ESTIMATING TIME TO ACHIEVE GROUNDWATER PROTECTION STANDARDS USING EXPONENTIAL DECLINE PLOTS

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Abstract. Groundwater concentrations tend to decline exponentially over time and distance due to natural attenuation or remedial actions. Exponential decline plots make use of existing data to empirically predict the time or distance to achieve groundwater protection standards and can be used in lieu of numerical modeling where there is a large amount of historical groundwater monitoring data for the site.

INTRODUCTION

Estimating the time to achieve groundwater protection standards (GWPS) is a necessary part of evaluating corrective measures around municipal solid waste (MSW) landfills where groundwater contamination is present. This paper describes an empirical method for estimating this length of time. The method consists of applying an exponential decline model to existing groundwater monitoring data. The method works when concentrations are already in decline through natural attenuation or active remediation.

CONTAMINATION IN MSW

Hazardous substances are typically dispersed throughout a large mass of MSW and tend to be absorbed into the waste. When water percolates through the waste, the hazardous substances can be leached out. Groundwater contamination can result if the leachate passes into the groundwater. When landfill gas is generated, highly volatile substances can be leached by the gas or can be generated through reaction with methane. Once landfill gas leaves the warmth of the waste cell, heavier substances can condense and contaminate the groundwater.

Concentrations in leachate tend to decline over time as the hazardous substances in the waste are depleted. Concentrations within the waste can also decline by biodegradation, dechlorination, and other processes. It is not necessary to know the specific reasons for this decline, but only to know that it can be observed to occur.

Concentrations in landfill gas are more likely to be at a steady state level, with the concentration controlled by the rate of landfill gas production. This means that groundwater contamination originating from landfill gas is not as likely to decline over time until gas production itself finally declines. Gas-related contamination is likely, however, to decline over distance. The causes of the distance decline are the same as decline over time. Again, it is not necessary to know the specific reasons for declining concentrations, but only to observe them through historical groundwater monitoring data.

MATHEMATICAL TREATMENT

Contaminant concentrations tend to decline as multiples, or percentages, of themselves. The amount of contaminant lost each day is a percentage of the concentration on that day. Even though the percentage rate remains constant, the amount of contamination lost is less each day because the starting value is less each day. The same applies per year or per minute, except that the percentage rate will change accordingly.

A relationship that varies as a percentage of itself takes the form of an exponential function:

$$C_t = C_o A^t \qquad \text{Eq. 1}$$

which, by the rules of logarithms, is equal to both

$$\log(C_t) = t \log(A) + \log(C_o) \qquad \text{Eq. 2}$$

$$\log(C_t/C_0) = t \log(A) \qquad \text{Eq. 3}$$

where C_t is the concentration at time t, C_o is the initial concentration, and $\log(A)$ is the slope of the exponential decline curve.

Equation 2 is useful if the data is first converted to log concentrations and then plotted on a graph with standard linear axes. Equation 2 is the equation for a line of the form $y = mx + b$, where t is x and the slope m is $\log(A)$. Equation 3 is better if the raw data is plotted directly on a semi-log plot, where the vertical axis has the log scale and represents concentration.

The units of the equations and the graphs are best explained using Equation 3. The horizontal axis is time (t) and can be in any convenient unit, such as years or months. The vertical axis is dimensionless because the units of concentration cancel out in the ratio C_t/C_0. This leaves the slope, log(A), in units of "per year" or "per month," depending on the units chosen for time.

The mathematics described above also applies for decline over distance. The only difference is that time t is replaced by distance x. The horizontal axis becomes the distance and slope is in units of "per meter" or "per foot."

DECHLORINATING COMPOUNDS

Certain hazardous substances go through chemical degradation processes that produce daughter compounds that are also hazardous. A good example is the dechlorination series from tetrachloroethene (PCE) to trichloroethene (TCE) to cis 1,2-dichloroethene (DCE) to vinyl chloride (VC) to ethene. Of the five, VC has the lowest GWPS (2µg/L) and ethene is not a hazardous substance.

These reactions occur at certain rates when the geochemical conditions are right. The conditions are nearly always right within an MSW landfill cell and are right in many cases downgradient from MSW landfills. The fact that the daughter products DCE and VC exist is sufficient evidence to know that these reactions are occurring. PCE and TCE are very common solvents found in MSW. Neither DCE nor VC should normally be found in an MSW waste stream.

These dechlorination reactions can cause the daughter products to increase in concentration for a time. For example, if TCE is degrading to DCE, then the concentration of TCE will decline through normal decline plus through degradation. However, DCE will increase as TCE degrades, but also have a normal decline of its own. If TCE degrades to DCE faster than DCE declines on its own, then the concentration of DCE will increase, even though the total amount of contamination is decreasing. This problem can be solved by considering the molar concentrations instead of the mass concentrations.

One mole of a substance is 6.02×10^{23} molecules. The mass of one mole is that number times the molecular weight of the compound. When TCE degrades to DCE, the mass decreases because one chlorine atom is released. The number of moles does not decrease, however, since one molecule of TCE produces one molecule of DCE.

The total decline for the series PCE to TCE to DCE to VC can be estimated by calculating the number of moles per liter for each, and then adding all the moles together. The resulting plot will show the decline rate for the system. Decline will be caused by the reasons given previously, plus the conversion of hazardous VC to non-hazardous ethene.

The maximum time to reach GWPS can be estimated by assuming that all moles are VC and then using the molar equivalent of the GWPS for VC. This approach is very conservative, because some of the moles will still be DCE, TCE, or PCE, and therefore counted separately when looking at GWPS.

DECLINE PLOTS

Figure 1 is an example of an exponential decline plot. The estimated time to achieve GWPS occurs where the decline model (sloping line) intersects the GWPS. The horizontal axis is years from present. The vertical axis is the total of PCE + TCE + DCE + VC in micromoles per liter.

The line can be fit visually or fit using least-squares methods. If least squares methods are used, then the concentration data needs to be converted to logarithms first and then plotted on a standard linear graph using Equation 2. In either case, hydrogeological judgment must be used in selecting which points are representative of the standard decline and which points are anomalies.

The plot contains points that plot above the decline model and below the decline model. These anomalies are caused by external changes that affect the groundwater flow system. The points that plot above the line at "A" on the graph were collected following the excessive rainfall that occurred in 2003. The points that plot below the line at "B" on the graph were collected following the severe droughts of 2000 and 2002. Over the long term, however, the overall trend is rather consistent.

Other external factors can also complicate the plots, such as installation of a landfill cap or a gas recovery system. It should be noted that the factors that complicate a decline plot will also complicate other methods of

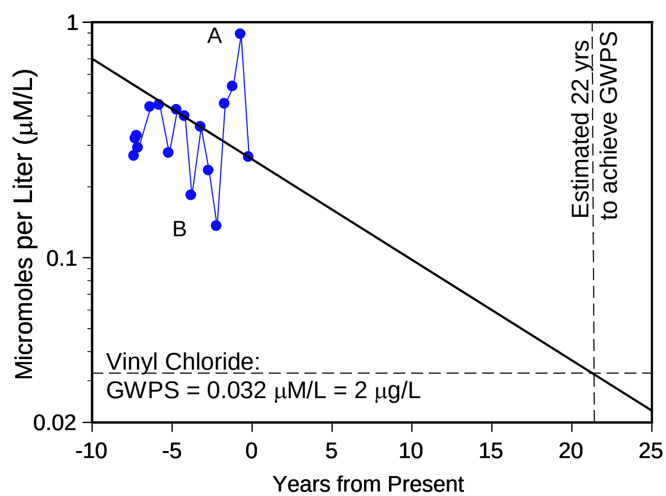

Figure 1. Exponential Decline Plot.

estimating time to achieve GWPS, such as numerical fate and transport modeling.

The GWPS used in Figure 1 is the GWPS for vinyl chloride (VC). The regulatory GWPS for vinyl chloride is 2 µg/L, which is equivalent to 0.032 micromoles of vinyl chloride per liter. Vinyl chloride was chosen because it has the lowest GWPS among PCE, TCE, DCE, and VC. This approach is very conservative because it assumes that all PCE, TCE, and VC will be converted to vinyl chloride in 22 years. It is more likely that there will be residual concentrations of PCE, TCE, and DCE that are below the detection limit or below their respective GWPS's. When these residual concentrations are subtracted from the total molar concentration, the actual amount of vinyl chloride will be less than predicted by the decline plot. Since GWPS are based on concentrations of individual constituents, not on the whole mix, GWPS for each constituent are likely to be achieved sooner than predicted by the decline plot.

Detection limits also affect exponential decline plots. When the concentration of an individual chemical reaches its detection limit, it will suddenly disappear from the calculations of total molar volume. This will cause the data points to deviate downward from the straight line as the concentrations become low. Likewise, if the concentrations are already low, and a constituent suddenly appears just above its detection limit, it can cause a large jump in concentrations. Some of the jumps in Figure 1 were caused in part by the appearance and disappearance of PCE near its detection limit.

CONCLUSIONS

Time to reach GWPS can be estimated empirically using existing groundwater monitoring data. This approach does not require developing complex numerical models. It does not require the user to estimate various attenuation factors or conduct special tests. Reliance on existing data makes this method robust, especially where there is several years or more of monitoring history. Points that plot off the decline model need to be handled with patience, with the realization that groundwater flow systems cycle through periods of drought and excessive rainfall.