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The influence of geology and land use on arsenic in stream sediments and ground waters in New England, USA

Gilpin R. Robinson Jr. [a,*], Joseph D. Ayotte [b]

[a] US Geological Survey, 954 National Center, Reston, VA 20192, United States
[b] US Geological Survey, 361 Commerce Way, Pembroke, NH 03275-3719, United States

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Abstract

Population statistics for As concentrations in rocks, sediments and ground water differ by geology and land use features in the New England region, USA. Significant sources of As in the surficial environment include both natural weathering of rocks and anthropogenic sources such as arsenical pesticides that were commonly applied to apple, blueberry and potato crops during the first half of the 20th century in the region. The variation of As in bedrock ground water wells has a strong positive correlation with geologic features at the geologic province, lithology group, and bedrock map unit levels. The variation of As in bedrock ground water wells also has a positive correlation with elevated stream sediment and rock As chemistry. Elevated As concentrations in bedrock wells do not correlate with past agricultural areas that used arsenical pesticides on crops. Stream sediments, which integrate both natural and anthropogenic sources, have a strong positive correlation of As concentrations with rock chemistry, geologic provinces and ground water chemistry, and a weaker positive correlation with past agricultural land use. Although correlation is not sufficient to demonstrate cause-and-effect, the statistics favor rock-based As as the dominant regional source of the element in stream sediments and ground water in New England. The distribution of bedrock geology features at the geologic province, lithology group and map unit level closely correlate with areas of elevated As in ground water, stream sediments, and rocks.

1. Introduction

National and regional studies of As occurrence in drinking water (Welch et al., 2000; Peters et al., 1999; Ayotte et al., 1999, 2003) have identified areas within New England, USA, where ground water wells have As concentrations that frequently exceed the maximum contaminant level (MCL) value of 0.01 mg/L for drinking water (US Environmental Protection Agency, 2002; Smith et al., 2002). Water samples from drilled wells in bedrock have the highest As concentrations, and it is estimated that as many as 10 to 40% of bedrock ground water wells in some areas exceed the MCL standard (Peters et al., 1999; Ayotte et al., 1999, 2003; Montgomery et al., 2003). Most water samples from ground water wells in surficial sediments have As concentrations below the MCL (Ayotte et al., 1999).

* Corresponding author. Fax: +1 703 648 6383.
E-mail address: grobinso@usgs.gov (G.R. Robinson Jr.).

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Previous local and regional studies have identified correlations between areas with elevated ground water As and geologic features and units (Peters et al., 1999; Ayotte et al., 1999, 2003; Montgomery et al., 2003). In some studies, the possibility that anthropogenic activity can affect ground water As concentrations have been acknowledged but correlations have not been found (Marvinney et al., 1994; Boudette et al., 1985; Zeuna and Keane, 1985). The widespread use of arsenical pesticides and herbicides on crops and shrubs in the region has been suggested as the dominant source of anthropogenic As to surficial soils and sediments (D'Angelo et al., 1996; Marvinney et al., 1994; Peryea, 1998; Nriagu and Pacyna, 1988). Stream sediment chemistry in the New England region appears to be influenced by both geologic and arsenical pesticide sources (Chormann, 1985; Robinson and Ayuso, 2004). The objective of this study is to compare As distributions and covariation map patterns to evaluate spatial associations between As concentrations in rock, sediment and water with geology, lithology and land-use features.

1.1. Occurrence and distribution of arsenic in the surficial environment

1.1.1. Rocks, soils, and sediments

Although the average concentration of As in the earth's crust is low, on the order of 1.7 mg/kg (Wedepohl, 1995), As is widely distributed and commonly found in many rock types, sediments, and soils at concentrations near or exceeding this level (Smedley and Kinniburgh, 2002). Arsenic concentration in rocks varies by mineralogy, rock type, and geologic setting. In its reduced form, As is commonly concentrated in sulfide and sulfosalt minerals (Rose et al., 1979). Pyrite, a common sulfide mineral in many rock types, is a prevalent host of As in most rocks (Kolker and Nordstrom, 2001). Weathering of As-containing rocks is considered to be the dominant source of natural As in the environment (Tamaki and Frankenberger, 1992). The baseline concentration of As in stream sediments and soils is in the order of 5–8 mg/kg (Smedley and Kinniburgh, 2002); soils in the USA. have an average concentration of approximately 7.4 mg/kg (Shacklette et al., 1974). In sediments, soils, and other oxidized weathered environments, As has an affinity for sorption and concentration with hydrous Fe oxide minerals and mineral coatings (Goldberg, 2002; Stollenwerk, 2003; Smedley and Kinniburgh, 2002). In similar weathering environments, where As concentrations are high, it also occurs in metal-arsenate–phosphate phases (Ayuso and Foley, 2002; Wauchope, 1975; Yan-Chu, 1994; Woolson, 1977). Stream sediments and soils integrate As from both natural and anthropogenic sources. The dominant natural source of As in sediments and soils is geologic and is dependent upon the nature of the weathering environment and the concentration and mineral form of As in the parent rock material (Tamaki and Frankenberger, 1992).

1.1.2. Anthropogenic sources of environmental arsenic

The most significant anthropogenic source of As in the region is believed to be from cumulative applications of arsenical pesticides and herbicides that were used in New England from the late 1800s until the late 1960s (Peryea, 1998; D'Angelo et al., 1996). The application of arsenical pesticides in New England predates systematic record-keeping and the exact locations and amounts of pesticide applications are unknown, but it is estimated, based on cultivation practices and history, that cumulative application rates of As could have been 22 g/m^2 in some cultivated areas in the region (equivalent to 200 lbs of elemental As per acre of cultivation, as reported by D'Angelo et al. (1996)). Widespread use of arsenical agricultural compounds occurred during the 1920s to 1950s on agricultural lands containing potato fields, apple orchards and blueberry fields (D'Angelo et al., 1996); cultivation data for these crops during this time period (US Department of Agriculture, 1935-1997) indicate, where arsenical pesticides and herbicides were used most extensively in the region.

1.1.3. Ground water wells used for drinking water

Arsenic is found at low levels in many natural waters (Smedley and Kinniburgh, 2002) and typical water concentrations are low in relation to the typical abundance of As in the rocks, mineral coatings and sediments that are in contact with ground water in most settings. A very small amount of dissolution or desorption of bound As from these materials can lead to high concentrations of As in local ground water, explaining why many ground water areas high in dissolved As are found in areas with near average As concentrations in rocks and soils (Welch et al., 2000; Stollenwerk, 2003).

Arsenic concentrations in ground water wells typically exhibit a high degree of variability on a well-to-well basis, even within close proximity to one another. It is difficult to predict the As concentration in a particular well based on the As concentrations in neighboring wells (Ayotte et al., 2003; Welch et al., 2000).

2. Data used in spatial analysis

2.1. Sample chemistry data sets

2.1.1. Rock arsenic chemistry

Rock chemistry data from 149 samples collected and analyzed for this study and geochemical data for 1125 rock samples from the New England region previously analyzed by US Geological Survey analytical laboratories were used in the study. The rock samples collected during this study were analyzed for As using hydride-generation atomic absorption spectrometry (HGAA) at a single laboratory facility, XRAL Laboratories (Canada). Analyses of reference materials and standards were used to standardize and calibrate the equipment. The HGAA method is described in Taggart (2002).

Additional analytical data for As concentrations in representative rock samples from the New England region were retrieved from the PLUTO database archive of geochemical data determined by US Geological Survey laboratories (Baedecker et al., 1998). Geochemical data was included only if the analytical technique reported a minimum detection level of 0.3 mg/kg or lower for As. Rock analysis data used in this study were restricted to representative rock samples from outcrop settings, where the rock type is identified. The rock samples are from a large variety of igneous and metamorphic rock types, but are dominated by samples of granite and felsic volcanics. Rock samples collected from the vicinity of mines, prospects, mine dumps, or otherwise mineralized settings were omitted.

The distribution of 1274 rock samples that meet the above criteria cluster along two NE-trending transects from (1) southern Connecticut to northern Vermont near the Vermont-New Hampshire border and (2) eastern Connecticut to coastal Maine. Other rock samples are clustered in areas across Maine (Fig. 1a).

2.1.2. Stream sediment arsenic chemistry

The stream sediment As data used in this study are a subset of 1597 stream sediment samples (Fig. 1b) that were re-analyzed by using similar methods to those described in Section 3 and with a reporting limit of 0.3 mg/kg. The samples were randomly selected from an archive of approximately

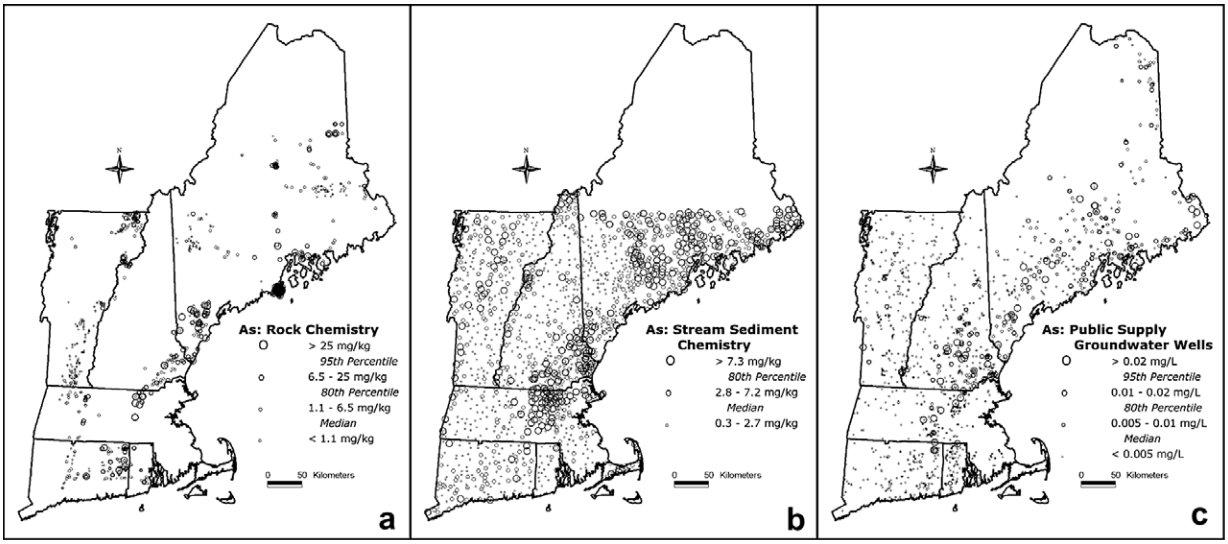

Fig. 1. (a) Rock chemistry sample locations in New England, showing As concentration ranges. The symbol legend for the As concentration data is based on percentiles for the ranked As concentrations. Symbol transitions occur at 0.5 (1.1 mg/kg), 0.8 (6.5 mg/kg), and 0.95 (25 mg/kg) percentile values. (b) Stream sediment chemistry sample locations in New England, showing As concentration ranges. The symbol legend for the As concentration data is based on percentiles for the ranked As concentrations. Symbol transitions occur at 0.5 (2.8 mg/kg) and 0.8 (7.3 mg/kg) percentile values. (c) Water chemistry sample locations from public-supply bedrock wells in New England, showing As concentration ranges. The symbol legend for the As concentration data is based on percentiles for the ranked As concentrations. Symbol transitions occur at 0.5 (0.005 mg/L), 0.8 (0.01 mg/L), and 0.95 (0.02 mg/L) percentile values.

7900 stream sediment samples distributed throughout New England collected from 1977 to 1980 by the National Uranium Resource Evaluation (NURE) Program conducted by the Department of Energy. The NURE program did not sample drainages in Maine north of 45° latitude. The sediment samples processed under the NURE program were sieved to below 100 mesh (<150 μm grain size). Information on the NURE sample-site attributes is given in Smith (2001a,b) and the reanalyzed analytical data are provided in Robinson et al. (2004).

2.1.3. Bedrock well arsenic chemistry

Arsenic data for ground water wells that penetrate bedrock in New England were obtained from state records on public-water supply wells collected for compliance with the Safe Drinking Water Act during the years of 1992–1999 (Fig. 1c). The data and criteria for selection are described in Ayotte et al. (1999, 2003). Sources of data include public-water supply records collected by the Maine Department of Health; the New Hampshire Department of Environmental Services, Water Division; the Massachusetts Department of Environmental Protection, Bureau of Resource Protection, Drinking Water Program; the Rhode Island Department of Health; and the Vermont Agency of Natural Resources. The laboratory reporting level (LRL) for the ground water samples used in this study was variable but not higher than 0.005 mg/L. Approximately 80% of the wells in the database have As concentrations that are below the highest LRL limit of 0.005 mg/L. For all censored and uncensored wells, where the reported analytical values for As are below 0.005 mg/L, ranks were assigned as tie values in the nonparametric statistical procedures and statistics.

2.2. Explanatory variable data sets

2.2.1. Bedrock geology and lithology spatial data layers

The geologic data sets were compiled from statewide maps of bedrock geology for Connecticut (Rogers, 1985), Maine (Osberg et al., 1985), Massachusetts (Zen et al., 1983), New Hampshire (Lyons et al., 1997), Rhode Island (Hermes et al., 1994), and Vermont (Doll et al., 1961). Over 1200 individual map units are named and portrayed in these state bedrock geology maps. Map units that were the site of 5 or more sediment or ground water samples were evaluated for differences in As distribution. For analysis of differences in As distributions, the bedrock map units were grouped into lithology and geologic province categories using map unit descriptions and other geologic information provided with the geologic maps. These lithology group categories (Robinson and Kapo, 2003) are shown in Fig. 2a. The bedrock map units have been divided into geologic provinces (Fig. 2b), using the geologic province categories presented in Robinson and Kapo (2003). Each province group shares common features of (1) lithology, (2) age of formation, (3) geologic setting, and (4) tectonic history. The province groups generally occur as NE trending belts that follow the structural fabric of the Appalachian foldbelt and faults in New England. Each province group was evaluated for differences in As distribution. The geologic province categories that are adjacent and have similar As distributions for ground water, sediment and rocks were combined to simplify the discussion and presentation of results.

2.2.2. Agricultural lands with As-pesticide use data

Robinson and Ayuso (2004) demonstrate that elevated As concentrations in stream sediments correlate with former agricultural areas in New England that used arsenical pesticides. Previous studies (Boudette et al., 1985; Marvinney et al., 1994; Zeuna and Keane, 1985) have suggested a link between areas with elevated ground water As and agricultural areas with historic application of large amounts of arsenical pesticides.

Long-term site-specific application rates of arsenical pesticides are not known in the region but can be inferred from regional crop production records and general pesticide application rates. This study uses agricultural census data for apple, blueberry, and potato crops in New England from 1935 to 1977 (US Department of Agriculture, 1935-1997) to define the location and estimate the relative intensity of arsenical pesticide applications in the region. D'Angelo et al. (1996) estimate that, on a per-acre-basis, the cumulative application rates for arsenical pesticides applied to apple, blueberry, and potato crops are comparable. The agricultural census data were compiled by crop type at county level for multiple agricultural census years. The GIRAS land-use database (scale 1:250,000; Hitt, 1994) compiled from high-altitude aerial photographs from the late 1960s to early 1970s was used to partition the county-scale agricultural census data into smaller units, based on census tracts, where agricultural land was located in each county (US Census

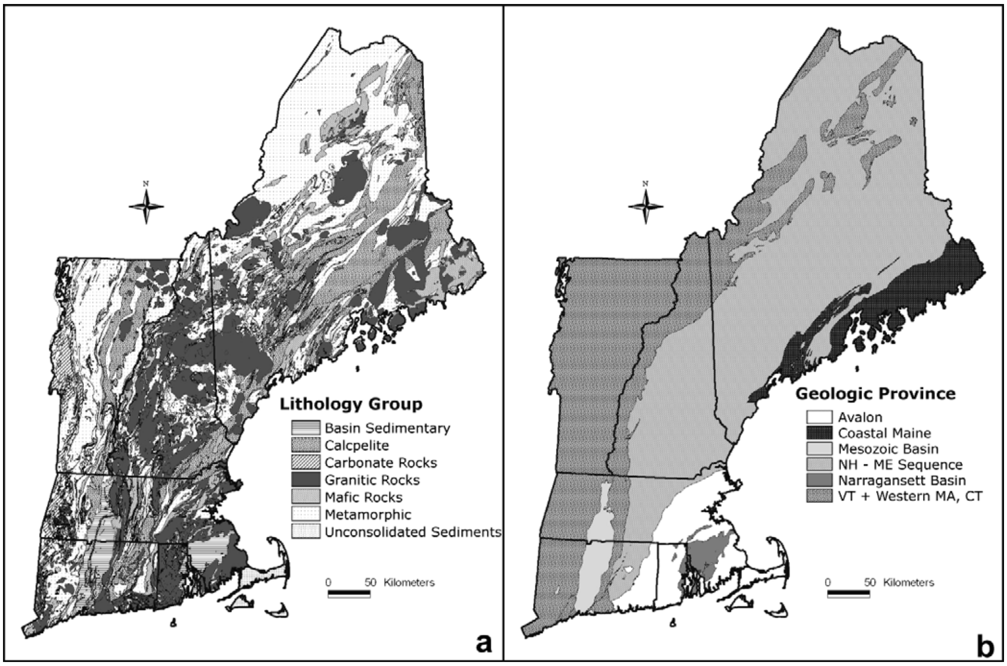

Fig. 2. (a) Generalized lithology of bedrock geologic units in New England. The rock types have been grouped into seven general categories based on map unit descriptions and depositional setting information summarized in Robinson and Kapo (2003). (b) Generalized geologic provinces in New England. The provinces have been grouped into 6 general categories based on descriptions and information summarized in Robinson and Kapo (2003).

Bureau, 2000a,b). The agricultural data from multiple census years were averaged on a census tract level to determine the area of apple, blueberry and potato cultivation per tract area. The agricultural-index (Agr-index) value is the ratio of cultivation area divided by tract area, given in percent units. These census-tract level agricultural cultivation estimates (areas on the order of a few tens of km^2) were compared to stream sediment data that are sampled in drainages in the order of a few tens of km^2. The Agr-index is used as a proxy for the arsenical pesticide application rate in the area (Fig. 3).

2.2.3. Interpolation maps for stream sediment and ground water well arsenic chemistry

The chemical data for stream sediments, rocks, and ground waters has been interpolated so that spatial comparisons could be made (Fig. 4a, b). The interpolation grids were produced using the GeoDAS System inverse-distance weighted (IDW) multifractal interpolation method (Cheng, 2003; Agterberg, 2001), with an output grid cell size of approximately 1 km^2. IDW techniques have been recommended in studies comparing interpolation methods (Weber and Englund, 1992, 1994; Englund et al., 1992). Multifractal IDW is a technique that fits the source data accurately and preserves local anomalies in the interpolation grid. The interpolation grids of stream sediment and ground water chemistry provide coverage over more than 70% of New England. Due to the unevenly scattered distribution of rock samples, the interpolation grid for rock As concentrations is poorly constrained. For this study, the rock As interpolation grid was restricted to areas within 2 km of a rock sample.

For the interpolation grid process, the censored data for ground water well As values below the LRL were assigned estimated values of one half the LRL value. After interpolation, all grid cell values less than the upper LRL value of 0.005 mg/L As were reassigned a value of <0.005 for data comparison evaluations. The interpolation grid process generates smoothed geochemical gradients that eliminate some of the local variability inherent in the point source data. Data smoothing is particularly evident in the interpolation grid for bedrock well water when compared to the well data that displays a high degree of well-to-well variability in areas, where higher As concentrations in well water are prevalent.

All statistical analyses in this study were performed on categorical or rank transformed data; these transformations are not sensitive to differences

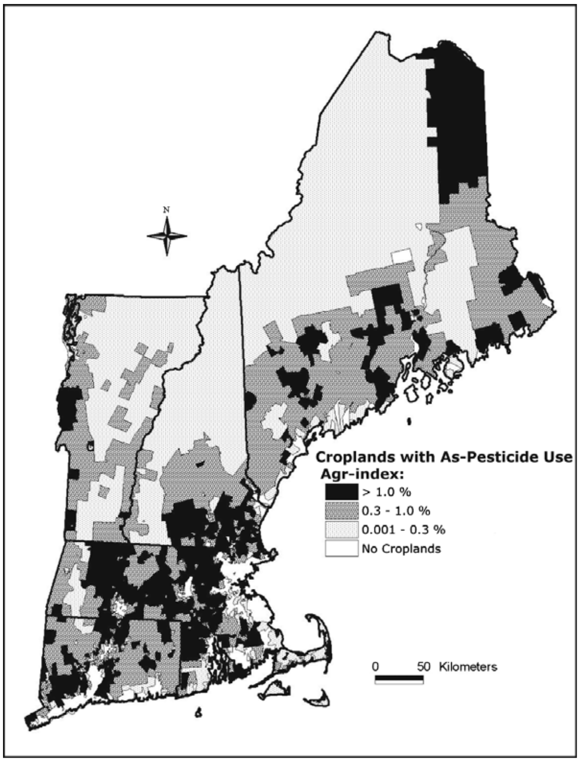

Fig. 3. Agricultural lands that used arsenical pesticides and herbicides in New England. The agricultural index value (Agr-index) portrays the ratio of average cultivation area of apples, blueberries and potatoes per census tract area. The Agr-index is based on agricultural census data from 1935 to 1977 (US Department of Agriculture).

in the concentrations portrayed by the interpolation process versus actual values.

3. Data comparison and statistical methods

3.1. Data comparison

The data for rock As concentrations were grouped by rock lithology and geologic province. The data for As concentrations in bedrock well-water and stream sediments were grouped according to geologic province, bedrock lithology, and Agr-index criteria. In addition, the data for As concentrations in bedrock ground water and stream sediments were grouped by the bedrock geology map units that were identified by this study and Ayotte et al. (1999) as having statistically elevated concentrations of As in ground water and stream sediments. Variation at geologic formation scale highlights differences in results for individual map units relative to the general lithology groups.

3.2. Statistical methods

Arsenic concentrations in the rock, stream sediment, and well water data sets are non-normally distributed and are positively skewed with infrequent extreme values. The data for ground water are censored at the lower end due to analytical limits and possibly at the high end due to well selection criteria. Based on population statistics in studies of private ground water wells that are not constrained by well selection criteria (Ayotte et al., 2003; Montgomery et al., 2003), the bias at the high end appears to be small.

Because of the non-normal distribution of data, nonparametric statistical procedures (Conover, 1980; Iman and Conover, 1983; Helsel and Hirsch, 2002) and contingency table tests (Agresti, 2002) are used to analyze the data. These procedures measure the degree of association between As concentrations in rocks, stream sediments, and ground water and describe and test differences between the distributions of As data when grouped by geologic, lithologic and past agricultural land use categories. The explanatory variable values are determined by spatial association of sample collection site locations (dependent variable) with (1) landscape features based on bedrock geology, (2) an Agr-index value based on the intensity of cultivation of crops that received arsenical pesticide applications, and (3) values for As in ground water and stream sediments estimated by spatial interpolation from sample data. Spearman rank correlation coefficients were calculated to measure the direction and strength of the association between ground water chemistry, stream sediment chemistry, and rock chemistry for As and for the Agr-index variable. These statistical analyses measure the degree of correlation between sample media, categorized by As concentration range, and landscape features without defining the causes and processes controlling the As concentrations in the stream sediment and ground water samples.

Hypothesis tests are used to test for differences in As chemistry between population groupings for the rock, stream sediment and water samples. Analysis of variance of rank transformed data were used to test the null hypothesis that the mean rank (an estimate of median) of the data from the different lithology group, geologic province, geologic map

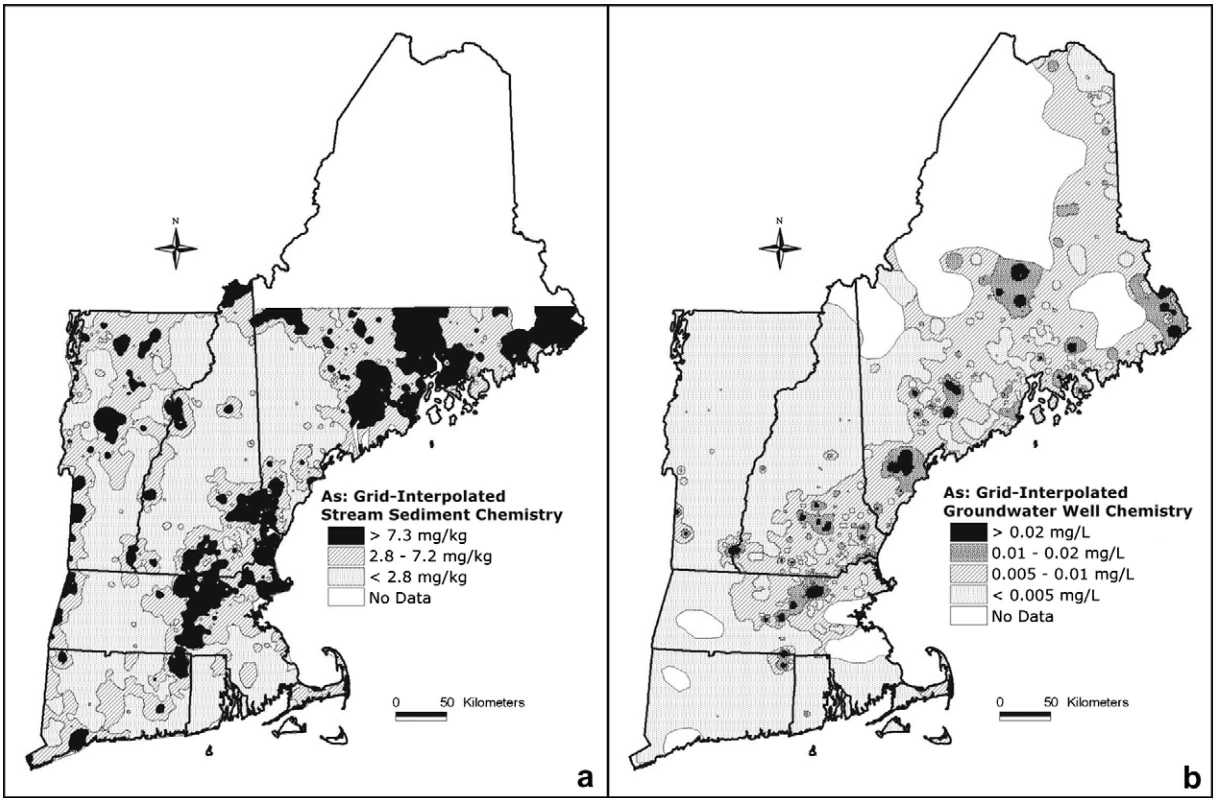

Fig. 4. (a) Inverse-distanced weighted interpolation grid of stream sediment As chemistry developed using the multifractal method in GeoDAS software (Cheng, 2003). The symbol legend for the As concentration data is based on percentiles for the ranked As concentrations in the stream sediment database. Symbol transitions occur at 0.5 (2.8 mg/kg) and 0.8 (7.3 mg/kg) percentile values. (b) Inverse-distanced weighted interpolation grid of As concentrations in bedrock groundwater based on water chemistry from public-supply bedrock well locations in New England. The interpolation grid was developed using the multifractal method in GeoDAS software (Cheng, 2003). The symbol legend for the As concentration data is based on percentiles for the ranked As concentrations in the well water database. Symbol transitions occur at 0.5 (0.005 mg/L), 0.8 (0.01 mg/L), and 0.95 (0.02 mg/L) percentile values. Areas of no data show, where bedrock well chemistry data are lacking.

unit, and agricultural class groups was equal (Sokal and Rohlf, 1969; Conover and Iman, 1981; Helsel and Hirsch, 2002). Rejection of the null hypothesis at the 95-percent confidence level ($\alpha = 0.05$) was considered evidence supporting the alternative hypothesis, that is, the existence of a relation between variation in the sample data and the tested landscape factor. The general linear models (GLM) procedure was used because the number of samples was not the same for all of the category groups (Helsel and Hirsch, 2002; SAS Institute Inc., 1999).

3.2.1. Kruskal–Wallis tests

Multiple comparison tests, based on Kruskal–Wallis rank sums and comparisons of means of ranks (Tukey) tests, were used to identify which groups differed from others (Hollander and Wolfe, 1973). Tukey's significant-difference test (Sokal and Rohlf, 1969; Stoline, 1981; Helsel and Hirsch, 2002) was used to discriminate which category group or groups of data differed when the analysis of variance rejected the null hypothesis.

3.2.2. Contingency table analysis

For the significant explanatory variables in Table 1, contingency table tests were used to evaluate which category groups had the strongest correlations while controlling for the influence of other variables. For these tests, both the sample (dependent variable) data and the explanatory (independent variable) data were categorized into binary groups. The sample data for rocks, stream sediments and bedrock well waters were divided into high and low data categories based on a threshold concentration defined by the 80th percentile value for As concentration in the sample population.

Table 1
Statistical summary of As concentrations in bedrock groundwater, stream sediments and rocks by geology and land use variables

Variable	Number of samples	Max	Percentile			Min	Tukey Group
			0.75	0.5	0.25		
Bedrock groundwater wells (As in mg/L units)							
Geologic Province	1572	(Total)					
Avalon	274	0.013	<LRL	<LRL	<LRL	<LRL	B
Coastal Maine (CM)	104	0.048	0.010	0.005	<LRL	<LRL	A
Mesozoic Basins	32	0.006	<LRL	<LRL	<LRL	<LRL	B
Narragansett Basins	21	0.380	<LRL	<LRL	<LRL	<LRL	B
NH-Maine (NHM)	729	1.100	0.006	<LRL	<LRL	<LRL	A
Vt.-W.Ma.-Ct	412	0.156	<LRL	<LRL	<LRL	<LRL	B
Lithology Groups	1572	(Total)					
Basin Sediments	44	0.016	<LRL	<LRL	<LRL	<LRL	BC
Carbonate Rocks	89	0.020	<LRL	<LRL	<LRL	<LRL	C
Calcpelite	311	0.820	0.007	<LRL	<LRL	<LRL	A
Granite	424	1.100	<LRL	<LRL	<LRL	<LRL	BC
Mafic Rocks	139	0.038	<LRL	<LRL	<LRL	<LRL	B
Metamorphic Rk, und	565	0.176	<LRL	<LRL	<LRL	<LRL	B
Bedrock MapUnits	1572	(Total)					
NHM-Ayer Granite	5	1.100	0.294	<LRL	<LRL	<LRL	B
NHM-Concord-Spaulding Gr.	37	0.038	0.014	<LRL	<LRL	<LRL	B
CM-Granite	14	0.260	0.010	0.005	<LRL	<LRL	AB
CM-Meta Rx	88	0.480	0.010	0.005	<LRL	<LRL	B
NHM-Calcpelite	311	0.082	0.007	<LRL	<LRL	<LRL	B
NHM-Waterville Fm	16	0.176	0.020	0.009	0.007	0.001	A
NHM-L. Rangley	37	0.034	0.009	<LRL	<LRL	<LRL	B
Other units, combined	1064	0.156	<LRL	<LRL	<LRL	<LRL	C
Land Use	1572	(Total)					
Agr-index > 1.0	581	1.100	<LRL	<LRL	<LRL	<LRL	A
Agr-index < 1.0	991	0.176	<LRL	<LRL	<LRL	<LRL	A
Stream Sediments (As in mg/kg units)							
Geologic Province	1597	(Total)					
Avalon	152	39.9	5.3	2.6	1.3	0.3	BC
Coastal Maine (CM)	141	98.3	13.5	7.6	4.8	1.0	A
Mesozoic Basins	37	6.9	4.1	2.8	1.7	0.7	BC
Narragansett Basins	19	7.1	2.9	1.7	1.2	0.3	C
NH-Maine (NHM)	721	52.7	6.6	2.8	1.3	0.3	B
Vt.-W.Ma.-Ct	525	86.9	4.1	2.3	1.3	0.3	BC
Lithology Groups	1597	(Total)					
Basin Sediments	49	7.1	3.1	1.9	1.3	0.3	C
Carbonate Rocks	104	16.1	4.1	2.3	1.2	0.3	BC
Calcpelites – NHM	295	46.8	8.0	4.2	1.9	0.3	A
Granite	429	39.6	4.0	2.0	1.0	0.3	BC
Mafic rocks	186	77.7	9.1	4.7	2.1	0.3	A
Metamorphic Rk, und	508	98.3	6.3	2.7	1.4	0.3	ABC
Bedrock MapUnits	1597	(Total)					
NHM-Ayer Granite	2	38.9	38.9	27.4	15.8	15.8	A
NHM-Concord-Spaulding Gr.	41	38.4	6.5	2.8	1.7	0.3	BC
CM-Granite	36	39.5	9.7	5.3	3.4	1.4	ABC
CM-Meta Rx	103	98.3	13.9	8.8	5.4	1.0	AB
NHM-Calcpelite	271	46.8	8.2	4.2	2.0	0.3	BC
NHM-Waterville Fm	19	34.1	10.5	6.7	3.9	1.5	ABC
NHM-L. Rangley	38	37.8	6.0	2.6	1.0	0.3	BC
Other units, combined	1085	86.9	4.5	2.2	1.2	0.3	C
Land Use	1596	(Total)					
Agr-index > 1.0	408	98.3	8.1	4.0	1.8	0.3	A
Agr-index < 1.0	1188	86.9	5.4	2.6	1.3	0.3	B

(*continued on next page*)

Table 1 (*continued*)

Variable	Number of samples	Max	Percentile			Min	Tukey Group
			0.75	0.5	0.25		
Rock Samples (As in mg/kg units)							
Geologic Province	1274	(Total)					
Avalon	81	182.0	2.0	1.3	0.8	0.2	BC
Coastal Maine (CM)	107	554.0	8.7	2.6	1.5	0.2	A
Mesozoic Basins	62	17.0	1.9	0.9	0.6	0.3	C
Narragansett Basins	351	366.0	9.4	2.3	0.6	0.2	AB
NH-Maine (NHM)	476	402.0	1.1	0.4	0.3	0.2	D
Lithology Groups	1200	(Total)					
Felsic Volcanics	270	57.0	14.0	6.0	0.7	0.2	B
Granite	428	179.0	1.5	0.6	0.3	0.2	C
Mafic Rocks	224	88.0	1.5	0.9	0.5	0.3	C
Calcpelite-NHM	124	366.0	21.7	6.0	2.5	0.3	A
Sulfidic Meta Rx	29	94.0	29.0	5.0	1.5	0.3	AB
Meta Rocks, other	125	554.0	3.5	0.5	0.4	0.2	C

Different sample populations (Tukey Groups) are designated by letter symbols (A, B, C); sample groups that share the same letter are not statistically different at $\alpha = 0.05$. Bedrock groundwater well samples listed as "<LRL" have As concentrations below the highest common laboratory reporting level (LRL); The LRL limit values range from 0.005 to 0.001 mg/L As for samples submitted to different laboratories for different state public supply records.

These threshold values for As concentration are 6.7 mg/kg, 7.3 mg/kg, and 0.005 mg/L for rocks, stream sediments and well waters, respectively. The 80th percentile was chosen because 80% of the bedrock well water As data is below the LRL value of 0.005 mg/L As. The choice of the 80th percentile provides discrimination at the high end of the As concentration range and also provides sufficient samples in each category to perform statistical tests.

The geologic features were combined into two binary explanatory variable categories used in the contingency table analysis. At geologic province scale, labeled the Province variable, the NH-Maine and Coastal Maine categories (Tukey group designations of A in Table 1) were combined into one category and all other provinces in the other. At geologic bedrock map unit scale, labeled the Geology variable, all bedrock map units with a Tukey group designation of A or B under the Bedrock Map Units heading in Table 1 were combined into one category and all other units were placed in the other. These groups were chosen at natural breaks between the categories in Table 1 so that not less than 30% of the total sample size occurs in any binary category.

The ordered explanatory variables were classified into binary categories using percentile criteria. The Agr-index variable was grouped into high and low categories using an Agr-index threshold value of 1.0%, which is the 80th percentile value based on area. The interpolated stream sediment chemistry grid was split into two categories, termed the SSgrid variable, using a threshold value of 7.3 mg/kg As, identical to the stream sediment threshold. For the SSgrid variable, 0.7% of sediment samples in the High category and 0.4% of sediment samples in the Low category are misclassified when the interpolated values are compared to the raw data. The interpolated bedrock well water chemistry grid was split into two categories, termed the Wellgrid variable, using a threshold value of 0.005 mg/L As, identical to the ground water well threshold. The well water data display a high degree of well-to-well variability, particularly in areas, where higher As concentrations in well water are prevalent. For the Wellgrid variable, 23% of wells in the High category and 5% of wells in the Low category are misclassified when the interpolated values are compared to the raw data used to generate the interpolation grid.

The interpolated rock chemistry grid was split into two categories, termed the Rockgrid variable, using a threshold value of 6.7 mg/kg As, identical to the rock chemistry threshold.

The relative influence of the geologic and landuse variables are of interest in the study. Therefore, a stratified analysis using a cross tabulation contingency table approach is used to measure strength of the spatial associations between As in rocks, sediments, and ground waters while controlling for the influence and covariance of geologic and landuse (Agr-index) variables. Because of data smoothing resulting from the interpolation process, matched associations are measured between pair-wise combinations of point (actual) and grid data in the contingency table analysis. Differences in the correlation between the matched data sets measured by the contingency table analysis reflect the effects of data smoothing in the interpolation. Due to these differences, the contingency table correlations are grouped by dependent variable.

3.2.2.1. Cochran–Mantel–Haenszel statistics. The stratified analysis approach using Cochran–Mantel–Haenszel statistics (Agresti, 2002; Stokes et al., 1995) provides a way to adjust for the possible confounding effects of the geology and landuse variables without estimating parameters for them. In this approach, 3 test statistics are estimated to measure the overall association between 2 variables while controlling for the influence of others. They are: (1) the Cochran–Mantel–Haenszel (CMH) test, (2) the Mantel–Haenszel (MH) test, and (3) the Breslow–Day (BD) test. All tests use a 95-percent confidence interval.

The CMH statistic tests the conditional independence of the relationship between two variables in relation to other variables by measuring the probability that the dependent variable subgroups, defined by independent variable, when adjusted for the controlled variable, have similar data distributions (Agresti, 2002). The null hypothesis tested is that the distribution frequency of As is conditionally independent of the explanatory variable criteria, given the control variable criteria. Rejection of the null hypothesis is evidence of a significant relationship between the dependent and the independent variables, after adjusting for the control variable. Spearman correlation coefficients (Rho) have been calculated for the continuous dependent and independent data variables when the CMH statistic indicates significant group differences.

The Mantel-Haenszel Case-control odds ratio, OR_{MH}, measures the strength of the relationship between the two variables, when adjusted for the control variable. An odds ratio of 1 indicates no effect while a ratio greater than 1 indicates that the independent variable category increases the odds of occurrence of high concentrations in the sample media. The magnitude of the common odds ratio is a measure of the strength of association between the two variables. The data in Table 2 are grouped by dependent variable and are listed in order of decreasing association strength (decreasing OR_{MH}) for each dependent variable group.

The Breslow-Day statistic, p(BD), measures the probability that the odds ratio of the groups defined by the control variables are homogeneous. Acceptance of the null hypothesis means that it is possible to summarize the conditional association between the dependent and explanatory variable by a single odds ratio. A low p-value result for the BD statistic means that the odds ratios differ between the control variable categories and the control variable influences the results. This situation occurs when the explanatory and control variables are influenced by each other but have differing associations with the dependent variable.

4. Results and discussion

Table 1 is a tabulation of As distributions by group percentile for bedrock ground water, stream sediment and rock samples grouped by bedrock geology, lithology and land-use explanatory variable variables. Concentrations of As in waters, rocks, soils and sediments vary by more than 3 orders of magnitude. The As concentrations show a positively skewed distribution with median values of 1.1 mg/kg, 2.8 mg/kg, <0.005 mg/L for rocks, sediments and ground water, respectively.

Different sample populations identified by multiple comparisons of ranked means tests (Tukey groups) are designated by letter symbols; sample groups that share the same letter are not statistically different at a 95-percent confidence level. Sample populations designated by the letter A have the highest concentration values.

4.1. Data comparison by geologic variables

The geologic feature categories are discussed in order of decreasing scale of combined map units, from province scale to lithology group scale to individual bedrock map units.

4.1.1. Geologic province and lithology group scale

The Tukey groups and statistics tabulated in Table 1 indicate that As concentrations in rocks, stream sediments and water from wells in the Coastal Maine and NH-Maine Geologic Provinces are significantly higher than As concentrations in the other groups. Arsenic concentrations in rocks, stream sediments and water from wells from the geologic provinces grouped into the Vt.-W.Ma.-Ct

Table 2
Summary of ranked Cochran–Mantel–Haenszel statistics for rock (rocks), stream sediment (sseds), and groundwater well (wells) sample populations evaluated relative to grouped geologic province (Province), geologic bedrock map unit (Geology), agricultural index (Agr-index), stream sediment As interpolation grid (SSgrid), rock As interpolation grid (Rockgrid), and groundwater well As interpolation grid (Wellgrid) variables

Dependent variable	Threshold	Independent variable	Threshold	Controlled variable(s)	Threshold	p(CMH)[a]	OR_{MH}[b]	p(BD)[c]	Rho[d]
Rocks	6.7 mg/kg As	Wellgrid	0.005 mg/L As	Agr-index	1.0%	<0.0001	7.435	0.1783	0.454
Rocks	6.7 mg/kg As	Province	Favorable units	Agr-index	1.0%	<0.0001	5.488	0.5213	
Rocks	6.7 mg/kg As	Geology	Favorable units	Agr-index	1.0%	<0.0001	5.124	0.3689	
Rocks	6.7 mg/kg As	SSgrid	7.3 mg/kg As	Agr-index	1.0%	<0.0001	4.385	0.4784	0.438
Rocks	6.7 mg/kg As	Wellgrid	0.005 mg/L As	Geology & Agr-index	Favorable units 1.0%	<0.0001	3.050	0.0012	
Rocks	6.7 mg/kg As	Agr-index	1.0%	Geology	Favorable units	0.6127	0.897	0.3708	
sseds	7.3 mg/kg As	Rockgrid	6.7 mg/kg As	proximity[e]	<2 km from rock	<0.0001	4.146	–	
sseds	7.3 mg/kg As	Wellgrid	0.005 mg/L As	Agr-index	1.0%	<0.0001	3.566	0.1971	0.291
sseds	7.3 mg/kg As	Geology	Favorable units	Agr-index	1.0%	<0.0001	3.186	0.3817	
sseds	7.3 mg/kg As	Province	Favorable units	Agr-index	1.0%	<0.0001	2.844	0.0032	
sseds	7.3 mg/kg As	Agr-index	1.0%	Province	Favorable units	<0.0001	1.831	0.0032	0.154
sseds	7.3 mg/kg As	Agr-index	1.0%	Geology	Favorable units	0.0006	1.629	0.3820	
Wells	0.005 mg/L As	Province	Favorable units	Agr-index	1.0%	<0.0001	13.621	0.3856	
Wells	0.005 mg/L As	Geology	Favorable units	Agr-index	1.0%	<0.0001	8.755	0.5369	
Wells	0.005 mg/L As	Rockgrid	6.7 mg/kg As	proximity[e]	<2 km from rock	<0.0001	7.763	–	
Wells	0.005 mg/L As	SSgrid	7.3 mg/kg As	Agr-index	1.0%	<0.0001	3.413	0.0434	0.283
Wells	0.005 mg/L As	SSgrid	7.3 mg/kg As	Geology & Agr-index	Favorable units 1.0%	0.0008	1.696	0.0003	
Wells	0.005 mg/L As	Agr-index	1.0%	Province	Favorable units	0.3959	1.125	0.3860	
Wells	0.005 mg/L As	Agr-index	1.0%	Geology	Favorable units	0.1602	0.819	0.5387	

The threshold values used to group the samples and independent variables into binary categories are identified. The Cochran–Mantel–Haenszel statistic, p(CMH), measures the probability that the dependent variable subgroups defined by the independent variable, when adjusted for the controlled variable, have similar data distributions. Rejection of the null hypothesis is evidence of a significant relationship between the dependent and the independent variables, after adjusting for the control variable. The Mantel–Haenszel Case-control odds ratio, OR_{MH}, measures the strength of the relationship between the two variables, when adjusted for the control variable. An odds ratio of 1 indicates no effect while a ratio greater than 1 indicates that the independent variable category increases the odds of occurrence of high concentrations in the sample media. The data are grouped by dependent variable and listed in order of decreasing OR_{MH}. The Breslow–Day statistic, p(BD), measures the probability that the odds ratio of the groups defined by the control variables are homogeneous. Acceptance of the null hypothesis means that it is possible to summarize the conditional association between the dependent and explanatory variable by a single odds ratio. Spearmans' Rho correlation coefficients have been calculated for the continuous dependent and independent data variables when the CMH statistic indicates significant group differences. All tests use a 95-percent confidence level.

[a] Cochran–Mantel–Haenszel statistic nonzero correlation probability.
[b] Mantel–Haenszel case-control odds ratio statistic.
[c] Breslow–Day test odds ratio homogenity probability.
[d] Spearmans' Rho correlation coefficient, significant at $p < 0.0001$.
[e] Dependent variable samples restricted to those within 2 km of a rock sample.

category have significantly lower concentrations. At geologic province scale, the general pattern of Tukey Group associations is consistent for the bedrock well, stream sediment and rock sample groups, implying an association of the geologic province feature with As sources in rocks and As occurrence in stream sediments and ground water.

At the lithology group scale, As concentrations in rocks, stream sediments and bedrock well water in the Calcpelite lithology group in the NH-Maine geologic province are significantly higher than As concentrations in the other groups. The Calcpelite group includes lithologies classified as Calcpelite and Calcgranofels by Robinson and Kapo (2003, Rock Group B) and as lithogeochemical group M_c by Ayotte et al. (1999) in the NH-Maine Province. Rocks also show higher As concentrations in the sulfide-rich metamorphic rock category (Sulfidic Meta Rocks, Table 1) and felsic volcanics than in the other lithology groups, but these rock types cover relatively small areas of New England and have not been individually characterized as host sites for stream sediment and well sample locations.

4.1.2. Bedrock map unit scale

The bedrock geology map units that contain five or more ground water well sample sites were evaluated for elevated As distributions in stream sediment and well water samples. The bedrock map units identified by this study as having statistically elevated concentrations of As in ground water and stream sediments all occur in the NH-Maine and Coastal Maine geologic provinces (Fig. 5) and include the bedrock map units identified by Ayotte et al. (1999) that contain high percentages of wells with elevated As concentrations. To simplify discussion, these map units have been combined into grouped categories in Table 1 under the bedrock map unit category. For comparison, data for all other bedrock map units have been combined in the "Other units, combined" category under the Bedrock Map Units heading.

This variation at geologic formation scale highlights differences in results for the map units relative to their general lithology groups. Some of the bedrock map units with statistically elevated As concentrations in stream sediment and well water occur in lithology groups that collectively show statistically low concentrations of As in the rocks in that group. These include the Ayer Granite (Zen et al., 1983), the Concord Granite and Spaulding Tonalite (Lyons et al., 1997) in the granite lithology group and the Waterville Formation and Rangely Formation, lower part, in New Hampshire (Lyons et al., 1997) and its correlative (Rindgemere Formation, lower member; Osberg et al., 1985) in Maine in the metamorphic rocks, undivided lithology group (Fig. 5). These are consistent with the formations listed in Ayotte et al. (1999).

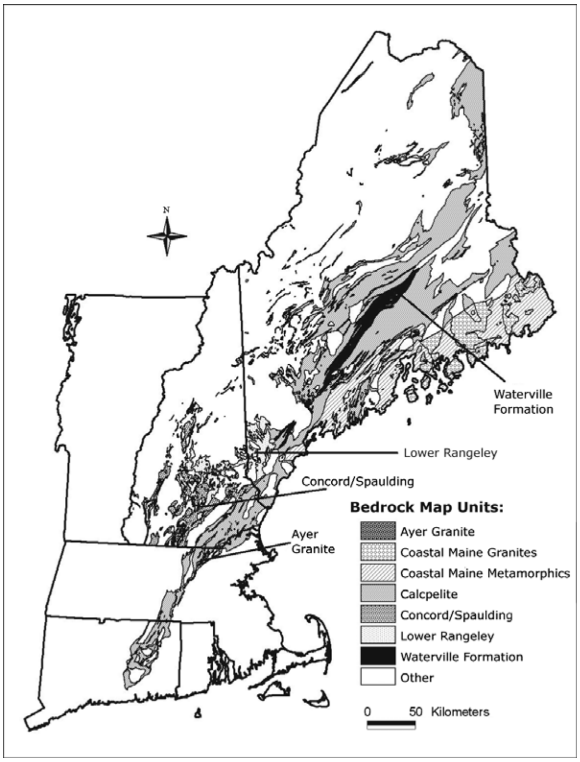

Fig. 5. Areal distribution of selected bedrock geologic units that have elevated As concentrations in stream sediments and groundwater. The bedrock units are from information summarized in Robinson and Kapo (2003).

4.2. Data comparison by land use (Agr-index) categories

The Agr-index explanatory variable, used as a proxy for the intensity of cumulative application of arsenical pesticides in the region, was split into high and low categories to test for differences in As distributions. An Agr-index value of 1.0% (80th percentile of Agr-index data by area) was chosen as the threshold value to split the datasets into high and low Agr-index categories.

The Tukey groups and statistics tabulated in Table 1 indicate that As concentrations in stream sediments and water from bedrock wells in the Agr-index >1.0 category are significantly higher than As concentrations in the lower Agr-index category, consistent with a hypothesized influence on As distributions related to arsenical pesticide contamination.

4.3. Statistics for rocks, steam sediments and well waters relative to other explanatory variables

Table 2 provides a summary of the Cochran–Mantel–Haenszel statistics for rock (rocks), stream sediment (sseds), and ground water well (wells) sample populations evaluated relative to grouped geologic province (Province), geologic bedrock map unit (Geology), agricultural index (Agr-index), stream sediment As interpolation grid (SSgrid), and ground water well As interpolation grid (Wellgrid) variables. The threshold values used to group the dependent and independent variables into binary categories are listed in Table 2.

4.3.1. Rock chemistry associations

The CMH scores for rock As distributions, adjusted for the Agr-index variable, indicate significant correlation with the following explanatory variables, in decreasing strength of correlation as indicated by the MH Odds Ratio: (1) wellgrid, (2) geology (Geologic Province categories and favorable bedrock map units), and (3) SSgrid variables (Table 2). For all of these correlations, the high values of the BD test scores indicate that it is possible to summarize the conditional association between rock chemistry and the explanatory variables by a single odds ratio, independent of the Agr-index variable. The rock-wellgrid variables display the strongest association, as indicated by the largest OR_{MH} value and the largest Spearman's Rho correlation among all continuous variables. This may be due in part to the generalizing effect of the interpolation process that limits the well-to-well variability inherent in the water As data. The rock-wellgrid variables have a significant positive correlation even when the data are adjusted for both the geology and Agr-index variables. The correlation of rock As distributions with the Agr-index variable was not significantly different from random distribution ($p(\mathrm{CMH}) = 0.613$), which was expected because rock chemistry is not influenced by land use.

4.3.2. Stream sediment chemistry associations

The CMH scores for stream sediment As distributions, adjusted for the Agr-index, Geology, or Province variables, are significantly correlated with the following explanatory variables, in decreasing strength of correlation as indicated by the MH Odds Ratio: (1) Rockgrid, (2) Geology (Geologic Province categories and favorable bedrock map units), (3) Wellgrid, and (4) Agr-index explanatory variables. The Rockgrid association is based on a subset of 263 stream sediment samples that are located within 2 km of a rock sample site. The high values of the BD test scores indicate that the odds ratios estimated for the stream sediment-wellgrid and stream sediment-geology associations are independent of the controlled Agr-index variable and the stream sediment–Agr-index association is independent of the controlled geology variable. Although the stream sediment As chemistry correlations with the geology and Agr-index variables are both positive and significant, the strength of the stream sediment correlation with the Agr-index explanatory variable is significantly weaker than the correlations with the Geology explanatory variables. The low values of the BD test score for the stream sediment-Province and the steam sediment–Agr-index variables, when controlled for Agr-index and Province variables, respectively, may be due to the high degree of spatial covariance between the Agr-index and Province variables and the independent association of stream sediment As concentrations with both the Agr-index and Province variables.

4.3.3. Well water chemistry associations

The CMH scores for bedrock well As distributions, adjusted for the Agr-index variable, indicate significant correlation with the following explanatory variables, in decreasing strength of correlation as indicated by the MH Odds Ratio:(1) Geology (Geologic Province categories and favorable bedrock map units), and (2) SSgrid explanatory variables. The correlation between the well data and the SSgrid variables are significant even when the data are adjusted for both the geology and Agr-index variables (similar to the rock-wellgrid correlation). These data collectively indicate that elevated ground water As concentrations correlate most strongly with areas of elevated As concentrations in rocks and with sediments dominated by rock-derived As sources. The correlation of well As distributions with the Agr-index variable, when adjusted for either the Geology or Province variables, was not significant. For these correlations, the high values of the BD test scores indicate that the nonsignificant CMH statistic are likely the result of no association rather than an inconsistent pattern of association that does not have enough strength or consistency to dominate any other pattern in the controlled strata groups. The low value for the BD test scores for the well-SSgrid association when controlled for Agr-index may reflect the influence of the Agr-index variable on stream sediment As concentrations, as discussed above. The strength of the well-SSgrid association is positive in both Agr-index categories, but is weaker in the High Agr-index category than in the Low Agr-index category. This indicates that increasing Agr-index influence affects the SSgrid variable in a way that weakens its association with well water chemistry. The interpretation is that rock chemistry influences both well water and stream sediment chemistry. The Agr-index variable represents an independent source of As to stream sediment that is not correlated with well water chemistry, thereby weakening the well-SSgrid association in the high Agr-index category.

The high value for the BD test scores for the stream sediment–Wellgrid association, when controlled for Agr-index, does not reflect a similar degree of influence of the Agr-index variable on the Wellgrid variable, consistent with the above interpretation. Another possible explanation for the difference in influence of the Agr-index control variable on the stream sediment–well water association is the degree of generalization (data smoothing) created during the interpolation process used to generate the well water grid from the well water data.

5. Conclusions

Data on representative As concentrations in 1572 public-supply bedrock ground water wells, 1597 stream sediment samples, and 1274 representative whole-rock samples are used to define As distribution statistics for ground water, stream sediments and rock types in the region, map the occurrence and distribution of As in near surface materials throughout New England, and to measure spatial associations between As concentrations in rocks, stream sediments, and rocks in relation to geologic features and land use factors. Significant sources of As include those that occur naturally in rocks and soils and As that was applied in the form of arsenical pesticides on apple, blueberry and potato crops in the region. Calcpelite, felsic volcanic and sulfidic schist rock types in New England have the highest median values for As concentrations in rocks (Table 1). The bedrock geology map units and the geologic provinces, where these rock types predominate typically have higher frequencies of elevated As occurrence in stream sediments and ground water. Stream sediments integrate As from both rock and anthropogenic sources, and stream sediment statistics for As correlate both with bedrock lithology units, geologic provinces, and with an agricultural intensity index that is a proxy for the intensity of past arsenical pesticide use.

The correlations indicated by the statistical analysis of As distributions in rocks, stream sediments and ground water indicate that rocks are most likely the dominant source of As to most sediments and ground water. Anthropogenic sources of As, related to past use of arsenical agricultural chemicals, appears to be a significant independent source of As to stream sediments in many agricultural areas. Rocks with elevated As concentrations occur near areas with elevated concentrations of As in sediment and ground water. The causes and processes responsible for controlling As concentrations in ground water systems are complex and likely involve interaction between (1) the distribution and chemical form of As in soils and rocks that are part of the ground water flow system and (2) the characteristics of the ground water aquifer that influence the solubility and transport of As (Ayotte et al., 1999, 2003). For the New England region, it appears that As distribution patterns in rocks and stream sediments provide a guide to the occurrence and distribution of As in ground water used for drinking water supply. The well statistics and associations with geologic units, stream sediment chemistry patterns, and historic agriculture cultivation patterns may be useful to efforts related to predicting, where As is likely to be high in ground water in the region.

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