Two-way cluster analysis of geochemical data to constrain spring source waters

Susan K. Swanson [a,*], Jean M. Bahr [a,1], Michael T. Schwar [b,2], Kenneth W. Potter [b,3]

[a] *Department of Geology and Geophysics, University of Wisconsin, Madison, WI 53706 1692, USA*
[b] *Department of Civil and Environmental Engineering, University of Wisconsin, Madison, WI, USA*

Abstract

The purpose of the study was to use geochemical characteristics and apparent ages of sampled groundwaters to determine which of the two regionally extensive bedrock aquifers, the lower bedrock aquifer or the upper bedrock aquifer, is a more likely source of water discharging to springs in the Nine Springs watershed. The use of summary statistics and our knowledge of the regional hydrostratigraphy resulted in the identification of three groups of monitoring points that are representative of groundwaters with distinct geochemical characteristics. Two-way cluster analysis of the geochemical data supports these groupings and further identifies subtle geochemical characteristics of the groups. One spring, which is representative of smaller springs and seeps found in the watershed, belongs to a group that is characterized by variable nitrate and chloride concentrations. Water discharging from this spring has a groundwater residence time of approximately 8 years based on the tritium/helium 3 dating method. The water discharging to this small spring is thought to have traveled primarily through the unlithified aquifer, as opposed to either of the major bedrock aquifers. Most of the springs in the watershed belong to a group that is characterized by elevated, but consistent, nitrate, sodium, and chloride concentrations. In addition, cluster analysis revealed that potassium and alkalinity concentrations are somewhat low. Apparent groundwater ages for this group range from 10 to 15 years. The water discharging from the majority of the springs in the watershed is thought to have traveled primarily through the unlithified aquifer and the upper bedrock aquifer before discharging into the former glacial lakebed wetland complex. Due to the relatively short groundwater residence times, spring water quality and flow in the Nine Springs watershed are likely to be vulnerable to the rapid urban expansion occurring within the watershed. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

The Nine Springs watershed, located in south-central Dane County, WI (Fig. 1), contains an unusually high concentration of cold-water springs. The springs are representative of those sometimes associated with former lakebed wetlands in the glaciated Upper Midwest where they often provide an important and consistent source of high quality water needed to maintain diverse and sensitive wetland

* Corresponding author. Tel.: +1-608-262-8960; fax: +1-608-262-0693.
  E-mail addresses: sskswanso@geology.wisc.edu (S.K. Swanson), jmbahr@geology.wisc.edu (J.M. Bahr), schwar@cae.wisc.edu (M.T. Schwar), kwpotter@facstaff.wisc.edu (K.W. Potter).
  [1] Fax: +1-608-262-0693.
  [2] Fax: +1-608-262-5199.
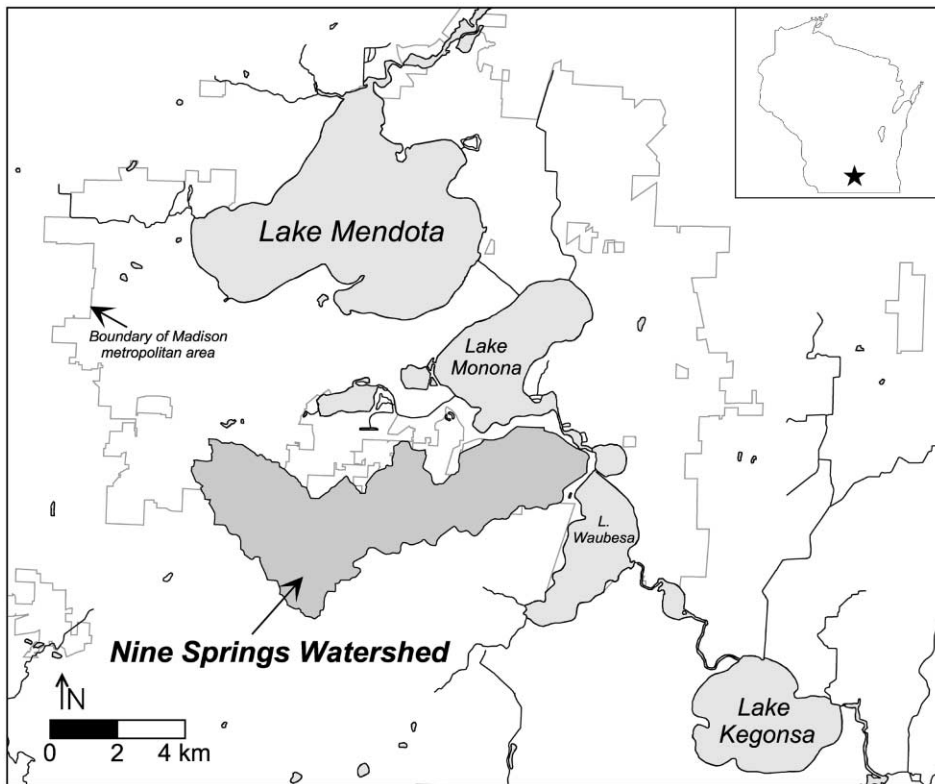 [3] Fax: +1-608-262-5199.

Fig. 1. The Nine Springs watershed, Dane County, WI.

plant communities (Eggers and Reed, 1997). Ongoing research shows that in the Nine Springs watershed, the springs also contribute significantly to the hydrologic budget of the system (unpublished data).

The Nine Springs watershed is situated in an area of rapid urban expansion, and it is faced with problems that are typical of urbanizing watersheds. Documented declines in wetland plant diversity (WRM, 1996) are likely due to increased surface water inputs in combination with land use changes and decreased groundwater inputs (Galatowitsch et al., 2000). In the past, the reduced groundwater inputs were primarily a result of agricultural practices (tiling); however, urban land use acreage has now surpassed agricultural land use acreage in the watershed (WRM, 1996).

An increase in the area of impervious surfaces, as well as an increase in municipal pumping, has accompanied the urbanization, which continues to take place. Planned land uses within the next 10 to 20 years will shift another 16% of the total watershed acreage from open space and agricultural uses to commercial and medium to high-density residential uses (WRM, 1996). In addition, groundwater supplies nearly all of the water for domestic and industrial uses in Dane County, and the City of Madison alone, which lies directly north of the watershed in central Dane County (Fig. 1), accounts for over half of this water use (based on 1995 water usage). Water use in central Dane County is expected to increase by about 21% between 1995 and 2020 (Dane County RPC, 1999).

Despite the hydrological and ecological importance of the springs, it is currently unclear what effects development is having on them and how spring flow will be impacted by further development. The springs have not been studied in detail and thus are poorly understood. This is partially due to the inaccessible nature of the geologic features ultimately responsible for their formation. This study is

the first step in the refinement of a conceptual model of the hydrogeologic system responsible for flow to the springs. In this paper, we describe the use of (i) summary statistics, (ii) two-way cluster analysis, and (iii) apparent groundwater ages based on the tritium/helium 3 dating method to test proposed sources of spring water. Two-way cluster analysis proves to be especially useful in identifying subtle geochemical characteristics of the groundwater discharging to the springs in the Nine Springs watershed.

2. Site description

The Nine Springs watershed is a sub-basin of the Yahara–Monona watershed. The uplands in the watershed are composed primarily of sandy till belonging to the Horicon Member of the Holy Hill Formation (Clayton and Attig, 1997). The bedrock in the area consists of a sequence of sandstones and dolomitic sandstones of Cambrian age that overlie Precambrian granite and undifferentiated igneous and metamorphic rocks (Fig. 2). The geologic units in Dane County have been divided into three aquifers and one aquitard for purposes of describing and modeling regional groundwater conditions (Bradbury et al., 1999; Krohelski et al., 2000). Because more detailed hydrostratigraphic characterization has not yet been conducted in the Nine Springs watershed,

we adopt this interpretation as our conceptual model of the hydrogeologic system. The major aquifers are the lower bedrock aquifer, the upper bedrock aquifer, and the unlithified aquifer. In addition, within much of Dane County the Eau Claire Formation contains a shale and siltstone facies that constitutes a leaky confining unit (the Eau Claire aquitard) between the lower bedrock aquifer and the upper bedrock aquifer. The lower bedrock aquifer is composed of the Mt. Simon Formation. The upper bedrock aquifer is composed of the Wonewoc, Tunnel City, St. Lawrence, and Jordan Formations in the vicinity of the field area, but also includes Ordovician bedrock units elsewhere in the county (Bradbury et al., 1999).

The low-lying areas in the Nine Springs watershed occupy a preglacial erosional bedrock valley that was subsequently filled with glacio-lacustrine deposits and till (Bradbury et al., 1999). It is likely that the bedrock valley deepens and widens to the east where it joins a larger buried erosional valley system. Many of the low-lying areas within the watershed are occupied by groundwater-fed wetlands with peat accumulations of up to 3 m. The wetlands historically consisted of shrub carr, shallow marsh, and sedge meadow. They were dominated by *Carex* spp. and *Salix* spp., which are often indicative of poor fen conditions (Owen, 1995). These wetland plant communities need a consistent source of groundwater inflow rich in calcium and magnesium bicarbonates, and they are frequently associated with
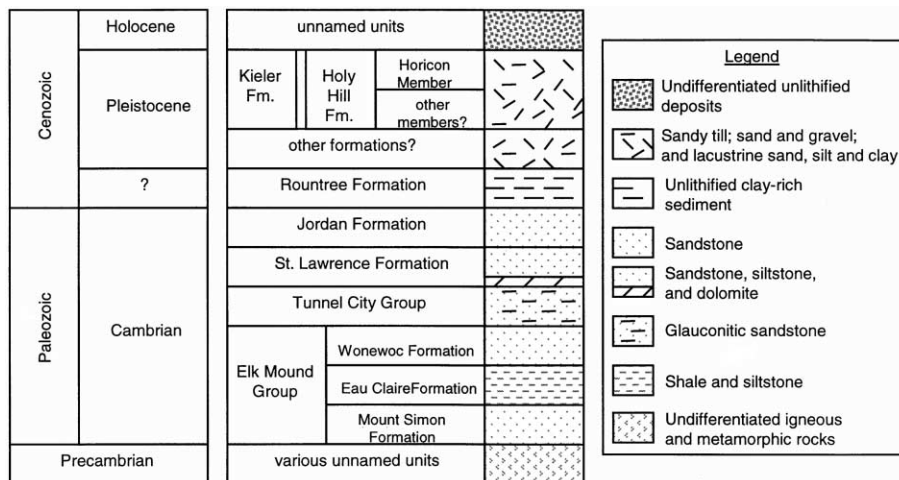

Fig. 2. Stratigraphic section for the study area (modified from Clayton and Attig, 1997).

springs or spring complexes (Eggers and Reed, 1997). Due in part to past agricultural practices including tiling and introduction of exotic plant species, large portions of the wetlands are now dominated by a monoculture of reed canary grass (*Phalaris arundinacea* L.) (Owen, 1995); however, pockets of high-quality sedge meadow remain primarily in the western and southern parts of the watershed, south of Nine Springs Creek. Nine Springs Creek, which was straightened and channelized in the 1930s, flows east through the wetland area and discharges to Mud Lake (WRM, 1996).

Two field sites, the Gunflint Trail site and the Syene Road site, were chosen on the basis of their proximity to major springs (Fig. 3). Two large springs ($> 8.5e - 03$ m^3/s), hereafter referred to as the big spring and the nursery spring, are located near the Gunflint Trail site. Many smaller springs or seeps, including one referred to as the peat spring, are also present in the vicinity of this site. One large spring, the Syene Road spring ($> 4.3e - 03$ m^3/s), is located in the vicinity of the Syene Road site. Each

field site was instrumented with at least 10 monitoring wells installed in nests; however, only the wells that were included in the groundwater quality monitoring program, which is discussed below, are shown in Fig. 3. Most of the well nests consist of a water table well, an intermediately screened well installed in sandy till, and a well screened in a highly weathered zone at the top of the dolomitic sandstone bedrock. The uppermost bedrock unit in the vicinity of the two field sites is the Tunnel City Group, which is described as a medium-grained, cross-bedded, dolomitic, and in some places glauconitic, sandstone (Ostrom, 1970).

In general, groundwater within the watershed flows downward from the surrounding uplands and towards Nine Springs Creek and its associated wetlands where it discharges. Vertical hydraulic gradients at the Gunflint Trail site range from positive gradients (downward flow) of approximately 0.04 between MW2A and MW2B to negative gradients (upward flow) of as high as 0.52 in the vicinity of the big spring. MW2A and MW2B are both screened
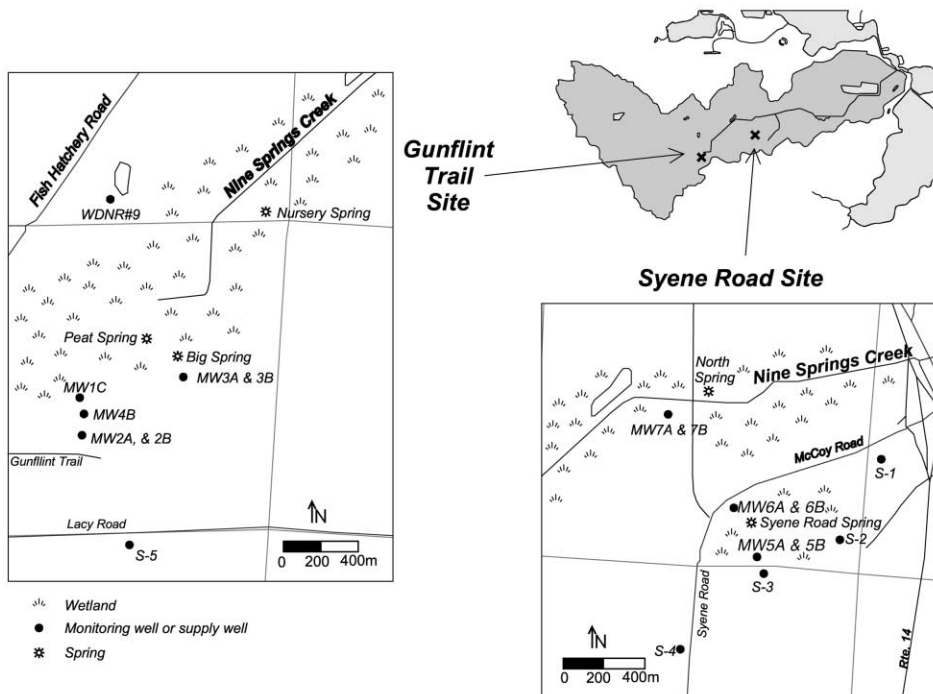

Fig. 3. Location of the field sites and sampling locations within the Nine Springs watershed.

in sandy till; however, MW2A is a water table well, whereas MW2B is screened approximately 3 m below the water table. Vertical gradients between MW3A and MW3B, which are situated at the margin of the wetland area, vary between -0.03 and $+0.01$ depending on the season and/or individual storm events. MW3A is screened in sandy till and MW3B is screened in the weathered bedrock zone approximately 11 m below the land surface.

Vertical hydraulic gradients at the Syene Road site are consistently negative and range from a minimum magnitude of 0.001 between MW7B and MW7A to a maximum magnitude of 0.14 between MW5B and MW5A, which are located near the Syene Road spring. MW5A and MW5B are screened in sandy till and within the zone of weathered bedrock (12 m below land surface), respectively, as are MW6A and MW6B. MW7A and MW7B are located in an area where the preglacial bedrock valley deepens. MW7A is screened in sandy till and MW7B, which is over 21 m deep, is screened in glacio-lacustrine fine sand and silt.

Continuous flow records for the big spring and the Syene Road spring show that spring flow is extremely consistent throughout the year; it does not respond to precipitation events or seasonal recharge events. The 1999 flow record (Jan.–Oct.) for the big spring is shown in Fig. 4. This lack of observed variation in spring flow in combination with high measured rates of flow would suggest an abundant source of water that is not greatly affected by any short-term or seasonal changes to the water budget. One such source could be groundwater discharging from the lower bedrock aquifer, which also supplies the majority of Madison's drinking water (Dane County RPC, 1999). The Eau Claire aquitard is partially absent in the central part of the county where a preglacial bedrock valley extends into the Mt. Simon sandstone (Bradbury et al., 1999). The lower bedrock aquifer could be providing a significant source of water to the springs if (i) the preglacial bedrock valley underlying the Nine Springs Creek and its associated wetlands, which is tributary to the larger erosional valley, also extends into the lower
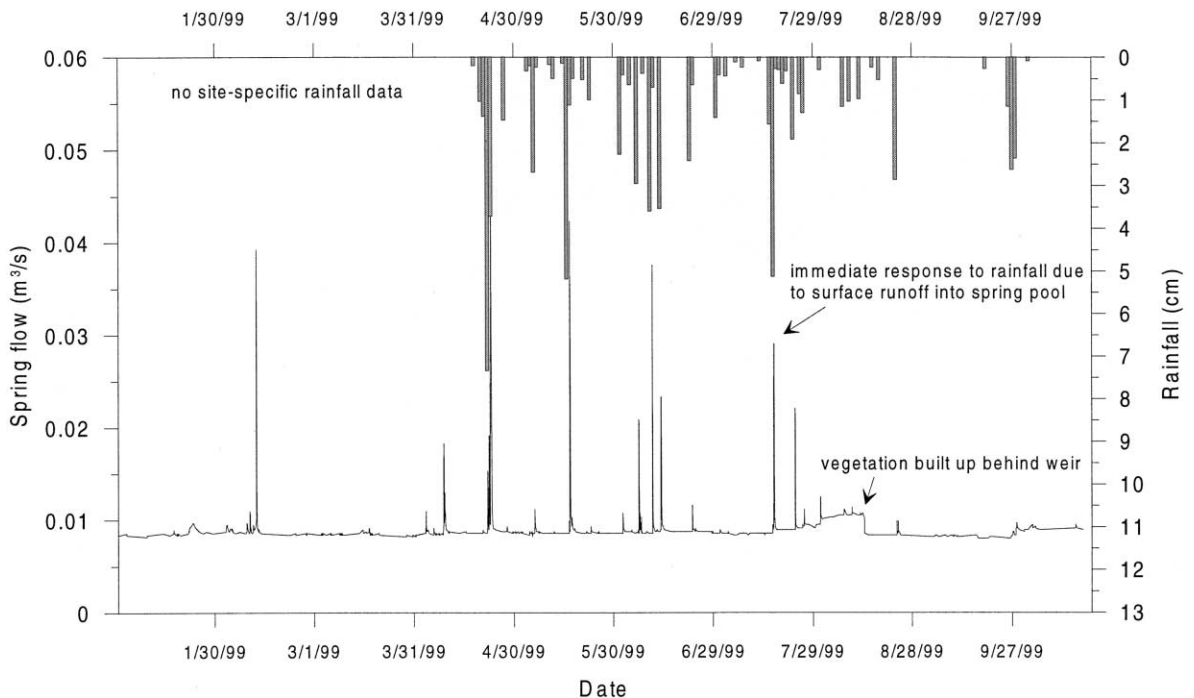

Fig. 4. 1999 flow record (Jan.–Oct.) for the big spring.

bedrock aquifer and (ii) sufficiently negative gradients exist. If this is the case, the springs could be especially vulnerable to increased municipal pumping in the region.

Another source could be groundwater discharging from the upper bedrock aquifer (Wonewoc and Tunnel City sandstones), as long as flow paths or residence times are sufficiently long to damp any seasonal variations in flow. If this is the case, the springs could be especially vulnerable to decreased groundwater recharge due to an increase in the area of impervious surfaces in a more local area. While the surficial unlithified aquifer is sometimes used for domestic water supply in the area, it is unlikely that it could consistently provide the volume of observed spring flow.

The purpose of our study is to use geochemical characteristics and apparent groundwater ages of sampled groundwaters to test whether the lower bedrock aquifer or the upper bedrock aquifer is a more likely source of spring water. Clearly, heterogeneities within these bedrock aquifers are critical to the existence of the springs and may strongly influence groundwater flow paths to the springs. Future work will include detailed hydrostratigraphic characterization and numerical modeling of the system. This geochemical survey is designed to constrain spring source waters and guide the more detailed hydrostratigraphic characterization to follow.

3. Methods

3.1. Geochemical analysis

Groundwater samples were first collected in November of 1997, and sample locations were added to the quarterly sampling program as new wells were installed. All sampling locations are shown in Fig. 3. In order to sample groundwater that is representative of water flowing through the bedrock aquifers in the vicinity of the sites, several domestic supply wells within the watershed were included in the monitoring network. Supply wells were chosen on the basis of their proximity to the field sites, the availability of a well construction report and driller's log on file at the Wisconsin Geologic and Natural History Survey, and the limited screened or open interval of the well (< 15 m) (Table 1). Supply well sampling began in August of 1998 and was also conducted on a quarterly basis. Sampling activities continued through March of 2000.

All samples were analyzed at the Wisconsin State Laboratory of Hygiene for major cations (Mg^{2+}, Ca^{2+}, K^+, Na^+) by ICP/atomic emission spectrometry and anions (NO_3^-, SO_4^{2-}, Cl^-) by automated colorimetry. Concentrations of total dissolved solids (TDS) were calculated by summing the concentrations of cations and anions for each monitoring point

Table 1
Summary of supply wells

Well identification	Well depth (m)	Approximate ground surface elevation (m amsl)	Screened or open	Screened or open interval (m)	Minimum and maximum elevation of open interval (m amsl)	Inferred geologic unit at screened or open interval
S-1	65	262–265	screened	1	197–201	Horicon Member, Holy Hill Fm.
S-2	44	265–268	open	8	221–232	Tunnel City Group
S-3	42	268–271	open	10	226–226	Tunnel City Group
S-4	31	274–277	open	11	244–258	Jordan Fm.
S-5	75	308–311	open	13	233–249	Jordan Fm.
WDNR #9	52	259–265	open	11	207–224	Wonewoc Fm. and Tunnel City Group

from each sampling event. The laboratory also reported total alkalinity. However, total alkalinity, as well as temperature, pH, conductivity, and dissolved oxygen, were measured in the field at the time of sample collection. Alkalinity and dissolved oxygen were measured using Chemetrics® colorimetric ampoules, which use a hydrochloric acid titrant with a pH indicator and an indigo carmine method, respectively. The field-measured values are considered more accurate, but due to the characteristically high alkalinity of the sampled waters, the precision of the colorimetric ampoules was poor ($\pm$50–100 ppm). Therefore, laboratory alkalinity values were compared to field alkalinity values to check the accuracy of the laboratory-measured results. Because the laboratory measured values were considered accurate and they are also more precise, they were used in the analyses discussed in this paper. Dissolved oxygen also tends to be very high in the sampled groundwaters (generally ≥ 6 mg/l). The precision of the dissolved oxygen colorimetric ampoules also decreases at high dissolved oxygen concentrations. Therefore, dissolved oxygen was not used in the analyses discussed in this paper except to note large deviations from a concentration of 6 mg/l.

3.2. Summary statistics

Preliminary observations and conclusions were based on the use of simple summary statistics including the sample mean and coefficient of variation for each analyte at each monitoring point. Comparison of means was used to assess spatial variations among monitoring points while the coefficient of variation reflected temporal variability (Table 2).

It should be noted that duplicate samples were not collected as part of the sampling program. Therefore, we were unable to assess the contribution of analytical uncertainty to the calculated measures of spatial and temporal variability. However, the differences in the magnitude of calculated means that are used to assess spatial variability are greater than differences that would be expected as a result of analytical error. Differences in the magnitude of the coefficients of variation that are used to assess temporal variability are also greater than differences that would be expected as a result of analytical uncertainty.

3.3. Cluster analysis

Cluster analysis refers to a set of techniques designed to classify observations so that members of the resulting groups are similar to each other and distinct from the other groups. Hierarchical clustering, which successively joins the most similar observations, is the most common approach (Davis, 1986). Because groups are simply based on their similarity to each other, hierarchical cluster analysis can be useful when abundant data are available and clear hydrogeologic models have not yet been developed (Colby, 1993; Suk and Lee, 1999). While other multi-variate techniques, such as factor analysis or principal component analysis, provide more insight into the underlying structure of a data set, the use of these techniques might require further analyses to identify distinct groups. Cluster analysis, on the other hand, may be thought of as a useful way of objectively organizing a large data set into groups on the basis of a given set of characteristics. This can ultimately assist in the recognition of potentially meaningful patterns. The set of characteristics chosen for inclusion in the cluster analysis is assumed to include the important distinguishing characteristics of the entities that are being clustered. It is recommended that the simplest characteristic applicable to the data set be chosen because this is likely to ease interpretation of the final results (Everitt, 1993). Therefore, we chose local standardized means, while other groundwater studies have involved the clustering of standardized raw data (Colby, 1993), rank-transformed data (Reeve et al., 1996), and factor scores estimated through factor analysis (Suk and Lee, 1999).

All analytical data were standardized using the global mean for each analyte. As an example, the global mean calcium concentration refers to the mean concentration of all calcium data collected at all monitoring points during all sampling events. Standardization is necessary because concentrations vary over a wide range among the analytes (Colby, 1993; Everitt, 1993). Standardization ensures that each analyte is weighted equally later on when computing a measure of similarity (Davis, 1986). Because each monitoring point also has multiple sampling events, a local mean for each analyte at each sampling location was then calculated. For example, the local

Table 2
Mean concentrations and coefficients of variation for analytes within Groups I, II, and III

Sampling location	n	Nitrate, mg/l		Chloride, mg/l		Sulfate, mg/l		Alkalinity, mg/l		Calcium, mg/l	
		Mean	CV	Mean	CV	Mean	CV	Mean	CV	Mean	CV
Group I											
MW2A	10	14.0	0.53	4.9	0.40	31.7	0.46	421.7	0.15	95.4	0.10
MW2B	10	10.3	0.13	11.9	0.22	37.5	0.31	384.7	0.05	93.6	0.06
MW3A	10	11.7	0.31	8.2	0.17	18.8	0.52	306.9	0.13	82.6	0.04
Peat Spring	10	6.1	0.62	21.9	0.17	19.6	0.36	297.1	0.12	77.5	0.08
Group II											
Big Spring	10	11.2	0.03	31.1	0.04	27.2	0.11	297.5	0.03	82.4	0.03
Nursery Spring	7	10.4	0.15	23.5	0.13	23.5	0.27	292.3	0.04	80.9	0.04
Syene Spring	7	10.2	0.02	38.3	0.02	23.9	0.35	312.3	0.04	86.7	0.02
MW4B	10	10.9	0.03	32.8	0.05	27.8	0.25	309.0	0.01	84.6	0.03
MW1C	8	10.2	0.04	39.4	0.06	22.3	0.41	310.3	0.07	82.6	0.06
MW5A	8	15.9	0.03	40.8	0.01	41.0	0.05	314.3	0.02	94.5	0.02
MW5B	6	10.5	0.05	37.1	0.01	27.1	0.16	310.3	0.04	85.7	0.02
MW6A	8	10.7	0.02	37.5	0.02	24.9	0.32	312.3	0.04	86.0	0.02
MW6B	8	10.6	0.02	37.2	0.02	24.7	0.33	313.6	0.02	86.4	0.02
S-4	6	10.3	0.04	35.8	0.01	25.7	0.25	312.2	0.04	86.7	0.02
S-3	6	12.7	0.03	33.3	0.03	32.2	0.04	297.5	0.02	88.2	0.03
S-5	5	18.4	0.03	21.7	0.02	25.3	0.45	282.4	0.02	86.2	0.02
Group III											
MW7A	8	2.3	0.03	2.8	0.07	4.2	0.67	294.9	0.05	65.8	0.02
MW7B	8	nd	–	1.2	0.30	5.5	0.46	320.0	0.05	69.6	0.01
S-1	6	1.2	0.09	1.8	0.07	3.9	0.89	276.7	0.06	62.5	0.02
Exceptions											
MW3B	10	13.9	0.09	25.6	0.03	30.4	0.26	322.2	0.05	88.8	0.08
S-2	6	9.5	0.06	21.1	0.13	21.7	0.19	289.3	0.03	79.7	0.04
WDNR #9	6	5.2	0.05	18.7	0.04	20.9	0.24	279.0	0.03	71.7	0.03

CV = Coefficient of variation.
nd = Non-detection.
– = Not calculated.

mean calcium concentration at MW7A was calculated by summing the standardized data from individual sampling events and dividing by the total number of samples collected at MW7A. It is important to note that by choosing the local standardized mean as the representative summary statistic for the geochemical data, the cluster analysis did not consider within-group variation (i.e. temporal variation) in analyte concentration at each sample location.

A two-way cluster analysis was performed on 22 monitoring points and 10 analytes to provide a check on interpretations of the geochemistry results that we made on the basis of a more subjective evaluation using summary statistics in combination with hydrostratigraphy. While both analytes and monitoring

points were clustered, the primary purpose of the exercise was to identify relationships among monitoring points. However, by also clustering analytes, the characteristics of the monitoring point clusters are more apparent.

The two-way analysis was performed by (i) clustering the sample locations, (ii) clustering the analytes, and then (iii) creating a two-way dendrogram or tree diagram to illustrate the results. This was accomplished using the statistical software Statistica (StatSoft, 1997). Cluster analysis requires a measure of similarity to be computed between every pair of objects (i.e. monitoring points or analytes), and Euclidean distances are often used for this purpose (Davis, 1986). The Euclidean distance between any

Magnesium, mg/l		Potassium, mg/l		Sodium, mg/l		Conductivity, μmhos/cm		TDS, mg/l	
Mean	CV	Mean	CV	Mean	CV	Mean	CV	Mean	CV
49.7	0.10	48.1	0.50	4.1	0.41	976.0	0.13	643.3	0.08
51.7	0.04	13.7	0.20	5.7	0.08	924.0	0.07	601.2	0.03
40.7	0.06	0.7	0.29	4.4	0.18	751.4	0.11	473.8	0.11
40.0	0.13	0.7	0.51	6.2	0.12	713.3	0.10	468.7	0.10
43.7	0.02	1.0	0.28	8.1	0.06	797.7	0.06	501.7	0.02
42.3	0.03	0.9	0.15	7.8	0.06	773.0	0.13	480.9	0.04
44.4	0.02	1.0	0.16	13.7	0.04	829.2	0.12	530.0	0.02
45.5	0.02	1.3	0.15	7.7	0.06	867.7	0.17	519.1	0.01
45.9	0.04	1.8	0.38	10.3	0.07	847.4	0.10	522.3	0.05
47.5	0.02	1.3	0.17	12.3	0.04	912.4	0.08	566.5	0.01
44.2	0.02	1.3	0.12	13.0	0.00	838.9	0.09	528.7	0.02
44.4	0.02	1.0	0.24	13.4	0.04	853.8	0.07	529.6	0.02
44.4	0.02	1.1	0.14	13.4	0.04	840.8	0.08	530.6	0.01
44.0	0.01	0.9	0.17	13.5	0.04	820.2	0.10	528.5	0.02
44.2	0.02	1.2	0.07	9.4	0.04	845.8	0.10	517.7	0.01
44.2	0.01	0.8	0.32	4.7	0.03	788.3	0.13	483.2	0.03
34.0	0.02	1.1	0.16	2.9	0.05	573.6	0.13	407.3	0.04
36.1	0.02	1.1	0.18	3.2	0.03	581.7	0.09	436.3	0.05
32.7	0.02	1.0	0.08	2.7	0.04	538.9	0.05	381.8	0.05
47.5	0.06	2.3	0.99	9.0	0.06	901.9	0.15	539.1	0.03
40.5	0.02	1.0	0.11	5.5	0.08	753.8	0.06	467.5	0.03
38.0	0.02	1.5	0.07	5.6	0.06	634.8	0.11	439.7	0.01

given pair of either monitoring points or analytes is equal to the geometric distance in multidimensional space (Everitt, 1993):

$$d_{AB} = \left\{ \sum_{i=1}^{p} \left(x_{Ai} - x_{Bi} \right)^2 \right\}^{1/2} \qquad (1)$$

where d = the Euclidean distance, A and B = any given pair of monitoring points or analytes, x = local standardized mean concentration, and p = number of variables (10, the number of analytes when clustering monitoring points; 22, the number of monitoring points when clustering analytes).

Calculating the distance between all possible pairs of monitoring points and analytes results in two matrices of Euclidean distances. The first matrix includes the Euclidean distances between the monitoring points and the second matrix includes the Euclidean distances between the analytes. It should be noted that if data were not standardized, the calculated distances would be influenced most strongly by the variables that have the greatest magnitude (Davis, 1986). The distance matrices are useful for initially determining similarity between all of the variables and for illustrating the relative similarity in the final dendrogram. However, a linkage rule, or clustering method, is necessary to determine hierarchical clusters. Ward's hierarchical clustering method was chosen for this purpose. It aims to minimize the loss of information at each step in the

clustering process. Information loss is defined in terms of an error sum-of-squares (ESS) criterion. Given g clusters, the procedure sequentially reduces the number of clusters to $(g-1)$ by considering the loss of information associated with the union of all possible $\{g(g-1)/2\}$ sets (Ward, 1963). The error sum-of-squares for each initial cluster is given by:

$$\text{ESS}_i = \sum_{j=1}^{n_i} \sum_{k=1}^{q} \left(x_{ijk} - \bar{x}_{ik} \right)^2 \qquad (2)$$

where n = the number of objects grouped together in a cluster (2), q = the number of variables (the number of analytes when clustering monitoring points, the number of monitoring points when clustering analytes), x_{ijk} = local standardized mean analyte concentration, $\bar{x}_{ik}$ = mean analyte concentration of objects grouped together in a cluster.

The total ESS can be evaluated as the sum of multiple separate sums of squares.

$$\text{ESS}_{\text{total}} = \sum_{i=1}^{g} \text{ESS}_i \qquad (3)$$

where g = number of sets evaluated.

After variables are combined into initial clusters, the ESS for each subsequent cluster is computed by:

$$\text{ESS} = |\overline{\boldsymbol{m}}_U - \overline{\boldsymbol{m}}_V|^2 / (1/n_U + 1/n_V) \qquad (4)$$

where U and V = two clusters combined to form a new cluster, $n_U = n_V$ = the number of analytes (22) or monitoring points (10) in U and V, respectively, $\overline{\boldsymbol{m}}$ = a vector that contains an average concentration for each of the n analytes (or monitoring points), calculated on the basis of the two previously merged monitoring points (or analytes) (Ward, 1963; Suk and Lee, 1999).

Finally, a dendrogram is created. The dendrogram illustrates the groupings made at each successive stage of the clustering process (Everitt, 1993); the branches of the dendrogram are scaled to represent the normalized Euclidian distances between members of each cluster.

3.4. Tritium / helium 3 analysis

A selected number of monitoring points were sampled for analysis of tritium (3H) and its stable decay product helium 3 (3He) for purposes of groundwater age dating. The 3H/3He dating method extends the usefulness of the mid-1960s tritium groundwater inputs to cases where radioactive decay and dispersion have significantly reduced the amount of 3H in groundwater (Solomon et al., 1992). In this study, the apparent ages calculated by the 3H/3He method place constraints on our conceptual model of groundwater flow.

Groundwater samples were collected from 10 monitoring points including MW3A, MW3B, MW4B, MW5A, MW5B, MW7A, MW7B, the big spring, the nursery spring, and the peat spring. In addition, a small spring on the north side of Nine Springs Creek was sampled. This spring was not included in the cluster analysis because the limited number of geochemical samples precluded the calculation of meaningful summary statistics.

Tritium samples were collected from the monitoring wells using a Waterra inertial pump, which consists of a footvalve connected to a length of polyethylene tubing. When oscillated up and down in the well, the pump produces a flow of water. Prior to collecting the samples, two to three well volumes of water were purged from the monitoring wells. Spring samples were collected by fully submerging sample bottles in the spring pool as close to the point of discharge as possible. Before filling and capping, bottles were rinsed with sample. Samples were collected in 250 ml glass bottles with tight sealing caps, and were submitted to the University of Utah Noble Gas Laboratory for analysis of tritium by the tritium in-growth method.

Dissolved gas samples were collected in copper tubes that were cold-welded using refrigeration clamps. After purging a monitoring well, a copper tube was attached to the discharge end of the plastic tubing. Water was then pumped through the plastic tubing and the in-line copper tube for several minutes to minimize bubble entrapment within the copper tube. Refrigeration clamps on either end of the copper tube were then tightened, and the ends of the copper tube capped. Samples were collected in a similar manner from the springs; however, water was drawn through the plastic tubing and in-line copper tube using a hand-held vacuum pump. Samples were submitted to the University of Utah Noble Gas Laboratory for analysis of dissolved gases by mass spectrometry.

The 3H/3He dating method was first proposed by Tolstikhin and Kamensky (1969) and has proved useful in many groundwater studies (e.g. Torgersen et al., 1979; Solomon et al., 1992, 1993). When measurements of tritiogenic 3He (3He*), which results exclusively from the decay of 3H, are made in association with 3H, the measurements can be used to calculate the time since the water was isolated from the atmosphere. The 3H/3He age ($t_{3H/3He}$) is calculated by:

$$t_{3H/3He} = \lambda_{3H}^{-1} \ln \left(\frac{3He^*}{3H} + 1 \right) \qquad (5)$$

where λ_{3H} is the decay constant for tritium.

Helium isotopes in groundwater, including both 3He and helium 4 (4He), come from several different sources. In order to compute 3He*, these additional sources and the 3He/4He ratio in the atmosphere must be taken into account. The total dissolved 3He is the sum of atmospheric 3He, 3He*, and nucleogenic 3He. The total dissolved 4He is the sum of atmospheric and radiogenic 4He. In this study, 3He* was computed using the following equation derived by Solomon et al. (1992):

$$3He^* = \left(R_{t=0} 4He_m - R_{sol} \left[\alpha'(4He_m - 4He_{sol}) \right. \right.$$
$$\left. \left. + 4He_{sol} \right] \right) \Big/ \left(1 + \alpha' \left(\frac{4He_m}{4He_{sol}} - 1 \right) \right) \qquad (6)$$

where $R_{t=0}$ = 3He/4He ratio at the time of sampling, R_{sol} = 3He/4He ratio of water in isotopic equilibrium with the atmosphere, $4He_m$ = measured 4He, $4He_{sol}$ = 4He resulting from equilibrium solubility with the atmosphere, α' = air/water fractionation factor ($\alpha' = 1.012$ at 10°C, Weiss, 1971).

This equation assumes that samples are supersaturated with respect to atmospheric nitrogen and helium, resulting from bubble entrapment inside the copper sampling tubes. In addition, one sample was analyzed by a different equation, also derived by Solomon et al. (1992), which assumes samples are undersaturated with respect to atmospheric nitrogen and helium:

$$3He^* = \left(R_{t=0} 4He_m - \left[(R_{sol} 4He_{sol}) \right. \right.$$
$$\left. \left. / \{ \alpha'(4He_{sol} - 4He_m)/4He_m \} + 1 \right) \right]. \qquad (7)$$

Eq. (7) assumes that gas stripping by CH_4 and/or CO_2 occurs at the water table and that no radiogenic 4He is present in the groundwater sample (Solomon et al., 1992).

4. Results and interpretation

4.1. Geochemical results and summary statistics

The geochemical results show that waters sampled cannot be distinguished on the basis of their major ion facies alone. Due to the high carbonate content of both the unconsolidated glacial deposits and the sedimentary bedrock units in the area, all waters sampled are a calcium–magnesium bicarbonate type. A Piper diagram of the March 1999 analytical results, which is representative of all the sampling events, is shown in Fig. 5.

The magnitude and temporal variation of individual ions, primarily nitrate (NO_3^-) and chloride (Cl^-), proved to be more useful in distinguishing between possible source waters, groundwater flow paths, and residence times. Preliminary observations and conclusions were based on the use of simple summary statistics including the sample mean and coefficient of variation (Table 2) in combination with our understanding of the hydrostratigraphy. On the basis of the geochemical analytical results and the use of these simple summary statistics, three "groups" of waters were identified. Table 3 presents the geochemical characteristics of the groups and identifies the sampling locations that define each group. The distinguishing geochemical characteristics of each group (defined relative to the other two groups of waters) are also discussed below.

4.1.1. Group I

Group I consists of monitoring wells MW2A, MW2B, and MW3A, and a small spring or seep called the peat spring. This group shows temporal variability in nitrate concentrations (CV = 0.13–0.62) and, relative to the other groups, somewhat higher variability in chloride concentrations (CV > 0.17). In some cases (MW2A and MW2B), potassium concentrations are elevated. Sodium concentrations tend to be low and somewhat more variable (CV = 0.08–0.41) than at other sampling locations. Alkalinity also tends to be more variable (CV = 0.05–0.15).
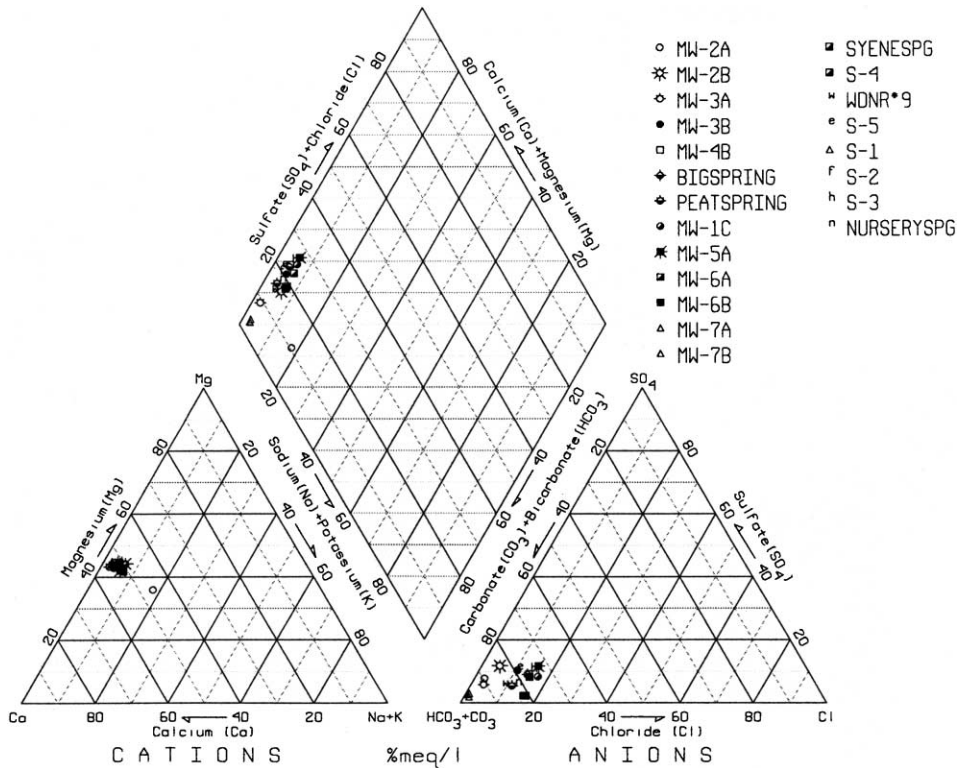
Fig. 5. Piper diagram showing the results of the March 1999 groundwater sampling event. All waters sampled are a calcium–magnesium bicarbonate type.

Positive vertical gradients exist between MW2A and MW2B and both wells are screened in sandy till. MW2A is screened across the water table, while MW2B is approximately 11 m deep. MW3A is also screened in sandy till. MW2A and MW2B are located in a field that was farmed through the 1997

Table 3
Characteristics of geochemical groups based on the use of summary statistics

Group	I	II	III	Exceptions
Monitoring points	MW2A, MW2B, MW3A, peat spring	MW4B, MW1C, MW5A, MW5B, MW6A, MW6B, S-3, S-4, S-5, big spring, nursery spring, Syene Road spring	MW7A, MW7B, S-1	S-2, WDNR #9, MW3B
Characteristics	· Variable NO_3^- and Cl^-	· Elevated, but consistent NO_3^-	· Low and consistent NO_3^-, SO_4^{2-}, Ca^{2+}, Mg^{2+} and Na^+	
	· Low and somewhat variable Na^+	· High and consistent Cl^-	· Low Cl^-	
	· Somewhat variable alkalinity	· High and consistent Na^+	· Lower TDS and conductivity	

agricultural season, and an actively farmed field is located less than 150 m upgradient and to the south. MW3A and the peat spring are located downgradient of MW2A and MW2B, approximately 60 and 90 m to the north, respectively. The high and temporally variable nitrate and potassium concentrations observed in these wells are probably a result of seasonal fertilizer application, while the variable chloride concentrations may be a remnant of seasonal road salt application. The high nitrate and chloride concentrations; the general variability in analyte concentrations observed in MW2A, MW2B, and MW3A; and the materials in which the wells are screened suggest that (i) groundwater travels along short flow paths and/or has short residence times and (ii) probably has traveled primarily through the unlithified aquifer. The water discharging to the peat spring probably travels along similar flow paths.

4.1.2. Group II

Group II consists of monitoring wells MW4B, MW1C, MW5A, MW5B, MW6A, and MW6B; supply wells S-3, S-4, and S-5; and the three larger springs: the big spring, the nursery spring, and the Syene Road spring. The geochemical characteristics of this group include elevated (generally > 10 mg/l), but relatively consistent (generally CV < 0.05) nitrate concentrations and high (generally > 20 mg/l) and consistent (generally CV < 0.06) chloride concentrations. In addition, sodium concentrations tend to be higher than concentrations detected at other monitoring points and consistent (CV < 0.07) throughout the sampling period.

All of the monitoring wells in this group are screened in areas with negative vertical gradients. MW5A and MW6A are screened in till while the other monitoring wells are screened at the top of the dolomitic sandstone bedrock surface. The supply wells (S-3, S-4, and S-5) are drilled to various depths in the bedrock; however, all supply wells are screened within the upper bedrock aquifer. From the well construction reports, it appears that S-3 is open to the Tunnel City Group, and S-4 and S-5 are open to the overlying Jordan Fm., which is described as fine to medium grained, thick-bedded quartzarenite (Ostrom, 1970). The high nitrate and chloride concentrations at these locations are probably due to the application of agricultural fertilizers and road salt, but it is likely

that either flow paths or residence times are longer than those for Group I because temporal variations in nitrate and chloride concentrations are not apparent in these quarterly samples. We conclude that Group II is representative of water that is traveling through or has traveled through the upper bedrock aquifer. Therefore, the water discharging to the big spring, the nursery spring, and the Syene spring may have also traveled through the upper bedrock aquifer.

4.1.3. Group III

Group III consists of monitoring wells MW7A, MW7B, and supply well S-1. None of the springs that were monitored have characteristics that are similar to this group. The geochemical characteristics of this group include very low (< 2.3 mg/l) and consistent (CV ≤ 0.09) nitrate concentrations throughout the sampling period and low (< 2.8 mg/l) mean chloride concentrations. In addition, mean sulfate concentrations were somewhat lower (< 5.5 mg/l) throughout the sampling period at these locations. Sodium concentrations are consistently (CV ≤ 0.05) less than 3.2 mg/l throughout the sampling period. Mean concentrations of calcium and magnesium are consistently lower (CV ≤ 0.02), and TDS concentrations in general are consistently (CV ≤ 0.05) lower than other sampling locations. The lowest conductivity measurements recorded in groundwater samples were also collected from MW7A, MW7B and S-1, and MW7B has low dissolved oxygen concentrations ($2–4$ mg/l) compared to approximately 6 mg/l at all other sampling locations.

MW7B and S-1 are screened in fine sandy lacustrine material that fills the preglacial bedrock valley below Nine Springs Creek. MW7A is screened in the overlying sandy till. The negative vertical gradient between MW7B and MW7A ranges in magnitude from only 0.001 to 0.005. The low nitrate and chloride concentrations might represent background levels of these constituents in more regionally derived groundwater, i.e. water that is representative of that flowing through the lower bedrock aquifer or the sandstones comprising the Elk Mound Group. Kammerer (1984) reports geometric mean concentrations of 0.8 and 3.3 mg/l for nitrate and chloride, respectively, in the Elk Mound Group sandstones. It is likely that either (i) fertilizer or road salt sources do

not exist in the recharge area or (ii) elevated concentrations of nitrate and chloride, resulting from heavy use of fertilizers and road salt beginning in the 1930s, have not yet reached these locations due to long flow paths and/or residence times.

4.1.4. Exceptions

Exceptions to the groups defined above include monitoring well MW3B and supply wells S-2 and WDNR #9. Monitoring well MW3B is screened in till, near the top of the bedrock surface at the Gunflint Trail site. It is located in an area where vertical groundwater gradients alternate between negative and positive, depending on the season and/or individual storm events. Therefore, it is not surprising that the groundwater shows some characteristics that are consistent with Group I (elevated and somewhat variable nitrate concentrations) and some that are consistent with Group II (elevated, but consistent chloride concentrations).

The supply wells (S-2 and WDNR #9) are open to bedrock at somewhat lower elevations than the other supply wells. While detailed geologic logs are unavailable for the supply wells, S-2 is probably completed in the Tunnel City Group based on the elevation of the open interval. The sampling results from this well are very similar to the characteristics of Group II, with a few exceptions. For example, groundwater shows lower, but still consistent, nitrate concentrations.

WDNR #9, which is a flowing well, is open to the Tunnel City Group and the underlying Wonewoc Fm., which is described as fine to medium grained, thick-bedded quartzarenite (Ostrom, 1970). The groundwater discharging from this well has lower nitrate, chloride, and sodium concentrations than those detected for Group II; however, the concentrations are higher than those detected for Group III. The water discharging from WDNR #9 may be a mixture of these two groups of waters.

4.2. Cluster analysis

While the use of summary statistics and our knowledge of the hydrostratigraphy resulted in three groups of monitoring points (plus several exceptions) with similar geochemical characteristics, cluster analysis offers a secondary, objective test of the groupings. Specifically, we were interested to see if the cluster analysis would identify a similar number of clusters of monitoring points (3 to 4) and if so, whether groups and clusters consisted of similar members. The two-way tree diagram, or dendrogram, that was generated by the cluster analysis is shown in Fig. 6. The linkage distances shown on the tree diagram are normalized Euclidian distances that represent the relative similarity between the clusters of sampling locations and analytes. Large differences in the levels of fusion into clusters can be used as a means to distinguish the number of clusters resulting from the analysis (Everitt, 1993). The first level where there appears to be a consistently large distance between levels of fusion of monitoring points occurs at approximately 40% of the maximum linkage distance. The four resulting clusters are labeled A–D in Fig. 6. The relatively low normalized distance between the four clusters emphasizes their geochemical similarity, but also shows the utility of the method in identifying subtle geochemical characteristics that might not be recognized by only reviewing the summary statistics.

By clustering the analytes in addition to the monitoring points, the subtle characteristics of each of the four monitoring point clusters are more easily identified. Furthermore, the results could be used to guide a sampling program in a similar hydrogeologic setting if resources were limited. Sodium and chloride are clustered together as are potassium and alkalinity. The remaining analytes also form a general cluster. Because chloride (specific ion electrode), alkalinity (colorimetric ampoules), and conductivity (electronic field meter) are all easily measured in the field, these three parameters might be good choices as broad indicators of geochemical similarity.

The monitoring point clusters are labeled A, B, C, and D in Fig. 6, which also shows the characteristics of each cluster in terms of mean standardized analyte concentrations. Table 4 summarizes the characteristics of each monitoring point cluster.

4.2.1. Cluster A

Cluster A is composed of monitoring wells MW2A and MW2B, and is characterized by nitrate, sulfate, calcium, magnesium, conductivity, total dissolved solids, alkalinity, and potassium concentrations that tend to be higher than the mean. Sodium and chlo-
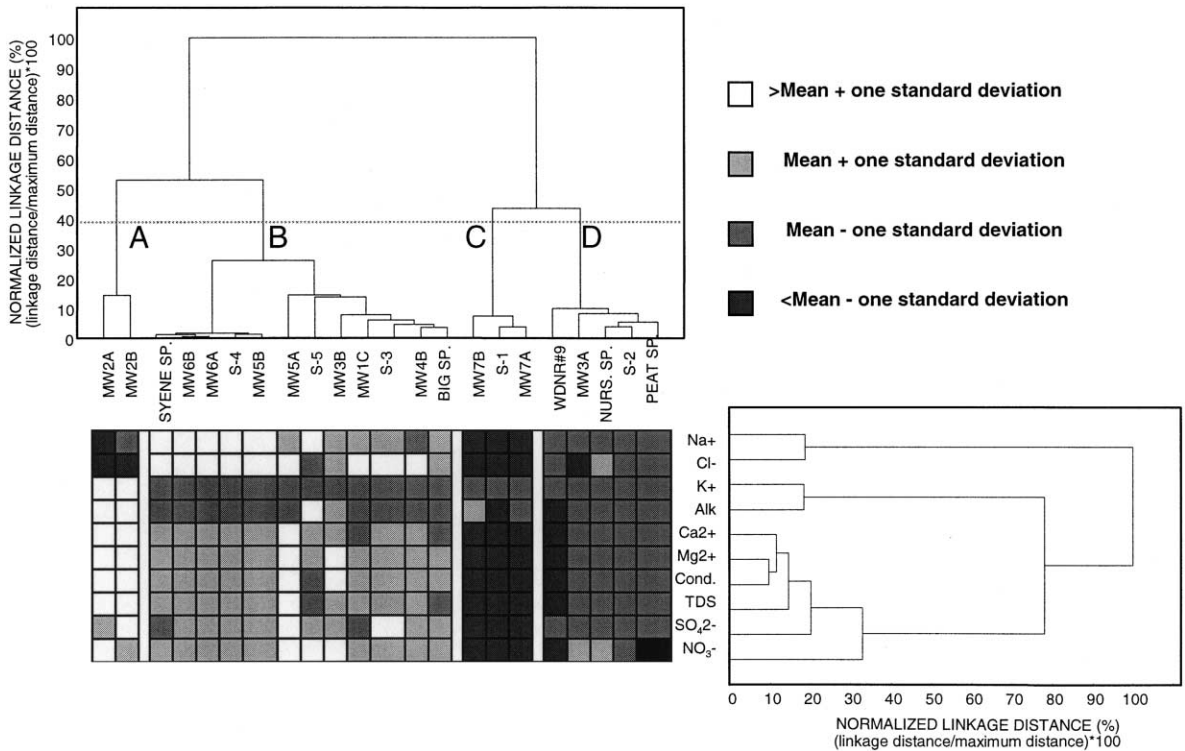
Fig. 6. Dendrogram resulting from the two-way cluster analysis.

ride concentrations are lower than the mean. MW2A and MW2B are both members of Group I, discussed earlier.

4.2.2. Cluster B

Cluster B comprises the majority of the monitoring points and two major springs, the big spring and the Syene Road spring. All of the monitoring points in Cluster B, with the exception of MW3B, are members of Group II discussed above. MW3B is considered an exception to Groups I, II, and III, with characteristics of both Groups I and II. Analyte concentrations tend to be within one standard deviation of the mean. The cluster analysis revealed, however, that potassium and alkalinity are consistently below the mean.

4.2.3. Cluster C

Cluster C groups MW7A, MW7B, and S-1 together. MW7A, MW7B, and S-1 are all members of Group III discussed above. Within this cluster, nitrate, chloride, calcium, magnesium, sulfate, sodium,

conductivity, and total dissolved solids are lower than one standard deviation below the mean. The cluster analysis also reveals that potassium concentrations are lower than the mean, but are within one standard deviation of the mean.

4.2.4. Cluster D

Cluster D consists of WDNR #9, S-2, MW3A, the nursery spring, and the peat spring. In general, analyte concentrations are lower than the mean. WDNR #9 and S-2 were considered exceptions to the groups defined above. MW3A and the peat spring are both members of Group I. The distinguishing characteristics of Group I are the variability of nitrate, chloride, potassium, and sodium concentrations. As previously mentioned, the mean was chosen as the representative summary statistic for each analyte at each monitoring point for the cluster analysis. Therefore, the cluster analysis did not consider within-group variation in analyte concentration at each sample location. On average, the analyte

Table 4
Characteristics of monitoring point clusters

Cluster	A	B	C	D
Monitoring points	MW2A, MW2B	MW4B, MW1C, MW3B, MW5A, MW5B, MW6A, MW6B, S-3, S-4, S-5, big spring, Syene Road spring	MW7A, MW7B, S-1	S-2, WDNR #9, MW3A, nursery spring, and peat spring
Characteristics	· NO_3^-, SO_4^{2-}, Ca^{2+}, Mg^{2+}, conductivity, total dissolved solids, alkalinity, and K^+ are greater than the mean · Na^+ and Cl^- are less than the mean	· Na^+ and Cl^- are greater than the mean · Alkalinity and K^+ are slightly less than the mean · Most other analytes are close to the mean	· NO_3^-, Cl^-, Ca^{2+}, Mg^{2+}, SO_4^{2-}, Na^+, conductivity, and total dissolved solids are less than the mean · K^+ is slightly less than the mean	· Na^+, K^+, alkalinity, Ca^{2+}, Mg^{2+}, conductivity, and SO_4^{2-} are somewhat less than the mean

concentrations may be somewhat lower at these locations; however, the variability in analyte concentrations is thought to be a more distinguishing characteristic of the geochemical results. The nursery spring is a member of Group II. It does tend to have somewhat lower nitrate and chloride concentrations than the other members of Group II; however, the concentrations are relatively consistent, higher than those of Group I, and much higher than those of Group III (Table 2). Finally, MW3A is a shallow water table well screened in till, whereas WDNR #9 is a flowing well open to sandstone bedrock, and is approximately 52 m deep. For all of these reasons, we believe that Cluster D is an artifact of the cluster analysis method and that it cannot be justified hydrogeologically.

4.3. Tritium and helium 3 results

The apparent ages calculated by the 3H/3He method are shown in Table 5. Seven of the ages were calculated using Eqs. (5) and (6), because the samples were supersaturated with respect to atmospheric nitrogen and helium. The age for the nursery spring was calculated using Eqs. (5) and (7) because the sample was undersaturated with respect to atmospheric nitrogen and helium. Ages could not be

calculated for MW7A and MW7B because very little or no tritium was present in the samples.

The shortest residence times were calculated for the nursery spring (1.5 years), MW3A (3.3 years) and the peat spring (8.5 years). However, we believe that the age calculated for the nursery spring is probably unreliable. The high level of CO_2 detected in the sample in association with its undersaturation with respect to atmospheric nitrogen and helium suggest that gas stripping probably occurred. The spring pool at the nursery spring is shallow (< 0.3 m), and the points of discharge are numerous, but relatively small. Therefore, it is likely that the sample that was collected is not representative of water discharging directly from the spring.

MW3A is a shallow well that is screened in till. Both MW3A and the peat spring are members of Group I, which we concluded are representative of groundwater that probably travels through the unlithified aquifer along short flow paths and/or has short residence times. The 3H/3He ages support these conclusions. The residence time associated with the peat spring is higher than that for MW3A because it is a point of discharge.

Residence times for MW3B, MW4B, MW5A, MW5B, the big spring, and the nursery spring range

Table 5
Results of 3H, He, CO_2, and N_2 analyses, and calculation of 3H/3He ages

Location	Tritium samples				4He (cm^3/kg)	3He (TU)	$R_{t=0}$	3He* (TU)	$t_{3H/3He}$ (years)	N_2 (cm^3/kg)	CO_2 (cm^3/kg)
	TU	+	−	Sample date							
MW3A	8.54	0.43	0.43	8/20/99 16:00	6.64e−05	3.93e+01	1.47e−06	1.75e+00	3.3	21.27	0.0248
MW3B	10.29	0.51	0.51	8/20/99 15:30	5.83e−05	4.71e+01	2.00e−06	1.17e+01	13.4	18.15	0.0439
MW4B	12.90	0.65	0.65	8/20/99 14:20	6.25e−05	4.78e+01	1.89e−06	9.66e+00	9.8	20.90	0.0189
MW5A	12.78	0.64	0.64	8/21/99 13:00	7.16e−05	6.51e+01	2.26e−06	1.64e+01	14.5	22.82	0.1009
MW5B	10.42	0.52	0.52	8/21/99 12:30	6.59e−05	5.24e+01	1.98e−06	1.12e+01	12.8	21.58	0.0107
MW7A	1.02	0.06	0.13	8/21/99 11:00	NA	NA	NA	NA	NA	NA	NA
MW7B	0.00	0.14	0.27	8/21/99 11:15	6.46e−05	2.60e+07	NA	NA	NA	20.38	0.0075
Big spring	10.99	0.55	0.55	8/19/99 14:30	6.01e−05	4.56e+01	1.88e−06	9.36e+00	10.7	18.85	0.0206
North spring	9.99	0.50	0.50	8/19/99 11:30	6.74e−05	5.53e+01	2.04e−06	1.23e+01	14.1	13.92	0.0392
Nursery spring	11.60	0.58	0.58	8/19/99 17:00	2.72e−05	1.61e+01	1.46e−06	1.05e+00	1.5	13.01	1.0656
Peat spring	11.42	0.57	0.57	8/19/99 16:00	9.75e−05	6.92e+01	1.76e−06	7.14e+00	8.5	32.01	0.0144

NA = not available.
Eq. (6) was used to calculate ages for MW3A, MW3B, MW4B, MW5A, MW5B, big spring, north spring, and peat spring.
Eq. (7) was used to calculate ages for the nursery spring.

from 9.8 to 14.5 years. With the exception of MW3B, all of these monitoring points are members of Group II, and all of the monitoring points are members of Cluster B. We concluded that Group II might be representative of water that flows through or has flowed through the upper bedrock aquifer rather than just the unlithified aquifer. The $3H/3He$ ages suggest that groundwater ages for these monitoring points are indeed greater than those for MW3A and the peat spring, which is probably an indication of longer flow paths.

Very little or no tritium was detected in the samples collected from MW7A and MW7B. These wells are members of Group III and Cluster C, which are considered to be representative of regionally derived groundwater with long flow paths and/or residence times. The apparent groundwater ages support this conclusion. It is likely that the groundwater at these monitoring points was recharged prior to, or only shortly after, the initiation of nuclear weapons testing in the 1950s and 1960s.

5. Conclusions

We believe that our conceptual model of the monitoring points in Group I being representative of water that travels primarily through the unlithified aquifer along short flow paths and/or that has short residence times is valid, and that the results of the cluster analysis and age dating support this interpretation. The variability in analyte concentrations was initially an important factor in grouping the sampling locations in Group I together. Because the cluster analysis was based on local mean analyte concentrations, it was unable to capture this within-group variability. However, the results of the cluster analysis still predominantly agreed with the conclusions based on the use of both the sample means and coefficients of variation. This reinforces the assumption that for purposes of this study, the local standardized mean was an adequate choice for a characteristic of the entities that were clustered. While Cluster A contains some of the monitoring points in Group I, it did not identify MW3A and the peat spring. However, on the basis of the $3H/3He$ ages, the groundwater samples from these two locations do represent young water.

The majority of the sampling points and springs were grouped and linked together in Group II and Cluster B. It is likely that the characteristics of the sampled waters represent water that travels through or has traveled through the upper bedrock aquifer. The high, but consistent concentrations of nitrate and chloride suggest flow paths that are longer than those for Group I because the temporal variability in analyte concentrations is not apparent. $3H/3He$ ages support this conclusion, as ages range from approximately 10 to 15 years.

Group III and Cluster C contain monitoring wells MW7A, MW7B, and S-1. We conclude that these monitoring points are representative of more regionally derived groundwater with longer residence times and/or groundwater that has traveled along longer flow paths. Group III may be representative of water that has flowed through the lower bedrock aquifer, or at least the Elk Mound Group sandstones. The apparent lack of tritium in the samples collected from MW7A and MW7B supports these conclusions.

Relatively short groundwater residence times ($<$ 15 years) and the apparent lack of regionally derived groundwater input to the springs suggest that the water discharging to the larger springs travels primarily through the unlithified and upper bedrock aquifer as opposed to the lower bedrock aquifer. Water discharging to some of the smaller springs and seeps may only flow through the unlithified aquifer. This implies that both the larger springs and the smaller seeps are particularly vulnerable to reduced discharges caused by the reduction in groundwater recharge that is expected to accompany urbanization. It also calls for a more detailed characterization of heterogeneities within the upper bedrock aquifer in order to better quantify impacts to the springs. As seen in the elevated nitrate and chloride concentrations, spring water quality has already been compromised due to past agricultural practices and maintenance of roads. Further development is likely to exacerbate water quality degradation, thereby hampering wetland restoration and preservation efforts.

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