RELATION OF ARSENIC, IRON, AND MANGANESE IN GROUND WATER TO AQUIFER TYPE, LITHOGEOCHEMISTRY, AND LAND USE

Ground-water quality in natural systems is a result of many environmental factors. Climate, geology, biochemistry, composition of atmospheric precipitation, and the nature of the hydrology are among the more important factors (Hem, 1985). Hem (1985) also notes that the source of most dissolved ions in natural waters is the mineral assemblages in the rocks near the land surface. Rock composition is only one of many related geologic factors; other geologic factors, such as nature of minerals, texture, porosity, and regional structure, can affect the composition of waters (Hem, 1985, Robinson, 1997). Ground-water quality in the stratified-drift and bedrock aquifers of New England evolves according to similar reaction types but differs primarily in the degree of chemical evolution (Rogers, 1989). Rogers (1989) further notes that the bedrock-aquifer waters are more chemically evolved probably because of longer contact time between the water and the aquifer matrix in the bedrock aquifer than in the stratified-drift aquifer. In the New England Coastal Basins study unit, aquifer type, bedrock lithology, and land use are expected to play an important role in the chemical character of ground water. This section focuses on how existing water-quality data relate to geologic and land-use factors on a regional scale.

Occurrence of Arsenic, Iron, and Manganese by Aquifer Type

The frequency of detection of arsenic, iron, and manganese was compared between stratified-drift and the bedrock aquifers in the study unit. Water-quality data were available for 145 public-supply wells in stratified-drift aquifers in Maine, New Hampshire, and Rhode Island. These were compared to data from 607 bedrock public-supply wells in those same states (table 3). Arsenic, at concentrations of 0.005 mg/L or greater, was detected in 7.6 percent of the 145 public-supply wells in the stratified-drift aquifers and in 25.5 percent of the public-supply wells in the bedrock aquifers (fig. 5, table 3). Results of contingency-table analysis indicate that the detection rate of arsenic in

Table 3. Percent of wells in stratified-drift and bedrock aquifers in the New England Coastal Basins study unit yielding water with detectable concentrations of arsenic, iron, and manganese, and Chi-square statistics

[mg/L, milligrams per liter]

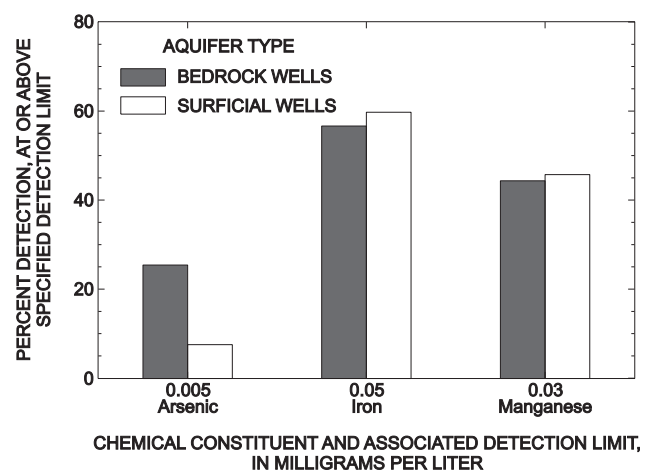| Chemical (detection limit) | Percent detected | | Chi-square statis-tic | p-value |
	Surficial aquifer (145 wells)	Bedrock aquifer (607 wells)		
Arsenic (As) (0.005 mg/L)	7.6	25.5	21.65	0.0001
Iron (Fe) (.05 mg/L)	59.8	56.7	.300	.584
Manganese (Mn) (.03 mg/L)	45.8	44.4	.064	.801

Figure 5. Percent detection of arsenic, iron, and manganese concentrations in ground water by aquifer type.

the two aquifer types is significantly different (p = 0.0001). This is consistent with previous studies (Marvinney and others, 1994; Peters and others, 1999). The detection rates for iron and manganese, however, are virtually identical and the contingency-table test indicates no difference by aquifer type for either constituent.

The difference in detection rate by aquifer type could be related to the type of aquifer materials, differences in ground-water residence times, and geochemical factors related to contact time and redox conditions. Shallow, surficial wells are more likely to

contain measurable dissolved oxygen, have lower pH, and the reaction-path length is short. In deep bedrock wells, the water is more likely to be in contact with the aquifer materials for a long time, have higher pH, and redox conditions tend to be reducing.

Occurrence of Arsenic, Iron, and Manganese by Lithogeochemical Group

Arsenic, at concentrations of 0.005 mg/L or greater, was detected in 20.4 percent of the 804 public-supply wells in the bedrock aquifer; however, the frequency of arsenic detection is significantly different among the six major lithogeochemical groups defined in this study (fig. 6, table 4). Analysis of arsenic concentrations in water from wells associated with the 6 lithogeochemical groups shows that 44 percent of the water samples from wells in the

metasedimentary lithogeochemical group M_c (primarily calcareous or calc-silicate rocks) had arsenic detections at or above the 0.005 mg/L level, whereas water samples from wells in the other 5 lithogeochemical categories had arsenic detections of 28 percent or less. Thus, in group M_c, which extends from northern Massachusetts through southeastern New Hampshire and northeastward into Maine, arsenic is detected in water from public-supply wells about 2 to 10 times the rate of detection in water from public-supply wells in the other major lithogeochemical groups (fig. 6). In the northern half of the study unit, rock units in group M_c underlie some of the most populated parts of those states, including southeastern and coastal New Hampshire and south-coastal Maine (Flanagan and others, 1999, fig. 16a). Water from the igneous lithogeochemical group I_f, (mostly felsic igneous rocks; primarily granites) had an overall arsenic detection rate of 11.9 percent (table 4).

EXPLANATION

[a] Populations that have the same letter designation
     do not differ significantly at the alpha = 0.05 level

M_c Major lithogeochemical group. See figure 3 for explanation

p   Attained significance level for the multiple-comparison test
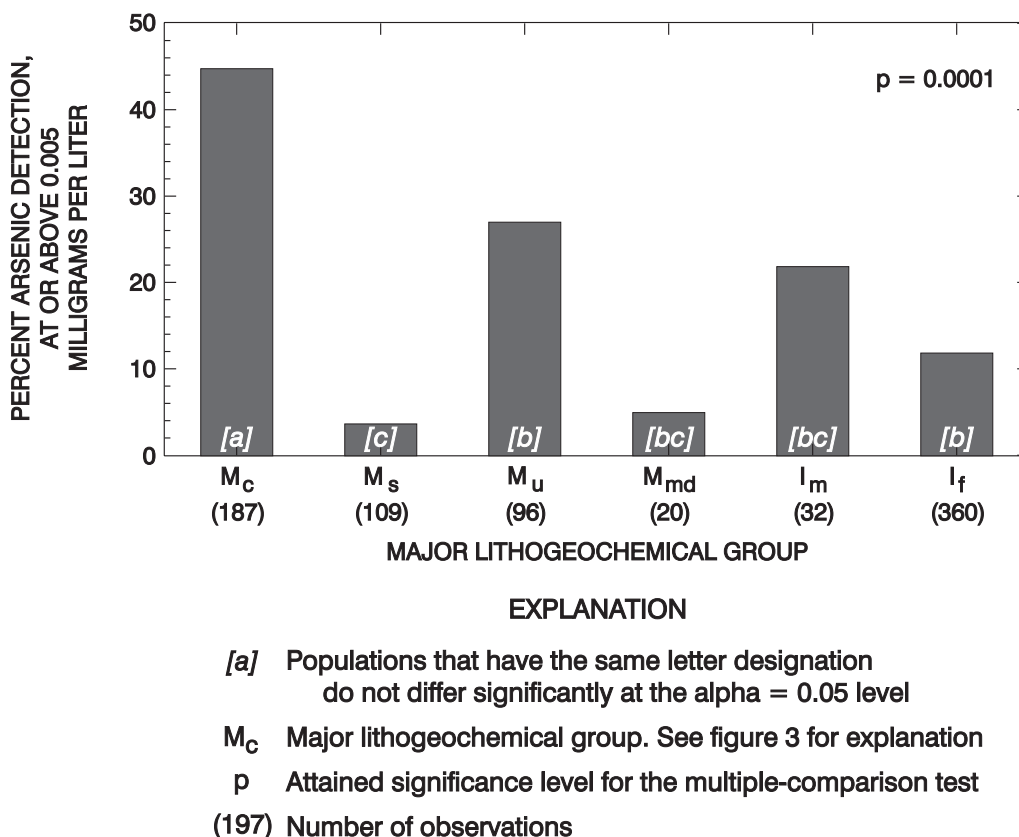
(197) Number of observations

Figure 6. Percent detection of arsenic concentrations in ground water, at or above 0.005 milligrams per liter, in selected bedrock geologic units in lithogeochemical group M_c.

Table 4. Summary statistics for concentrations of arsenic, iron, and manganese in ground water by major lithogeochemical group in the New England Coastal Basins study unit

[mg/L, milligrams per liter; <, less than]

Major litho-geochemical group	Number of wells	Percent at or above detection limit			Percentiles								
					Arsenic (mg/L)			Iron (mg/L)			Manganese (mg/L)		
		Arsenic (0.005 mg/L)	Iron (0.05 mg/L)	Manga-nese (0.03 mg/L)	50th	75th	Maxi-mum	50th	75th	Maxi-mum	50th	75th	Maxi-mum
M_c	187	44.4	51.6	49.7	< 0.005	0.008	0.058	0.05	0.13	7.42	< 0.03	0.07	3.53
M_s	109	3.7	73.2	75.6	< .005	< .005	.018	.14	.47	4.69	.06	.1	2.2
M_u	96	27.1	52.6	52.6	< .005	.005	.176	.05	.13	6.16	.03	.09	.4
M_{md}	20	5.0	80.0	70	< .005	< .005	.016	.335	1.09	38.9	.12	.29	.62
I_m	32	22.0	61.9	42.9	< .005	< .005	.046	.07	.24	1.5	< .03	.08	5.88
I_f	360	11.9	52	36.8	< .005	< .005	1.1	.05	.17	21.6	< .03	.06	3.29

Many of the arsenic concentrations above the detection limit in water from wells in group I_f were associated with specific intrusive igneous rocks with anomalously high arsenic levels (Peters and others, 1998; Peters and others, 1999).

Arsenic detections in water from wells in the metasedimentary group M_s was the lowest, at 4 percent. Many sulfide minerals commonly contain arsenic, and when oxidized, could contribute arsenic to ground water (A.H. Welch, written commun., April 1999). The low frequency of detection suggests that sorption of arsenic on iron-oxide precipitates, or other solubility controls, may limit the concentration of arsenic in drinking water derived from aquifers in group M_s. Because of the limitations of using public-supply drinking water data for this analysis, certain biases could be responsible for the low detection of arsenic in these variably sulfidic bedrock aquifers. One such bias could be that drinking-water wells are not drilled as commonly in the aquifers of the metasedimentary group M_s. Another could be that wells are placed in order to avoid certain parts of these rock types.

Seven of the 804 wells yielded water with maximum reported arsenic concentrations that ranged from greater than the USEPA MCL of 0.05 mg/L to 1.1 mg/L. Four of these wells were in group M_c and three were in group I_f.

Kruskal-Wallis tests indicate a significant difference in concentrations of arsenic in ground water between different lithogeochemical groups (table 5, p = 0.0001). Results of subsequent multiple comparisons of means tests (Tukey) of arsenic concentrations by lithogeochemical group indicate, by pair-wise comparison, which groups are different from the others. Results are shown in figure 6 and indicate that arsenic concentrations in water from wells in the group M_c (fig. 6, [a]) were significantly higher than concentrations in the other five groups ([b] and [c]) and that there was no significant difference in the concentrations among the other five groups with one exception: the concentrations of arsenic in water from wells in group M_s [c] were significantly lower than in water in wells in group M_u [b].

Within the metasedimentary group M_c, most of the geologic units (rock formations and formation members) have a high percentage of wells with water containing detectable arsenic (fig. 7). These units, although commonly quite variable in composition

Table 5. Summary of attained significance levels (p-values) for Kruskal-Wallis tests of the concentrations of water-quality variables compared by lithogeochemical and land use variables in the New England Coastal Basins study unit
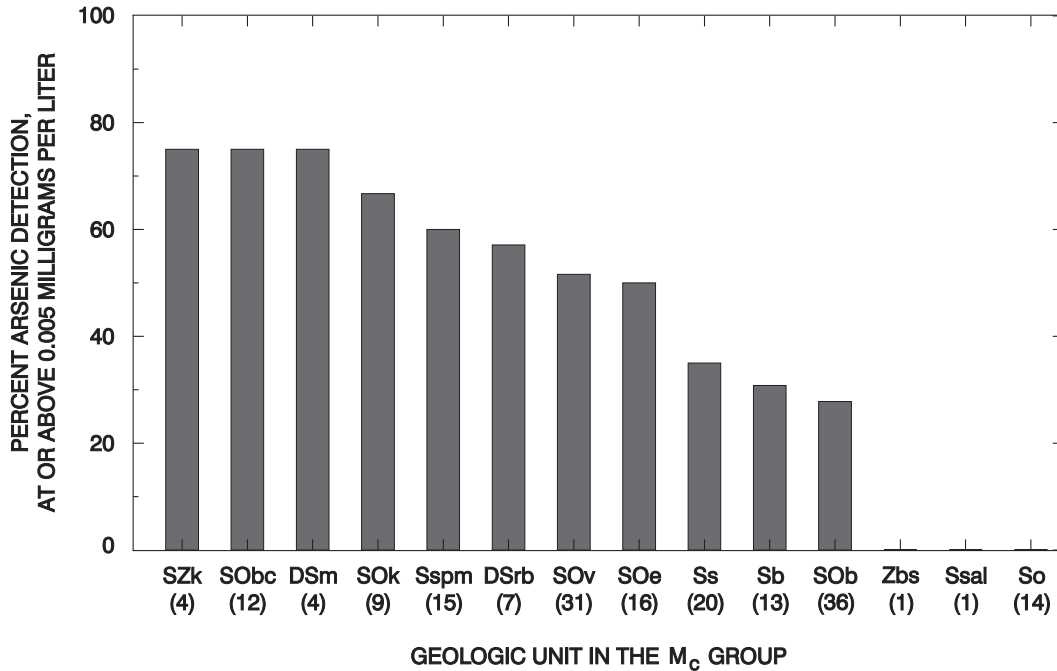
[p-values, the probability that the observed differences are due to chance rather than the factor tested, are for SAS General Linear Models Type III sum of squares (SAS Institute Inc., 1990); p-values significant at a = 0.05 are shown in bold; --, none computed]

Water-quality variable	Factor	
	Lithogeochemistry	Land use
Arsenic	**0.0001**	**0.0128**
Iron	**0.0023**	--
Manganese	**0.0002**	--

within any given unit, are grouped as calcareous or calc-silicate rocks according to descriptive information on the state bedrock geologic maps of Maine (Osberg and others, 1985), New Hampshire (Lyons and others, 1997), Massachusetts (Zen and others, 1983), and Rhode Island (Hermes and others, 1994). The Madrid Formation in Maine, and an unnamed member of the Berwick Formation in New Hampshire, have detectable arsenic in ground water from 75 percent or more of the wells in their respective units (fig. 7).

Variation in the occurrence of iron and manganese was analyzed by lithogeochemical group. Kruskal-Wallis analysis showed significant differences in iron concentration by lithogeochemical group (table 5), and a subsequent multiple comparison test (Tukey) showed that water from wells in group M_s [a] had significantly greater concentrations than water from wells in group M_c [b] and group I_f [b] (fig. 8). Concentrations of iron in water from wells in groups M_u, M_{md}, and I_m [ab] were not significantly different from those in water from any other lithogeochemical group. The highest median concentration of iron was in water from wells in group M_{md}; however, only 10 samples were collected from wells in this lithogeochemical group (fig. 8).

A Kruskal-Wallis test on the manganese data also indicates differences in concentration by lithogeochemical group (table 6). For manganese, the multiple comparison test (Tukey) showed that water from wells in the group M_s [a] had significantly higher concentrations of manganese than did water from wells in the group I_f [b], but that manganese in water from the other four groups [ab] was not significantly different from water from groups M_s and I_f (fig. 8).

Figure 7. Percent detection of arsenic concentrations in ground water, at or above 0.005 milligrams per liter, in selected bedrock geologic units in lithogeochemical group M_c. [Bedrock geologic unit names from Lyons and others, 1997; Hermes and others, 1994; Osberg and others, 1985; and Zen and others, 1983; Lithogeochemical group described in figure 3.]
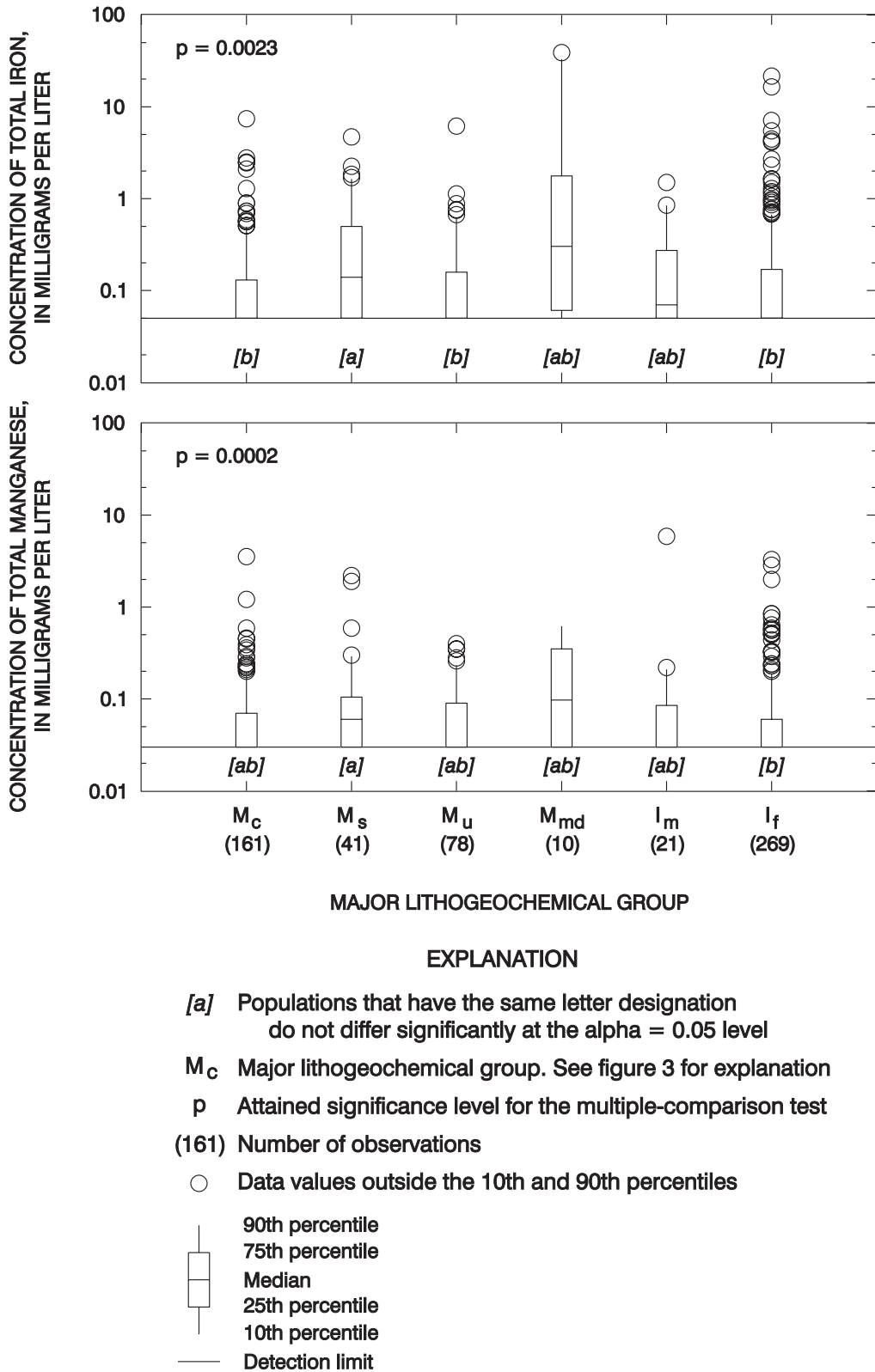
Figure 8. Iron and manganese concentrations in ground water by major lithogeochemical group.

Table 6. Summary of Spearman's rho rank-correlation coefficients for concentrations of arsenic and iron, arsenic and manganese, and iron and manganese in the New England Coastal Basins study unit

[Significant correlations, the probability that the observed correlations are due to the relation tested rather than to chance, at alpa =0.05, are shown in bold; see figure 3 for lithogeochemical group explanation]

Lithogeochemical group	Spearman's correlation coefficients for correlation of well water concentrations of		
	Arsenic and iron	Arsenic and manganese	Iron and manganese
M_c	0.03362	0.16096	**0.60472**
M_s	.05433	.10787	**.77128**
M_u	-.10321	.02278	.31353
M_{md}	-.05838	-.41248	**.86072**
I_m	-.01091	-.06781	.26320
I_f	-.01490	.02278	**.47104**