

Ground Water Flow in a Desert Basin: Challenges of Simulating Transport of Dissolved Chromium

by Charles B. Andrews¹ and Christopher J. Neville²

Abstract/

A large chromium plume that evolved from chromium releases in a valley near the Mojave River was studied to understand the processes controlling fate and migration of chromium in ground water and used as a tracer to study the dynamics of a basin and range ground water system. The valley that was studied is naturally arid with high evapotranspiration such that essentially no precipitation infiltrates to the water table. The dominant natural hydrogeologic processes are recharge to the ground water system from the Mojave River during the infrequent episodes when there is flow in the river, and ground water flow toward a playa lake where the ground water evaporates. Agricultural pumping in the valley from the mid-1930s to the 1970s significantly altered ground water flow conditions by decreasing water levels in the valley by more than 20 m. This pumping declined significantly as a result of dewatering of the aquifer, and water levels have since recovered modestly.

The ground water system was modeled using MODFLOW, and chromium transport was simulated using MT3D. Several innovative modifications were made to these modeling programs to simulate important processes in this ground water system. Modifications to MODFLOW include developing a new well package that estimates pumping rates from irrigation wells at each time step based on available drawdown. MT3D was modified to account for mass trapped above the water table when the water table declines beneath nonirrigated areas and to redistribute mass to the system when water levels rise.

Introduction

Cooling water from an industrial facility containing chromium as a corrosion inhibitor was discharged to unlined ponds for a 14-year period between 1952 and 1965 (Ecology and Environment 1988). This release of chromium to the ground water system in the Hinkley Valley in the Mojave Desert, California, was studied to understand the processes controlling fate and migration of chromium in ground water. The chromium plume has served as a tracer to study the dynamics of a basin and range alluvial ground water system, a ground water flow system in which the main source of recharge is infiltration from the bed of a desert stream that flows infrequently, and the main discharge area is a playa lake. Unlike most anthropogenic releases of contaminants, the timing and magnitude of the contaminant release at this site was documented, making this an excellent site to study the evolution of a ground water plume.

The ground water systems in many of the alluvial valleys in the southwestern United States have been significantly affected by urban development and agricultural developments over the last 60 years. Ground water pumping to support this development has lowered water levels, in many cases by well over 30 m, and has significantly changed ground water flow directions in many areas. Relatively coarse-grained materials and relatively high ground water velocities characterize the hydrogeologic settings of these alluvial valleys. Because of this, the ground water systems in alluvial valleys are unduly susceptible to ground water contamination, and many alluvial valleys have ground water plumes that are several kilometers long.

An overview of the migration and fate of organic contaminants in alluvial valleys is presented in Jackson (1998). Jackson notes that whereas the physical hydrogeology of alluvial-fan environments is complex, the chemical hydrogeology with respect to oxidation-reduction is more straightforward, as the alluvial-basin aquifers are predominately oxic sedimentary environments. Izbicki et al. (1995) presented a geochemical model of the evolution of water quality in the alluvial aquifers in the upper part of the Mojave River basin.

Ground water modeling of the changes in hydrogeologic conditions in alluvial aquifers over the last 60 years is

¹S.S. Papadopoulos & Associates Inc., 7944 Wisconsin Ave., Bethesda, MD 20814-3620; (301) 718-8900; candrews@sspa.com

²S.S. Papadopoulos & Associates Inc., 90 Frobisher Dr., Unit 2B, Waterloo, Ontario N2V 2A1; (519) 579-2100; cneville@sspa.com

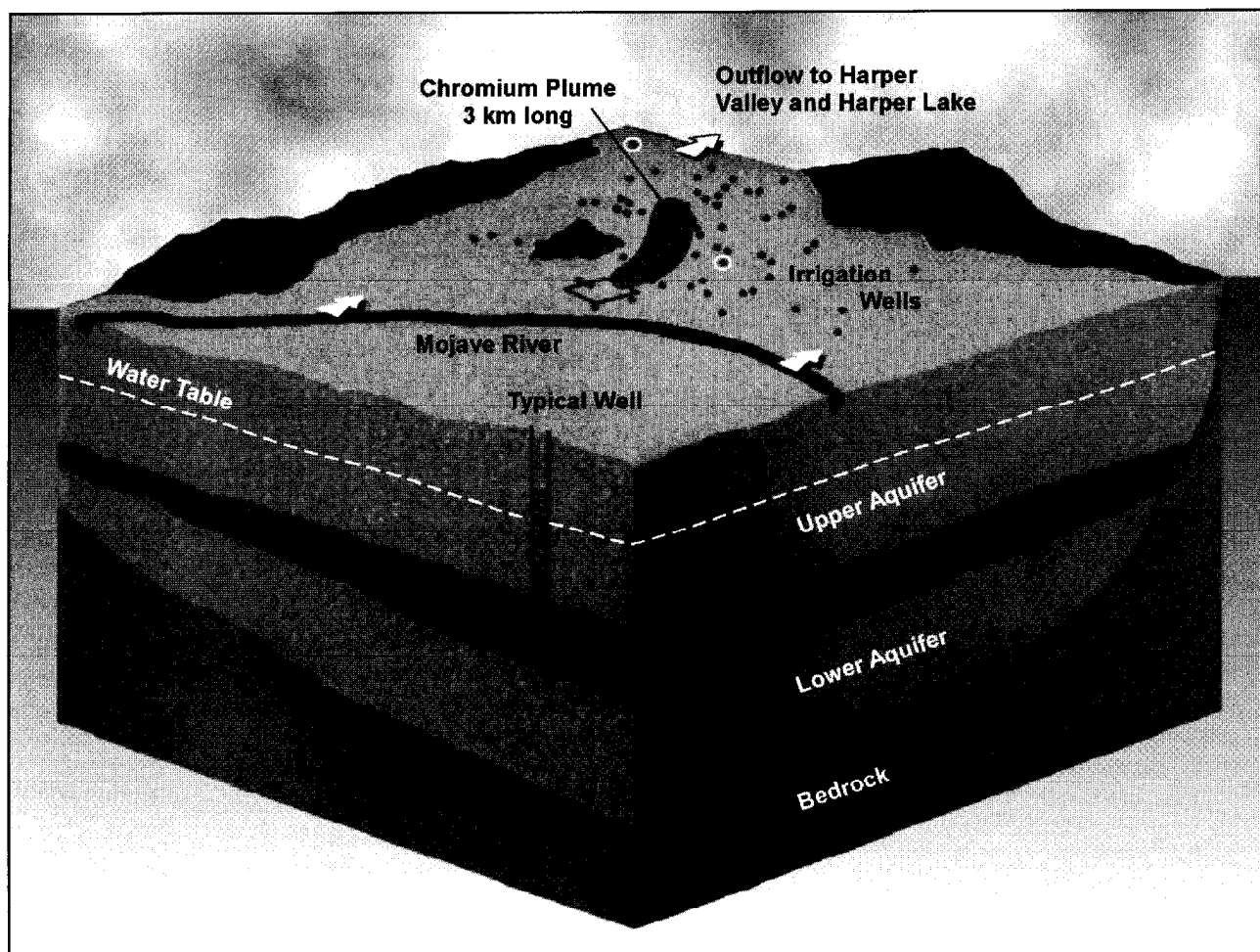


Figure 1. Schematic of the Hinkley Valley showing the major hydrogeologic units, location of irrigation wells, typical well construction, and the areal location of the chromium ground water plume. Two wells with long-term hydrographs are denoted by the circled dots. The major hydrogeologic units are projected onto the front face of the diagram. The schematic represents an area of $\sim 16 \times 16$ km \times 90 m.

challenging because of the large changes in water levels and ground water flow directions that have occurred. Modeling the transport of inorganic redox-sensitive solutes, such as chromium, is also challenging even in relatively simple environments, because their fates cannot be predicted by thermodynamic considerations alone. This paper describes a case study of the application of MODFLOW (McDonald and Harbaugh 1988) and MT3D (Zheng 1996) to simulate the migration of chromium in an alluvial valley characterized by large fluctuations in water levels, and describes techniques that were developed to address important processes influencing migration that have not been addressed in the standard simulation codes.

Geologic and Hydrogeologic Setting

The Hinkley Valley is north of the Mojave River, west of Barstow, California. The main valley averages ~ 11 km in length and 4.5 km in width, and the axis of the valley is relatively flat with a gentle slope toward the northwest away from the river. The valley connects in the north to the Harper Valley, the center of which is occupied by a playa called Harper Lake, through a narrow break in the bedrock hills (Mojave Water Agency 1983). The ground water system in Hinkley Valley is shown schematically in Figure 1.

The Hinkley Valley is a narrow northwest-trending alluvium-filled depression between uplifted ridges of Mesozoic or older igneous intrusive granitic rocks, Tertiary volcanics, and Precambrian sedimentary and metamorphic rocks (Dribblee 1967). The total thickness of alluvial sediments along the axis of the valley is only ~ 90 m. The alluvium in the valley consists of three distinct lithologic units: (1) a basal unit of alternating layers of coarse sand and silt, (2) a middle unit of lacustrine clay, and (3) an overlying unit consisting of primarily sand and gravel layers that have alternating thin silt and clay layers along the axis of the valley grading to finer-grained deposits along the valley margins. The lacustrine clay, which averages ~ 12 m in thickness in the center of the valley, represents deposits from a late Pleistocene lake. Along the axis of the valley the coarse deposits above the clay unit, referred to as the upper aquifer, represent recent alluvial deposits along an abandoned route of the Mojave River, which once flowed northward through the valley. These deposits range in thickness along the valley axis from 36 m in the southeast to 27 m in the northwest. The finer-grained deposits along the margin of the valley above the clay unit represent fan and alluvial deposits derived from the bedrock ridges.

The estimated hydraulic conductivities of the materials comprising the upper aquifer range from 46 m/day along



Figure 2. View of the dry Mojave River downstream of the Hinkley Valley. The riverbed is fine white sand with no visible flow; dust clouds of fine sand rising from the bed of the river are shown in the background.

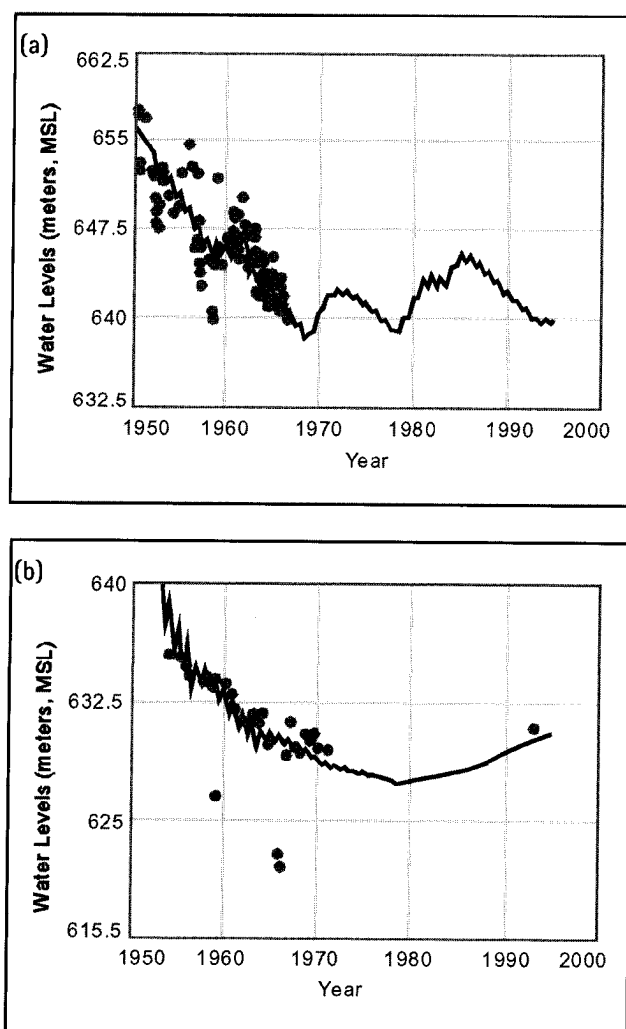


Figure 3. Water levels in typical shallow wells in the Hinkley Valley from 1952 to 1992; calculated water levels are shown with solid line and measured water levels are shown as solid dots. The hydrograph shown in (a) is from a well located in the central part of the basin, and the hydrograph shown in (b) is from a well located in the northern part of the basin. The approximate locations of these shallow wells are shown in Figure 1 as the circled dots.

the present course of the Mojave River, to 30.5 m/day along the ancestral channel through the center of the valley and 7.6 m/day along the valley margins. The hydraulic conductivities were estimated from a number of aquifer tests in the Hinkley Valley and model calibration. The thickness and continuity of the lacustrine clay is such that there is little hydraulic communication between the upper and lower aquifer.

Historic ground water flow in the Hinkley Valley was northward from the Mojave River toward the playa lake in the Harper Valley, and the depth to ground water in much of the valley was less than 30 feet. The Mojave River is the main source of recharge to the ground water system in the Hinkley Valley, but the Mojave River is mainly a river of white sand that seldom contains surface flows (Hardt 1971). The dry riverbed is shown in Figure 2. Between 1932 and 1994, the Mojave River flowed only on 23 occasions in the reach adjacent to the Hinkley Valley, thus providing an intermittent source of recharge. Precipitation is not a significant source of recharge as the average annual precipitation is only 13 cm/year. Some recharge occurs following infrequent but intense summer thunderstorms, but this recharge is insignificant relative to that which occurs from the river.

Ground water flow in the Hinkley Valley has been significantly influenced by ground water withdrawals for irrigation (Durbin and Hardt 1974). More than 150 irrigation wells are reported in the valley (USGS 1960). Irrigation pumping, primarily for the irrigation of alfalfa, began in the early 1930s and peaked in the mid-1950s, when $\sim 3.4 \times 10^8$ m³ (278,000 acre-feet) per year were extracted for irrigation. The irrigation pumping significantly dewatered the shallow aquifer; water-level changes from 1930 to 1970 were more than 20 m in the center of the valley (California Department of Water Resources 1967; Mojave Water Agency 1983). Water levels in two wells, one in the central and one in the northern part of the basin, are shown in Figure 3. The water levels demonstrate a significant downward trend from 1950 to at least 1970, and the measured water levels during a given year show significant variability as the result of seasonal operation of the wells for irrigation. These long-term downward trends in water levels effectively reduced pumping yields. As a result, much of the irrigated land was abandoned during the next three decades. In the early 1990s only $\sim 1.6 \times 10^8$ m³ (130,000 acre-feet) per year were extracted for irrigation, less than 50% of mid-1950s withdrawals (Mojave Water Agency 1983).

Chromium Plume

Chromium in the cooling water discharged to unlined ponds for a 14-year period from 1952 to 1965 was in the form of chromium (VI), an active ingredient in the corrosion inhibitor. The alkaline cooling waters containing chromium (VI) were discharged to surface ponds constructed in the relatively permeable surface deposits at the site. The infiltration rates from the ponds were sufficiently high that the travel time from the ponds to the water table was less than one year. The chromium (VI) that reached the water table formed a plume that migrated northward from

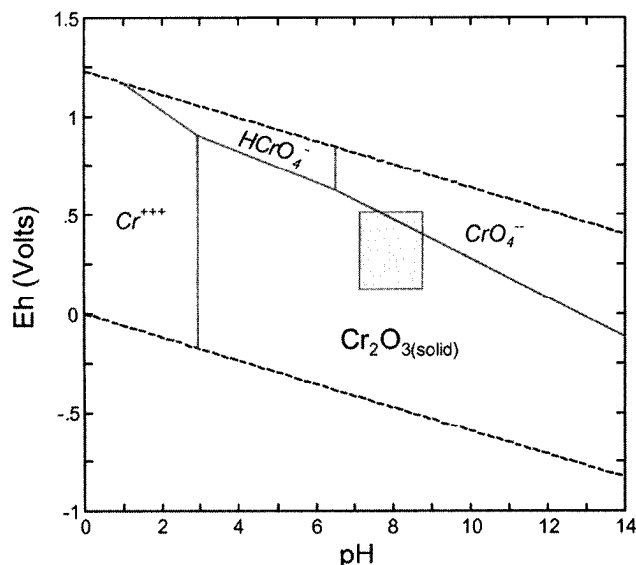


Figure 4. Chromium Eh-pH diagram for total aqueous chromium of 0.5 mg/L. The Eh-pH conditions that exist in ground water in the Hinkley Valley fall within the shaded region. Stable forms of chromium in the ground water are a dissolved chromium (VI) species in the upper right corner of the shaded region and a solid phase chromium (III) oxide elsewhere within the shaded region.

the location of the ponds in the direction of ground water flow.

The approximate location and length of the plume as defined by chromium concentrations greater than 0.01 mg/L in the mid-1990s is shown in Figure 1. The highest chromium concentrations in the plume in the mid-1990s occur in the vicinity of the source area, even though discharges of chromium to the subsurface ceased more than 30 years ago. Extensive monitoring of the plume did not begin until the late 1980s; but since monitoring began, the plume has expanded toward the north.

The fate of chromium (VI) in the subsurface is a function of geochemical conditions in the subsurface and the nature and composition of the matrix surfaces. The shallow ground water in the upper aquifer in the central part of the basin has a total dissolved solids concentration of <400 mg/L; calcium and sodium are the dominant cations; and bicarbonate, sulfate, and chloride are the dominant anions. Measured pH values are typically in the range of 7 to 8.5, and measured Eh values are in the range of 0.1 to 0.4 volts. The stability fields for various chromium species are shown in Figure 4 (Ball and Nordstrom 1998). The thermodynamically stable chromium species within much of the range of the observed Eh and pH conditions in the shallow ground water is $\text{Cr}(\text{OH})_3$, a reduced chromium (III) precipitate. This precipitate is relatively insoluble, and as a result the dissolved concentrations of chromium (III) in equilibria with this precipitate are very small. Electron donors, such as iron (II)-containing minerals and organic matter, are required to reduce chromium (VI) to chromium (III), and the long-term persistence of chromium (VI) in the upper aquifer indicates that electron donors are limited.

Chromium (VI) adsorbs to hydrous metal oxides on matrix surfaces, but adsorption on coarse-grained matrix

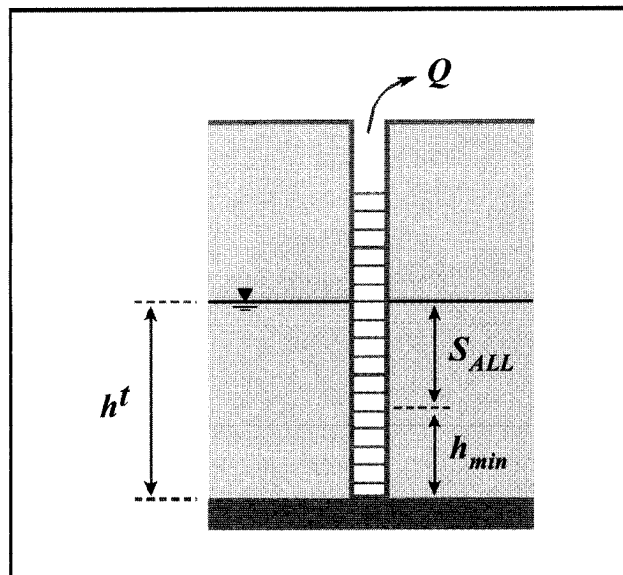


Figure 5. Schematic of a typical irrigation well.

materials is usually minor because of limited availability of sorption sites (Kent et al. 1994). Evaluation of the rate of chromium (VI) transport in the upper aquifer indicated that dissolved chromium (VI) migrated at approximately the same rate as ground water. This indicated that adsorption or other retardation processes were not significant in the coarser-grained materials in the upper aquifer.

Initial model simulations indicated that the highest concentrations in the 1990s should be downgradient of the source area as the result of the insignificant retardation of chromium (VI). However, in the 1990s the highest chromium (VI) concentrations were still found directly beneath the ponds where the cooling waters were originally discharged. In developing a model of chromium migration, it was hypothesized that during the long period of declining water levels from 1952 to 1970, significant mass of chromium would be retained in pore water in the unsaturated zone, and that this chromium would subsequently be released to the ground water system when water levels were rising in subsequent years.

Modeling Approach

Ground water flow and the transport of chromium in the Hinkley Valley were simulated with MODFLOW and MT3D. A steady-state model was developed to simulate conditions prior to settlement and initiation of irrigation pumping. The water levels simulated with this steady-state model were used as the initial conditions for a transient simulation of the period 1930 to 1995.

The successful simulation of ground water flow and chromium transport required addressing several difficult issues, including (1) estimation of irrigation pumping, (2) estimation of infiltration rates from the Mojave River, (3) understanding the chemical processes affecting chromium in the source area, (4) simulation of chromium reactions in infiltrating irrigation water, and (5) simulation of chromium retention in retained water above the water table. Each of these issues is described in the following.

Irrigation Pumping

No records of irrigation pumping were available. Therefore, aerial photographs were used to estimate irrigated acreage for 11 time intervals between 1952 and 1995 in each 40-acre (16.2 hectare) tract in the Hinkley Valley. During the period when flood irrigation was practiced, prior to the 1970s, an application of 2.7 m during the irrigation season was specified in the model, based on reported usage rates for irrigating alfalfa in the desert areas of southern California. For the period following the introduction of spray irrigation, an application of 2.1 m during the irrigation season was specified (Duffin 1971). One-half of the applied water was specified as recharge to the ground water system (Owen-Joyce and Kimsey 1987). Recharge was only specified in those areas where irrigation was occurring, and recharge was assumed to occur only during the irrigation season.

A record of wells in the Hinkley Valley was compiled based on published records and maps, and pumping rates were assigned to wells based on location relative to irrigated fields and reported well yields. As the water table in the valley fell, in many instances the existing wells had insufficient yield to satisfy the full irrigation demand. To simulate this condition, the pumping rate specified at each irrigation well was checked at each time step to ensure that the well had sufficient yield to satisfy the irrigation demand, given the current saturated thickness. If the yield was less than the irrigation demand, the pump rate was reduced to the calculated yield.

A schematic representation of a typical irrigation well screened through the upper aquifer is shown in Figure 5. The Theis solution was used to calculate the allowable yield of a typical irrigation well at each time step:

$$Q_{\text{all}} = \frac{4\pi T s_{\text{all}}}{W\left(\frac{r_w^2 S}{4T \Delta t}\right)} \quad (1)$$

where T is the transmissivity (product of current saturated thickness and horizontal hydraulic conductivity); s_{all} is the allowable drawdown, defined as shown in Figure 5 based on the head in the node with the well at the end of the last time step; $W(\bullet)$ is the Theis well function; r_w is the radius of the irrigation well; S is the storage coefficient; and Δt is the duration of the time step. If the calculated well yield was greater than the estimated pumping rate specified for the well, the pumping rate was specified as the calculated well yield for the current time step.

Recharge from the Mojave River

Recharge from the Mojave River was initially estimated from U.S. Geological Survey (USGS) gauging stations that straddle the model area. Gauging stations are located at Hodge, just upstream of the modeled area, and at Barstow, ~6.5 km downstream of the modeled area. Data for the Hodge station date back only to 1971, and flow data for earlier periods were estimated by developing a regression based on the period when data were available for both stations.

The initial approach adopted for simulating the recharge from the Mojave River consisted of using the

available flow data to assign an infiltration rate per surface area of the riverbed. This infiltration rate was then used to allocate the available surface-water flow beginning at the upstream end of the modeled area. It was necessary to allocate flow in this manner because our observations indicated that the decrease in surface flow through the model area was dramatic: On April 5, 1995, we observed the river flowing bank to bank at the upstream end of the modeled area and observed a dry riverbed at the downstream end of the modeled area. However, this approach proved unsatisfactory in simulating observed water levels, as recharge was not accurately distributed along the river reach, likely because of a large uncertainty in the estimated width of the river at various stages. The width of the river during high flood stages can exceed 1.5 km, but is difficult to calculate for a given flow because elevations of the broad valley are not well known.

The approach ultimately used to simulate the recharge from the river represented the river as a transient head-dependent boundary condition using the MODFLOW general-head boundary (GHB) package. The head-dependent boundary condition was applied for only those periods during which river flow data indicated there were losses from the river. In this application, the MODFLOW GHB or river packages could be used, but not the drain package. The drain package can withdraw ground water only from the aquifer, when the water level in the aquifer exceeds the stage of the drain. At this site, there are episodic surface flows in the Mojave River that recharge the ground water system; i.e., for some flood periods, the water level in the Mojave River exceeds the water levels in the aquifer and the GHB package adds water to the aquifer. The time-dependent heads along the river were initially specified on the basis of the observed water levels in two wells adjacent to the river, with long historical water-level records and the differences in surface elevations between nodal points representing the river and the two wells. The initial specified river levels were adjusted by a constant additive factor during model calibration to achieve a match between the calculated and observed ground water levels at two wells near the river. The final step was to compare the total river recharge produced with the head-dependent boundary condition to the recharge estimated from the stream gaging data. The correspondence was excellent.

Chemical Processes in Source Area

An enigma of the chromium (VI) plume was that in the 1990s the highest chromium (VI) concentrations were still found directly beneath the ponds where the cooling waters were originally discharged in both the coarse-grained and fine-grained sediments. Initial model simulations indicated that the highest concentrations in the 1990s should be downgradient of the source area as the result of the insignificant retardation of chromium (VI). The situation is similar to that found at a highly heterogeneous aquifer at the Columbus Air Force Base in Mississippi, as reported by many researchers including Zheng and Gorelick (2003). Several hypotheses were developed to explain the high concentrations of chromium (VI) beneath the ponds. One hypothesis was that some chromium was adsorbed to oxide

surfaces in finer-grained silt and clay layers in the upper aquifer and at the base of the upper aquifer. Kent et al. (1994) conducted a tracer test of chromium (VI) in a sand aquifer and measured asymmetric breakthrough curves with steep rising limbs and extensive tails, not unlike the breakthrough curves observed in the Hinkley Valley. Another hypothesis was that some of the chromium (VI) was precipitated as calcium, calcium-aluminum, calcium-aluminum-sulfate and barium minerals, and these minerals later dissolved re-releasing chromium (VI) to the ground water (Davis and Olson 1995; Nikolaidis et al. 1994; Palmer 1998).

It was not possible within the context of the present study to conclusively identify the mechanisms behind the retained high chromium concentrations near the source. In the model simulation, a high retardation coefficient ($R = 8.0$) was specified in the fine-grained sediments at the base of the upper aquifer beneath the ponds to simulate the long-term retention of chromium (VI)/chromium in this area. No retardation was specified in the coarser-grained sediments in the upper aquifer. No data were available to test the hypotheses for elevated chromium concentrations, and their cause is still not satisfactorily explained. We consider the approach described here to be pragmatic in the absence of a clear understanding of the controlling processes.

Chromium Reactions in Infiltrating Irrigation Water

The irrigation wells in the Hinkley Valley acted as a large ground water containment system for the chromium (VI) plume. The water pumped from the irrigation wells was applied to the fields prior to the 1970s by flood or furrow irrigation, and later by spray irrigation. A number of studies have shown that chromium (VI) can be reduced to chromium (III) in soils by redox reactions with aqueous inorganic species, electron transfers at mineral surfaces, reaction with nonhumic organic substances such as carbohydrates and proteins, or reduction by soil humic substances (Wittbrodt and Palmer 1995; James 1996). The processes causing the reduction of chromium (VI) to chromium (III) in the soils in the Hinkley Valley were believed to be reduction by soil organic matter, but this was not rigorously determined. Soil data collected from the site, though, showed that chromium (VI) in the applied water was reduced to chromium (III) in the soils. Chromium (III) minerals are relatively insoluble and studies have demonstrated that under the geochemical conditions that exist in the Hinkley Valley, chromium (III) minerals are unlikely to be subsequently oxidized to chromium (VI) (Davis and Olson 1995; Nikolaidis et al. 1994). The chromium (VI) that was applied to the irrigated fields likely has accumulated in the surface soils as chromium (III) minerals.

All the chromium (VI) in the irrigation water was assumed to be reduced to chromium (III) in the soils; therefore, the water infiltrating from the irrigated fields to the water table was assumed to contain no dissolved chromium (VI) or chromium (III). As a result, the irrigation pumping was an effective pump-and-treat system that contained the chromium (VI) plume. The mass-balance routine in MT3D was modified to keep track of the mass of chromium pumped from irrigation wells and subsequently reduced to

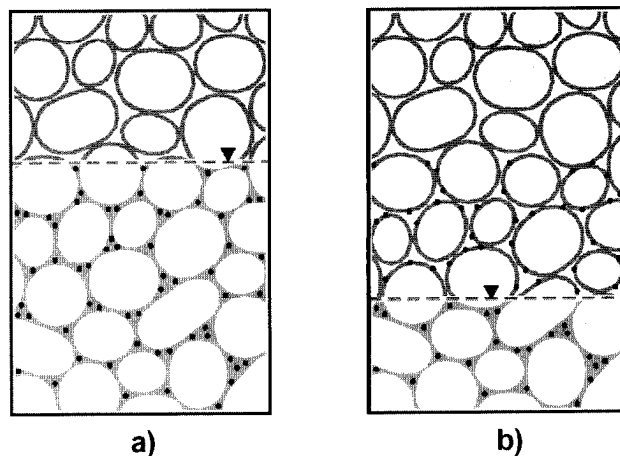


Figure 6. Distribution of dissolved chromium (VI) in ground water downgradient of source area: (a) distribution of chromium (VI) with steady water level, dissolved chromium (VI) occurs below the water table; (b) distribution of chromium (VI) after a period of declining water table, dissolved chromium (VI) occurs below the water table and above the water table in residual water around the matrix grains.

chromium (III) in the organic-rich soils in the irrigated areas.

Pore Water

During the first 20 years after discharge of cooling water to the ponds began, the water table in the shallow aquifer in the Hinkley Valley was declining rapidly. This decline in the water table is hypothesized to have trapped large quantities of chromium (VI) in the pore water above the water table. (Pore water is defined here as the water remaining in the aquifer materials after gravity drainage, or simply as total porosity minus specific yield.) The chromium (VI) was retained in the pore water in all areas in the Hinkley Valley where recharge rates were negligible, essentially everywhere except beneath the irrigated fields. Beneath the irrigated areas, the recharge of irrigation water was sufficient to flush the chromium (VI) out of the pore water as the water table declined.

The chromium (VI) trapped in the pore water is hypothesized to have subsequently acted as a source of chromium (VI) to the ground water when the water table rose. A schematic of this process is shown in Figure 6. The microscale processes affecting chromium (VI) in the retained water are not well understood. It is possible that some of the chromium (VI) was reduced by iron (II)-containing mineral coatings on the matrix surface and that some diffused into the matrix; however, in this study it was assumed that these processes were insignificant relative to the total amount of chromium (VI) contained in the retained water.

These hypotheses were supported by an apparent increase in mass in the dissolved plume during the periods when water levels were rising. The solute transport code MT3D was modified to account for the mass retained in the pore water. A mass-balance approach was developed to keep account of the retained mass. The retained mass was

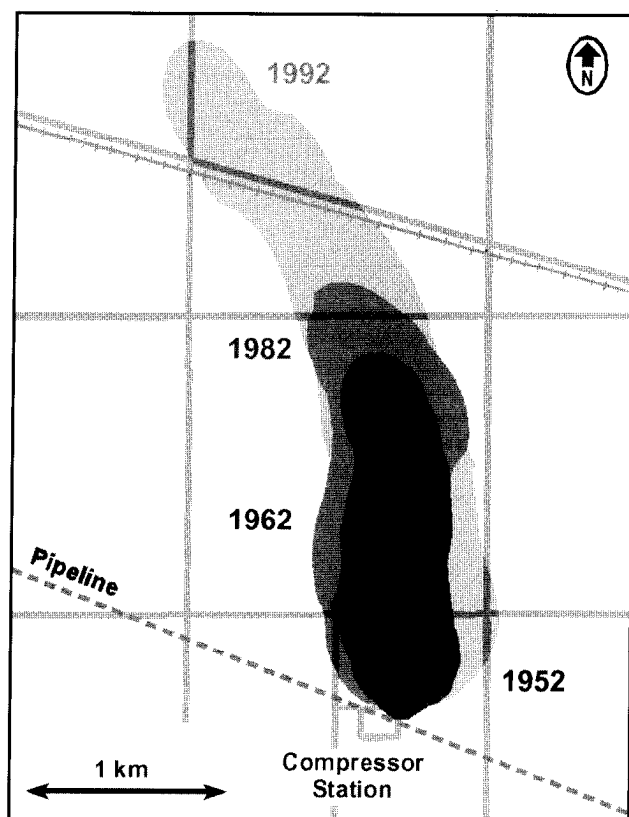


Figure 7. Calculated extent of chromium (VI) ground water plume in 1952, 1962, 1982, and 1992 at concentrations >0.01 mg/L.

accounted for in a three-dimensional array dimensioned as: number of rows times the number of columns in the finite-difference grid times 100, where 100 represented the maximum decline in the water table from initial conditions, in feet. When the water table was falling, at each time step the amount of mass of chromium (VI) retained for each foot decline in the water table was calculated. Mass retained per unit area per foot decline of the water table was calculated as the product of the concentration, the retardation coefficient and the difference between total porosity and specific yield. When the water table was rising, at each time step a check was made to determine if mass had accumulated in the interval through which the water table was rising during the previous period(s) when the water table was falling. If mass had accumulated, this mass was added to the water table aquifer as a source, and accumulated mass in the mass-balance array was reset to zero.

Summary of Results

A ground water model was developed to simulate the evolution of a chromium plume over a 40-year period. The model successfully simulated observed chromium concentrations in ground water during a period in which large changes in water levels and ground water flow directions had occurred. The chromium plume rapidly evolved to a relatively steady configuration due to the containment of the plume by irrigation pumping. In later years, the plume began expanding again as irrigation pumping was curtailed and rising water levels remobilized chromium that had

been retained in the unsaturated zone during periods when water levels were falling. The evolution of the chromium plume from 1952 to 1992 is shown in Figure 7.

The ground water transport model developed in this study used simplified representations of the processes affecting the fate of chromium in the subsurface. These simple representations were adequate for simulating the large-scale evolution of the chromium plume, but are inadequate for understanding dissolved chromium concentrations in the aquifer over the long term. In this study, the retention and release of dissolved constituents in the unsaturated zone as the result of fluctuating water levels was successfully simulated. This is a process that is often overlooked in transport modeling, despite the fact that it may be important. The standard transport models conserve the mass constituents within the saturated domain, but do not account for solute left above a declining water table.

The evolution of the chromium plume over the last 50 years indicated that irrigation pumping and recharge from the river have controlled the dynamics of the ground water system in the Hinkley Valley during this period. The dominant process during this period was irrigation pumping. Irrigation pumping resulted in a significant dewatering of the upper aquifer and reversed the natural direction of ground water flow in the northern part of the valley. Although it was not intended for this purpose, the irrigation pumping significantly slowed the rate of migration of the chromium plume, acting as a large pump-and-treat system. With the curtailment of irrigation pumping, the rate of migration of the plume increased significantly.

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