

**U.S. Geological Survey
Toxic Substances Hydrology Program—
Proceedings of the Technical Meeting,
Charleston, South Carolina,
March 8-12, 1999**

David W. Morganwalp and Herbert T. Buxton, Editors

U.S. GEOLOGICAL SURVEY

Water-Resources Investigations Report 99-4018C

Volume 3 of 3 - Subsurface Contamination From Point Sources

West Trenton, New Jersey

1999

Recharge Conditions and Flow Velocities of Contaminated and Uncontaminated Ground Waters at Cape Cod, Massachusetts: Evaluation of $\delta^2\text{H}$, $\delta^{18}\text{O}$, and Dissolved Gases

John-Karl Böhlke, Richard L. Smith, Tyler B. Coplen, Eurybiades Busenberg, and Denis R. LeBlanc

ABSTRACT

The isotopes of H and O in H_2O , and the concentrations of dissolved Ar, N_2 , and O_2 , were used to investigate recharge conditions and flow velocities in parts of a ground-water contaminant plume originating from disposal of treated domestic waste water and in surrounding uncontaminated ground water at the Massachusetts Military Reservation on Cape Cod. Contrasting patterns of isotope and gas abundances in the two water types are attributed to their different recharge sources and conditions: a low rate of areally distributed recharge of precipitation producing closely spaced, horizontal isochrons above the plume resulted in significant vertical variation in the H_2O isotope ratios but relatively little variation in atmospheric gases; conversely, a high rate of local recharge of recycled ground water producing more widely spaced, tilted isochrons in the plume resulted in significant horizontal variation in atmospheric gases but almost no variation in the H_2O isotope ratios. In addition, waters enriched in heavy isotopes by evaporation were detected in a pond and in the aquifer downgradient from the pond.

Concentrations of Ar and N_2 were consistent with recharge at temperatures ranging from about 8-24°C, followed by varying amounts of denitrification within the plume. Plume waters were anoxic, but O_2 concentrations above and below the plume averaged about 80-90 % of air saturation values at the temperatures implied by corresponding Ar concentrations, indicating relatively little O_2 reduction at time scales of up to at least 25 years. Vertical variations in ground-water isotope ratios above the plume at a site 140 m from the source in November 1996 were consistent with a precipitation recharge rate of 0.6-1.0 m/yr, an age of 1.0-1.5 yrs at the top of the plume, and a horizontal flow velocity of 140-210 m/yr. Longitudinal variations in Ar concentrations and H_2O isotopes in March 1998 were consistent with the position and age of the trailing edge of the plume following cessation of waste-water disposal in December 1995, and with horizontal flow velocities between about 120 and 240 m/yr. The isotope and dissolved-gas results are consistent (to within about $\pm 50\%$) with travel times indicated by $^3\text{H}/^3\text{He}$ dating, injected tracer tests, regional flow modeling, and passage of other conservative tracers representing the trailing edge of the plume.

INTRODUCTION

Conditions of ground-water recharge and short-term ground-water velocities commonly are reflected in the stable isotopic composition of H_2O and the concentrations of dissolved atmospheric gases. The H and O isotopes in atmospheric moisture vary systematically as air masses move away from moisture sources, cool, condense, and precipitate rain or snow (Craig, 1961; Rozanski and others, 1993). A common result is that the $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values of precipitation are positively correlated with temperature, so that winter values are more negative than summer values. Regular seasonal variations in the $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values of precipitation may be evident at the water table if

recharge occurs by piston flow, and they may persist for some distance downward within the saturated zone if vertical ground-water dispersion is limited. In favorable situations, seasonal isotope signals can be used to determine ground-water flow velocities within a few years of recharge (Stichler and Moser, 1979). Similarly, the concentrations of dissolved atmospheric gases vary inversely with the temperature of equilibration at the water table (Weiss, 1970) and, if recharge and isolation occur rapidly enough, seasonal variations in concentrations of Ar and other stable gases may be used to determine ground-water flow velocities (e.g., Sugisaki, 1961). Dispersion may be expected to reduce the

amplitudes of seasonal variations in the gas concentrations and isotopic compositions of recharging ground waters as they flow through aquifers, but the rate at which this occurs is not well known from direct evidence and may be expected to vary depending on the geometry of recharge and flow.

Applications of the isotope and gas methods to determining recharge conditions and ground-water velocities are most likely to succeed where recharge is rapid and/or dispersion is limited. In unconfined aquifers where recharge is areally distributed, isochrons are approximately parallel to the water table, and seasonal variations in water isotopes or gas concentrations are most likely to be found in short vertical profiles near the water table. In confined aquifers or in unconfined aquifers with high local recharge rates, isochrons are spaced more widely in the vertical dimension and seasonal variations in recharge characteristics may be detectable in longitudinal (subhorizontal) transects. The Toxic Substances Hydrology Program research site at the Massachusetts Military Reservation (MMR) on Cape Cod includes both types of recharge environments. In addition, the MMR includes numerous surface-water bodies in which isotope signals related to evaporation and/or seasonal precipitation may originate. The current study is a preliminary evaluation of the distribution of H and O isotopes of water and the concentrations of Ar, N₂, and O₂ in those different environments. The data were collected as a result of two major projects investigating the transport and reaction of N and O species in a contaminated waste-water plume (Böhlke and others, 1997; Smith and others, 1997; Smith and others, 1999; Miller and others, 1999; Revesz and others, 1999).

CONTAMINATED AND UNCONTAMINATED GROUND WATERS

The surficial aquifer at the MMR study site consists largely of fluvial-deltaic sands and gravels deposited from glacial melt waters in Late Wisconsin time. Distributed recharge to the surficial aquifer from precipitation in the vicinity of the MMR was estimated to be about 0.55 m/yr based on water balance calculations (LeBlanc and others, 1986), and 0.66 m/yr based on a calibration of a ground-water flow model (Masterson and others, 1998). Those distributed recharge rates would result in annual isochrons

roughly parallel to the water table with a vertical spacing of around 1.4-1.7 m near the water table (for the average porosity of 0.39). Most of the natural precipitation recharge occurs in late fall and early winter (LeBlanc and others, 1986).

The Ashumet Valley ground-water contaminant plume was formed in the surficial aquifer by artificial recharge of treated domestic waste water starting in 1936 and ending on December 13, 1995 (LeBlanc, 1984; Hess and others, 1996). The high rate of artificial recharge beneath the waste-water disposal beds caused water-table mounding and rapid downward vertical movement of contaminated water, which then joined the regional flow system and moved more horizontally to the south (Masterson and others, 1997; Figures 1 and 2). The result after 60 years was a plume of contaminated ground water approximately 5000 m long, 500-1000 m wide, and 20-25 m thick. The plume was overlain by a wedge of uncontaminated locally-recharged ground water that increased in thickness to the south, and it was underlain by relatively uncontaminated ground water from recharge areas north of the disposal beds. The contaminated plume was anoxic (O₂ < 10 µM) and had relatively high concentrations of NO₃⁻, Cl⁻, SO₄⁻, dissolved organic C, dissolved inorganic C, B, and other constituents; whereas, the surrounding ground waters generally were oxidic. Vertical chemical gradients between the plume and the surrounding ground waters above and below were fairly abrupt. Since cessation of waste-water recharge in December, 1995, the trailing edge of the plume has been replaced by ground waters recharged under more normal conditions (LeBlanc and others, 1999).

The 8 southernmost (downgradient) disposal beds were active from 1983 until the end in 1995 (Hess and others, 1996; Figure 1). The amount of treated waste water discharged to the disposal beds averaged approximately 950 m³/d spread over an area of about 2000 m² at any given time, or 16,000 m² overall). The normal rotation cycle for disposal among the individual beds was in the order of 1 day; for time scales longer than a few days, the 950 m³/d recharge may be considered to have been distributed evenly over 16,000 m², corresponding to a local recharge rate of about 6 cm/d or 22 m/yr. At that rate, the 20-25 m thickness of the plume would have been filled vertically in less than half a year. The horizontal travel time from the upgradient edge to the downgradient edge of the southern disposal area could be as much as 1 yr, consistent with

significant lateral spreading of the plume beneath the source. In recent years, rates of water use and disposal at the site averaged around 10-20 % higher in summer months than in winter months (F. Creighton, Otis ANG Base, written commun., 1998).

From the longitudinal $^3\text{H}/^3\text{He}$ age gradient in the core of the plume, Shapiro (1998) estimated that the long-term average velocity of the plume was 126 ± 2 m/yr., but the data also indicate significant variations in the vertical age gradients within the plume. Horizontal velocities estimated from aquifer hydraulic properties and from injected tracer tests range from about 0.2-0.6 m/d (70-220 m/yr) (LeBlanc, 1984; LeBlanc and others, 1991). Because of seasonal and other variations in water use at the MMR, and because of variations in aquifer hydraulic properties, it is possible that age gradients within the plume exhibit significant irregularities with a resolution of months to years (Figure 2). Nevertheless, limited data support the conceptual model that calls for annual isochrons within the plume generally to dip downward toward the point source of recharge (Shapiro, 1998).

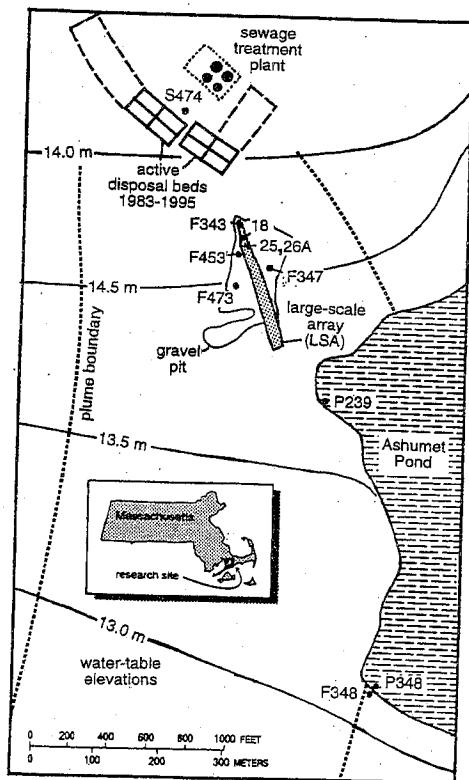


Figure 1. Map showing the location of sampling sites in the northern (proximal) part of the study area. Average water table contours are from LeBlanc (1984). Sites F168 and F593 (Appendix) are off the map approximately 2600 m downgradient (south) from the disposal beds.

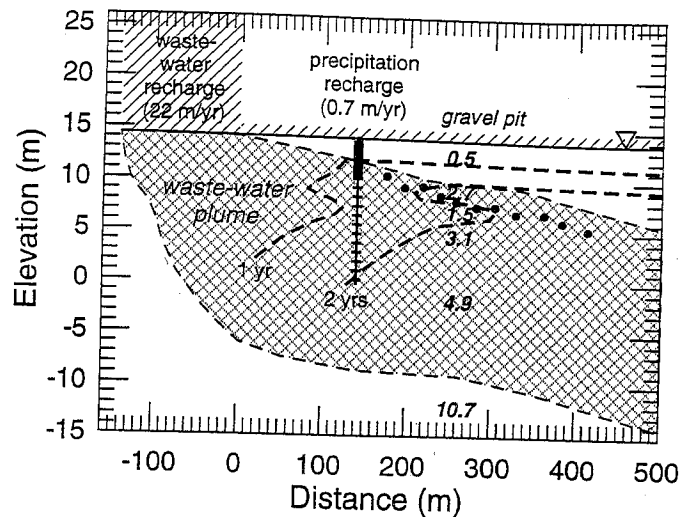


Figure 2. Schematic longitudinal vertical section through the waste-water plume showing the locations of sample profiles. The boundaries of the plume (shaded area) correspond approximately to the limits of anoxia. Dashed lines indicate approximate configuration of isochrons. $^3\text{H}/^3\text{He}$ ages (in years) are given for samples collected in October, 1994 from F347 (Shapiro, 1998). Filled circles indicate samples in the longitudinal dissolved gas transect in the LSA multiports (see Figure 6); crosses indicate samples in the vertical isotope profile in F343 (see Figure 4).

METHODS

Ground-Water Sampling

Most of the ground-water samples were collected from multilevel sampling devices located either within the gravel pit (about 140-420 m down-gradient from the nearest waste-water infiltration bed) or in Ashumet Valley (about 2600 m downgradient) (Figure 1). A multilevel sampler (LeBlanc and others, 1991) is a 3.2-cm diameter PVC pipe containing a bundle of 6-mm diameter polyethylene tubes that exit the pipe at 15 discrete elevations separated by 0.25-1.0 m intervals. Samples were pumped from the polyethylene tubes through Norprene tubing by a peristaltic pump at the land surface, approximately 4-7 m above the water table. Other ground waters were obtained with submersible pumps from 5-cm diameter PVC observation wells with screens ≤ 1 m long.

Stable Isotopes of Water

Samples for H and O isotope analysis were obtained from multilevel samplers, observation wells, a MMR water-supply well, faucets in the laboratory and living quarters of the MMR, and Ashumet Pond. The isotope samples were collected unfiltered in glass bottles with polyseal caps. For hydrogen isotope measurement, a 2-mL split from each sample was equilibrated with H₂ gas at 30°C and 1 atm for 1 hour. The H₂ gas was then admitted to a dedicated mass spectrometer for analysis against a H₂ reference gas. For oxygen isotope measurement, a 2-mL split from each sample was equilibrated with CO₂ gas at 25°C and 0.5 atm for 7 hours. The CO₂ was then admitted to a dedicated mass spectrometer for analysis against a CO₂ reference gas. The hydrogen and oxygen isotope analyses were calibrated by interspersed analyses of laboratory standard waters whose values are known with respect to the normalized scale defined by the Vienna Standard Mean Ocean Water (VSMOW) and Standard Light Antarctic Precipitation (SLAP) reference waters (Coplen, 1988). The stable isotope ratios are reported relative to a standard as delta (δ) values in units of parts per thousand (‰), as defined for each element by $\delta_x = 1000 \cdot [R_x/R_s - 1]$, where R_x and R_s are the ratios ²H/¹H, or ¹⁸O/¹⁶O of the sample and standard, respectively. $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values are reported relative to VSMOW, with overall uncertainties of around ± 1.5 ‰ and ± 0.1 ‰, respectively. H₂O isotope data are given in the Appendix; the data for F453 are from Reilly and others (1996).

Dissolved Gases

Dissolved O₂ was measured in the field by electronic probe (O₂ > 30 $\mu\text{mol/L}$) or by colorimetry (O₂ < 30 $\mu\text{mol/L}$; Chemetrics, Inc.). Samples for laboratory analysis of N₂, Ar, O₂, and CH₄ were collected in 125 mL glass serum bottles with no headspace. A dry KOH pellet (approximately 100 mg) was added to each bottle as a preservative (pH > 12), and a rubber stopper was inserted with a syringe needle in place to allow excess water to escape. In the laboratory, low-pressure headspace was created by vacuum-extraction of approximately 10 % of the water, the remaining water and headspace were equilibrated for several days at constant temperature, then the concentrations of gases in the headspace were measured by gas chromatography and converted to aqueous concentrations with corrections for the

lab solubilities (E. Busenberg, M. Doughten, and P. Widman, USGS, unpublished data). Overall uncertainties, including sampling artifacts, leakage, and GC analysis, generally were less than ± 2 -4 %, except for low O₂ concentrations. All samples analyzed by GC had CH₄ < 0.1 $\mu\text{mol/L}$.

RESULTS AND DISCUSSION

Water Sources from H and O Isotopes

In most vertical profiles, the H and O isotopic compositions of water in the plume were significantly different from those of overlying and underlying oxic ground waters and there were abrupt vertical gradients in the water isotope values between the two water types (see Appendix for data). Plume waters had relatively uniform isotopic compositions (Figure 3): at sites under the gravel pit (140-270+ m from the source) between 1995 and 1998, plume samples had $\delta^2\text{H} = -41.5 \pm 1.5$ ‰ and $\delta^{18}\text{O} = -6.8 \pm 0.2$ ‰ ($\pm \sigma$, n=59); at F168 and F593 under Ashumet Valley (2600 m from the source) in 1997, plume samples had $\delta^2\text{H} = -44.0 \pm 1.0$ ‰ and $\delta^{18}\text{O} = -7.3 \pm 0.1$ ‰ (n=28). Seasonal variations in the isotopic composition of precipitation were not detected within the plume, which consisted almost entirely of recycled waste water (the normal precipitation recharge rate was only 2 % of the waste-water recharge rate in the disposal beds).

Plume samples from beneath the gravel pit in 1995-1998 were similar isotopically to water samples collected from a water-supply well (J-well) in 1998 and from tap waters collected at several locations and times at the MMR in 1996 and 1998, all of which had $\delta^2\text{H} = -43.0 \pm 1.0$ ‰ and $\delta^{18}\text{O} = -6.9 \pm 0.1$ ‰ (Appendix). Those data indicate that the isotopic composition of the water was not altered significantly between the time it was extracted from the ground and the time it was re-introduced to the aquifer after having been used. That is, there is no evidence for isotopic fractionation caused by any parts of the anthropogenic hydrologic cycle including (1) extraction, (2) treatment for human consumption, (3) consumption or other use on the MMR, (4) sewage treatment including aeration, or (5) disposal in the infiltration beds.

Oxic ground waters above, below, upgradient from, and elsewhere in the vicinity of the waste-water plume (e.g., S474, S313) had relatively variable isotopic compositions, with $\delta^2\text{H}$

= -61 ‰ to -37 ‰ and $\delta^{18}\text{O}$ = -9.9 ‰ to -6.4 ‰. In several profiles beneath the gravel pit, the $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values of the overlying oxic waters decreased immediately above the plume. At F343, the isotopes varied cyclically with depth above the plume (Figure 4). The relatively large isotopic variations in the oxic ground waters are consistent with those of meteoric waters in which $\delta^2\text{H} = 8 \cdot \delta^{18}\text{O} + \text{"H-excess"}$ (Dansgaard, 1964), where $\text{"H-excess"} = 15 \pm 2$ (Figure 3). Though no precipitation measurements were made locally for this study, it is considered likely that seasonal isotope variations at the MMR were somewhat larger than those at a coastal site at Lewes, DE (around 40 ‰ in $\delta^2\text{H}$ and 5 ‰ in $\delta^{18}\text{O}$), but not as large as those at an inland site at Underhill, VT (around 70 ‰ in $\delta^2\text{H}$ and 9 ‰ in $\delta^{18}\text{O}$) (T.B. Coplen, unpublished data). Thus, the magnitude of the isotope variation in the MMR ground waters (about 24 ‰ in $\delta^2\text{H}$ and 3.5 ‰ in $\delta^{18}\text{O}$) probably was somewhat less than that of local precipitation.

Surface-water samples collected from Ashumet Pond in December, 1996 were relatively enriched in ^2H and ^{18}O and also were relatively far from the meteoric-water trend, with low apparent ^2H -excess values of 8 ± 2 (Figure 3). Those features are consistent with evaporation having altered the isotopic composition of the pond water. The apparent degree of heavy-isotope enrichment was slightly more for a sample taken near F348 at the southwest (downgradient) shore of the pond and less for a sample taken near F239 at the mid-western (upgradient) shore, possibly because of ground-water discharge near the upgradient shore. Ground waters from the F348 well nest had isotope ratios similar to the pond values, indicating that evaporated pond water recharged the aquifer and moved to depths of at least 30 m near the down-gradient edge of the pond (Figure 1).

The reason for the small apparent enrichment of ^2H and ^{18}O in the MMR treated waste-water plume with respect to the average of the overlying oxic ground waters is not known. Other examples have been reported of ground-water contaminant plumes having $\delta^2\text{H}$ and (or) $\delta^{18}\text{O}$ values slightly different from those of surrounding ground waters, but the reasons for the differences have not been clear. Fritz and others (1976) reported relative enrichment of ^2H and ^{18}O in a leachwater plume from a sanitary landfill, and speculated that the contrast might be due to evaporation in the landfill, different water sources, $\text{CO}_2\text{-H}_2\text{O}$ exchange, or organic matter decomposition.

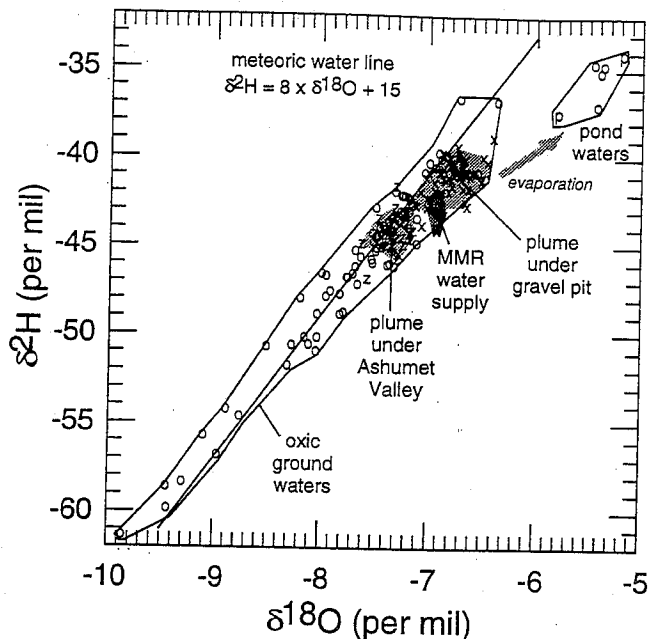


Figure 3. Relation between $\delta^2\text{H}$ and $\delta^{18}\text{O}$ in ground waters, tap waters, and pond waters. Oxic ground waters are indicated by symbol "o"; anoxic plume waters are indicated by symbols "x" and "z" (Appendix); pond waters are indicated by symbol "p".

Aravena and others (1993) attributed a small relative depletion in ^2H and ^{18}O in a domestic septic tank drainage water plume to the fact that the domestic water source was a relatively deep confined aquifer with an isotopic composition different from that of the surficial aquifer. Enrichment of ^2H caused by methanogenesis is common in ground waters from some types of sources (e.g., Hackley and others, 1996), but is not consistent with the plume data. The plume data (with ^2H excess = 13 ± 2) could be consistent with a minor component of evaporated pond water in the MMR water supply that was not present in the ground-water wedge overlying the plume (Figure 3). However, Masterson and others (1998) indicate that the source area for the J-well does not include major surface-water bodies.

Though the data are sparse, the slightly lower $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values of the older (downgradient) plume waters at Sites 168 and 593 under Ashumet Valley could indicate a long-term (decade-scale) shift in the isotopic composition of the shallow ground-water source of the MMR water supply, possibly due to a shift in the local climatic conditions affecting recharge to the water-supply aquifer, or possibly because of a

shift in the amount of pond-evaporated water in the aquifer being used. By interpolation between the ^3H - ^3He ages of plume waters at F411 (14 yrs) and F350 (26 yrs) (Shapiro, 1998), the ages of waters in the core of the plume at F168 and F593 are estimated to be about 22 yrs.

Vertical Ground-Water Velocity and Recharge Rate from Variations in Stable Isotope Ratios Above the Plume

At F343, the vertical distributions of H and O isotope ratios in oxic ground waters above the plume (Figure 4) appear to be consistent qualitatively with seasonal cycles in precipitation contributing to recharge (though damped significantly in amplitude compared to likely precipitation variations). If so, then it would appear that the multiports sampled about 1.0-1.5 years of recharge in a vertical distance of 2.5 m, corresponding to a vertical linear velocity of about 1.7-2.5 m/yr. Multiplied by the average porosity at the site (0.39), those velocities would correspond to recharge rates between about 0.6 and 1.0 m/yr, similar to the value used recently in a regional ground-water flow model (0.66 m/yr; Masterson and others, 1998). Differences between long-term regional recharge estimates and the isotope recharge rate at F343 could be due to local deviations from average recharge conditions, or to non-average precipitation in the period between Summer, 1995 and Fall, 1996, which may have been somewhat higher than usual (McCobb and others, 1999). The isotope pattern at F343 also is consistent with the timing of the sampling in November, 1996, as the $\delta^{18}\text{O}$ values near the water table may be interpreted to have just begun to decrease after the summer high values (sampled between 13 and 14 m elevation). The water at the bottom of the oxic wedge (11.5 m elevation) would have been recharged during the previous summer, perhaps 3-6 months before the waste-water disposal ended in December, 1995. These results indicate that closely spaced vertical profiles of $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values of H_2O may yield reasonable estimates of ground-water vertical velocity and recharge rate in the parts of the flow system that are not affected by the waste-water plume to a depth of at least 2.5 m, corresponding to at least 1 yr of precipitation recharge. Similar techniques cannot be used within the plume because the isotopic composition of the MMR water supply was relatively homogeneous.

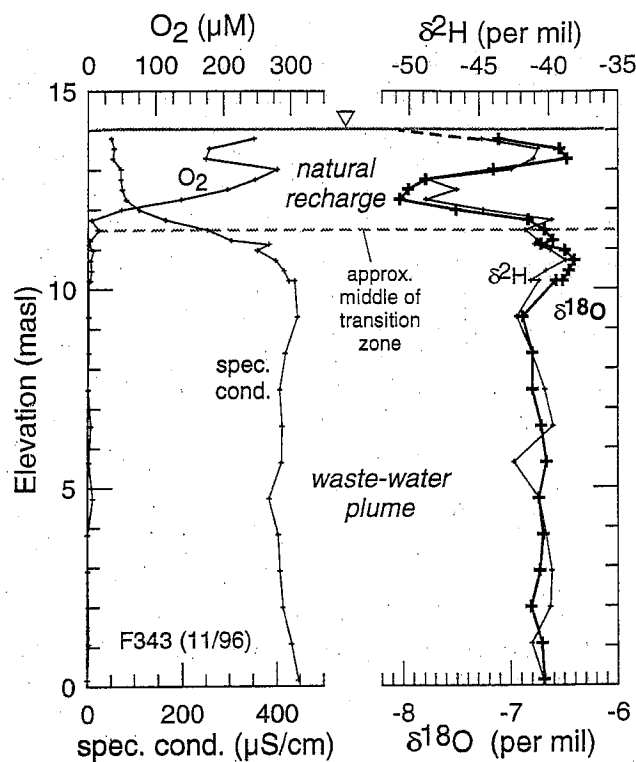


Figure 4. Vertical profiles of specific conductance, O_2 concentration, $\delta^2\text{H}$, and $\delta^{18}\text{O}$ values near the top of the contaminated plume in F343 (Figures 1 and 2). The transition zone between plume water and overlying natural recharge is indicated by the specific conductance gradient between 11 and 12 m elevation. The upper plume boundary is shown at 11.5 m elevation near the middle of the transition zone.

Recharge Temperatures from Dissolved Nitrogen and Argon Concentrations

Concentrations of Ar and N_2 (Figure 5) and $\delta^{15}\text{N}[\text{N}_2]$ values (Böhlke and others, 1997), in oxic ground waters above and below the waste-water plume were similar to those of air-saturated waters at approximately 12-20°C (Weiss, 1970) with $0 \pm 2 \text{ cm}^3/\text{L}$ of excess air (Heaton and Vogel, 1981), some of which could have been gained (positive values) or lost (negative values) during sampling. Plume waters had slightly more variable Ar concentrations corresponding to those of air-saturated waters at approximately 8-24°C. Plume waters also had more variable N_2 concentrations and $\delta^{15}\text{N}[\text{N}_2]$ values that are attributed in part to denitrification (Smith and others, 1991; Böhlke and others, 1997).

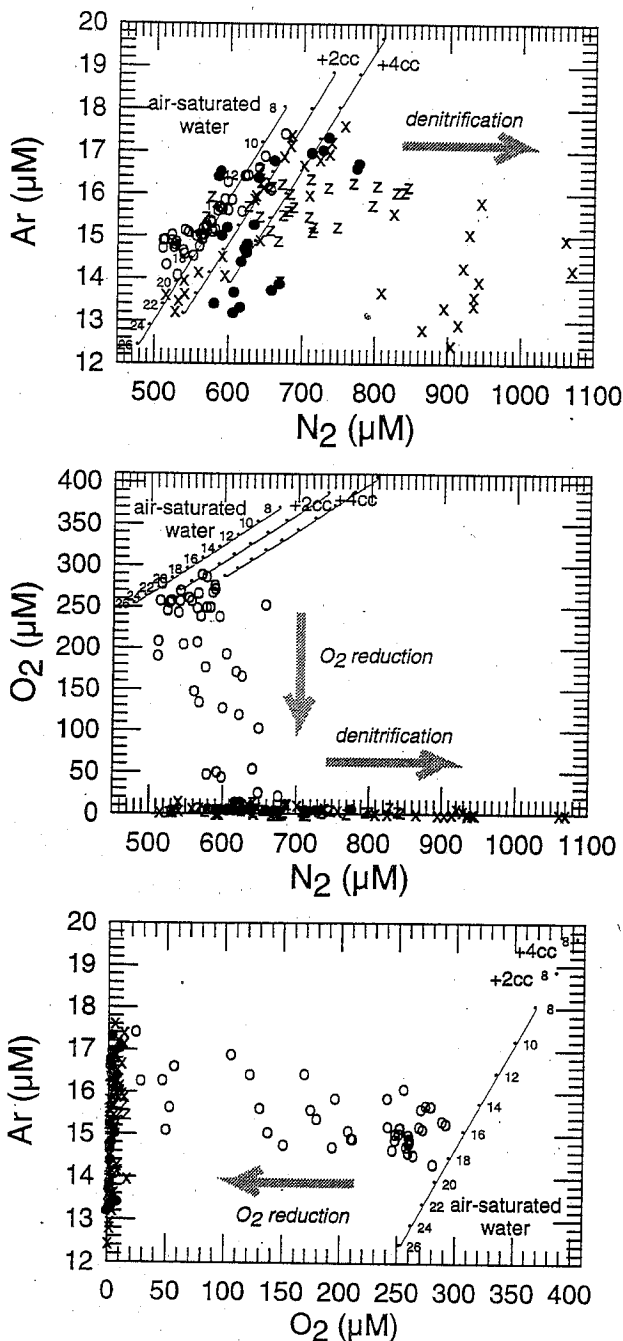


Figure 5. Ar, N₂, and O₂ concentrations in contaminated and uncontaminated ground waters. Oxic ground waters are indicated by symbol "o"; anoxic plume waters are indicated by symbols "x" and "z" (Appendix 1); filled circles indicate samples in the longitudinal dissolved gas transect (see Figure 6); curves indicate concentrations of gases in equilibrium with air (Weiss, 1970) at 100 % humidity, 14 m elevation, over a range of temperatures (8-24°C) and with varying amounts of excess air (0- 4 cm³/L).

Variations in the concentrations of Ar may be attributed largely to seasonal variations in the temperatures of recharge. Relatively large variations in apparent recharge temperatures were recorded and preserved within the plume near its source, possibly because the high local rate of recharge and the relatively large distances between isochrons minimized the effects of dispersion or re-equilibration on the Ar concentrations. Ar concentrations at F168 and F593 (2600 m downgradient from the disposal beds) indicate more uniform recharge temperatures (13-17°C), consistent with dispersion of the seasonal signal over long travel times. The relatively small variations in the apparent recharge temperatures of the oxic waters may indicate effects of vertical dispersion or of partial equilibration with changing temperatures near the water table.

Whereas the majority of precipitation recharge is believed to have occurred in the colder months, there may have been a slightly higher rate of waste-water disposal in the summer months. However, the Ar concentrations do not indicate that recharge temperatures were systematically higher in the plume than outside the plume, possibly because the variability of both groups is large and the sample set is not representative, or because of delay or partial re-equilibration between infiltration and isolation.

Horizontal Ground-Water Velocity from Variations in Apparent Recharge Temperatures and H₂O Isotopes

A one-dimensional survey of Ar concentrations in ground waters just below the upper boundary of the contaminated plume in March, 1998 indicates a range of apparent recharge temperatures from about 10 to 22°C (Figure 6), similar to the range observed in other samples from various localities at the site. The systematic cyclic variation of apparent recharge temperatures in the 240 m longitudinal transect could be consistent with a 1.0-1.1 year-long record of seasonal changes in recharge temperature of the plume, in which case the Ar transect would indicate a horizontal flow velocity of around 220-240 m/yr. However, because those samples were collected 2.2 yrs after the cessation of waste-water disposal, it is possible that upgradient ground waters may have replaced plume waters in parts of the transect. This is supported by significant deviations of δ²H and δ¹⁸O from plume values about half-way through the transect (Figure 6),

indicating that the trailing edge of the plume water was around 250-300 m downgradient from the edge of the disposal beds (around LSA rows 40-50). The isotope data are in agreement with the distributions of other conservative tracers such as B, which indicate the trailing edge of the plume was about 250-300 m downgradient in May-June, 1998 (LeBlanc and others, 1999). As the isotope samples were taken about 1-3 m below the top of the plume (that is, at plume depths between 5 and 15 % of the total plume thickness of 20 m), their recharge points may be assumed to have been upgradient from the southern edge of the infiltration beds by 5-15 % of the total distance across the infiltration beds (about 100 m), yielding total flow-path distances about 5-15 m longer than those given in Figure 6. In that case, allowing time for waste-water recharge, the H₂O isotope data would indicate a minimum velocity of about 120-140 m/yr for the trailing edge of the plume. This interpretation is supported by the observation that the trailing edge of the plume defined by the H₂O isotopes occurs where Ar concentrations are relatively high, consistent with the timing of source cessation in December, 1995.

The plume transect results can be compared with several other independent indicators of the horizontal ground-water flow velocities beneath the gravel-pit area. For example, the ground-water age at the top of the plume indicated by the H₂O isotope profile in F343 in 1996 was 1.0-1.5 yrs, which, for a travel distance of 140 m, would correspond to a horizontal velocity of 140-210 m/yr. In a large-scale tracer experiment monitored from July, 1985 to December, 1986 (LeBlanc and others, 1991), the trailing and leading edges of a Br⁻ cloud advanced at rates ranging from 0.2 to 0.9 m/d (70-330 m/yr); whereas the center of mass of the cloud moved with an average velocity of 0.42 m/d (153 m/yr). The shape of the cloud was irregular and the apparent velocities varied spatially, being relatively high near the water table (LeBlanc and others, 1991). The overall average velocity of the contaminated plume estimated from the distribution of ³H-³He ages was 126 ± 2 m/yr (Shapiro, 1998). However, an apparent age reversal at F347 beneath the gravel pit may indicate significant variations in the velocities at different depths (Figure 2). The apparent ages and corresponding velocities from estimated recharge points within the disposal beds to the sample elevations in F347 are: to 4.5 m elevation, 310 m in 3.1 yrs = 100 m/yr; to 7.0 m elevation, 290 m in 1.6 yrs = 180 m/yr; to 9.1 m elevation, 270 m in 2.7 yrs = 100 m/yr. The elevation of the dissolved

gas transect at Row 41 (nearest F347) was 7.9 m, possibly within a zone of relatively rapid flow (Figure 2).

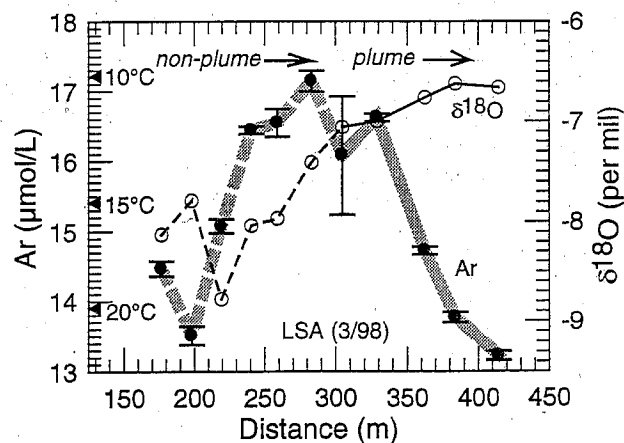


Figure 6. Ar concentrations and $\delta^{18}\text{O}$ values in a longitudinal transect in the upper part of the waste-water plume (Figure 2). Samples were collected in the large-scale array (LSA) in March, 1998. The horizontal flow-path distances are measured from the nearest edge of the waste-water disposal beds. Data points and error bars represent averages and ranges for analyses of duplicate samples. Temperatures are indicated for Ar concentrations in equilibrium with air at 100 % humidity, 14 m elevation, with no excess air (Weiss, 1970). The solid lines indicate the part of the transect in which H and O isotopes are consistent with plume water; the dashed lines indicate the part of the transect in which plume water may have been replaced by upgradient ground water.

Distribution of Dissolved Oxygen

Dissolved O₂ concentrations were high in uncontaminated ground waters both above and below the contaminated plume (Figure 2; Appendix). Maximum O₂ concentrations in samples collected for Ar and N₂ analyses averaged about 260 µM, approximately 85 % of the saturation value (310 µM) at the average Ar recharge temperature of 16°C. Larger sets of field measurements at the site indicate maximum O₂ concentrations ranging between about 250 and 340 µM (Savoie and LeBlanc, 1998), equal to or slightly less than saturation values over the range of apparent recharge temperatures. O₂ concentrations of at least 250 µM occur in ground waters at least as old as 25 yrs (Savoie and LeBlanc, 1998; Shapiro, 1998), indicating that the glacial-fluvial sediments in the surficial aquifer

were not capable of supporting a high rate of O₂ reduction outside the plume. Corresponding cumulative reaction rate constants derived from some of the relatively old oxic ground waters (assuming maximum recharge concentrations of around 340 μM) would be less than 0.013/yr (first-order) or less than 4 μM/yr (zero-order). The data do not indicate systematic decreases in O₂ concentrations with age; instead it is possible that the oxic ground waters were recharged with 80-90 % of the air-saturation values owing to O₂ reduction in the unsaturated zone, or that they lost 10-20 % of their O₂ relatively quickly after recharge, perhaps by oxidation of small amounts of reactive DOC. In this case, reaction rates after the first few years may have been significantly smaller than the estimated maximum values for the cumulative rates.

O₂ concentrations decreased abruptly in the dispersive transition zones at the upper and lower boundaries of the plume (Figures 2 and 4), and were consistently low (< 10 μM) within the plume. O₂ reduction apparently was associated with oxidation of reduced constituents in the plume water, and occurred at a relatively high rate near the source beds. Complete loss of O₂ within 1 year of recharge implies O₂ reduction rates within the plume greater than 1/yr (first-order) or greater than 350 μM/yr (zero-order), at least two orders of magnitude higher than the rates outside the plume. O₂ reduction rates in the transition zone between the plume and overlying ground water apparently were intermediate between those above and below (Smith and others, 1999).

SUMMARY

Evidence was found for seasonal variations in the stable isotope ratios and dissolved atmospheric gas concentrations of recharging ground waters at the MMR. In the vicinity of the waste-water treatment plant, the distributions of stable isotopes and dissolved gases were consistent with 2 contrasting isochron configurations caused by the high local recharge rate in the waste-water disposal beds: Outside the plume, isochrons were parallel to the water table and closely spaced. Inside the plume, isochrons were at a higher angle to the water table (with some apparent reversals) and more widely spaced. Seasonal variations in stable isotope ratios with depth below the water table were used to determine vertical velocities and recharge rates outside the plume, while seasonal variations in

atmospheric gas concentrations with horizontal distance from the source beds were consistent with horizontal velocities within the trailing edge of the plume. There is approximate agreement on travel times and velocities in the first few years of flow near the top of the plume derived from (1) ³H/³He dating, (2) vertical recharge from H₂O isotopes, (3) displacement of the plume after cessation of waste-water disposal indicated by H₂O isotopes and other conservative tracers, (4) horizontal gradients in dissolved gas concentrations in the plume, (5) injected tracer tests, and (6) regional flow simulations.

Discrepancies or uncertainties of around ± 50 % may be due in part to incorrect assumptions in some of the methods (including the configuration of the flow field under the disposal beds), but real variations of the same magnitude are also evident. Specifically:

1. Three sources of ground-water recharge were distinguishable within the surficial aquifer on the basis of H and O isotope values of the H₂O: Local recharge water overlying the treated waste-water plume and elsewhere in the vicinity had variable δ²H (-61 ‰ to -37 ‰) and δ¹⁸O (-9.9 ‰ to -6.4 ‰) values that were consistent with meteoric waters with ²H-excess values of 15 ± 2. Waters in and downgradient from Ashumet Pond but outside the plume had relatively high δ²H (to -34 ‰) and δ¹⁸O (-5.2 ‰) and significantly lower apparent ²H-excess values (8 ± 2) indicating isotopic enrichment by evaporation. Plume waters within 420 m of the disposal beds had relatively constant and generally higher average δ²H (-43.0 ± 1.0 ‰) and δ¹⁸O (-6.9 ± 0.1 ‰) with slightly lower apparent ²H-excess values (13 ± 2), consistent with a relatively homogeneous source and possibly indicating a minor component of evaporated pond water in the MMR ground-water supply.
2. The artificial hydrologic cycle of H₂O at the MMR, involving ground-water extraction, purification, use, treatment, disposal, and infiltration, had little or no effect on the H and O isotope ratios of the water (Δδ²H ≤ 2 ‰; Δδ¹⁸O ≤ 0.2 ‰).
3. A ground-water isotope profile at F343 indicated a vertical ground-water flow velocity of around 1.7-2.5 m/yr, corresponding to a recharge rate of around 0.8 ± 0.2 m/yr, roughly consistent with other estimates of the local natural recharge rate.
4. Concentrations of dissolved atmospheric gases indicate that plume waters were recharged at

temperatures ranging from about 8 to 24°C with 0 ± 2 cc/L of excess air.

5. A March, 1998 transect near the top of the plume beneath the gravel pit was truncated as a result of source cessation in 1995. Changes in gas recharge temperatures and H₂O isotopes indicated horizontal ground-water flow velocities in the order of 120-240 m/y, near the high end of the range of velocities derived from tracer tests and ³H/³He dating.

ACKNOWLEDGMENTS

This study was supported in part by the USDA (National Research Initiative Competitive Grants Program), EPA (NSF/EPA Water and Watersheds Program), and the USGS-WRD National Research Program and Toxic Substances Hydrology Program, in collaboration with T. Yoshinari (NY State Health Dept.) and K. Revesz (USGS). T. Peacock, M. Nimiroski, K. Revesz, J. Hannon, and T. Yoshinari assisted with field sampling. P. Widman, M. Doughten, B. Baldrige, I. Hamblen, and K. Plummer assisted with laboratory analyses. T. Councill and K. Revesz reviewed the manuscript.

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AUTHOR INFORMATION

John Karl Böhlke, U.S. Geological Survey, 431 National Center, Reston, VA 20192
[jkbohlke@usgs.gov]

Richard L. Smith, U.S. Geological Survey, 3215 Marine St., Boulder, CO 80303
[rlsmith@usgs.gov]

Tyler B. Coplen, U.S. Geological Survey, 431 National Center, Reston, VA 20192
[tbcoplen@usgs.gov]

Eurybiades Busenberg, U.S. Geological Survey, 432 National Center, Reston, VA 20192
[ebusenbe@usgs.gov]

Denis R. LeBlanc, U.S. Geological Survey, 28 Lord Road, Marlborough, MA 01752
[dleblanc@usgs.gov]