradient water quality among the four sites. Therefore, analysis of major and trace constituents for site A will be discussed.

Concentrations of major and trace constituents in groundwater-quality samples collected at site A upgradient and downgradient from Route 25 are presented in Figure 4 (note that the concentrations are presented on a logarithmic scale). The calculated concentration of each constituent expected from mixing the upgradient water with road salt also are presented. Concentrations expected from the constituents of road salt were calculated by assuming the excess chloride in wells downgradient from the highway was from road salt. The calculated downgradient concentration of each con-

stituent was determined by adding the concentration measured in upgradient groundwater to the product of the excess chloride and the constituent-chloride mass ratio in road-salt samples collected in 1991, 1992, and 1993 from the MHD Route 25 maintenance facility.

The quality of groundwater downgradient from the highway was notably different from the upgradient-groundwater quality and the water quality expected from the addition of road salt (Figure 4). The measured and calculated concentration of chloride were equal because all calculations were based on excess chloride. Sodium shows an attenuation in downgradient-groundwater samples from concentrations measured in road-salt samples. Concentrations of calcium and magnesium are much greater in downgradient groundwater samples than in road-salt samples, potentially indicating CMA loading at site A. Concentrations of all major and trace cations are much greater in groundwater downgradient from the highway (in some cases more than an order of magnitude higher), but dissolved silica (a neutral compound) seems to be slightly attenuated. Results for the anion sulfate are ambiguous. Sodium, calcium, magnesium, potassium, barium, strontium, copper, iron, and zinc concentrations appear to be highest when chloride concentrations are high and lower when chloride concentrations are low, which indicates that mobilization may be caused by deicing chemical migration. For brevity, Figure 4 does not show all of the constituents analyzed in the major and trace constituent samples. Chromium, cyanide, and nickel concentrations were less than the detection limits of 0.005, 0.01, and 0.01 mg/L, respectively, in all samples.

None of the concentrations measured in the analysis of major and trace constituents from samples collected during February and

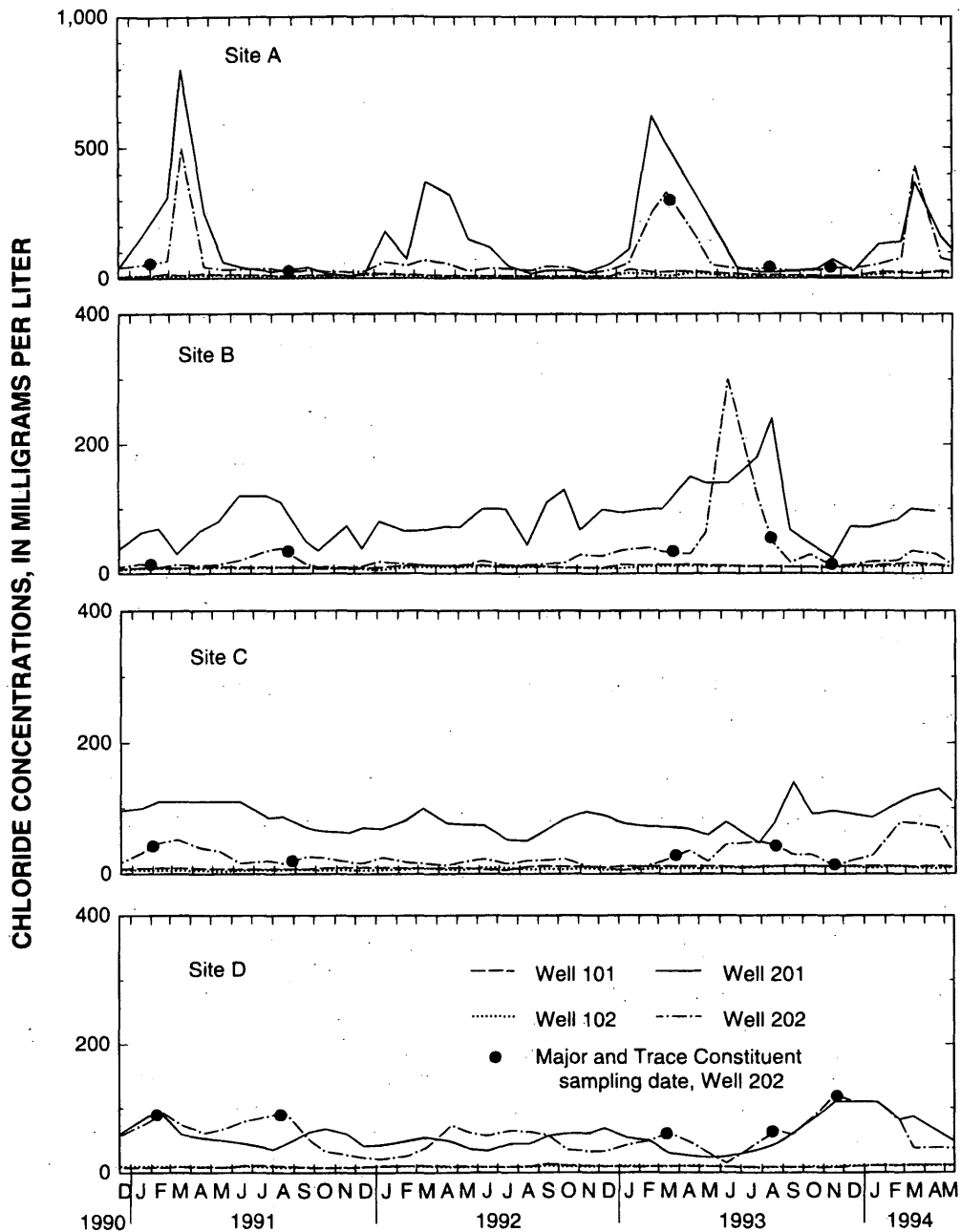


FIGURE 3 Monthly chloride concentrations in groundwater at wells 101 and 102 upgradient and wells 201 and 202 downgradient from the highway, and chloride concentrations measured during the major and trace sampling rounds along State Route 25 in southeastern Massachusetts.

August 1991 and March, August, and November 1993 exceeded national primary drinking-water standards (37). Secondary standards for chloride (250 mg/L) and manganese (0.05 mg/L) were exceeded (37), and recommendations for surface-water criteria (38) were exceeded for chloride (230 mg/L), cadmium (0.0039 mg/L), and copper (0.018 mg/L). However, chloride concentrations in groundwater from well 202 during the major and trace constituent sampling rounds were less than the maximum annual concentrations measured at the water table in well 201 (Figure 3). If major and trace constituents of highway runoff are mobilized by deicing

chemical migration, then these concentrations also may be higher in well 201 at each site.

DISCUSSION OF RESULTS

The results presented in Figure 4 raise many questions rather than provide answers, indicating the need for further study of the mobilization of the major and trace constituents of highway runoff in groundwater that may be caused by deicing-chemical migration.

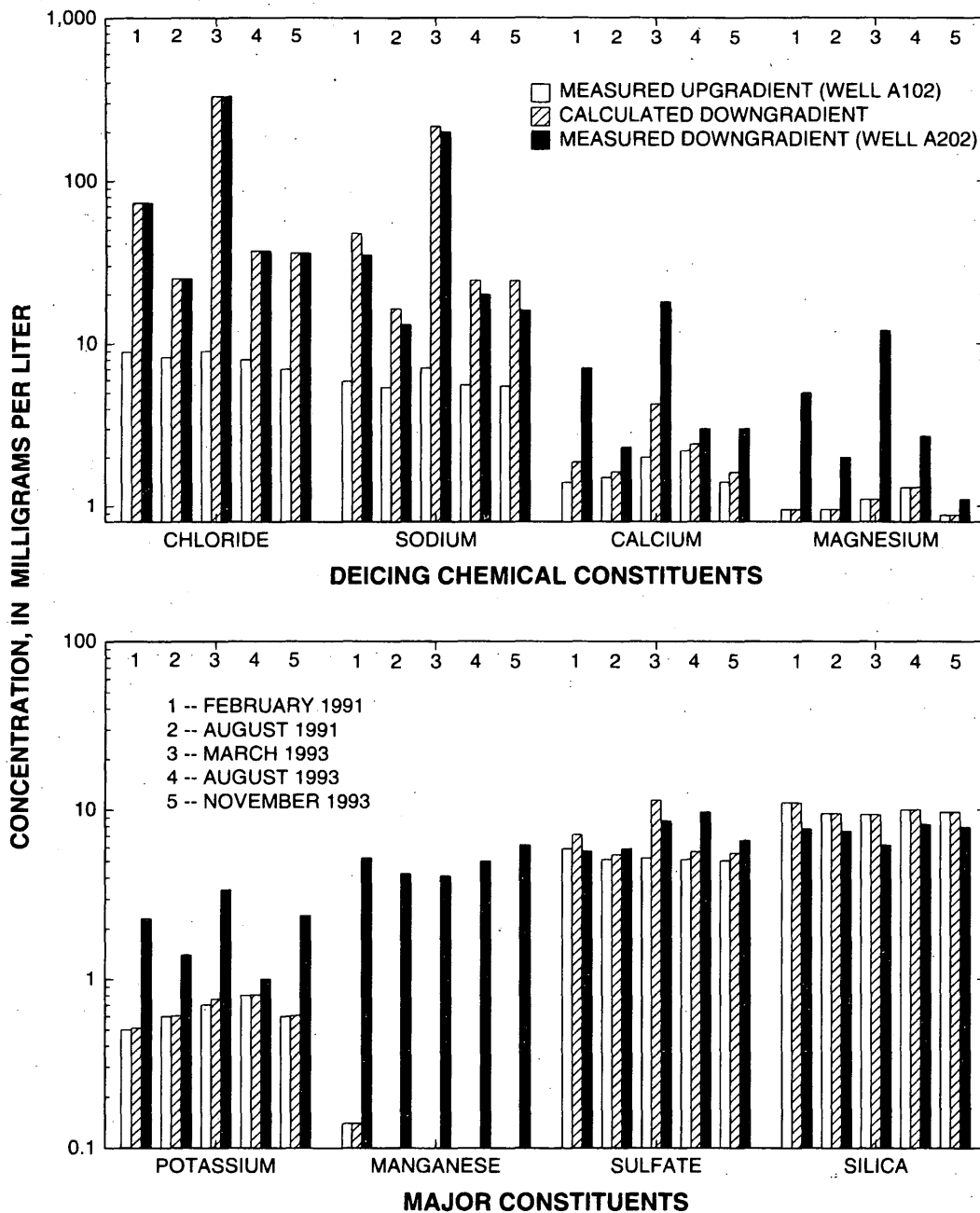


FIGURE 4 Constituent concentrations in groundwater measured upgradient and downgradient from the highway compared with constituent concentrations expected from road salt, based on the excess chloride measured in downgradient groundwater at site A along State Route 25 in southeastern Massachusetts.

Many field studies (7,11-16) indicate that the trace constituents of highway runoff are immobilized in the first 20 cm of the soil. However, the analysis of major and trace constituents from samples collected during February and August 1991 and March, August, and November 1993 indicates that mobilization may occur with deicing-chemical migration. These analyses show consistent increases in constituent concentrations in groundwater downgradient from the highway at a site with an 18-m-thick unsaturated zone with no contaminant sources other than the highway. Additionally, the ADT of 28,000 vehicles was less than the threshold of

30,000 vehicles expected for measurable effect on receiving water quality (12).

The sampling conducted during February and August 1991, and March, August, and November 1993 was designed to provide synoptic water-quality information but was not specifically designed to quantify the processes of major and trace constituent mobilization. However, this information, when combined with water-level measurements and water-quality analyses of groundwater samples collected monthly from November 1990 to May 1994 and water-quality analyses of highway-runoff samples collected since 1988,

indicates several potential mobilization processes related to deicing chemical migration. In the following sections, several hypotheses including winter recharge, effects related to ion exchange, acidification from deicing chemicals, and mineral weathering are proposed to explain the differences in groundwater quality upgradient and downgradient from Route 25.

Winter Recharge

The potential geochemical importance of deicing chemicals is enhanced by the annual recharge cycle in latitudes where road salting is a common practice. Low rates of evapotranspiration in the winter months increase groundwater recharge (39,40). Recharge during the winter road-salting months—December, January, February, and March—accounts for 75 percent of the annual recharge in southeastern Massachusetts as calculated from 60 years of precipitation data from the East Wareham meteorological station along Route 25 (41).

Annual fluctuations in recharge also are indicated by measured groundwater levels at each site. Water-table altitudes upgradient and downgradient from Route 25 (Figure 5) show rising water tables in the winter and spring because of infiltrating recharge water. Therefore, recharge near the highway occurs during the period when deicing chemical concentrations in the infiltrating water are highest and when the geochemical effects associated with the migration of deicing chemicals are the greatest during the year.

Effects Related to Ion Exchange

Winter recharge of salt-laden water alone cannot account for the quality of groundwater downgradient from the highway. Comparison of measured and calculated concentrations (Figure 4) indicates sodium attenuation; however, all of the other cations were greater than would be expected from road-salt contamination (the calculated downgradient concentrations). In March 1993 the sodium attenuation was about 0.67 meq/L, and the other species combined are 1.8 meq/L greater than expected from conservative transport of road-salt constituents in winter recharge. Therefore, in this case sodium exchange accounts for about 37 percent of measured constituent concentrations in groundwater contaminated by highway runoff. Migration of CMA and ion exchange involving the divalent cations calcium and magnesium therein also may represent part of this imbalance.

The cation-exchange capacity of aquifer sediments is low compared with peak salt concentrations. Peak salt concentrations are about 70 times the cation-buffering capacity of aquifer sediments. However, conservative transport of cations will not occur because cation exchange acts as a temporary buffer in non-steady state situations, such as pollutant migration, acidification, or moving freshwater/saltwater interfaces (18).

The ion-exchange process must be inferred from analysis of groundwater samples; therefore, it is difficult to demonstrate conclusively that ionic exchange is the driving process controlling water quality. Data on multicomponent displacements at varying concentrations are rarely available (18). Ion exchange in natural water that contains various ions is complicated because of different ions competing for the same site, and theories that explain changes in activity coefficients of ions on soils are not complete (18). Ion-

exchange interactions between major and trace ions are difficult to quantify because changes in trace-ion concentrations do not affect the major-ion distributions, but changes in major-ion concentrations do affect the trace-ion distributions (18).

Despite these complexities, a comparison of analyses of highway-runoff and downgradient groundwater samples indicates the occurrence of sodium for calcium exchange (Figure 6). The shift in the mean mass ratio of sodium to chloride from 0.625 to 0.550 in 181 highway-drainage samples and 297 groundwater samples from all four sites indicates attenuation of sodium in infiltration water. A modified *t*-test based on Tukey's bi-weight estimator (42) was used because the populations were not normally distributed. Statistical results indicate that estimates of the population means were significantly different, with a probability of less than .0001 that they were the same. The sodium ratio shift in infiltrating water cannot be explained by mixing with upgradient groundwater because the mean mass ratio of sodium to chloride in upgradient water is 0.611. Population means of the mass ratio of calcium to chloride also were significantly different with a probability of less than .0001 that they were the same. The shift in the mean mass ratio of calcium to chloride from 0.031 in the highway runoff to 0.067 in downgradient groundwater indicates enrichment of calcium during infiltration. Sodium was attenuated by 0.11 meq, and calcium increased by 0.02 meq/meq of chloride in winter recharge water on the basis of mean concentrations. Therefore, sodium may exchange for other cations as well as calcium on the sediments as highway runoff migrates through the unsaturated zone and downgradient in groundwater.

These findings are supported by several laboratory and field studies indicating that sodium exchange is important to the quality of groundwater affected by road-salt contamination (10,21,25,43). Other studies indicate that ion exchange precedes metal-chloride, metal-acetate, and metal-ligand complexation, which increases the mobility of the metals because these complexes do not seek the next available exchange site (21,22,24–27).

Sodium-related ion exchange also may indirectly increase the mobility of other ionic constituents. One such phenomenon is clay dispersion and clay swelling because of ion-exchange reactions between sodium and divalent ions such as calcium or magnesium as freshwater replaces saltwater in aquifer sediments (44,45). Amrhein et al. (23,24) documented mobilization of metals by organic-matter solubilization, clay dispersion, and colloid-assisted transport in soil cores flushed with deicing-chemical solutions.

Acidification from Deicing Chemicals

Differences in pH were significant between 190 samples collected from water-table wells upgradient and 187 samples collected from water table wells downgradient from Route 25 (Figure 7). A modified *t*-test based on Tukey's bi-weight estimator (42) was used because the populations were not normally distributed. Statistical results indicated that estimates of the population means were significantly different, with a probability less than .0001 that they were the same. Although the difference between mean pH of the populations may seem small (5.45 upgradient, 5.13 downgradient from the highway), there are twice as many hydrogen ions in solution in downgradient groundwater than in upgradient groundwater. Additionally, the pH seems to decrease with increasing chloride concentrations. Groundwater pH may not reflect the extremes of acidification (lowest pH) in infiltrating water because

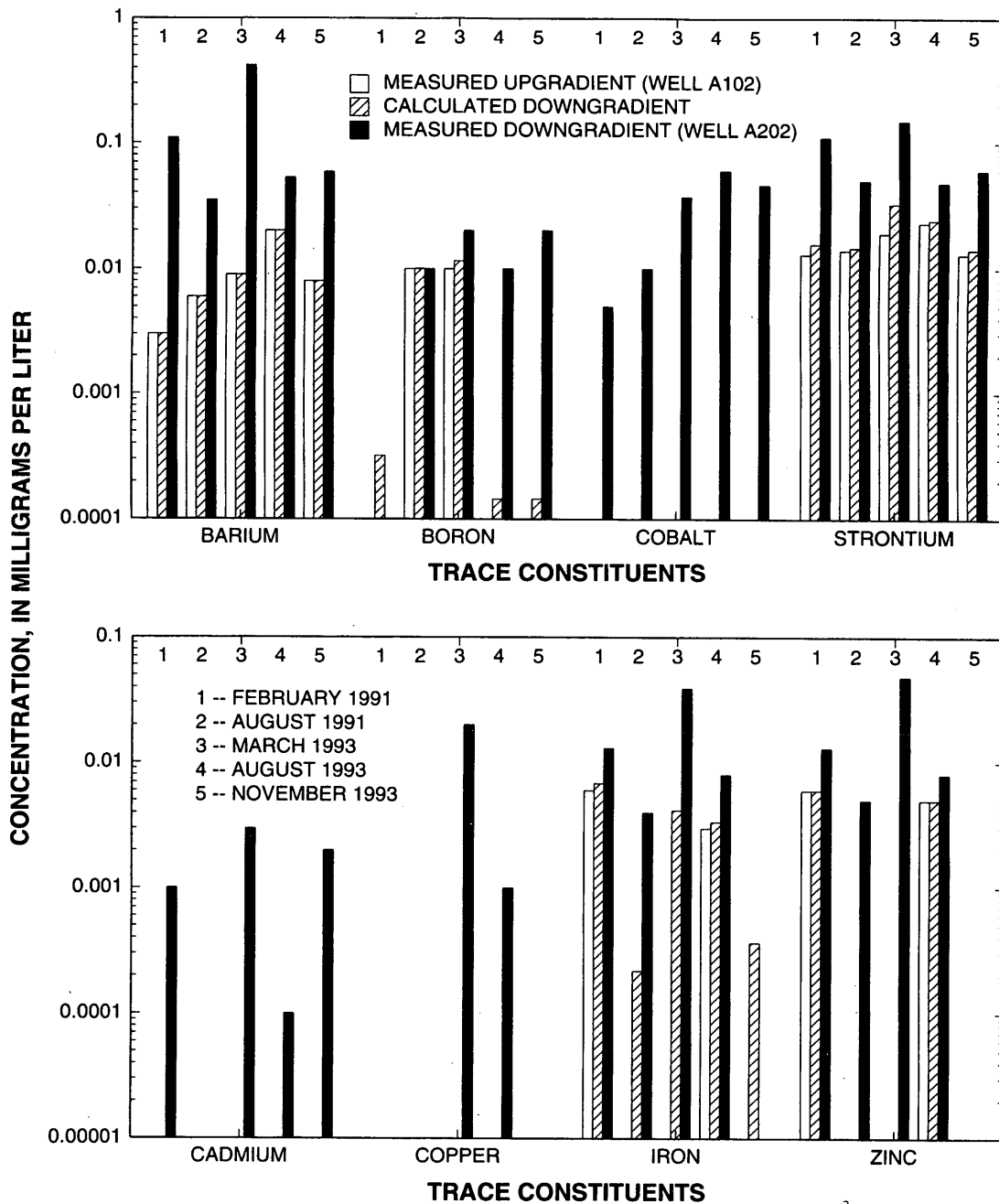


FIGURE 5 Water table altitudes upgradient (well 101) and downgradient (well 201) from the highway along State Route 25 in southeastern Massachusetts.

equilibration processes in the unsaturated zone tend to increase pH (18).

Studies examining the role of neutral sea salts in episodes of natural acidification have determined that sodium from salt-laden precipitation or sea-spray exchanges for hydrogen and aluminum ions on the soil, which decreases the pH of the infiltrating water (46,47). Although several road-salt researchers have noted a pH effect in laboratory tests (21,24,32), acidification caused by neutral sodium chloride is not currently under field conditions. Also, CMA may decrease pH of groundwater by the production

of acetic or carbonic acid produced from biodegradation of the acetate (27).

The role of pH is more important than many other factors in determining the solubility of metal species (17,18). Although it is well established that many trace metals are more soluble at low pH (12,30,31), many of the studies done to determine the partitioning of metals in soils were done at neutral pH (19,20,48). Studies indicate that mobilization of trace constituents in highway runoff can be associated with a decrease in pH (17,21,25,31,32). Therefore, acidification caused by deicing chemical migration may change the spe-

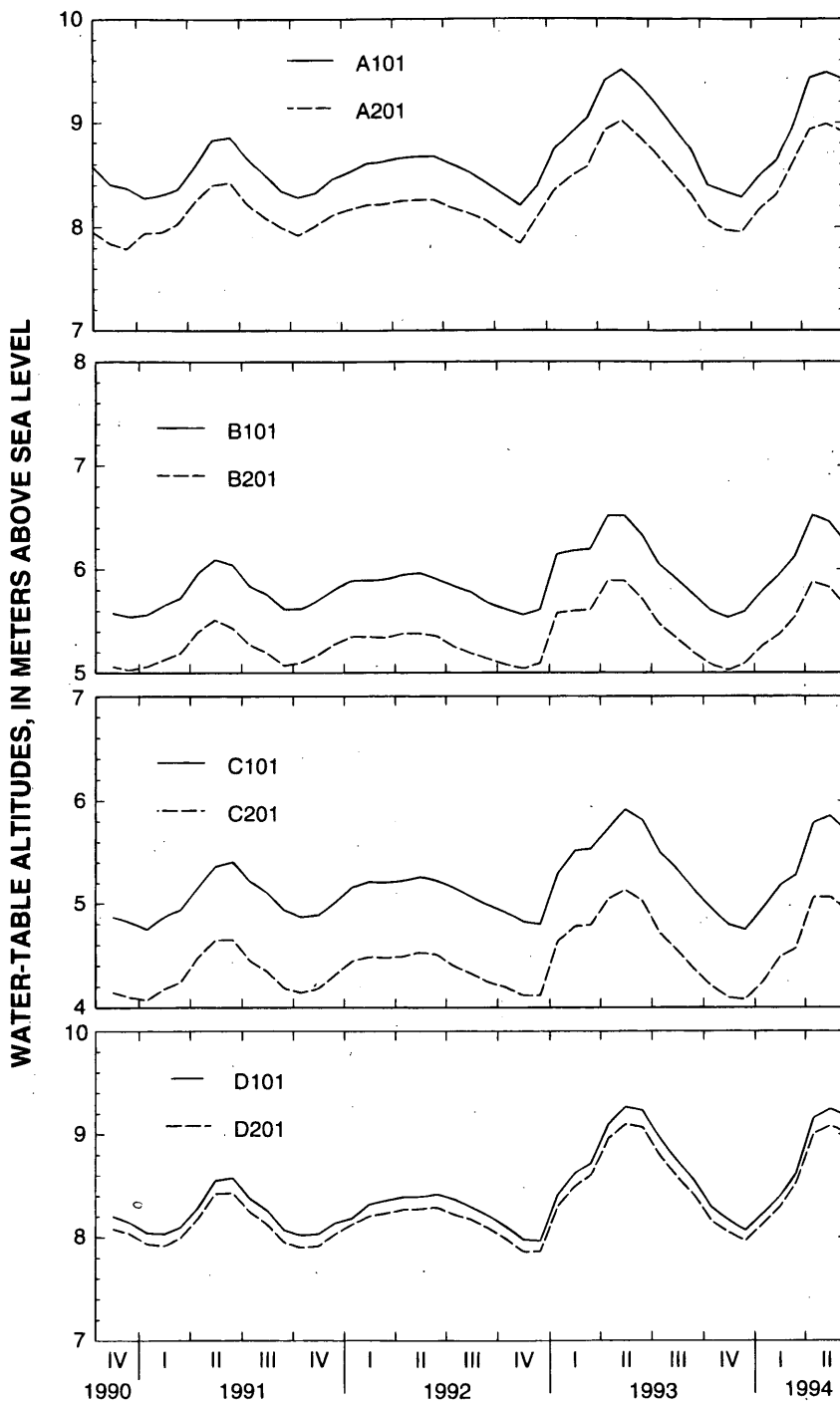


FIGURE 6 Ion exchange indicated by shifts in the population of the mass ratio of sodium and calcium in groundwater and in highway runoff collected at test sites A, B, C, and D along State Route 25 in southeastern Massachusetts, November 1990 through June 1994. (continued on next page)

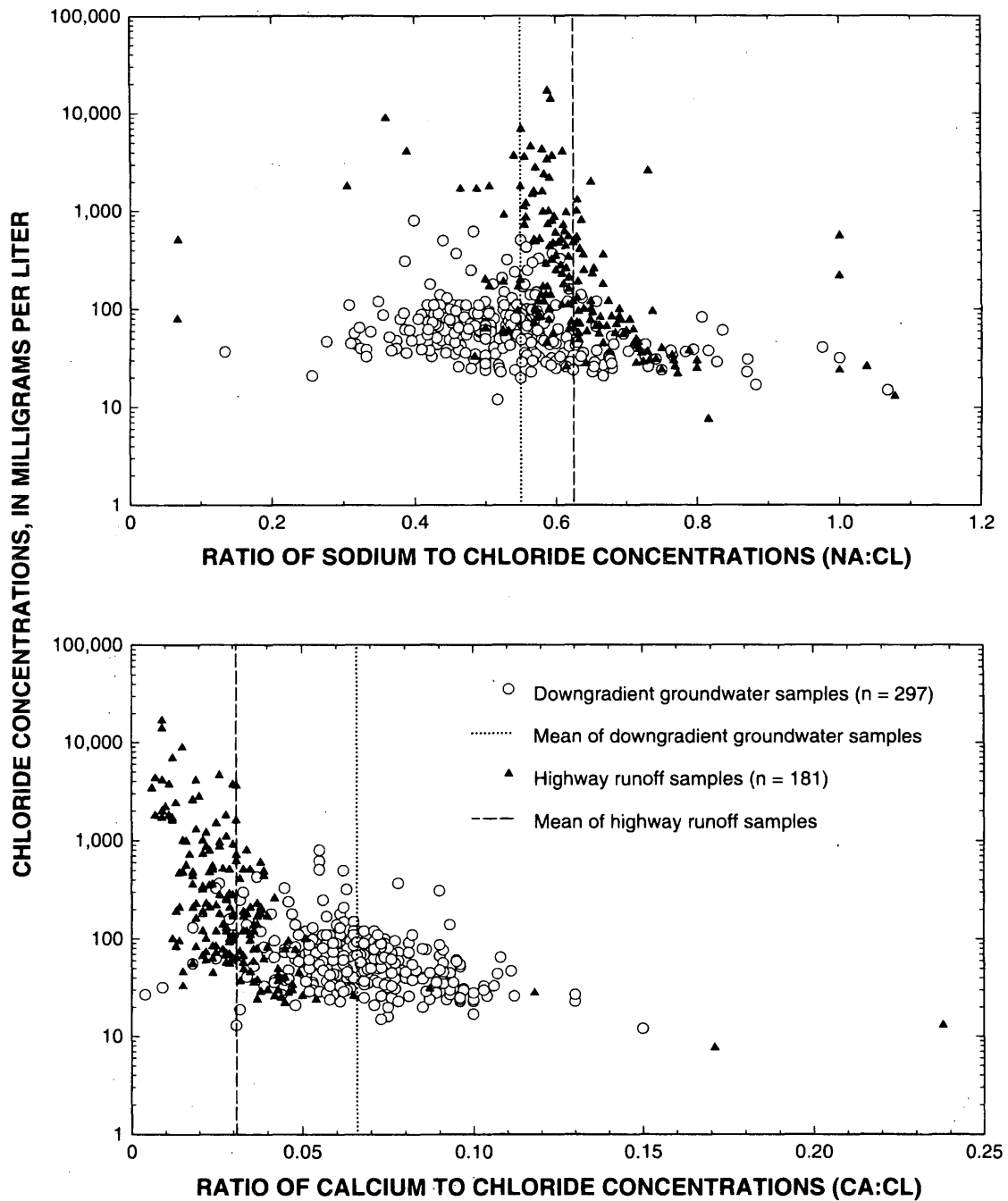


FIGURE 6 (continued)

ciation of soil-bound metals and make them more soluble in groundwater.

Mineral Weathering

Mineral weathering not associated with geochemical changes attributable to highway runoff is not considered to be a significant source or sink for the major or trace constituents between the wells upgradient and downgradient from State Route 25. Analysis of sediments

from drill-core samples does not indicate any significant changes in lithology between upgradient and downgradient wells. Major-ion analyses of groundwater from deep wells, unaffected by highway runoff, do not show any significant changes in water quality from well 120 upgradient to well 220 downgradient from Route 25 at the four sites. However, the concentrations of silica, a species indicative of changes caused by mineral weathering (43), are consistently lower downgradient in the major and trace constituent analyses shown in Figure 4 indicating the possibility that the deicing chemicals affect mineral weathering.

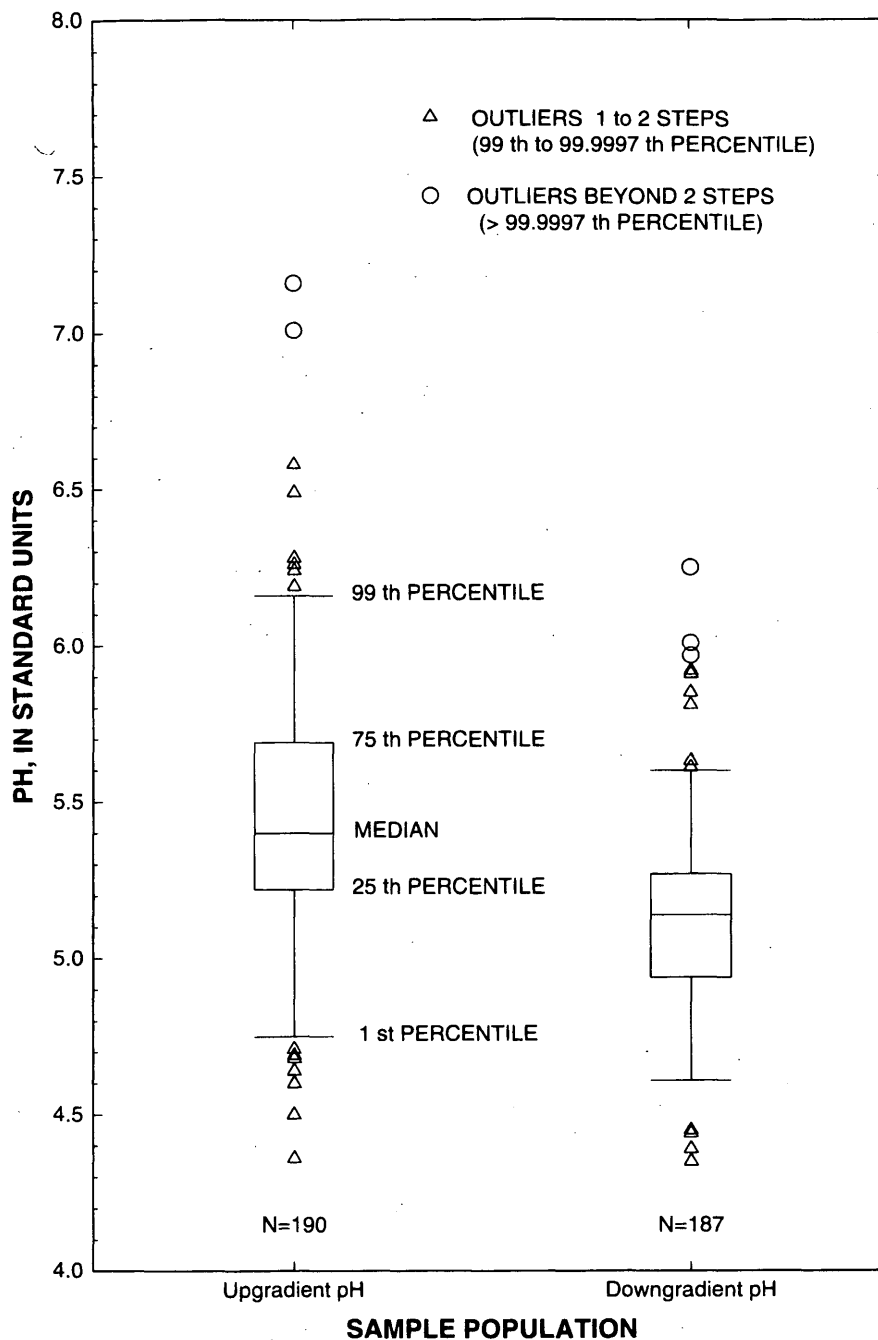


FIGURE 7 pH populations upgradient and downgradient of the highway at sites A, B, C, and D along State Route 25 in southeastern Massachusetts, March 1992 through June 1994.

SUMMARY

Mobilization of major and trace constituents of highway runoff in groundwater is hypothesized to be caused by deicing chemical migration at a site where highway runoff is locally discharged to the land surface (an open drainage system typical of many national highways) and both CMA and road-salt loads are significant. This hypothesis is supported by groundwater-level measurements and analyses of groundwater samples from clusters of wells upgradient

and downgradient from Route 25 in southeastern Massachusetts that indicate the following:

1. Concentrations of major and trace constituents in groundwater downgradient from the highway were notably greater than concentrations in groundwater upgradient and concentrations expected from the addition of road salt. For some constituents, downgradient concentrations were more than an order of magnitude greater than upgradient concentrations.

2. Seventy-five percent of annual recharge, which carries highway runoff through the unsaturated zone to groundwater, occurs during the winter road-salting months.
3. Cation exchange is indicated by decreases in sodium concentrations and corresponding increases in calcium concentrations in infiltrating water.
4. Acidification from road salt is indicated by a significant decrease of pH in groundwater downgradient from the highway.

Analyses of major and trace constituents from samples collected during February and August 1991 and March, August, and November 1993 in groundwater are indicative, rather than conclusive because more spatial and temporal data are needed to define mobilization processes. However, this information when combined with water-level measurements and water-quality analyses of groundwater and highway-runoff samples collected monthly from December 1990 to May 1994 indicates potential mobilization processes, which include winter recharge, effects related to ion exchange, and acidification and mineral weathering caused by deicing chemical migration. Therefore, these processes need further investigation to assess fully the possible mobilization of the major and trace constituents of highway runoff in groundwater caused by deicing chemical migration.

None of the measured concentrations of the major and trace constituents in groundwater samples exceed national primary drinking-water standards, but secondary standards were exceeded for chloride and manganese. Also, recommendations for surface-water criteria were exceeded for chloride, cadmium, and copper. If mobilization is caused by deicing chemical migration then concentrations of the major and trace constituents of highway runoff in groundwater are likely to be higher when deicing chemical concentrations are higher.

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