THE CLEANUP OF CHEMICAL WASTE SITES -

A RATIONAL APPROACH

Charles A. Staples and Richard A. Kimerle

Monsanto Co., St. Louis, Missouri

ABSTRACT

A conceptual hazard assessment design is presented here for addressing waste site cleanup. Three main steps to be carried out in an evaluation of any potential waste site include, identification of potential chemical exposure, assessment of that exposure in relation to established 'safe' concentrations, and control measures to remediate the exposure. Hazard assessment techniques are used to establish the appropriate 'how clean is clean enough' endpoints based on calculated margins of safety (MS), where MS = toxicologically safe concentration/exposure concentration. A successful remedial action endpoint is achieved when the targeted exposure reduction action results in a margin of safety that is greater than 1.0 (MS > 1.0) including the uncertainty of the estimate. This assessment program is carried out in a cost effective step by step tiered approach to guide selection of a remediation endpoint.

INTRODUCTION

There are estimated to be well over 20,000 solid and contained liquid waste sites (both legal and illegal) in the U.S. (1-3). Many of the sites have been abandoned and are perceived as or are known to be sources of chemical contamination. Costs for cleanup of these sites has been estimated at up to $10-20 billion. The 1984 RCRA amendments (4) are forcing review of current waste disposal practices and are geared towards prevention and reduction of future problems from hazardous waste facilities. The 1980 'Superfund' Law is aimed at cleaning up those past sites which are or may threaten human health and the environment. Technically sound, cost effective approaches are needed to determine 'how clean is clean' for remedial or corrective action under both programs. A hazard assessment based approach is presented here to utilize rational decision making in addressing the cleanup of any contaminated site. The hazard assessment approach suggested here addressed the critical issue of how extensive the remedial practices must be to protect the ecosystem and humans from exposure to toxic chemicals (5).

How Clean Is Clean?

A key factor in any remedial action program must be the establishment of a justifiable endpoint which is established by answering 'how clean is clean?'. This endpoint is a reduction in the concentration of the chemical(s) to a point where no adverse impact is expected to man or the environment now or in the future. The factors that affect the establishment of the target performance standard include subsurface or surface hydrology, chemical fate and transport properties and toxicological characteristics.

The answer to, 'how clean is clean?' is indeed complex. All aspects of a problem resolution scheme must take part (Figure 1). The potential problem must be identified in terms of what compound(s) or groups of compounds are present. The levels of these compounds must be quantified. This is to be followed by a comprehensive assessment. The assessment addresses both chemical exposure and chemical effects in a rational manner. Both short and long term exposures and effects are addressed. This assessment process allows the thorough understanding of the implications of the exposure. The general formula for addressing both exposure and effects together also considers uncertainty of exposure calculations (equation 1).

$$\text{Margin of Safety (MS)} = \frac{\text{Safe Concentration}}{(\text{Exposure Conc.})(\text{Uncertainty})} \qquad (1)$$

We will assume that a safe concentration can be established for a particular exposure scenario. A margin of safety, then, is a function of the measured exposure concentration and the uncertainty or variability that exists in the exposure determination. The exposure concentration is unacceptably high when the MS is less than 1.0 (6) An exposure concentration is desired that causes the MS to exceed 1.0. Assessment, then is the coupling of chemical exposure concentrations (whether measured or predicted) with the toxicologically safe concentrations that is appropriate for the exposure scenario (figure 2). This type of assessment guides the choice and development of control actions and provides an iterative review of post-remedial action results. The site is 'clean' when these processes are complete and margin of safeties are scientifically judged to be adequate.

Decision-making Steps for Cleanup at Waste Sites

Cleanup of any waste site may be carried out in a stepwise fashion as described in Figure 3 and Table 1 The steps required include both decision points and more complex activity steps Moving through the described decision-making process represented in the simple flowchart results in a rational stepwise approach to correctly ascertaining the necessary extent of remediation of an identified waste site problem

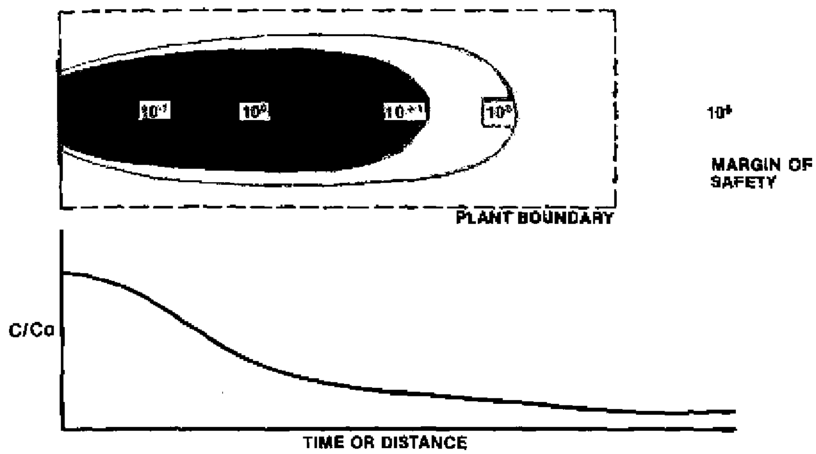

Figure 1

Predicted Concentrations and Margins of Safety

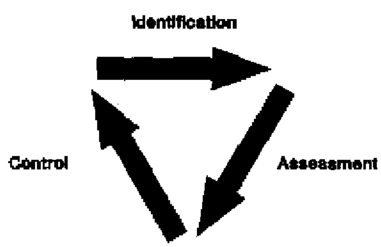

Figure 2

The Cycle of Problem Solving

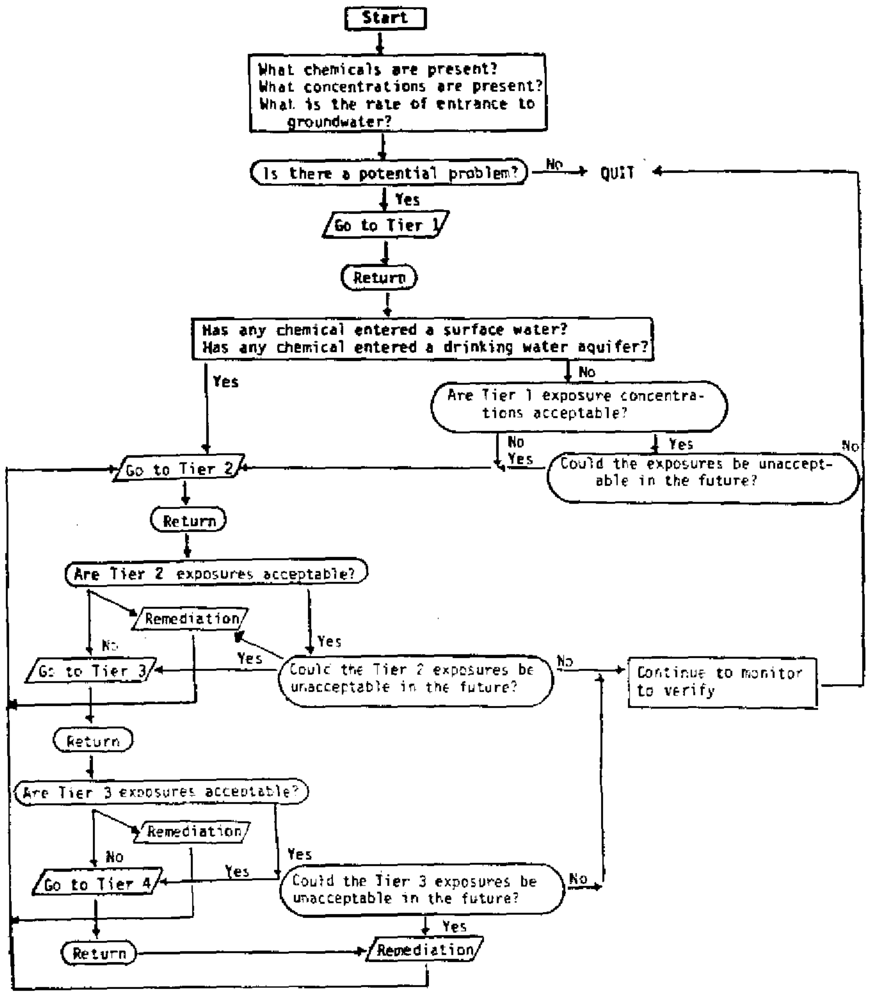

Figure 3

Decision Pathway for Evaluation of Potential Waste Site Problems

Table 1

Summary of Risk Results and Research Recommendations from a Hypothetical Million BPD Oil Shale Fuel Cycle

Tier	Data Requirements	Cost	Uncertainty of Exposure Calc.	Required Exposure: Conc. = $\frac{\text{Safe Conc.}}{(\text{MS})(\text{Uncertainty})}$
I	• Monitoring onsite • General site geology & characteristics • ADI's and/or Screening Toxicology Tests • Simple one dimensional modeling	$	LARGE $(10^0 - 10^5)$	10^{-5}
II	• Monitoring (con't) • Leachate rate or source loading rate • Hydrologic characteristics • 2 dimensional solute transport in groundwater or surface waters • ADI's	$$	MEDIUM $(10^0 - 10^3)$	10^{-3}
III	• Offsite (if needed) hydrologic data • Offsite monitoring (if needed) • 2-3 dimensional solute transport modeling • Sorption, biodegradation, hydrolysis rates • Toxicity data for complex mixtures • ADI's	$$$	SMALL $(10^0 - 10^1)$	10^{-1}
IV	• Complete field chemical analyses (spatial & temporal) • ADI's for all constituents	$$ to $$$$	ONE (10^0)	10^{-0}

* $MS = \frac{\text{Safe}}{\text{Exposure}}$, MS ≥ 1.0 is required so rearranging allows calculation of maximum allowable exposure:

Exposure = Safe/(MS)(Uncertainty)

Four main assumptions are considered here. First, the existence of contamination substantial enough to be of potential concern has been established. Second, the source is considered sufficiently large such that the problem will not rapidly correct itself. Third, an acceptable safe concentration has been or can be established for the chemicals of concern. Fourth, when safe concentration is used a margin of safety (MS) in excess of 1.0 is an appropriate 'clean' target. The concept of a safe level is used by EPA and others in an attempt to establish safe chemical concentrations for the protection of human life and the environment (7). The use of the term safe concentration in this paper directly assumes that an acceptable or safe concentration can be correctly established. The exact technical procedures for establishment of safe or acceptable levels of exposure are not an issue here.

Beginning with Figure 3, the first steps for the site evaluation include ascertaining the scope of the problem. The main emphases are 'what chemicals are found where and in what concentrations?' This is followed by determination of approximate rates of continued chemical input from the source. Rapid or catastrophic release of chemicals to groundwater would call for a different response than a slow leaching of a source. The leaching could, for example, be defined by the Toxicity Characteristic Leaching Procedure (TCLP) being developed by EPA. These data provide definition of the contaminants at the waste site. Then, the following question is asked: Does this preliminary data suggest any potential problems? If not, one ends the investigation. If potential problems are indicated, a Tier 1 assessment (Table 1) is carried out to estimate the existing exposure concentrations.

Tier 1 Assessment

Tier 1 assessments include continued monitoring of chemicals at the site as well as conducting a hydrogeologic evaluation of the site. Identified compounds would have a 'safe' concentration determined. The safe concentration must be selected with regard to the existing and future exposure scenarios.

Determining the correct exposure scenario is critical. Chronic toxicity requires chronic exposure. Carcinogenicity requires lifetime (70 years) exposures. Long term exposures must be considered possible if the source is very large and is essentially considered infinite. However, if a contaminated aquifer is not a drinking water aquifer (it may be saline, for example), application of a carcinogenic endpoint may be inappropriate. Discharge of the chemical into a surface water body from such a saline aquifer would then alter the useful endpoint to perhaps a site specific water quality criteria. It is therefore possible to require different endpoints for the different aspects of the exposure scenario. Initial analytical data plus site hydrogeologic characteristics can then be coupled with simple one dimensional modeling to yield short and long term chemical exposure estimates. Necessary exposures (that result in MS > 1.0) can then be calculated based on the safe concentration, required margin of safety and the related uncertainty (eq. 1). At this point, return to the flow chart (Figure 3).

More specific data concerning leaching rates, transport times (which take into account appropriate chemical for the processes) and exposure estimations with lower uncertainty would be required if the chemical(s) have entered either a drinking water aquifer or surface water body from subsurface flow. No further testing would be required if drinking water supplied were not in the chemical flow path and Tier 1 exposures were acceptable. If the exposures are unacceptable than Tier 2 assessment is required.

Tier 2 Assessment

Tier 2 assessments focus on improvement of understanding of existing and future chemical exposure, fate and transport. Existing chemical exposure is further evaluated by additional chemical measurements made both spatially and temporally. These measurements may require more monitoring wells and an expanded site based on the results of Tier 1 assessments. Additionally, a leachate rate (from TCLP) should be generated if deemed necessary and not already accomplished. Additional hydrogeologic parameters required for exposure analysis that may not be known or are needed for 1 dimensional solute transport modeling, should be generated. Properly calibrated 2 dimensional models can generate exposure concentrations with less uncertainty than 1 dimensional models. A lesser gap between exposure concentrations and uncertainty factors is allowed with the Tier 2 efforts, while still achieving a MS > 1.0.

Upon return to Figure 3, judgment of Tier 2 exposure predictions are made. Acceptable MS's (MS > 1.0), coupled with continued monitoring for verification purposes allow the site investigation to move to completion. Unacceptable MS's require moving to Tier 3 or carrying out remediation.

Tier 3 Assessment

Tier 3 assessments may require offsite (i.e. expanded beyond original natural site boundaries) hydrogeologic data to be determined. Many solute transport models carry assumptions of homogeneity and isotropy. These assumptions are often valid for short distances or areas but usually become unsupportable with greater distances from a source. Variability over a site of transmissivities, conductivities and dispersivities can lead to unacceptable uncertainty factors. Therefore, improvement of future chemical exposures may require more extensive and costly data. Existing analytical data may not fully describe chemical transported beyond initial discovery (Tier 1 and 2) efforts. This may be especially important if deeper aquifers are potentially impacted.

These more extensive data collection efforts are coupled with estimated or measured chemical equilibrium and decay processes for key individual compounds. These loss (sink) mechanisms become increasingly important as greater exposure prediction accuracy is required. In place of toxicological data that may not be available, 'safe' toxicologic endpoints may have to be established for the complex mixtures of compounds that may exist (8-10). These tests may include acute tests (plant root elongation, algal assays, Ceriodaphnia mortality) or chronic tests (earthworm growth or Ceriodaphnia reproduction that are currently being evaluated by EPA). New exposure concentrations can be determined for each set of new data, modeling predictions and their uncertainty factors. More comprehensive data sets obtained under Tier 3 guidelines (chemical and hydrogeologic data) should reduce uncertainty related to predicted exposure concentrations from that of Tiers 1 and 2. The allowed exposure concentration to achieve MS > 1.0 would be greater by an equivalent margin.

Tier 4 Assessment

Complete field chemical analyses would be required (spatially and temporally) throughout the entire site if Tier 3 exposure values are considered inadequate to guide remedial actions. Many more monitoring points (than with Tier 1 to 3) would be needed to analytically describe a chemical waste site fully 3 dimensionally. Costs could become prohibitive relative to possible remedial practices.

Decision points for remedial action can occur at any of the return points in Figure 3 from Table 1. A remediation is selected that will obtain a particular tier's required exposure concentration yielding MS > 1.0. If the remediation is judged to be excessive in either cost or scope then the next tier assessment is conducted. Determination of the necessity, extent and specifics of remediation at any site must be carried out using these assessment procedures. Data requirements may include chemical specific parameters such as soil partitioning, degradation rates, aqueous solubility and aquifer characteristics such as permeabilities, gradients, densities, direction of flows and storage. Needed toxicological data, if absent, may include aquatic acute and chronic tests and mammalian chronic studies. Obtaining these data may become expensive should the scale of the site be large. However, control of chemical exposure without sufficient assessment could result in gross over-expenditures far in excess of assessment costs.

Identifying appropriate remedial actions to address the various affected regions is the next step to carry out. Possible remedial actions of groundwater contamination are many in number. Various categories range from simple water withdrawal to walls or trenches to divert groundwater flow to complete removal of contaminated aquifer material. The specific actions taken must reflect both the desired goal of reducing chemical exposure as well as being cost effective. Following choice of remedial actions, mathematical modeling should again be used to estimate the new or altered chemical concentrations. Plotting the new exposure isopleths gives guidance as to the ultimate success of the remediation.

Hypothetical Use of the Waste Site Decision Tree

Examination of a hypothetical case study illustrates the principles behind the approach. The demonstration involves a leachate moving from a waste site through soil to groundwater, then to a stream. The chemical of concern is tetrachloroethylene, a slightly soluble solvent (Table 2). Chemical concentrations were measured in surface soils, a groundwater and surface waters. Concentration isopleths were drawn. Long term tetrachloroethylene fate predictions through mathematical modeling were used to evaluate the steps that follow.

Choice of toxicological endpoints requires examination of the exposure scenario. The aquifer is not considered to be a potential drinking water source (salinity > 4%) nor used to feed stock animals. The groundwater discharges into a stream. Fish may be consumed from the stream. The safe concentration utilized here will be the aquatic life criteria (1500 ug/L).

Calculated uncertainty can then be overlain on the exposure concentration isopleths (Figure 2). Now the identified chemical exposures can be adequately understood through this assessment. Clearly, all of the chemical levels present are not unsafe (based on exposures). The extent to which the site must be remediated can now be clearly identified. Exposures considered unacceptable would trigger either further work (e.g. advanced tiers) to better establish chemical concentrations or remedial action.

Remedial activities are called for by the decision tree analysis when exposure concentrations are deemed unacceptable. Possible remedial actions include: (1) doing nothing, (2) using a combination of best engineering practices or (3) digging it up. Chemical fate modeling is used to evaluate the results of the various remedial actions. The overall effect of doing nothing may cause exposures to get worse (i.e. MS's smaller) as the concentrations increase through time. The combination of engineering practices reduces chemical levels. Evacuation and removal from the site of all contaminated material does improve the margin of safeties. However, consideration of another factor, cost, reveals the drawbacks of the 'dig-it-up' approach to cleanup. Excavation of even a small (1 acre) site 30-40 feet deep (to bottom aquifer) generates over 80,000 tons of aquifer material. A 200 acre site with a contaminated aquifer 100 feet deep would generate 40,000,000 tons of aquifer material. Even a combination of source excavation and removal coupled with complete aquifer withdrawal and treatment would be unduly costly for such a large site. Clearly, rational remedial actions or control measures must be dictated by all facets of the identification and assessment processes.

SUMMARY

Cleanup of contaminated waste sites is possible in a manner that is scientifically adequate, technologically feasible and cost effective. Remedial activities must be guided by a complete comprehension of the identified problems through assessment. Failure to do so can be costly. Efficient use of existing resources can yield the best results not only for a particular site but also for effectively addressing the nation's overall toxic wastes problems.

The general approach to the addressing of waste site cleanup is not new. The principles elucidated here have been used to address work place chemical exposure limits, set permitted effluent discharge limits and guide industrial waste treatment plant designs. The approach outlined here should not be considered as an 'out' or as a means to avoid acceptance of responsibility by affected parties. Rather, use of the methods presented here can successfully guide the cleanup of contaminated waste sites in the most rational and feasible manner.

REFERENCES

Adrian, G.W., 1981, Development of a National Groundwater Strategy. In: Proceedings AWWA Seminar entitled, 'Organic Chemical Contaminants in Groundwater: Transport and Removal'. AWWA (American Water Works Association) Denver, CO.

Cairns, J., Jr., K.L. Dickson and A.W. Maki, 1978. Estimating the Hazard of Chemical Substances to Aquatic Life. ASTM STP 657. American Society for Testing and Materials, Philadelphia, PA.

Callahan, C.A. 1984, Earthworms as Ecotoxicological Assessment Tools, U.S. environmental Protection Agency Report No. EPA-600/D-84-272.

Frost, E.G., 1982. Risk Assessment Under the Revised National Contingency Plan to Superfund. In: Risk Assessment of Hazardous Waste Sites. Edited by F.A. Long and G.E. Schweitzer, ACS No. 204, American Chemical Society, Washington, D.C.

Gilford, J.H. 1985, Environmental Effects Assessment of New Chemicals under the Toxic Substances Control Act. Presented at 1985 Summer National Meeting, American Institute of Chemical Engineers, Seattle, WA.

Houk, V.N., 1982, Determining the Impact on Human Health Attributable to Hazardous Waste Sites. In: Risk Assessment of Hazardous Waste Sites, Edited by F.A. Long and G.E. Schweitzer, ACS No. 204, American Chemical Society, Washington, D.C.

PL-98616, 1984, Hazardous and Solid Wastes Amendments of 1984.

Stephan, C.E., D.A. Mount, D.J. Hausen, J.H. Gentile, G.A. Chapman and W.A. Brungs, 1983. Draft U.S. Environmental Protection Agency Document.

Thomas, J.M., 1984, Characterization of Chemical Waste and its Extent Using Bioassays. Report to U.S. Environmental Protection Agency. Contract D.E.-AC06-76RLO 1830, Pacific Northwest Laboratory, Richland, WA

Thomas, J.M. and J.F. Cline, 1985. Modification of the Neubauer Technique to Assess Toxicity of Hazardous Chemicals in Soils. Environmental Toxicology and Chemistry, 4:201:207.