An environmental risk assessment using CalTOX

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Abstract

R & P Electroplating, Inc. (R & P) operated on the site at 2000 Pump Station Road, Fayetteville, Arkansas, from 1977 to 1997. Contaminants from the facility include an assortment of heavy metals, vinyl chlorides, and other solvents. These contaminant stressors potentially pose a risk to aquatic systems, wildlife and human life within the vicinity of the site, as well as humans in Northwest Arkansas who consume drinking water from Beaver Lake Reservoir. Using the CalTOX model, simulations were performed for the main contaminants of concern (COCs) to determine their potential contamination risk. CalTOX represents the environment using seven different compartments: air, surface water, plants, sediments, surface soil, root-zone soil, and vadose-zone soil. The chemicals of concern were 1,1,1 trichloroethane; 1,1 dichloroethene; vinyl chloride; methylene chloride; arsenic; chromium; and lead. The results of the CalTOX simulations provided concentrations leaving the site in groundwater and surface water for each COC as a distribution. All COCs were determined to be present at concentrations below the Maximum Contaminant Levels (MCL) at the downstream drinking water supply.

Keywords: electroplating, uncertainty, drinking water, MC, fish consumption.

1 Introduction

R & P Electroplating, Inc. (R & P) operated from 1977 to 1997. Electroplating is a subset of the fabricated metal products industry (Standard Industrial Classification (SIC) code 34) which is comprised of establishments that fabricate metal products and those that perform finishing operations such as electroplating,
plating, polishing, anodizing, coloring, and coating operations on metals [1].
The industry is largely composed of small, independently owned companies. A
typical “job shop” employs 15 to 20 people and generates $800,000 to
$1,000,000 in annual gross revenues. In 1987, there were 213 companies in
Arkansas covered by SIC 34 [1].

Electroplating and other metal deposition operations and numerous finishing
operations at R & P generated wastes that were mainly associated with the
solvents and cleansers applied to the surface and the metal-ion-bearing aqueous
solutions used in the plating tanks. Metal-ion-bearing solutions are commonly
based on hexavalent chrome, trivalent chrome, copper, gold, silver, cadmium,
zinc, and nickel. The cleaners (acids) may appear in process wastewater; the
solvents may be emitted into the air, released in wastewater, or disposed of in
solid form; and other wastes, including paints, metal-bearing sludges, and still
bottom wastes may be generated in solid form [1].

1.1 Location description

The R & P Electroplating site is located at 2000 Pump Station Road,
Fayetteville, Arkansas (Figure 1). This is approximately three miles southeast of
downtown Fayetteville. The site consists of 5.77 acres of land adjacent to the
West Fork of the White River in Fayetteville’s Industrial Park. The company was
contained in a single story, 20,000 sq ft building. When R & P was abandoned
in April 1997, over 90 unsecured containers of hazardous substances were left,
which included cyanides, metal solutions, acids, and bases.

To help prevent future contaminant environmental releases, many of the
drums of chemical contaminants that were left on the R&P Electroplating Site at
the time of closing were removed from the site by the Arkansas Department of
Environmental Quality (ADEQ). This has contributed to protecting the
ecosystem from further COC releases from R & P.

1.2 Source and stressor characteristics

The sources of contamination at R & P can be divided into two categories 1) sources from historic use of the facility and 2) potential sources presently on site
at the facility.

1.2.1 Sources from historic use

Historic use of the facility has resulted in potential contamination of groundwater
(hence surface water) and soil. To determine which stressors might be emitted
by the identified sources from historic use, past monitoring (the most recent
occurring in 2003) and reports for R & P were reviewed:

- A 2002 EPA report indicated that the monitoring well nearest the stream had
  concentrations of vinyl chloride, 1,1-dichloroethene, and arsenic at levels
  above the residential tap water standards.
- Contaminants found in surface soil were arsenic, chromium, copper, and
  lead [2].
In subsurface soil samples; chromium, nickel, 1,1 dichloroethene, methylene chloride, 1,1,1 trichloroethane, trichlorethene, beryllium, cadmium, chromium and nickel were found above the EPAs screening levels [2].

1.2.2 Potential sources presently on site
The abandoned R & P facility still contains potential sources of contamination:

- Drums are still located onsite that are not properly maintained and are not secure;
- Large concrete sumps in the floor of the facility are filled with water contaminated with arsenic, beryllium, cadmium, chromium, lead, and nickel above residential tap water standards [2];
- Structural beams and floors in the interior of the building are contaminated with chromium and lead posing additional sources [2]; and
- Dust with heavy metals within the structure may become air borne and contaminate air within the building and surrounding areas.
1.3 Systems potentially at risk

Systems presently at risk due to stressors released from the R & P facility include:

- Aquatic ecosystems in the West Fork of the White River and waters downstream from the site, including Beaver Lake Reservoir;
- The drinking water supply provided by Beaver Water District and hence the majority of the population of NW Arkansas;
- Less obvious systems such as the natural, non-domesticated animal inhabitants of the area (e.g. bird, rodent, and other small animal communities within the contaminated area); and
- Humans working or recreating within the vicinity (this is particularly a concern due to the proximity of the site to a community baseball field).

![Conceptual model representing contaminant sources and pathways.](image)

Figure 2: Conceptual model representing contaminant sources and pathways.

1.4 Assessment endpoints (hazard identification)

Assessment endpoints were selected based on the population exposed to risk from COCs. Although many different entities are at risk (including microbes in the soil, meiofauna in the river), only those that would be agreed upon by a majority of the population are included in this assessment. Decisions regarding appropriate endpoints also included consideration of economical issues and ecological services. Assessment endpoints were selected based on best available knowledge at the time of this assessment.
• *Children’s health* (the health of 2-3 year old children/toddlers) was selected as an assessment endpoint because of their higher vulnerability to stressors compared to adults [3]. The main exposure pathway of the contaminants to this endpoint is through drinking water consumption.

• The aquatic biota endpoint selected was *COC bioaccumulation and biomagnification in fish located in the adjacent stream*. Assessment of aquatic biota indirectly provides a measure of potential water quality problems and hence potential contamination of the drinking water supply. It also provides information on the human risk associated with eating fish exposed to the COCs.

### 2 Approach

#### 2.1 Conceptual model

A conceptual model consisting of the sources, stressors, and endpoints with consideration to their relationship to each other was developed for this site (Figure 3).

#### 2.2 CalTOX modeling

The conceptual model included inhalation, oral ingestion, and primary contact as the modes of exposure to contaminants from the R & P Site. Potentially, children playing in a recreational area adjacent to the site could be exposed to contaminants through inhaling or ingesting dust from the site, or children could be exposed through drinking water containing contaminants from the site or by eating fish that have assimilated the contaminants. The probabilities of these exposures were assessed using CalTOX, a computer selected due to its availability, documentation, computational abilities, and ease of use [4].

CalTOX was developed in Microsoft Excel and consists primarily of a spreadsheet with built in macros that were designed with some database linkages for specialized parameterization. It has historically been used to set soil clean-up levels at hazardous waste sites. Input parameters that are used to describe the fate and transport of contaminants in CalTOX were created so distributions could be used in defining their value. By using a distribution instead of a discrete value for a model parameter, model predictions can be simulated that more accurately represent the uncertainty in predictions. We implemented the CalTOX model in this manner to determine source-dose-risk relationships in respect to the R & P Site.

CalTOX is a multimedia fugacity-based model used for screening level risk assessment of sites with contaminated soils [5]. The model includes a fate and transport module that drives the exposure assessment, and a toxicity assessment that relates the different media concentration to the human toxicity analysis leading to a calculation of predicted risk. CalTOX partitions contaminants between the compartments of air, water, soil layers, sediment, vegetation, and aquatic biota based on their relative fugacity. CalTOX groups environmental
processes into three categories: adjective, intermedia, and degradation. Adjective processes include runoff, infiltration, plant uptake, and plug flows in and out of the different compartments. Intermedia transfers include such processes as volatilization and adsorption between air and water. Degradation losses included in the multimedia approach are considered first-order decays based on the contaminant’s estimated half-life in different compartments [5]. Mass balance of contaminants is maintained between the different compartments. The model allows up to 23 different exposure pathways.

2.2.1 CalTOX model parameterization
The COCs that were identified for the R & P Electroplating site. The COCs were selected based on information from sampling events that indicated the presence and quantity of each chemical. The initial screening of contaminants indicated eleven chemicals present at levels higher than the Human Health Medium-Specific Screening Levels (HHMSSLs). Analysis of the risk of increased cancer and the hazard ratio of these chemicals with CalTOX concluded that bis (2 ethylhexyl) phthalate, copper, beryllium, and cadmium posed negligible risk and needed no further analysis. In addition, it was determined that ingestion through drinking water was not a route for exposure to methylene chloride, so that chemical was also eliminated from this assessment. The remaining chemicals from the initial screening then were: arsenic (As); chromium (Cr); lead (Pb); 1,1,1 trichloroethane (TCE); 1,1, dichloroethene (DCE); and vinyl chloride. Because of the different properties of metals and volatiles, CalTOX parameterization was different for each group.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Symbol</th>
<th>Default value</th>
<th>New value</th>
<th>Additional information</th>
</tr>
</thead>
<tbody>
<tr>
<td>Contaminated area</td>
<td>AREA</td>
<td>1.38E11 m²</td>
<td>2.34E04 m²</td>
<td>Site is 5.77 acres</td>
</tr>
<tr>
<td>Runoff</td>
<td>RUNOFF</td>
<td>1.16E-03 m/d</td>
<td>2.62E-03 m/d</td>
<td>Assumed 80% of precipitation becomes runoff b/c of gravel, pavement, and soil compaction</td>
</tr>
<tr>
<td>Groundwater recharge</td>
<td>RECHARGE</td>
<td>1.62E-04 m/d</td>
<td>3.27E-04 m/d</td>
<td>Assume 10% of precipitation infiltrates</td>
</tr>
<tr>
<td>Thickness of vadose zone</td>
<td>D_V</td>
<td>7.03E-01 m</td>
<td>1.05E00 m</td>
<td>From monitoring well data</td>
</tr>
<tr>
<td>Thickness of aquifer</td>
<td>D_Q</td>
<td>3.00E00 m</td>
<td>1.25E00 m</td>
<td>From monitoring well data</td>
</tr>
</tbody>
</table>
The CalTOX model provides default parameters for chemical characteristics, landscape variables, and exposure characteristics. Default values for parameters in CalTOX were used except for parameters identified in Table 1. Although additional parameters are used in the CalTOX model, they were not modified (hence default values were used) because information was not available to estimate a more appropriate value.

Table 2: Chemicals with their respective input values for CalTOX.

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Soil zone</th>
<th>Distribution (mg/L)</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar</td>
<td>Root</td>
<td>Triangle (5.0, 8.1, 11.3)</td>
<td>Min, mean, and max of data</td>
</tr>
<tr>
<td></td>
<td>Vadose</td>
<td>Triangle (0.001, 0.0015, 0.0023)</td>
<td>No hits above detection limit</td>
</tr>
<tr>
<td></td>
<td>Groundwater</td>
<td>Triangle (15.0, 1010.0)</td>
<td>Min, mean, and max of data</td>
</tr>
<tr>
<td>Cr</td>
<td>Root</td>
<td>Triangle (59.0, 98.9, 130.0)</td>
<td>Min, mean, and max of data</td>
</tr>
<tr>
<td></td>
<td>Vadose</td>
<td>Triangle (0.0005, 0.00088, 0.002)</td>
<td>Min, mean, and max of data</td>
</tr>
<tr>
<td></td>
<td>Groundwater</td>
<td>Triangle (0.002, 0.003, 0.004)</td>
<td>Min, mean, and max of data</td>
</tr>
<tr>
<td>Pb</td>
<td>Root</td>
<td>3.293</td>
<td>No hits above detection limit</td>
</tr>
<tr>
<td></td>
<td>Vadose</td>
<td>0.0</td>
<td>Min, mean, and max of data</td>
</tr>
<tr>
<td></td>
<td>Groundwater</td>
<td>Triangle (0.001, 0.0015, 0.0023)</td>
<td>Min, mean, and max of data</td>
</tr>
<tr>
<td>TCE</td>
<td>Root</td>
<td>Uniform (0.0, 0.025)</td>
<td>Min and max of data, the majority of the data was below the detection limit so the mean value was not used.</td>
</tr>
<tr>
<td></td>
<td>Vadose</td>
<td>Uniform (0.0, 9.27)</td>
<td>Min and max of data, the majority of the data was below the detection limit so the mean value was not used.</td>
</tr>
<tr>
<td></td>
<td>Groundwater</td>
<td>Triangle (0.0025, 0.3712, 1.835)</td>
<td>Min, mean, and max of data</td>
</tr>
<tr>
<td>DCE</td>
<td>Root</td>
<td>1.0</td>
<td>Min and max of data, the majority of the data was below the detection limit so the mean value was not used.</td>
</tr>
<tr>
<td></td>
<td>Vadose</td>
<td>Uniform (0.145, 0.22)</td>
<td>Min and max of data, the majority of the data was below the detection limit so the mean value was not used.</td>
</tr>
<tr>
<td></td>
<td>Groundwater</td>
<td>Uniform (0.25, 0.775)</td>
<td>Min and max of data, the majority of the data was below the detection limit so the mean value was not used.</td>
</tr>
<tr>
<td>Vinyl Chl.</td>
<td>Root</td>
<td>0.0</td>
<td>No hits above detection limit</td>
</tr>
<tr>
<td></td>
<td>Vadose</td>
<td>0.0</td>
<td>No hits above detection limit</td>
</tr>
<tr>
<td></td>
<td>Groundwater</td>
<td>Uniform (0.044, 0.06)</td>
<td>No hits above detection limit</td>
</tr>
</tbody>
</table>

2.2.2 CalTOX model uncertainty propagation
Uncertainty is an inherent component of complex system modeling. Quantifying and communicating uncertainty within any modeling context is critical. CalTOX
is designed for propagation of uncertainty using spreadsheet ad-on programs. The variability of concentrations of chemicals in the different monitoring wells and soil borings reflected uncertainty as to the actual concentration of the chemical in runoff and groundwater flow. To account for this uncertainty, the input values for root zone, vadose zone, and groundwater concentrations in CalTOX were considered to be distributions instead of a discrete value (Table 2). The distributions were designated based on available monitoring data from 1998 to 2003.

Triangle distributions were used with the minimum value, the mean value, and the maximum value defining the vertices of the triangle. If there were only two values above the detection limit for the chemical, then a uniform distribution was used with the lower limit at 50% of the detection limit and the upper limit at the highest value reported. If only one value was recorded, that value was used as the model parameter.

The CalTOX model was run for each parameter using @RISK (Palisade Corporation, NY) to perform 100 simulations. The results were recorded as five number summaries (minimum, 5th percentile, 50th percentile, 95th percentile, maximum) of the distribution of risk of additional cancers and hazard ratio.

3 Results

3.1 Drinking water risk assessment

Exceedence probability plots characterize the percent of events that will occur that are greater than the corresponding concentration (Figure 3). For example, Vinyl Chloride values for the 5th percentile CCDF will exceed 5.25E-11 mg/L approximately 50% of the time. It is also interesting to note the relationship between the curves. All of the COCs appear to have a greater rate of exceedence probability to increased concentration for 5th and 50th percentile than to 95th percentile CCDFs. In addition, there appears to be a greater shift between 50th and 95th percentile CCDFs than between 5th and 50th percentile CCDFs. This can be explained by characteristics within the data distributions.

Since the primary exposure route of these contaminants was drinking water, the EPA guidelines for MCLs for each COC were compared with the probability of exposure [6].

Contaminants of concern are at concentrations many magnitudes below the drinking water MCLs set by the EPA (Table 3). The Maximum Contaminant Level (MCL), as defined by EPA, is the maximum permissible level of a contaminant in water which is delivered to any user of a public water system [7]. For our purposes, it is the maximum concentration of a contaminant that can be present in drinking water. For example, the MCL value for Arsenic is 0.01 mg/L which is approximately 4 orders of magnitude greater than the 5th percentile estimated value of 2.02E-6 mg/L. A similar trend can be found with the other COCs (Table 3).
Figure 3: Summary of the Distribution of CCDFs of COC estimates. The 5th, 50th, and 95th percentile estimates of the distribution of the CCDFs are shown for a) Arsenic, b) Chromium, c) and 1,1,1 Trichloroethane (TCE).

4 Conclusions

The differences between reservoir COC concentrations and EPA MCLs suggests that considering only contributions from the R & P Site, none of the COCs listed in Table 3 are a human health concern for drinking water. It is important to note that this study was conducted under several constraints and results should be
considered with caution. Some of these constraints include: limited data collection, limited model calibration, and no validation (such as monitoring at the drinking water withdrawal). However, it does provide information on how to proceed with mitigation of this site and its potential impacts on the drinking water supply for Northwest Arkansas.

Table 3: The 5th, 50th and 95th percentile estimates of the distribution of CCDFs are presented for each contaminant as well as the Maximum Contaminant Level (MCL) allowed in Drinking Water by the Environmental Protection Agency.

<table>
<thead>
<tr>
<th>Contaminant</th>
<th>Reservoir contaminant Concentrations</th>
<th>EPA MCL (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>5th Percentile Estimate mg/l</td>
<td>50th Percentile Estimate (mg/l)</td>
</tr>
<tr>
<td>Arsenic (As)</td>
<td>2.02E-06</td>
<td>3.51E-06</td>
</tr>
<tr>
<td>Chromium (Cr)</td>
<td>1.21E-05</td>
<td>2.09E-05</td>
</tr>
<tr>
<td>Lead (Pb)</td>
<td>3.56E-05</td>
<td>1.24E-04</td>
</tr>
<tr>
<td>1,1 Dichloroethene</td>
<td>3.47E-07</td>
<td>5.84E-07</td>
</tr>
<tr>
<td>Methylene Chloride</td>
<td>4.10E-09</td>
<td>6.53E-09</td>
</tr>
<tr>
<td>1,1,1 Trichloroethane</td>
<td>4.03E-07</td>
<td>1.24E-06</td>
</tr>
<tr>
<td>Vinyl Chloride</td>
<td>3.16E-11</td>
<td>5.25E-11</td>
</tr>
</tbody>
</table>

References