

## Age dating of a chlorinated solvent plume in groundwater

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**Abstract** Groundwater in a well in southern New Jersey exhibited elevated concentrations of trichloroethylene (TCE), cadmium (Cd) and lead (Pb). The contaminant source was suspected to be wastewater lagoons at an industrial site located 550 m upgradient. Wastewater discharges were active at the site until the mid-1970s and TCE, Cd and Pb have been detected in underlying soils. The age of groundwater in the well was used to confirm the source of the contamination. To determine the age of the contaminants present, tritium ( $^3\text{H}$ ) analyses and groundwater migration rate calculations were performed.  $^3\text{H}$  analyses performed on the sample revealed that the age of the groundwater was about 24 years. Groundwater flow calculations confirmed that the travel time between the lagoons and the well for TCE and metals is between 20 and 25 years. Accordingly, the contaminant source was confirmed and the owner accepted liability.

### INTRODUCTION

In the United States, environmental consultants are often brought into litigation cases to provide expert testimony. Questions posed by plaintiff and defence attorneys often revolve around responsibility for contaminant releases and their time frame. Consequently, consultants such as hydrogeologists are often asked to provide opinions on the age of a contamination problem. There are several methods used to date a contaminant release; either one or a combination of methods may be used. The contaminants may be dated or the age of the groundwater in which they are present may be determined. The age of groundwater and associated contaminants may be estimated with methods such as: (a) site history; (b) groundwater migration rate; (c) index chemicals; (d) isotopes, and (e) chemical fingerprinting. The purpose of this paper is to provide a case study where a combination of methods was used to date a chlorinated solvent plume.

### BACKGROUND

In October 1993, a groundwater sample was collected from a well located in southern New Jersey. The well ("historical well") is part of an historical property built in the 1600s and was constructed to a depth of 31.4 m below ground surface. The well is located within 8 km of Philadelphia and extends into the Cretaceous-age Old Bridge Formation (Fig. 1). The sample was submitted to a laboratory for analysis of volatile organic compounds (VOCs). Detected VOCs included *cis*- and *trans*-1,2-dichloroethylene (DCE)

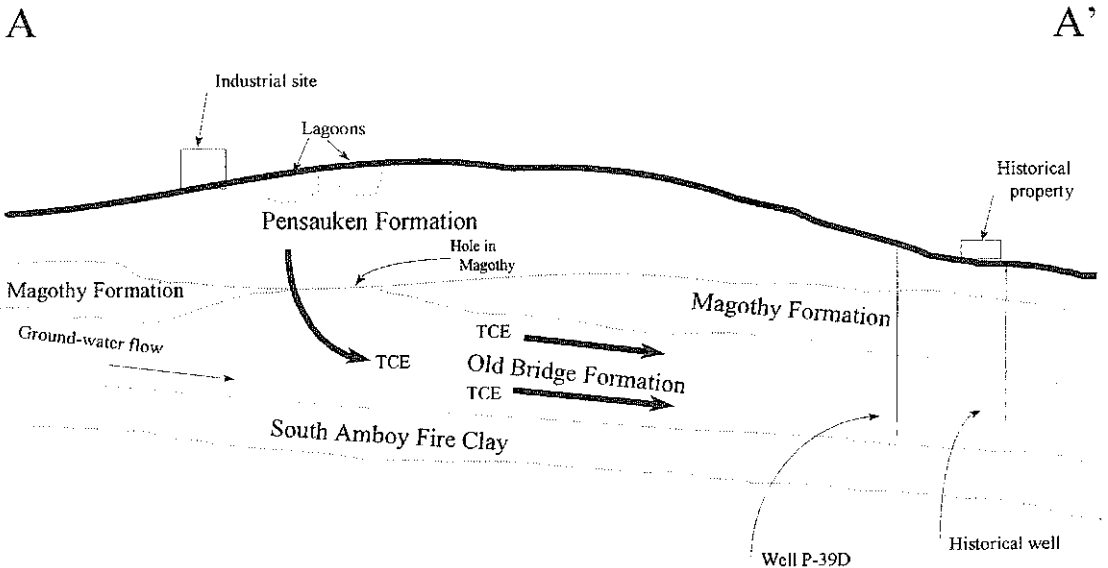


Fig. 1 Geological cross section depicting locations of the industrial site and historical well.

and trichloroethylene (TCE) at concentrations of  $0.6 \mu\text{g l}^{-1}$ ,  $22 \mu\text{g l}^{-1}$  and  $77 \mu\text{g l}^{-1}$ , respectively. The State of New Jersey's (State's) groundwater quality standard for TCE is  $1 \mu\text{g l}^{-1}$ . At a later date, elevated concentrations of cadmium (Cd) and lead (Pb) were detected. Use of the historical well ceased and the property was connected to a public supply.

Between 1993 and 1998, the State conducted investigations to identify the source of contamination in the Old Bridge Formation aquifer. Several sources were identified and investigated. One potential source is approximately 550 m upgradient of the historical well (Fig. 2). The site ("industrial site") was used since the 1950s for the re-manufacturing of automobile engines. The purpose of our investigation was to determine if contamination in the historical well originated from the industrial site.

## INVESTIGATIONS AT INDUSTRIAL SITE

From the early 1990s to the present, the owner of the industrial site conducted an investigation to determine if site operations had impacted the groundwater. The investigative work revealed that the groundwater had been impacted. However, the owner refused to accept responsibility for contamination detected in the historical well. Based on the State's investigations, wastewater generated at the industrial site was discharged to a lagoon system. The lagoons were constructed in the early 1960s, but were decommissioned in the mid 1970s. After decommissioning the lagoons, seepage pits were constructed for the wastewater disposal and used until early 1982.

Between 1994 and 1996, soil samples were collected from boreholes located in the vicinity of the former lagoons and seepage pits. TCE, DCE, benzene, Cd, Pb and arsenic (As) were detected at concentrations in excess of the State's cleanup standards.

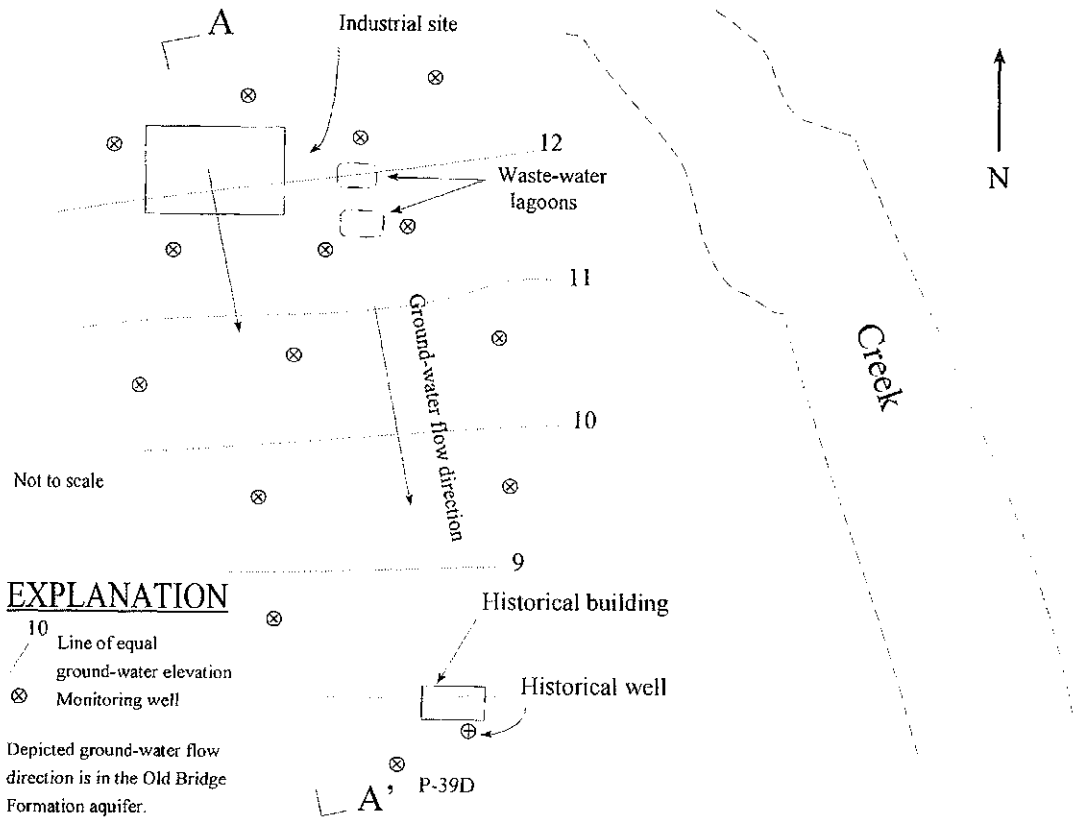


Fig. 2 Locations of the industrial site and historical property.

As part of the investigation, more than 50 monitoring wells were installed at and downgradient of the industrial site (Fig. 2). One monitoring well, designated P-39D and constructed within the Old Bridge Formation, was installed within 50 m of the historical well. Based on the laboratory analysis of groundwater samples collected from the monitoring wells, a contaminant plume is present in the aquifer underlying and downgradient of the industrial site and contains TCE, *cis*-DCE, *trans*-DCE, 1,1,1-trichloroethane (TCA) and toluene, among others.

## ENVIRONMENTAL SETTING

Surficial deposits beneath the industrial site and in the vicinity of the historical well consist of the unconsolidated, Quaternary-age Pensauken Formation and are comprised of medium- to coarse-grained sand and clay (Farlekas *et al.*, 1976). The Pensauken Formation is up to 18 m thick and underlain by clay of the Cretaceous-age Magothy Formation (Fig. 1). Based on borings completed at the industrial site, there are at least two holes within the Magothy Formation in the vicinity of the former lagoons and seepage pits. The Magothy Formation is up to 9 m thick.

The Magothy Formation is underlain by the Cretaceous-age Old Bridge Formation, a medium- to coarse-grained sand. The Old Bridge Formation is between 9 and 30 m

thick and a source of water supply (Zapeczka, 1984). The historical well is screened within the upper portion of the Old Bridge Formation aquifer, while monitoring well P-39D is screened within the lower. The Old Bridge Formation is underlain by the South Amboy Fire Clay, which is up to 3 m thick and laterally extensive. The unconsolidated, Cretaceous beds beneath the industrial site: the Magothy, Old Bridge, and South Amboy Fire Clay formations, are extensive throughout southern New Jersey. The formations strike northeast-southwest and dip southeast at approximately 10°. Therefore, the formations beneath the industrial site will also be found beneath the historical property, but at a lower elevation.

## HYDROLOGICAL CONDITIONS

Because of holes in the Magothy Formation beneath the industrial site, there is a hydraulic connection between the Pensauken and Old Bridge Formations (Fig. 1). In the vicinity of well P-39D and the historical well, the Old Bridge Formation is under confined conditions. The upper confining layer is the Magothy Formation, while the lower confining layer is the South Amboy Fire Clay. Therefore, at the location of the historical well, the Old Bridge Formation is not in hydraulic connection with the Pensauken Formation. Based on water-level measurements collected from monitoring wells installed into the Old Bridge Formation, the groundwater flow direction is to the south and south-southeast towards well P-39D and the historical well (Fig. 1). The hydraulic gradient ( $dh/dl$ ) was found to be  $1.4 \times 10^{-3} \text{ m m}^{-1}$ . Based on tests completed at the industrial site, the hydraulic conductivity ( $K$ ) of the Old Bridge Formation is approximately  $40 \text{ m day}^{-1}$ .

## FIELD SAMPLING

In January 1999, groundwater samples were collected from monitoring well P-39D and the historical well. Prior to sample collection, three water column volumes were purged with an electric, submersible pump. The groundwater sample from the historical well was submitted for analysis of VOCs, metals, tritium ( $^3\text{H}$ ), helium (He) isotopes and neon (Ne), while the P-39D sample was analysed for  $^3\text{H}$ , He isotopes and Ne. Samples collected for isotope analysis, such as He and Ne, must not be in contact with the atmosphere. Therefore, a special technique is required to collect the sample. After three water column volumes had been removed from the wells, a 45 cm (1.5 feet) length of 1 cm (3/8 inch) diameter copper tubing was attached to the pump discharge. To ensure that exposure to the atmosphere did not occur, the copper tubing was clamped on both ends while the pump ran. The sample for  $^3\text{H}$ , VOC and metals analysis was collected with a dedicated Teflon bailer, and placed in laboratory-supplied containers. The samples were sent to the University of Miami's Rothschild School Isotope Laboratory for the isotope analysis.

## IDENTIFICATION OF THE CONTAMINANT SOURCE

There are four lines of evidence to indicate that the former lagoons and seepage pits are the source of contamination of the historical well: the groundwater flow direction; suite of contaminants; groundwater migration rate; and the age of the groundwater.

**Groundwater flow direction** Based on water-level measurements collected from the monitoring wells, the groundwater flow direction in the Old Bridge Formation aquifer has been consistently to the south and south-southeast (Fig. 2). Therefore, groundwater in the Old Bridge Formation aquifer beneath the industrial site flows directly to the historical well and well P-39D.

**Suite of chemicals** Contaminants detected in groundwater samples collected from monitoring wells at the industrial site include 1,1-dichloroethane, *cis*-DCE, *trans*-DCE, toluene, TCE, TCA and vinyl chloride. Elevated concentrations of As, Cd and Pb were also detected in soil samples collected in the vicinity of the former lagoons and seepage pits. VOCs detected in samples collected from the historical well include *cis*-DCE, TCE and toluene and metals such as Pb and Cd were also present. Therefore, the same suite of chemicals is present in the groundwater samples collected from the historical well as detected beneath the industrial site.

**Groundwater migration rate** The groundwater migration rate may be estimated by:

$$V = (K \, dh/dl) / \phi_c$$

where  $V$  is the average groundwater migration rate in  $\text{m day}^{-1}$  and  $\phi_c$  is the effective porosity of the formation. Assuming a  $K$  value of  $40 \text{ m day}^{-1}$ , a  $dh/dl$  of  $1.4 \times 10^{-3} \text{ m m}^{-1}$  and an  $\phi_c$  for a medium to coarse grained sand of 0.30 (Freeze & Cherry, 1979),  $V$  is estimated at  $0.19 \text{ m day}^{-1}$ . VOCs such as TCE do not migrate at the same rate as groundwater. Natural organic carbon in the aquifer matrix causes a portion of the VOCs to adsorb. To determine the contaminant migration rate, the retardation factor must be calculated where:

$$R_d = 1 + (\rho_b K_d / \phi_c)$$

and  $R_d$  is the retardation factor,  $\rho_b$  is the bulk density of the material and  $K_d$  is the partitioning coefficient (Appelo & Postma, 1993). The  $\rho_b$  for medium to coarse-grained sand (Rawls *et al.*, 1982) is  $1.65 \text{ g cm}^{-3}$ . The partitioning coefficient is:

$$K_d = 0.63 f_{oc} K_{ow}$$

where  $f_{oc}$  is the fraction of organic carbon and  $K_{ow}$  is the octanol-water partitioning coefficient. Rutgers University has tested geological materials throughout New Jersey and  $f_{oc}$  ranges from 0.001 to 0.004 (C. Uchirin, verbal communication). An  $f_{oc}$  value of 0.0025 will be used and the  $K_{ow}$  for TCE is  $200 \text{ cm}^3 \text{ g}^{-1}$  (Montgomery & Welkom, 1990). The average contaminant migration rate is:

$$V_c = V / R_d$$

where  $V_c$  is the contaminant migration rate. Assuming the values given and  $R_d$  resulting in 2.73,  $V_c$  is estimated at  $24.7 \text{ m year}^{-1}$ . Therefore, for TCE to migrate 550 m from the industrial site to the historical well, it would take 22 years. TCE was first detected in the historical well in 1993. Consequently, this calculation confirms that the TCE originated at the industrial site in the early-1970s, when the wastewater discharges were active.

**Age of the groundwater** The age of groundwater can be estimated with several techniques. A recent technique used by researchers in the hydrological field is to

analyse groundwater samples for  $^3\text{H}$ , an isotope of hydrogen.  $^3\text{H}$  was introduced into the hydrological cycle in the early 1950s through the explosion of hydrogen bombs (Schlosser *et al.*, 1988). Therefore, as of 1953, all precipitation contains  $^3\text{H}$ . Because precipitation will percolate through the soil and recharge the water table, the presence of  $^3\text{H}$  can be used to determine the age of the water, or when it entered the hydrological cycle. Atoms of  $^3\text{H}$  are unstable and will disintegrate radioactively into a helium isotope ( $^3\text{He}$ ) at a half-life rate of 12.43 years. Therefore, to determine the concentration of  $^3\text{H}$  in the original precipitation, the quantity of both  $^3\text{H}$  and  $^3\text{He}$  must be quantified. Because  $^3\text{He}$  is prevalent in the atmosphere and can be derived from radioactive decay of uranium or lithium present in rocks or rock fragments (Aeschbach-Hertig *et al.*, 1998), the concentrations of the helium isotope ( $^4\text{He}$ ) and neon (Ne) must also be quantified to determine the concentration of  $^3\text{He}$  derived from  $^3\text{H}$ . Based on known ratios of Ne versus  $^3\text{He}$ , and  $^4\text{He}$  versus  $^3\text{He}$  in the atmosphere, the quantity of tritiogenic  $^3\text{He}_{\text{tri}}$  ( $^3\text{He}$  derived solely from the radioactive decay of hydrogen bomb  $^3\text{H}$ ) can be determined.

Prior to 1953, precipitation and groundwater contained  $^3\text{H}$  concentrations of less than 0.5 TU (tritium units). Water containing  $^3\text{H}$  concentrations greater than 10 TU is considered to be of post-1953 age, while water with  $^3\text{H}$  concentrations of between 0.5 and 10 TU may be a mixture of pre-1953 and post-1953 water (Mazor, 1991). Because the Old Bridge Formation is under confined conditions, it is unlikely that mixing of differing ages occurred in the aquifer.

In summary, because  $^3\text{H}$  decays at a known and constant rate and the concentration of  $^3\text{H}$  in historical precipitation is known, the age of the groundwater can be determined by quantifying the concentrations of  $^3\text{H}$  and its daughter product,  $^3\text{He}$ . The age of groundwater is determined by:

$$t = (T_{1/2}/\ln 2) \ln(1 + ^3\text{He}_{\text{tri}}/^3\text{H})$$

where  $t$  is the age of the water,  $T_{1/2}$  is the half life of  $^3\text{H}$  (12.43 years) and  $^3\text{He}_{\text{tri}}$  is the concentration of tritiogenic  $^3\text{He}$  (Schlosser *et al.*, 1989).

The concentration of  $^3\text{H}$  in the groundwater sample collected from the historical well was found to be  $11.3 \text{ TU} \pm 0.24 \text{ TU}$ . Based on the calculated values for  $^3\text{He}$ ,  $^4\text{He}$  and Ne, the age of the groundwater sample collected from the historical well is estimated at 24.3 years. Therefore, for groundwater to migrate 550 m from the industrial site to the historical well, it would take 24.3 years. Consequently, TCE present in the historical well originated at the industrial site in the mid-1970s, when the wastewater discharges were active.

The analysis conducted on the groundwater sample collected from well P-39D revealed similar results. The  $^3\text{H}$  concentration ranged from  $9.5 \text{ TU} \pm 2 \text{ TU}$  to  $10 \text{ TU} \pm 2 \text{ TU}$ . Based on the range, the age of the groundwater at the P-39D location would be from 22.9 to 28.7 years.

## CONCLUSIONS

Contaminant concentrations in samples collected from the historical well exceed the State's standards. Discharges of wastewater at the industrial site occurred from the early-1960s until 1982. The wastewater contained TCE, *cis*- and *trans*-DCE and

metals, such as Cd and Pb. Beneath the industrial site, the Old Bridge Formation aquifer is in hydraulic connection with the surficial, Pensauken Formation. Therefore, discharges from the former lagoons and seepage pits impacted the Old Bridge Formation aquifer. Groundwater flow direction in the aquifer is to the south and south-southeast, from the industrial site to the historical well. Sampling confirms that a plume of TCE is migrating downgradient of the industrial site. Contaminants detected in the Old Bridge Formation aquifer and at the historical well were also detected in samples collected from beneath the industrial site. TCE within the Old Bridge Formation aquifer migrates at a rate of approximately 24.7 m year<sup>-1</sup>. Therefore, TCE present in the historical well originated at the industrial site in the mid-1970s, when wastewater discharges through the seepage pits were active. The age of the groundwater in the historical well, as measured with the <sup>3</sup>H/<sup>3</sup>He method, is 24.3 years. Therefore, the water and the associated contaminants originated from the industrial site in the mid-1970s.

## REFERENCES

- Aeschbach-Hertig, W., Schlosser, P., Stute, M., Simpson, M. & Clark, J. F. (1998) A <sup>3</sup>H/<sup>3</sup>He study of ground water flow in a fractured bedrock aquifer. *Ground Water* **36**, 661–670.
- Appelo, C. A. J. & Postma, D. (1993) *Geochemistry, Groundwater and Pollution*. A. A. Balkema, Rotterdam.
- Parlekas, G. M., Bronius, B. & Gill, H. E. (1976) Geology and ground-water resources of Camden County, New Jersey. *US Geological Survey Water-Resources Investigations Report 83-4029*.
- Freeze, R. A. & Cherry, J. A. (1979) *Groundwater*. Prentice Hall Publishers, Englewood Cliffs, New Jersey, USA.
- Montgomery, J. & Welkom, L. (1990) *Groundwater Chemicals Desk Reference*. Lewis Publishers, Chelsea, Michigan, USA.
- Mazor, E. (1991) *Applied Chemical And Isotopic Ground Water Hydrology*. Halsted Press, New York.
- Rawls, W. J., Brakensiek, D. L. & Saxton, K. E. (1982) Estimation of soil water properties. *Trans. Am. Soc. Agric. Engrs* Paper no. 81-2510, 1316–1328.
- Schlosser, P., Stute, M., Dörr, H., Sonntag, C. & Münnich, K. O. (1988) Tritium/<sup>3</sup>He dating of shallow ground water. *Earth Plan. Sci. Lett.* **89**, 353–362.
- Schlosser, P., Stute, M., Sonntag, C. & Münnich, K. O. (1989) Tritogenic <sup>3</sup>He in shallow groundwater. *Earth Plan. Sci. Lett.* **94**, 245–256.
- Zapacza, O. S. (1984) Hydrogeologic framework of the New Jersey coastal plain. *US Geological Survey Open-File Report 84-730*.