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ORIGINAL ARTICLE

Persistence of vinyl chloride in ground water at the Woodlawn landfill Superfund site, northeastern Maryland, USA

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Abstract Since landfill operations ceased in the early 1980s at the Woodlawn landfill Superfund site in northeastern Maryland, USA, the carcinogen vinyl chloride monomer (VCM) has persisted in the site ground water at concentrations in places greater than 100 ppb. Investigations of VCM concentrations from monitoring well data from 1981 through 1991, which were published in 2001, concluded that concentrations were cyclic and were not dissipating. Data from 1991 to 2000 confirm VCM persistence, showing concentration peaks as late as 1997 in the eastern part of the site. These values are significantly above both drinking water standards (>MCL of 2 ppb) and lifetime excess cancer risk (E-6 risk level) from exposure since birth (>0.024 ppb). Sources for VCM are landfill wastes (PVC-sludge) and effluent from an on-site transfer station. In addition to direct release of VCM from wastes, other chlorinated hydrocarbons, trichloroethene and perchloroethene (TCE and PCE) are also present in the ground water, and these compounds can degrade into VCM. Persistence of VCM concentrations is the result of leachate generation, mostly from multi-source wastes in the vadose zone, with subsequent infiltration into the regional aquifer. Increases in VCM concentrations (new leachate generation) alternated with decreases in VCM concentrations (infiltration without leachate) in a cyclic fashion, during this 20-year period.

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Introduction

Computer simulation of ground-water flow and contaminant transport can be a useful tool in predicting the future fate and transport of contaminant plumes. Unfortunately, assumptions used in the simulation may not account for the numerous irregularities and field complexities. The site in question has heterogeneous terrain, multiple, waste source areas, and surges of leachate production. The present authors' review of a computer modeling study (Geraghty and Miller 1998) indicates that the model, although mathematically rigorous, presents predictions and conclusions that differ from observed monitoring results. The Geraghty and Miller study in (1998) and the previous study conducted by IT Corporation in (1992) assumed that: (1) all of the VCM contaminants were derived from wastes in Cells A and B/C (Fig. 1); and (2) no new leachate was generated decades after the initial burial period.

Cyclic peaks in contaminant concentrations subsequent to the remedial investigation (RI), the Geraghty and Miller modeling study (1998), and the second record of decision (ROD 1999) indicate that assumptions (1) and (2) above are incorrect. Assumption (1) is incorrect because contaminant plumes have been coming from many sources. These plumes were derived from indiscriminant dumping at numerous places on site (multiple, and unknown sources). Assumption (2) is incorrect because contaminant plumes are still being generated in surges, decades after the initial burial.

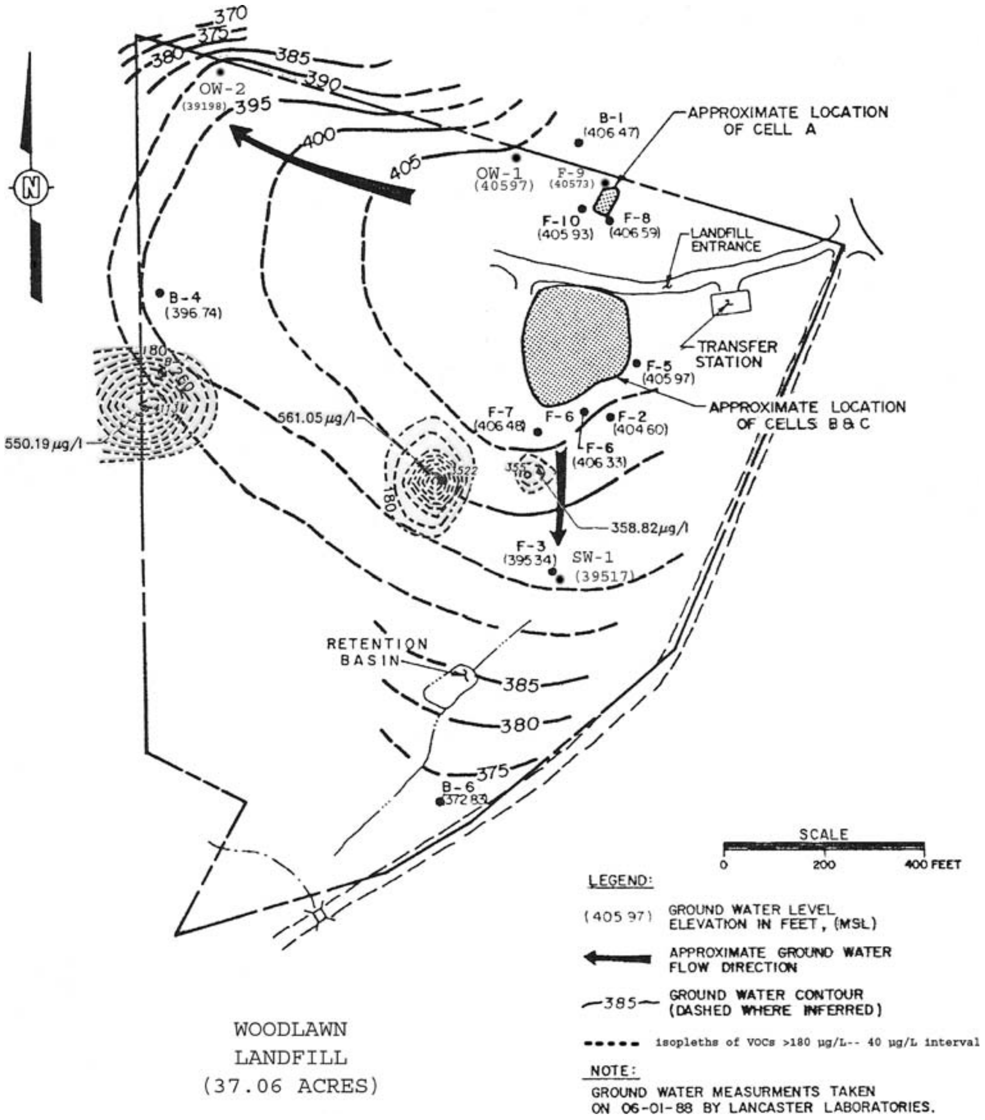


Fig. 1 Woodlawn Landfill Superfund Site, Cecil County, MD

Site history

The US Environmental Protection Agency (EPA) added the Woodlawn landfill to the National Priorities List (NPL, Superfund) in 1987 (Fig. 1). From 1960 to 1981, Bridgestone/Firestone (B/F) had disposed of polyvinyl chloride (PVC) sludge wastes that contained residual vinyl chloride monomer (VCM) in the landfill. The disposal was permitted by the State of Maryland; but in 1988, B/F and the County (site owner) became legally responsible for investigations and remediation of site contaminants, including VCM a known human carcinogen.

The remedial investigation (RI) and feasibility study (FS) were undertaken between 1987 and 1993 (IT 1992 and 1993). During the RI investigations, historical analytical records were compiled (IT 1989) and used in planning the installation of additional monitoring wells. These data were added to new data obtained during the RI. EPA issued a record of decision (ROD) in 1993 that included requirements for a pump-and-treat cleanup of ground water with estimated costs exceeding 12 million U.S. dollars ($) (US EPA 1993). Six years later, however, a ROD amendment allowed for natural attenuation of VCM without treatment but with continued monitoring, at a revised cost of about $6 million (US EPA 1998).

Natural attenuation can be adopted as a cleanup alternative to ground water treatment if site cleanup objectives can be achieved in a reasonable time (US EPA 1998). Natural attenuation is achieved without human intervention through biodegradation, dispersion, sorption, volatilization, stabilization, and recharge dilution.

At the time of the original ROD for this site (1993), cleanup objectives for VCM and other site contaminants in the ground water were not considered achievable with natural attenuation in a reasonable period of time. Detection of VCM in offsite wells to the northeast suggested that ground water flow was faster than modeling predicted, perhaps because of the local presence of linear fracture zones. Furthermore, several wells showed upward trends in VCM concentrations.

Later site-specific studies by Geraghty and Miller (1998), however, concluded that iron-reducing bacteria and reductive dechlorination would reduce the VCM concentration to 1 ppb in 15 years without groundwater treatment. Mandated, continuing monitoring of the contaminant concentrations (US EPA 1999) is being used by the authors of this paper to test this prediction.

After more than 18 years of study, this Superfund site is not slated for any aquifer remediation and is being, instead, reclassified as a ‘‘wildlife conservation area.’’

Site hydrogeology

The study area under investigation is a rural site that occupies 15 ha in the Appalachian piedmont. Ground water beneath the site is present in a local unconfined aquifer contained in two geologic units: unconsolidated sediments and fractured bedrock. The unconsolidated sediments consist of approximately 10 m of residual sandy–clay–loam and sand and gravel terrace deposits. The unconsolidated deposits overlie the crystalline, fractured bedrock (e.g., granitoid gneiss and metadiorite). The water table generally lies near the base of the unconsolidated deposits. The aquifer is mainly recharged by direct infiltration of rainfall and snowmelt.

Ground-water flow is to the south, except at the northern edge of the site where flow is to the northwest (Fig. 1). Slug tests (IT 1992) indicated that the hydraulic conductivity in the unconsolidated portion of the aquifer is 8.6E-5 to 2.8E-4 cm/s and in the bedrock, the fractured portion of the aquifer, is 2.7E-5 to 1.4E-2 cm/s. Step-drawdown aquifer tests (Geraghty and Miller 1998) indicated that the hydraulic conductivity in the unconsolidated portion is 3.2E-4 to 6.4E-4 cm/s and in the bedrock is 1.0E-4 cm/s to 1.7E-3 cm/s. In both tests, the hydraulic conductivity of the unconsolidated sediments was low (E-3 to E-5 cm/s) due to the presence of clay. The hydraulic conductivity of the bedrock was medium (E-1 to E-3 cm/s) to low (E-3 to E-5 cm/s)**,** depending on the degree of fracturing. Hydraulic gradients at the site range from almost zero (at a ground-water divide) to about 0.05.

Site model

Vinyl chloride concentrations from monitoring-wells indicate the extent of contamination of ground water from PVC-sludge wastes. Rain water and melted snow that infiltrated through contaminated soils and rock fractures flushed leachate into ground water aquifers. This process may be continuing to the present day.

Two possible scenarios explain increases and decreases in VCM concentrations over time (Fig. 2).

If the infiltration waters do not encounter VCM buried wastes or contaminated soil and rock, then the vinyl chloride concentrations in the aquifers decrease (by dilution). This could be the situation if all wastes have been flushed away or if the infiltration is up- or down-gradient from existing waste or contaminated soil and rock. For the moment, it is assumed that vinyl chloride is not degrading into or being formed from other chemicals within the aquifer. Decrease of vinyl chloride concentrations can also occur if vinyl chloride degrades (in an oxidizing environment) into hydrochloric acid, carbon dioxide, and water.

If the infiltration waters encounter VCM buried wastes or contaminated soil and rock, then the vinyl chloride concentrations in the aquifers increase. An increase in VCM concentration can also occur if other chemicals, such as trichloroethene (TCE) and perchloroethene (PCE), which are present, degrade into vinyl chloride (in a reducing environment).

Assuming no chemical production or degradation of vinyl chloride, the VCM concentration profile over time is an indication of the presence of waste residuals in the soil and bedrock near and up-gradient from the monitoring well in question.

VCM contamination

Polyvinyl chloride sludge was disposed of with other wastes at various times and places on site. In the 1980s, VCM was detected in monitoring wells adjacent to the waste at concentrations three orders of magnitude above drinking water standards (MCL) of 2 ppb and 4 to 5 orders of magnitude above risk-based human health goals of 0.02 ppb. The current MCL for vinyl chloride, now 1 ppb, is still orders of magnitude below actual levels.

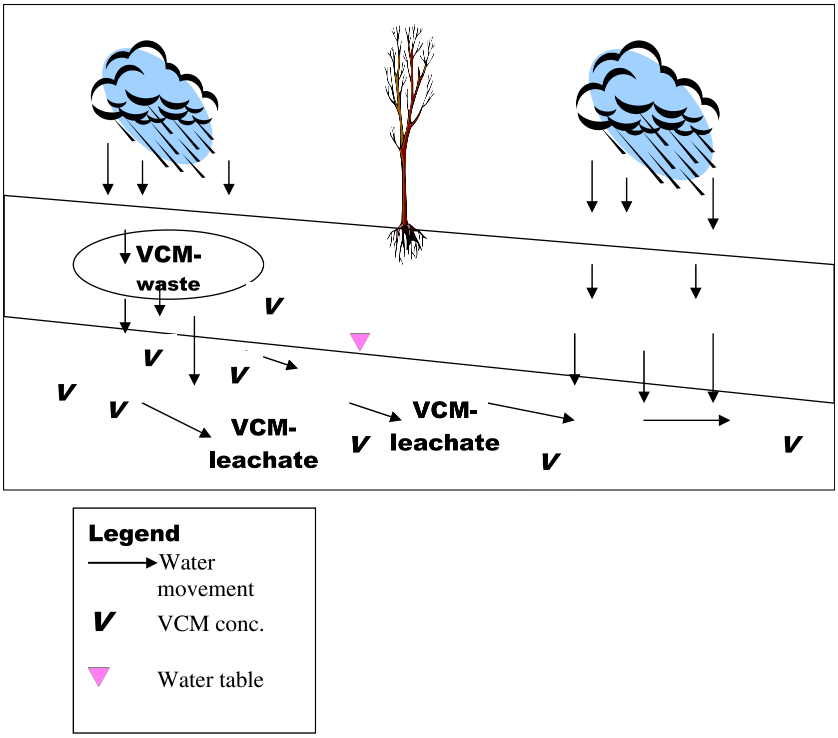


Fig. 2 Site ground water model

The sources of VCM can come from the PVC sludge, but also from breakdown products of other chlorinated hydrocarbon precursors, such as PCE, TCE, and dichloroethene (DCE). These VCM precursors were known to be disposed of at the site from various waste generators.

Vinyl chloride monomer concentrations in site ground water are affected by the following variable factors:

1. Placement of wastes in different areas of the entire site over a long period of time (spanning 1960–1981)
2. Percentage of VCM (unpolymerized PVC residues) in each waste area
3. Different mixtures of wastes
4. Additions of VCM from breakdown of PCE, TCE, and DCE
5. Different rates of leachate production and infiltration
6. Different natural attenuation rates of VCM through dilution, dispersion, volatilization, biodegradation, etc., in the vicinity of each well
7. Different physio-chemical factors affecting natural attenuation rates (dissolved oxygen, organic content, pH, etc.) in the unconsolidated and the bedrock portion of the aquifer in the vicinity of each well
8. Erratic flow rates from fracture zones in the bedrock, and
9. Continual influx of residual VCM from hot spots of waste in the subsurface.

Quantification of these factors through field measurements has not been adequately performed and may not be achievable. Such tasks may not be cost effective. For computer modeling, some of these factors were estimated or assumed to be negligible and indirectly evaluated with the use of sensitivity analyses. These factors, however, are real and very important to the resulting predictions used to protect human health and the environment. A more objective approach would be to rely on frequent monitoring and be guided by observed concentrations over time, which is the approach adopted in this study.

Discussion

VCM trends 1981–2000

Jacobs (2001) presented trend curves of VCM from data obtained during the period 1981–1991. VCM concentrations (1982–1991) from each of the existing site wells (IT 1989 and 1992) were documented during the RI. Subsequent to the RI, VCM concentrations from on-site wells have been monitored since 1991 as required by the US EPA. All these data are part of the Administrative Record and available to the public through the Freedom of Information Act (FIOA).

These data show that some of the most contaminated wells fluctuate in cycles. Furthermore, the concentrations in wells in 2000 were still the same orders of magnitude above MCLs and risk-based health goals as they were in 1991.

Vinyl chloride monomer trends from wells F-2, F-3, F-5, and B-4 are presented here (Figs. 3, 4, 5, and 6). Well B-4, in the western part of the site has had no detection of VCM since early 1996. Wells F-2, F-3, and F-5, in the eastern part of the site, have significant concentrations of VCM since 1995 and were on the rise. There are no post-1991 data from wells F-7 and B-1; these wells were decommissioned, no longer exist, and have been excluded from the present study.

Vinyl chloride monomer concentrations (Fig. 3) in well F-2 had reached their highest levels since monitoring at 250 ppb in 1991. Since then they have cycled lower, reaching a plateau at 149 ppb from February 1993 to January 1994. Then they decreased significantly to 27 ppb in November 1995, increased to 68 ppb in late 1996, and decreased to 46 ppb in March 1997. Then in late 1997 VCM increased to 208 ppb, which re-established 1987 levels.

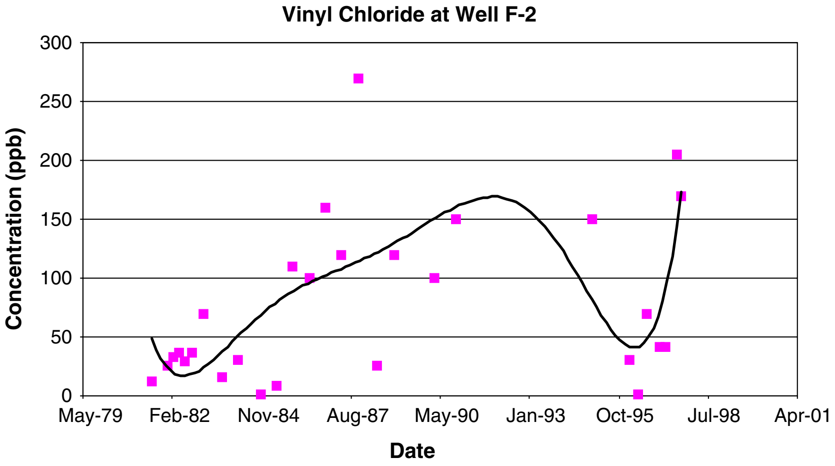
Vinyl chloride monomer concentrations in well F-3 (Fig. 4) from 1982 to 1991 were first measured at 4 ppb and decreased to less than 5 ppb in 1985 through 1990. Also between 1985 and 1990, VCM was frequently not detected (at a 1 ppb detection limit). Then in 1991 the concentration increased to 7.2 ppb. Since 1991, it decreased to 6 ppb in February 1993 and then increased to 15 ppb in January 1994. It decreased to 12 ppb in March 1997 and then jumped to 20 ppb (more than four times the 1982 concentration) later that year. At the beginning of 1998 the concentration was 12 ppb, equal to three times the 1983 concentrations. In summary, VCM in F-3 showed low or non-detect values from 1984 to 1990. However, since 1990, concentrations greatly exceeded pre-1984 values and exhibited more cyclicity than pre-1991 values.

Vinyl chloride monomer concentrations at well F-5 (Fig. 5) were very low or not detected until 1986 when they increased dramatically, peaking in 1990 at 160 ppb. As of the end of 1991, the concentration was 120 ppb, less than its peak values. When next seen in February 1993, VCM concentrations were 56 ppb and decreased subsequently to 34 ppb by November 1995. Then they cycled back up to 56 ppb and were 42 ppb when last sampled in 2000. In summary, the 1990 peak was not duplicated since then, but the concentrations have lately cycled around 1987 levels.

Vinyl chloride monomer concentrations in well B-4 (Fig. 6) from 1982 to 1991 were first measured at 20 ppb in February 1982 and decreased to less than 5 ppb in 1985 through 1990 and were on the rise in 1991. They increased to 10 ppb in February 1993 and then decreased to 1.6 ppb in November 1995 where they remained through 2000. Although data from year 2000 were detected at low levels, the 1991–2000 peaks at values more than twice the initial readings indicate that cyclicity is still the norm.

The wells that indicate a continued presence of significant VCM contaminations in the year 2000 include: F-2, 3, and 5. All these wells are on the east side of the site. The previous peak in VCM concentration occurred in about 1993 (7 years before 2000) in these wells and in many wells down gradient on the west and in the central part of the site. If this trend repeats itself, the wells in the down-gradient direction (west and central) should bear watching for a peak rise in contamination 7 years later, i.e., in the year 2007.

Fig. 3 Plot of VCM concentration (ppb) and trend line in well F-2



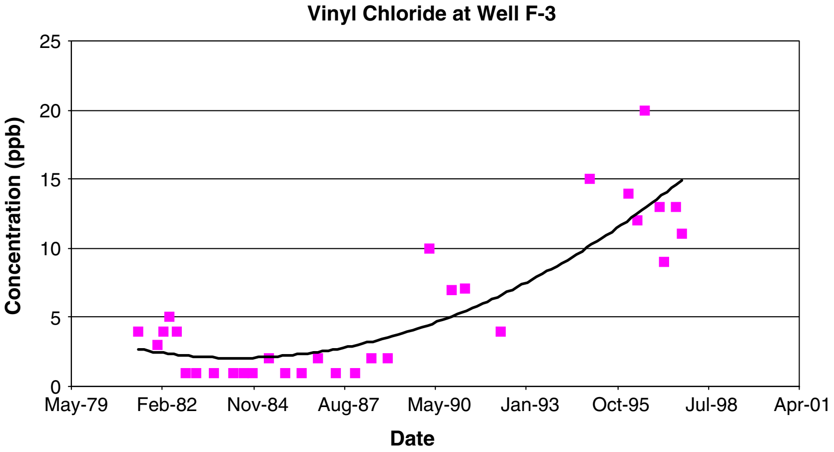


Fig. 4 Plot of vinyl chloride concentration (ppb) and trend line at well F-3

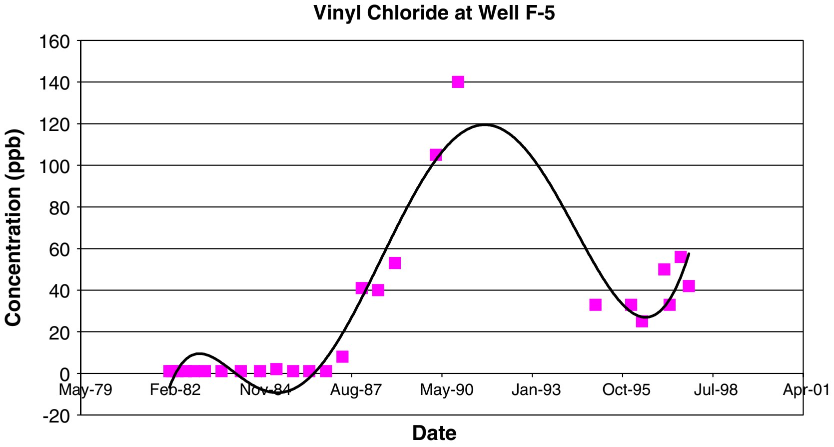


Fig. 5 Plot of vinyl chloride concentration (ppb) and trend line at well F-5

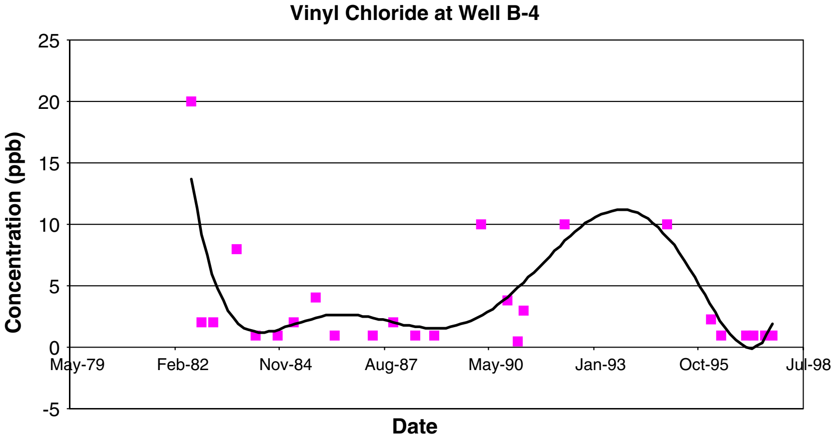


Fig. 6 Plot of vinyl chloride concentration (ppb) and trend line in well B-4

Possible source areas and environmental pathways

The remedial investigation phase I work (non-invasive testing) included a soil–gas survey that had unexpected results. Hot spots of total volatile organics were not at Cells A and B/C (Fig. 1), as expected, but rather in other areas on the landfill site. These hot spots indicate the areas of waste and potential leachate generation points. The hot spots were at the western boundary and south of Cells B/C.

The hot spot originally noted in the soil–gas survey at the western edge of the site bears watching. Barry

Belford, Cecil County Engineer (retired) (personal communication 1989) related his recollection of a truck of PVC sludge backing up to the edge of the western boundary of the site (at the location of the soil-gas hot spot) to dump its permitted load in the early 1980s. The monitoring wells in this area should record contamination coming from the eastern part of the site; they are down gradient from the eastern part of the site. Waste at the western boundary should affect wells to the west of the site (also down gradient), indicated by water analyses at wells at residences.

Pathways of ground water and contaminant transport in the subsurface include mostly vertical downward movement in the vadose zone, lateral movement along the water table in the unconsolidated portion of the aquifer, and movement along fractures in the crystalline bedrock portion of the aquifer. Therefore, granular porous media flow and fracture flow characterize contaminant transport mechanisms at the site.

Using modeling to predict future VCM concentrations with the assumptions in the Geraghty and Miller or IT computer simulations at this site led to incorrect predictions. Clearly the assumptions were too simplistic to account for the complexity of the ground-water flow system (fracture-granular porous media) and the heterogeneity of the waste sources at the site.

Reasons for cyclicity

Leachate production is generated by infiltration of precipitation (rain and snow melt) through the waste. After contaminants are dissolved or washed downward to the saturated zone, they add to the existing presence of contaminants and increase their concentrations. Following precipitation events, infiltration at waste locations can increase the generation of leachate. The addition of groundwater and contaminants to the pore spaces of the vadose zone will not immediately force groundwater and contaminants into the aquifer below. The vadose zone creates a reservoir of leachate in pore spaces. Flushed by additional infiltration, contaminants can later migrate into the aquifer.

Vinyl chloride monomer concentrations decrease in dilution as ground-water level rises and increase in concentration as ground-water level drops. Dilution/concentration explains in part the cyclicity in VCM concentrations in ground water at the site. In addition to the dilution/concentration mechanism, VCM concentration at a well also depends on whether a plume from one of the many waste sources (hot spots) at the site has passed by that well or not. Obviously, VCM concentration will decrease in the absence of supply from a plume independently of ground-water level fluctuations. This situation is observed when precipitation is lacking at the site. In this case, (1) no plume(s) will be generated, as flushing of VCM into the subsurface will not be possible, and (2) the ground-water levels will drop due to the lack of precipitation. Therefore, the lack of precipitation will result in lowering of ground-water levels and VCM concentrations. The data of ground-water levels and VCM concentrations at wells F-2, F-3, and F-5 that were evaluated in this study are only those that are measured at the same time period (1996–1997). During this period, well B-4 showed a constant VCM concentration of 1 ppb, which is below the drinking water standard (MCL) of 2 ppb. No correlation of VCM concentration and ground-water level fluctuations is possible at B-4; the VCM concentration reported is the detection limit, and fluctuations below the detection limit could not be measured.

Conclusions

The cyclic nature of VCM concentrations in wells on the Woodlawn landfill site has continued to the year 2000, and may still persist. Leachate was still being generated at hot spots where PVC sludge was placed (planned and indiscriminately dumped). In the year 2000, ten on-site wells still showed increasing VCM concentrations. Site complexities preclude the prediction from computer simulation of the success of natural attenuation of VCM. As mandated by the USEPA, monitoring is continuing for wells on site and in residential wells in the vicinity. As VCM still poses health risks at very low levels (greater than 0.2 ppb), human consumption of ground water adjacent and down gradient from the site should not be permitted.

Acknowledgments The authors wish to thank Mr. Anthony Iacobone, EPA Region III Remedial Project Manager in providing site ground water monitoring data.

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