Evaluation of Treatment Alternatives and Conceptual Design of a Reverse Osmosis Groundwater Remediation System: A Case Study

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ABSTRACT

Contaminated groundwater from a closed landfill site in Novato, California, was subjected to treatability testing. The groundwater contaminants included heavy metals, chlorinated hydrocarbons, polynuclear aromatic hydrocarbons and high levels of dissolved solids. Two discharge options were considered for disposal of the treated groundwater. The first option included discharge into the Novato Sanitary District publicly owned treatment works (POTW), while the second option included discharge into the San Pablo Bay.

Six treatment alternatives were evaluated for the remediation of groundwater prior to discharge. Reverse osmosis (RO) was selected among these six alternatives for conceptual design based on the results of the treatability evaluation. The treated groundwater should be capable of meeting limits for both discharge options. The RO treatment system included various pretreatment and sludge treatment processes. The effluent resulting from such treatment could be either discharged or appropriately reused.

INTRODUCTION

The Hamilton Air Force Base (AFB) is an inactive base located in Marin County, California, near the City of Ignacio and immediately adjacent to San Pablo Bay. A landfill located on that base, designated as Landfill No. 26, received household and military wastes during the 1940-1970 period. The military wastes were generated by industrial activities such as welding, plating, electronic maintenance and engine and frame repair.

The May 1988 results of a Long-Term Surface and Groundwater Monitoring Program conducted at the Landfill Site by Woodward-Clyde Consultants indicated the presence of contaminants at levels exceeding background concentrations in the groundwater. Therefore, a voluntary action remediation program was undertaken in order to remove these contaminants from the groundwater.

A groundwater treatability study was conducted by Sirrine based on the review of a feasibility study report for the Remediation of Landfill 26, dated July 1988, and on the review of the ROD-Remedial Alternative Selection, dated August 1989. The objective of this work was to evaluate the capability of various treatment alternatives to meet anticipated limits for the discharge of groundwater into the San Pablo Bay or into the Novato Sanitary District publicly owned treatment works (POTW). Another objective was to conceptually design a groundwater treatment system using the most appropriate treatment alternative.

PROJECT DESCRIPTION

Pollutant Concentration in the Groundwater

The projected concentration of pollutants in the groundwater was determined based on data acquired during the long-term monitoring study; the collected data involved 11 monitoring wells located in and around the landfill area. Table 1 summarizes the average concentrations of pollutants detected in samples collected from these monitoring wells.

Table 1
Projected Groundwater Characteristics
and Anticipated Discharge Limits

Pollutant	Concentration[a,d]		San Pablo Bay Discharge	Novato POTW Discharge Limits	
	Average	Background	Average Limits	Daily Max	Monthly Average
COD	170	21		–	1,000
BOD	7	4	30	--	400
TOC	42	3			
TSS	NDA[b]	NDA	30	--	400
pH				6.0-9.0	5.5-8.5
Phenol	0.004	ND[c]	0.5		
Total Oil & Grease	NDA	NDA		200	
Dissolved Phosphate	0.03	0.03			
Nitrate-N	0.015	2			
Chloride	706	87		420	
TDS	2060	580		1250	
Antimony	0.11	0.120		5	
Arsenic	0.003	ND	0.020	0.5	
Barium	0.38	0.037		5	
Berylium	0.006	0.009		1	
Boron	0.71	0.009		1	
Cadmium	0.007	0.007	0.010	0.11	
Chromium	0.014	0.013	0.011	1.0	
Cobalt	0.016	0.013			
Copper	0.014	0.014	0.020	1.5	
Iron	18	12.3			
Lead	0.09	0.087	0.0056	0.4	
Mercury	0.001	ND	0.01	0.01	
Molybdeum	0.021	0.02			
Nickel	0.017	0.015	0.0071	1.0	
Selenium	0.002	0.002		2	
Silver	0.011	NA	0.0023	0.2	
Thallium	0.12	0.14			
Vanadium	0.016	0.01			
Zinc	0.023	0.02	0.058	1.5	
Chlorobenzene	0.023	ND			
1,4-Dichlorobenzene	0.015	ND			
Jet Fuel	0.11	ND			
Diesel Fuel	0.78	0.05			
Motor Oil	1.0	ND			
Acenapthene	0.0013	ND			
Antracene	0.0012	ND			
Bis-phthalate	0.10	ND			
Chrysene	0.001	ND			
Flurantliene	0.0012	ND			
Fluorene	0.0013	ND			
Napthalene	0.014	ND			
Phenanthrene	0.0014	ND			
Pyrene	0.0035	ND			
1,2-Dichlorobenzene	0.0065	ND			
1,3-Dichlorobenzene	0.0015	ND			
Nitrobenzene	0.0012	ND			
Bis(2-chloropropyl)	0.001	ND			
2,4-Dimethylphenol	0.0015	ND			
Heptachlor	0.001	ND			
Total PNAs	0.027		0.015	0.10	
Cyanide	ND	ND			
Volatile & Chlorinated Organics					
TICH	0.047			0.015	

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[a] All quantities are expressed in mg/L.
[b] NDA - No Data Available
[c] ND - Not Detected
[d] Based on the 1988 Long Term Groundwater Monitoring Study

Discharge Options and Requirements

Two options were considered for the disposal of treated groundwater from the Hamilton AFB site. The first disposal option was discharge into the Novato Sanitary District POTW; the second option was discharge into the San Pablo Bay. The first option necessitates the removal of dissolved solids and chlorinated hydrocarbons from the groundwater. The second option necessitates the removal of polynuclear aromatic hydrocarbons (PAHs) and heavy metals from the groundwater in order to meet required discharge limits for these pollutants (Table 1).

GROUNDWATER SAMPLING AND CHARACTERIZATION

Groundwater Sampling

The groundwater that was tested was collected from four monitoring wells (MW), MW-75, MW-77, MW-86 and MW-88. These wells were selected among the 11 monitoring wells located in and around the landfill area (Figure 1).

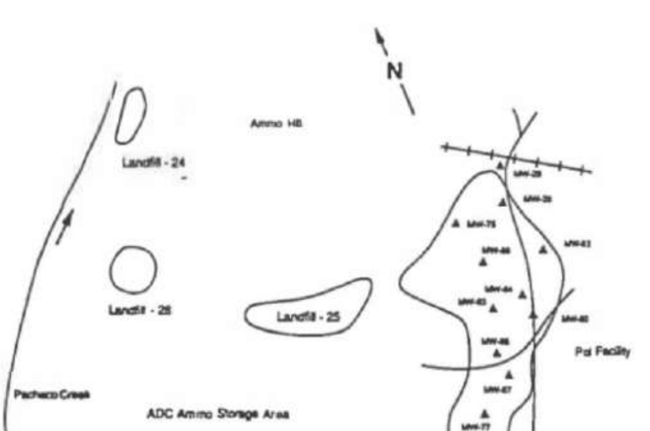

Figure 1
Groundwater Sampling Location Map

Five 100-gallon samples of groundwater were collected from MW-77, MW-86 and MW-88, and a 20-gallon sample was collected from MW-75. These wells were selected because of the projected presence of priority pollutants in significant concentrations (when compared to their discharge limits to the POTW or to the San Pablo Bay [1988 data]). MW-77 was selected because chlorinated organics such as chlorobenzene and 1,4-dichlorobenzene (1,4-DCB) were reported to be present in significant concentrations in samples from this well (1988 Groundwater Monitoring Report). Cadmium, lead and zinc were also reported to be present in MW-77 samples. MW-86 samples were reported to contain significant concentrations of PAHs such as naphthalene and phenanthrene as well as cadmium, nickel, copper, lead and zinc (1988 Groundwater Monitoring Report). Elevated concentrations of dissolved solids were reported in samples from MW-75. Finally, samples were collected from MW-88 because this well was subjected to extensive aquifer testing during the sampling process.

Groundwater Characterization

Analytical tests were carried out in the Sirrine laboratories and in the Radian Corporation laboratories. Table 2 summarizes the results of these tests. Jet fuel, diesel fuel and motor oil were not detected in the collected samples. Total BOD and COD concentrations were lower than 10 and 75 mg/L, respectively. Total organic carbon (TOC) and dissolved organic carbon (DOC) concentrations ranged between 10 and 160 mg/L and between 10 and 30 mg/L, respectively, in the tested samples. Chlorinated hydrocarbons were not detected in these samples and the concentrations of most metals were either below detection limits or below their discharge limits to the San Pablo Bay.

Table 2
Characteristics of Groundwater Samples Collected for Treatability Testing

Pollutant	MW-77	MW-86	MW-88	MW-75	Background Concentration[a]
	Monitoring Well Concentration, mg/L				
COD (filtered)	67	58	50	35	
COD (total)	74	60	60	35	21
BOD (filtered)	2	3	2	8	
BOD (total)	2	3	8	8	4
TOC	12	12	89	156	3
DOC	27	23	12	24	
TSS	28	33	38	158	
pH	6.9	6.8	7.7	7.1	
TKN	14.3	13.4	2.24	< 1	
Ammonia-N	13.0	11.5	1.1	<3.3	
Total Phosphorus	< 0.2	< 0.2	0.24	0.33	
Chloride	38	26	49	3000	87
TDS	655	491	948	7330	680
Total Oil and Grease	84	5	26	< 1	
Bicarb. Alkalinity	479	550	780	443	
Sulfate	3	32	83	1450	
Fluoride	0.18	0.1	0.17	0.3	
NO_3-N	< 0.1	0.09	3.58	< 0.1	
NO_2-N	< 0.1	0.23	< 0.1	–	
Phosphate-P	0.1	0.1	0.1	0.33	
SiO_2	43.3	43.3	40.5	43.8	
Carbonate	0	0	0	0	
Electrical Conductivity, μmhos/cm	–	–	–	11300	
Turbidity, NTU	–	–	20	110	
CN-	< 0.02	< 0.02	< 0.02	< 0.02	
Metals[b]:					
Aluminum	ND[f]	0.42	0.75	6.8	
Antimony	ND	ND	ND	ND	0.12
Barium	0.26	0.91	0.4	0.083	0.037
Boron	ND	ND	ND	2.1	0.009
Calcium	140	93	180	49	
Chromium	ND	ND	ND	0.011	0.013
Cobalt	ND	ND	ND	0.021	0.013
Iron	28	33	5.6	9.8	12.3
Magnesium	36	28	47	88	
Manganese	1.5	0.38	0.85	1.4	
Nickel	ND	ND	ND	0.025	0.015
Potassium	16	5.6	18	37	
Silicon	8.5	19	17	27	
Sodium	36	52	100	2200	
Strontium	0.79	0.79	1.3	0.88	
Vanadium	ND	ND	ND	0.023	0.01
Zinc	0.030	ND	0.023	0.029	0.02
Copper[c]	0.0033	ND	0.0091	0.016	0.014
Lead[d]	0.022	0.011	0.015	0.0048	0.087
Volatile Organics[g]:	ND	ND	ND	ND	ND
Xylenes	0.013	ND	ND	ND	
Semivolatile Organics[h]:	ND	ND	ND	ND	ND
Acenaphthene	ND	ND	ND	0.0028	ND
Fluorene	0.00026	ND	ND	ND	ND

[a] Data obtained from long term groundwater monitoring
[b] Concentration measured by ICP method
[c] Concentration measured by graphite furnace method
[d] Concentration measured by SW F421 method
[e] Concentration measured by cold vapor method
[f] Non detected
[g] Benzene, Chlorobenzene, 1,2-Dichlorobenzene, 1,3-Dichlorobenzene, 1,4-Dichlorobenzene, Ethyl benzene, Toluene
[h] Acenaphthalene, Anthracene, Benzo(a) pyrene, Benzo(b) fluoranthene, Benzo(g,h,i) perylene, Benzo(k) fluoranthene, Chrysene, Dibenzo(a,h) anthracene, Fluoranthene, Indeno (1,2,3-Cd) pyrene, Naphthalene, Phenanthrene, Pyrene

Iron and dissolved solids concentrations were also measured in the collected samples. Iron concentrations of 28, 33, 5.6 and 9.8 mg/L were measured in samples from MW-77, MW-86, MW-88 and MW-75, respectively. A total dissolved solids (TDS) concentration of 7,330 mg/L was measured in the MW-75 sample; this concentration is significantly higher than the Novato POTW discharge limit of 1,250 mg/L. However, TDS concentrations were lower than 1,000 mg/L in samples from the other three monitoring wells. Oil and grease concentrations of 84 and 26 mg/L were measured in the MW-88 and MW-77 samples, respectively. Suspended solids and chlorides were found at the respective concentrations of 156 and 3,000 mg/L in samples from MW-75. Elevated concentrations of sodium and sulfate were also characteristic of groundwater from this monitoring well.

Most of the contaminants that were projected to be present in the collected groundwater samples were not detected or were detected at levels lower than their background concentrations or discharge limits. Therefore, it was decided to spike the collected samples with selected chemicals in order to simulate their average concentrations in the groundwater as determined from the 1988 Groundwater Monitoring Report (Table 1).

GROUNDWATER TREATABILITY

Several technologies were evaluated for the removal of pollutants from the spiked groundwater samples. The evaluation was based on bench-scale treatability testing and on a literature search. Six groundwater treatment alternatives were considered. Three of these treatment alternatives (reverse osmosis [RO], precipitation and evaporation/distillation-carbon adsorption) were considered for the removal of dissolved solids and total identifiable chlorinated hydrocarbons (TICH) in order to meet the requirements for discharge into the POTW. The three remaining alternatives were considered for the removal of PAHs and heavy metals in order to meet the requirements for discharge into the San Pablo Bay. These alternatives included biological treatment, electrochemical-carbon adsorption treatment and electrochemical-UV/ozone/H_2O_2 treatment. Figure 2 shows a schematic of the various treatment alternatives considered.

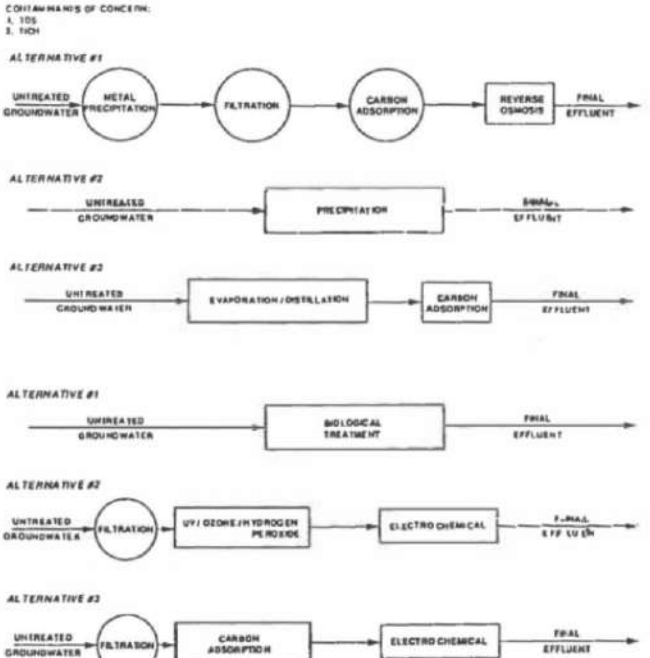

Figure 2
Alternatives Considered for the Treatment of Groundwater
from Landfill No. 26 in the Hamilton Air Force Base
Novato, California

Reverse Osmosis

Reverse osmosis is typically used for the removal of dissolved solids from water or wastewater. Pretreatment processes such as metal precipitation, filtration and carbon adsorption are necessary prior to RO treatment. Carbon adsorption and filtration remove TOCs, refractory organics, suspended solids and metals, whereas precipitation removes metals.

It was important in the course of the study to determine the extent of removal of dissolved solids from groundwater as well as the operational conditions required for such removal using RO treatment systems. The average TDS concentration in the groundwater is projected to exceed the Novato POTW daily maximum discharge limit of 1250 mg/L. RO treatment should be capable of lowering the TDS concentration in the groundwater to less than 500 mg/L. Therefore, an application test was carried out to determine the type of membrane required for RO treatment and the effectiveness of such a treatment in rejecting groundwater contaminants.

Materials and Methods

Fifty gallons of groundwater were sent to a reverse osmosis system manufacturer. The groundwater sample was prepared by mixing MW-75 samples with MW-88 samples in a 1:5 ratio. The 50-gallon sample was then sand-filtered before shipment. The TDS concentration of the mixture was 2014 mg/L, a concentration close to the average projected TDS concentration of 2,060 mg/L (Table 1). Table 3 reports the estimated characteristics of the 50-gallon sample.

Table 3
Estimated Characteristics of the Groundwater Mixture Sample
Subjected to RO Treatment

Constituent	Concentration, mg/L MW-88[a]	MW-75[a]	Mixture[b]
Total dissolved solids (TDS)	948	7330	2058
Total suspended solids (TSS)	36	156	56
TOC	249	167	234
COD (filtered)	50	35	47
COD (total)	60	35	56
BOD (filtered)	2	6	3
BOD (total)	8	6	7
DOC	39	–	–
Total oil and grease	26.1	< 1	21
Chloride	49	3000	562
Bicarb. alkalinity, as ($CaCO_3$)	760	443	705
Sodium	93	1393	319
Calcium	200	41	172
Magnesium	44.7	44	44.6
Sulfate	63	1460	306
Silica	40.5	43.8	41.1
Potassium	14.9	–	–
Iron	8.7	8.4	8.6
Total Kjeldahl nitrogen	2.24	< 1	< 2.0
NO3-N	3.58	< 0.1	< 3.0
NO2-N	< 0.1	–	–
Ammonia-N	1.1	< 0.3	< 0.9
Total phosphorus	0.24	0.33	0.26
Phosphate-P	0.1	0.33	0.14
Turbidity, NTU	020	110	35.7
Conductivity, micromhos		11300	
pH	7.7	7.1	

Mixture Characteristics as Tested

Conductivity	3150 micromhos
pH	7.6
Refractometer measurement	0.3 Brix
Appearance	clear pale yellow solution
Viscosity	similar to water viscosity

[a] Measured Concentration
[b] Estimated Concentration

Results

RO treatment effectively concentrated the groundwater contaminants. More than 90% of the treated groundwater was recovered with a permeate quality capable of meeting the required discharge limits. Over 96% of all ionic contaminants in the groundwater were retained during concentration processing. This result was achieved using an "ST10" sepralator (Osmonics Corporation, Minnetonka, Minnesota). The TDS concentration of the composite permeate, at 90% recovery, was less than 180 mg/L, well below the anticipated discharge limit for that pollutant. On the other hand, the measured TDS concentration of 360 mg/L in the permeate was more than doubled when recovery increased from 77% to 90%.

Discussion RO treatment of groundwater successfully reduced the dissolved solids concentration from approximately 2,000 mg/L to less than 500 mg/L. The permeate should, therefore, be capable of meeting the Novato POTW discharge limits for dissolved solids. It is recommended that the RO system be operated at a recovery level of 80% because of the increase of the composite permeate TDS concentration to 180 mg/L as recovery is increased from 77-to 90%.

The concentrate generated during the RO treatment process itself requires treatment. The concentrate is projected to have a TDS concentration of 10,000 mg/L when the RO system is operated at an 80% recovery level. This concentrate requires further concentration treatment via a second RO unit. The concentrate from the second unit is projected to have a TDS concentration of approximately 19,000 mg/L. It can be disposed of by deep well injection or by evaporation. The residue from the evaporation process can be transported off-site to an appropriate permitted disposal facility.

Membrane fouling is of concern due to the presence of iron at a concentration higher than 8 mg/L. Such fouling may result from iron precipitation which may form a relatively impenetrable scale at the membrane surface. Scale formation would reduce groundwater flow through the membrane. Removal of iron should, therefore, be considered in a pretreatment step.

Chemical Precipitation

Chemical precipitation with lime and caustic soda was evaluated for the removal of dissolved solids, metals and chlorinated hydrocarbons.

Materials and Methods

Groundwater samples were filtered and spiked with selected pollutants prior to chemical precipitation treatment. A 20-L sample of groundwater from MW-88 was passed through a glass-fiber filter; the filtrate was dosed with 25 ug/L copper, 20 ug/L nickel, 100 ug/L lead and 18 mg/L iron and 1,4-DCB and naphthalene at 75 and 40 ug/L, respectively.

Another 20-L sample of groundwater was also prepared for flocculation treatment by mixing MW-75 and MW-88 samples at a ratio of 1.5:1. This sample was also filtered and spiked with copper, nickel, lead, iron, 1,4-DCB and naphthalene at the same dosage levels used for the first sample.

Flocculation trials were carried out using a standard jar test apparatus with paddles and stirrer shafts made of stainless steel. Jars were fabricated from acrylic plastic with inside dimensions of 11.5 x 11.5 x 20.0 cm. Flash mixing at a speed of 220 rpm was initiated immediately following the addition of NaOH or $Ca(OH)_2$ and continued for 1 minute. Slow mixing at 40 rpm was continued for 5 minutes. At the end of a 30-min period of quiescent settling, a supernatant sample of 500 mL was transferred to a container. The influent and supernatant fractions were then analyzed for total and soluble iron, copper, nickel, lead and TDS. The concentration of 1,4-DCB was also analyzed for in the influent and supernatant fractions.

Results

The effect of lime treatment on pollutant concentration is summarized in Table 4. The concentrations of copper, nickel and lead in the effluent supernatant were reduced to levels lower than their discharge limits to the San Pablo Bay at pH > 10. The TDS concentration was reduced to a minimum (920 mg/L) as effluent pH was increased to 10.4. A further increase in effluent pH resulted in an increase in TDS concentration.

The iron concentration of 2.62 mg/L in the control supernatant was reduced to less than 0.5 mg/L by lime treatment. The concentration of iron in the control sample was reduced from 11.2 to 2.6 mg/L by settling, indicating that most of the iron in the groundwater was present in an insoluble form. Lime treatment had no effect on the removal of 1,4-DCB from the treated sample.

The results of the caustic treatment of the samples are summarized in Table 4. The TDS concentration increased from 825 mg/L to 973 mg/L when the effluent pH was increased from 8.8 to 10.1 during the first batch tests. The TDS concentration also increased from 1,396 to 1,660 mg/L when the effluent pH was increased from 9.6 to 10.8 during the second batch tests.

Iron was reduced to less than 0.5 mg/L by caustic treatment. Copper, nickel and lead concentrations in the treated effluent were lower than their discharge limits to the San Pablo Bay (@ pH ≥10.2). Caustic soda treatment had no effect on the removal of 1,4-DCB from the treated sample.

Carbon Adsorption

Batch isotherm tests were conducted in order to evaluate the efficiency of carbon adsorption in removing TOC, 1,4-DCB, naphthalene and metals. The ultimate objective of the carbon adsorption study was to determine the carbon utilization rates for the compounds under consideration.

Materials and Methods

Groundwater samples from MW-75 and 88 were mixed at an approximate ratio of 1:4 to obtain a sample with TDS and TOC concentrations similar to the ones projected in Table 1. The mixture was then passed through a glass fiber filter and dosed with 50 ug/L 1,4-DCB, 40 ug/L naphthalene and 100 ug/L lead.

The spiked groundwater samples were subjected to batch carbon isotherm testing. Aliquots (45-mL) of the spiked groundwater samples were transferred into glass containers and dosed with pulverized activated carbon (Calgon Filtrasorb 300, Calgon Corp., Charlotte, North Carolina) at concentrations ranging between 0 and 160 mg/450-mL aliquot. The containers were capped with nonreactive, Teflon-coated tops which allow less than 30 mL of headspace volume. They were then tumbled for 48 hours in the dark at room temperature (approximately 20 °C). Next, the activated carbon was removed from the samples by filtration through glass fiber filters. TOC, 1,4-DCB and lead concentrations were measured.

Table 4
Concentrations of Metals in Groundwater
to Lime and with Caustic Soda Treatment

Flocculant	Dosage mg/L (as $CaCO_3$)	Effluent pH	Metal Concentration[a], mg/L Fe	Cu	Ni	Pb	TDS
BATCH 1							
Control[b]	—	—	2.62	0.034	0.032	0.089	724
Influent[c]	—	—	11.2	0.033	0.025	0.083	825
Lime	223	8.5	0.155	0.006	0.017	BDL[e]	592
	513	9.5	0.111	0.007	0.012	BDL	518
	618	9.9	0.124	0.008	0.009	BDL	492
Caustic Soda	200	8.8	0.333	0.006	0.022	BDL	800
	450	9.6	0.141	0.006	0.017	BDL	839
	900	10.1	0.100	BDL	0.011	BDL	973
Flocculant	Dosage mg/L (as $CaCO_3$)	Effluent pH	Metal Concentration[a], mg/L Fe	Cu	Ni	Pb	TDS
BATCH 2							
Influent[d]		—	18.5	0.033	0.031	0.083	1640
Lime	618	9.5	0.224	0.006	0.008	BDL	984
	755	10.1	0.201	0.007	0.005	BDL	958
	838	10.4	0.327	0.008	<0.005	BDL	920
	1339	11.5	0.139	0.007	<0.005	BDL	1352
Caustic Soda	935	9.6	0.178	0.006	0.008	BDL	1660
	1420	10.2	0.753	0.006	0.007	BDL	1878
	1760	10.8	0.111	BDL	<0.005	BDL	1396
San Pablo Bay Discharge Limits				0.020	0.0071	0.0056	

[a] Total metal concentrations
[b] No lime or caustic soda were added during treatment
[c] MW-88; Influent pH = 7.3
[d] MW-88 + MW-75 (ratio=1.5:1); Influent pH=7.3
[e] BDL: Below detection limit
Detection Limit of Fe (Dissolved) = 0.030 mg/L
Ni = 0.005 mg/L
Pb = 0.005 mg/L

Results

Freundlich isotherms corresponding to 1,4-DCB, lead and TOC were generated from the results of the batch tests. Figures 3, 4 and 5 show the Freundlich isotherms corresponding to 1,4-DCB, lead and TOC, respectively. The K values determined from these figures for 1,4-DCB, lead and TOC were 0.10, 0.04 and 678 mg/g, respectively. The K value represents the adsorbate loading, X/M (mg adsorbate/g carbon) at a pollutant equilibrium concentration of 1.0 mg/L. Naphthalene was not detected in any of the samples from the isotherm testing. This result may be attributed to its volatilization from solution. The activated carbon requirements (G=c) for the removal of 1,4-DCB, lead and TOC are summarized in Table 5.

Biological Treatment

Alternative technologies evaluated for the biological removal of organic pollutants from groundwater included: (1) submerged fixed film bioreactors and (2) granular activated carbon fluidized bed systems. Most organic contaminants are biodegradable, although the relative ease of biodegradation varies widely with their concentrations. Chlorinated organic hydrocarbons and PAHs have been reported to be reduced to the ug/L level, in the presence of adequate concentrations of primary substrates.[1,2] On the other hand, heavy metals may inhibit the growth of microorganisms and consequently their ability to remove biodegradable organics.

The characteristics and concentrations of pollutants present in the groundwater play an important role in the selection of the type of biotechnology required for its treatment. Groundwater from landfill No. 26 was projected to have an average BOD concentration of 7 mg/L and an average TOC concentration of 42 mg/L. However, the samples collected for treatability testing contained BOD at a concentration range of 2 to 8 mg/L and TOC at a range of <5 to 250 mg/L. The elevated concentrations of TOC identified in the groundwater may be attributed to the presence of mostly nonbiodegradable or slowly degradable organics.

The concentration of biodegradable organics is not sufficient to support aerobic suspended growth systems. These systems usually work best at an influent BOD concentration in the range of 100 to 10,000 mg/L. Aerobic suspended growth systems were not considered in this study because of the low concentrations of BOD in the groundwater samples. However, fixed film systems and other types of nonconventional biological treatment technologies were further considered in the study.

Fixed Film Systems

Fixed film biological reactors have been used to treat low BOD wastewaters and polluted groundwaters. These systems operate under conditions of low carbon to surface area ratios and are capable of achieving significant removal of biodegradable pollutants from the groundwater. Nutrients such as nitrogen and phosphorus as well as primary substrates may be required for such treatments. Advantages of fixed film systems include low capital cost, minimal operating requirements and low biological solids generation.

Granular Activated Carbon—Biological Fluidized Bed Reactor (GAC-FBR) System

A biological GAC-FBR system couples the use of cost-effective biological treatment with carbon adsorption for the removal/degradation of contaminants present in small concentrations in the groundwater.

The unit typically consists of a carbon column operated at a flux rate sufficient to fluidize the carbon bed. The hydraulic detention time of groundwater through the system is approximately 7-8 minutes. The GAC-FBR system has been operated at COD loading rates ranging between 30 lb/day/1000 ft^3 and 450 lb/day/1000 ft^3 and at a hydraulic loading rate of approximately 12 gpm/ft^2. Benzene, toluene, ethylbenzene and xylene (BTEX) have been reported to be readily removed by GAC-FBR systems, with effluent concentrations as low as 7 ug/L.[3]

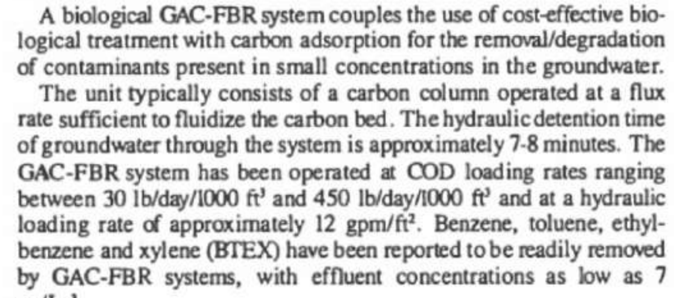

Figure 3
Freundlich Isotherm of 1,4-DCB in the Groundwater Matrix

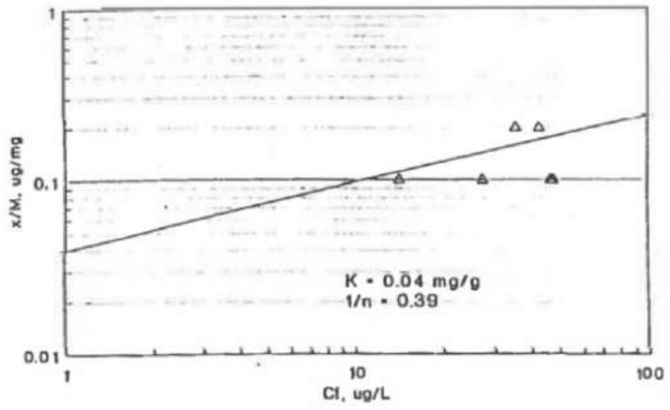

Figure 4
Freundlich Isotherm of Lead in the Groundwater Matrix

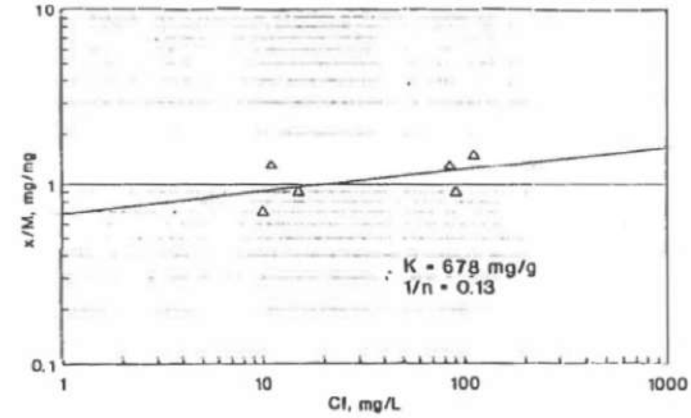

Figure 5
Freundlich Isotherm of TOC in the Groundwater Matrix

Table 5
Carbon Adsorption Study Results

Compound	Freundlich Isotherm Parameters		Influent Concentration	Lb. Carbon/Month at Q = 100 gpm
	K	1/n		
1,4-DCB	0.10 ug/mg	0.83	50 µg/L	700
Lead	0.04 ug/mg	0.38	80 µg/L	13000
TOC	680 mg/g	0.13	80 mg/L	2390

Aeration of the groundwater is achieved by predissolution of oxygen in order to prevent the loss of VOCs. Recycling provided a flowrate sufficient to maintain the activated carbon in the fluidized state and to dilute heavy loadings of contaminants to a reasonable concentration. Nutrients such as nitrogen and phosphorus must be added to the groundwater if it is deficient in these elements.

A pretreatment system would be necessary to remove iron which is present in significant concentration in the groundwater. The removal of the latter compound is necessary to prevent the generation of iron sludge in the reactor.

The GAC-FBR biological treatment system is considered to be the best available biotechnology for the removal of PAHs and TICHs through adsorption and biodegradation. This system was reported to be capable of absorbing a ten-fold increase in contaminant loading, due to the combined adsorptive capability of the biofilm coated GAC and to the bioregenerative capability of the activated carbon. The presence of chlorinated hydrocarbons in groundwater will necessitate periodic regeneration or replacement of the carbon following saturation.

The carbon utilization rate of this system will be lower than that of a conventional activated carbon system because adsorbed PAHs and chlorinated hydrocarbons are biodegraded. Metals, present at low concentrations, are expected to be removed from the groundwater through adsorption. The advantages and disadvantages of such a system are summarized in Table 6.

Table 6
Advantages and Disadvantages
of Biological GAC Fluidized Bed Reactors

ADVANTAGES

1. No volatilization of organics; no loss of BTEX (benzene, toluene, ethylbenzene, and xylene).
2. Biological regeneration of carbon eliminates the need for thermally regenerating carbon or hauling spent carbon.
3. Ability to remain biologically viable at low BTEX and organics concentrations.
4. Operates as a carbon column.
5. Small size of GAC FBR unit allows its use as a transportable unit.
6. Eliminates aeration process that would result in the stripping of BTEXs.
7. Minimum carbon replacement costs.
8. Organics are adsorbed onto carbon and are degraded at faster rates than when present in solution.

DISADVANTAGES

1. Slowly biodegradable organics such as 1,4-DCB will use up carbon capacity and will result in a larger carbon utilization rate than that of a system treating readily biodegradable organics.
2. Use of pure oxygen; expensive and must be generated on site.
3. Recycle is required to maintain fluidization and to dilute incoming waste in order to obtain adequate loading rates.

UV/Ozone/H_2O_2 Oxidation Treatment

UV/ozone/H_2O_2 treatment involves the photochemical oxidation of halogenated organic compounds and other selected organics. The oxidation process is induced by a controlled combination of ozone treatment and UV irradiation. The process involves bubbling ozone through contaminated water while it is being simultaneously subjected to UV irradiation. The effectiveness of the UV oxidation technology has been demonstrated for the removal of volatile and semivolatile organics such as trichloroethylene, perchloroethylene, PCBs, benzene, toluene, xylene and ethylbenzene. The effect of UV/ozone treatment on the concentrations of these VOCs in groundwater is summarized in Table 7. These concentrations are lower than the Novato District POTW or the San Pablo bay discharge limits.

Table 7
Effect of UV/Ozone Treatment on Pollutant Concentrations *

Pollutant	Concentration, ug/L	
	Influent	Treated Effluent
Trichloroethylene	5,000	<2
BTEX (Benzene, toluene, xylene, ethylbenzene)	10,750	4
Pentachlorophenol	50	<1
Lindane	60	<1
1,2-dibromo, 3-chloropropane (DBCP)	50	<1
Hexachlorobenzene	39	<1.5

Process Description

A pretreatment step is required in order to remove the soluble iron prior to oxidation. Iron removal can be accomplished using a slip stream of ozone either from an ozone generator or from the UV/O_3/H_2O_2 reactor off-gas. The pretreated groundwater is passed through filter bags prior to UV/O_3/oxidation. The system should be operated with a retention time of 20 to 25 minutes (in order to meet discharge limits to the San Pablo Bay).

The power requirement for the ozone generator, UV lamps, air compressors and pumps is estimated to be 30 kva. The ozone used for iron pretreatment could add between 5 and 15 kva in power requirements.

The UV oxidation treatment process is an attractive alternative for the removal of volatile and chlorinated organics from groundwater. Advantages of this treatment process over air stripping or carbon adsorption include the absence of VOCs released into the atmosphere by air stripping and the absence of a solids handling problem. Unlike air stripping or carbon adsorption that concentrate the pollutants, UV oxidation destroys them. Finally, the UV oxidation process offers considerable operational flexibility since it can be operated in an intermittent mode and under a wide range of operating conditions.

Electrochemical Treatment

Electrochemical treatment has been used for the removal of metals and dyestuff from wastewaters.[5,6] This process involves the circulation of groundwater between two oppositely charged iron electrodes. Iron is released by the anode and the ferrous and hydroxide ions that are generated and will form ferrous hydroxide. Heavy metals and possibly organic pollutants are adsorbed on the ferrous hydroxide molecules. The addition of a polymer causes flocculation and precipitation of the hydroxide along with the adsorbed compounds. The effluent from this process is filtered to remove suspended and precipitated solids. Electrochemical treatment is usually carried out at a neutral pH.

Materials and Methods

Two 1-gallon groundwater samples from MW-75 were filtered and dosed with 100 ug/L 1,4-DCB, 40 ug/L naphthalene, 20 ug/L nickel, 25 ug/L copper and 100 ug/L lead. The spiked samples were shipped to Andco Environmental Processes, Inc. (Amherst, New York) in order to evaluate the effectiveness of the electrochemical treatment process in removing the contaminants of concern. One of the two groundwater samples was subjected to electrochemical treatment, while the second sample was used as a trip blank.

Three 500-mL samples were electrochemically treated under oxidized iron conditions of 25, 50 and 100 mg/L. A polyacrylamide copolymer (98% active) was added to the spiked samples at a dosage of 5 mg/L during the treatment process. Cu, Ni and Pb concentrations were measured in the influent, in the trip blank and in each of the treated effluents samples. The concentrations of naphthalene and of 1,4-DCB were also measured in the influent, trip blank and treated samples.

Results

The results of electrochemical treatment are summarized in Table 8. The concentrations of Pb and Cu in the influent sample (50 and 25 ug/L, respectively) were reduced to less than 5.6 and 20 ug/L, respectively. On the other hand, nickel concentrations of 19, 18 and 17 ug/L were detected in the treated effluent at iron concentration levels of 25, 50 and 100 mg/L, respectively. The measured concentrations of nickel were significantly higher than the San Pablo Bay discharge limit (7.1 ug/L). Finally, the concentration of 1,4-DCB was reduced from 95 ug/L in the influent to 17 ug/L in the trip blank and to 6.8 ug/L in the treated effluent at the iron concentration level of 50 mg/L.

Discussion

The treatability study indicates that electrochemical treatment did not successfully achieve the San Pablo Bay discharge limits. While the electrochemical treatment process did successfully remove copper and lead from spiked groundwater samples to below discharge limits, it did not adequately remove nickel. The failure of the electrochemical process to remove nickel may be attributed to the neutral pH at which treatment was performed. Nickel was reported to exhibit minimum stability in solution at pH 10.[7] In fact, a repeat of the electrochemical treatment process at pH 10 resulted in a significant reduction in nickel concentrations.

Table 8
Effect of Electrochemical Treatment on Pollutant Concentrations

Pollutant	Concentration, mg/L					San Pablo Bay Discharge Limits
	INFL	Trip Blank	EFF Conc. of oxidized iron, mg/L 25	 50	 100	
Pb	0.05[a]	0.091	ND[b]	ND	0.004	0.006
Ni	0.02[a]	0.021	0.019	0.018	0.017	0.007
Cu	0.025[a]	0.027	0.010	0.010	0.006	0.020
Fe	–	1.2	0.64	0.92	.6	–
1,4-DCB	0.095	0.0017	–	0.0068	–	–

[a] Spiked concentrations
[b] Detection limit for Pb-0.003 mg/l.

The significant decrease in 1,4-DCB concentration in the trip blank and in the treated sample may be attributed to its volatilization during transportation. Thus, it was not possible to determine if electrochemical treatment is effective in reducing the concentration of chlorinated hydrocarbons.

SUMMARY OF THE TREATMENT ALTERNATIVE EVALUATIONS

The evaluation of the various treatment alternatives was based on the system performance, reliability and flexibility. Table 9 summarizes the effect of the various treatment alternatives on effluent quality with respect to possible discharge options.

RO treatment should be capable of producing effluent that would consistently meet the San Pablo Bay and the Novato POTW discharge limits. On the other hand, the effluent from the biological GAC-FBR system should be capable of meeting the San Pablo Bay discharge option. This latter system constitutes a cost-effective method for groundwater treatment as noted in Table 10. When used in conjunction with lime precipitation, the GAC-FBR system should be capable of producing an effluent that would meeting either discharge option (metals and dissolved solids are readily removed by lime treatment).

Table 9
Quality of Treated Effluents with Respect to the POTW or San Pablo Bay Discharge Options

Treatment Alternative	Effluent Discharge to the POTW	Residual Pollutant in Effluent	Effluent Discharge to the San Pablo Bay	Residual Pollutant in Effluent
Reverse Osmosis	+		+	
Lime Precipitation	-	TICH	-	PAH
Biological GAC-FBR	-	TDS	+	
Lime Precipitation - Biological GAC-FBR	+		+	
Evaporation/Distillation-Carbon Adsorption	+		+	
UV/Ozone/Hydrogen Peroxide-Electrochemical Treatment	-	TDS	-	Ni, other metals
Electrochemical Treatment-Carbon Adsorption	-	TDS	-	Ni, other metals

+ Effluent meets discharge limits
- Effluent does not meet discharge limits

The effluents generated by the UV/O_3/H_2O_2-electrochemical treatment train and by the carbon adsorption-electrochemical treatment train are not expected to meet the discharge limits into the San Pablo Bay for all the compounds under consideration.

Table 10
Cost Estimates of the Groundwater Treatment Alternatives

Treatment Alternatives	Total Present Worth, $
1. Reverse Osmosis	3,365,200
2. Lime Precipitation	1,088,100
3. Evaporation/Distillation (60 gpm) - Carbon Adsorption (100 gpm)	4,042,500
4. Biological Treatment	397,900
5. UV/O_3/H_2O_2 - Electrochemical Treatment	1,048,700
6. Electrochemical Carbon Adsorption Treatment	883,600

Evaporation/distillation constitutes the least cost-effective process both from the capital and from the operation and maintenance cost standpoints. However, the effluent from this process should be capable of meeting both the POTW and the San Pablo Bay discharge limits when used in conjunction with carbon adsorption.

RO treatment was retained for a concept design because the effluent from such a system should be capable of consistently satisfying both the San Pablo Bay and the Novato POTW discharge requirements and because the effluent could be possibly reused instead of being discharged. However, RO treatment is not the most cost-effective alternative for the remediation of the Hamilton AFB groundwater.

CONCEPTUAL DESIGN OF THE REVERSE OSMOSIS GROUNDWATER TREATMENT SYSTEM

A flow diagram of the proposed groundwater treatment system is presented in Figure 6. This treatment system will include groundwater equalization, oil removal, precipitation, filtration, carbon adsorption, a two-stage RO system and a flash evaporation system. The system will be designed for a peak flow of 100 gpm and an average daily flow of 65 gpm.

The groundwater to be treated is projected to contain dissolved solids, metals, chlorinated hydrocarbons, polynuclear aromatic hydrocarbons and oil and grease. The permeate from the RO system will be discharged into either the Novato district POTW or San Pablo bay or will be reused. The reject stream from the RO system will be directed to the evaporator. The residue from the evaporator, at 15-20% solids, will be dewatered and transferred to an appropriately permitted disposal facility.

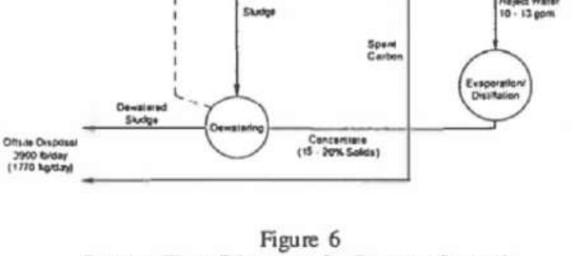

Figure 6
Process Flow Diagram of a Reverse Osmosis Groundwater Remediation System

Groundwater collected from different wells will be pumped to an equalization tank (10,000 gallons). The latter will allow for the equalization of pollutant concentrations prior to treatment. A rope skimmer will remove floating oil present in the groundwater.

Groundwater will be pumped from the equalization tank at 100 gpm to a small aeration tank in which ferrous iron will be oxidized. The groundwater will then be transferred to a lime precipitation unit. The latter will consist of a 500-gallon flash mix tank and a 1,500-gallon flocculation tank. The effluent from the precipitation tank will be pumped to a lamella type gravity settler at a loading rate of 0.5 gpm/ft^2. The settled sludge will be pumped to a filter press which will produce sludge with a total solids concentration of 30-35% The dewatered sludge will then be collected and transported to an appropriately permitted disposal facility. The supernatant from the clarifier will be pumped through a multimedia filter for the removal of suspended solids and through a 3,000-lb carbon adsorption unit. The latter unit will be used for the removal of TOC. Effluent groundwater will then be pumped to the first stage RO unit.

The RO units will be used for the removal of at least 90% of the dissolved solids from the groundwater. A two-stage RO system is proposed in order to minimize the volume of reject stream prior to its treatment by evaporation. The influent into the first RO unit will have a flow of 100 gpm and a TDS concentration of 1,750 mg/L. The effluent from the first-stage RO system will have a flowrate of 80 gpm and will have a TDS concentration of 165 mg/L, based on an 80% permeate recovery and more than 90% TDS removal. The reject stream from this system will have a flowrate of 20 gpm and a TDS concentration of approximately 10,000 mg/L. This reject stream will be transferred to the feed tank of a second RO unit. The second RO unit will generate 7-10 gpm of permeate with a TDS of approximately 1000 mg/L, based on a 33-50% permeate recovery and a 90% TDS removal. This permeate will be blended with the permeate from the first RO unit.

The treated effluent from the RO treatment system will have a TDS concentration of approximately 200-230 mg/L and a flowrate of 87–90 gpm. This effluent could be discharged to the San Pablo Bay or to the Novato district POTW or appropriately reused.

The 10-13 gpm of concentrate generated by the second RO unit will have a TDS concentration of approximately 19,000 mg/L. It will be transferred to the feed tank and then pumped to a triple-effect evaporator which will produce a slurry containing 15-20% solids. The condensate from the evaporator will be blended with the RO system permeate prior to discharge. The evaporator will have a maximum evaporation rate of 15 gpm. A diesel engine boiler unit will generate steam for the evaporation system at a flowrate of 1600 lb/hr and at a pressure of 10-12 psig.

The sludge from the evaporator (15-20% solids) will be pumped to a filter press. Dewatered sludge with 35% solids will be the end-product. Approximately 3,900 lb/day of dry solids will be generated by the RO treatment system, including 900 lb/day of suspended solids generated by the lime precipitation process and 3,000 lb/day generated by evaporation.

CONCLUSIONS

The following conclusions were made based on the results of this study:

- The groundwater sampling and characterization did not identify pollutants at levels reported in the 1988 Long-Term Groundwater Monitoring Report. This finding reflects the migratory nature of these pollutants in groundwater.
- Reverse osmosis should be capable of removing organic and metal pollutants as well as dissolved solids from the groundwater and be fully capable of producing an effluent that meets the San Pablo Bay and the Novato district POTW discharge limits. The effluent is expected to have a TDS concentration of less than 500 mg/L when the RO unit is operated at 80% recovery.
- Lime treatment of groundwater produced an effluent that meets the San Pablo Bay discharge limits for metals (at a reaction pH ≥ 10.5). TDS concentration in the lime-treated effluent was also lower than the Novato District POTW discharge limits.
- Caustic soda treatment of spiked groundwater samples produced an effluent that meets the San Pablo Bay discharge limits for metals. The TDS concentration was not reduced by caustic treatment, however.
- 1,4-DCB was not removed from spike groundwater samples by either lime or caustic precipitation treatment.
- The carbon utilization rates required for the removal of TOC and 1,4-DCB from spiked groundwater samples were determined as 1,300 and 700 lb/month, respectively.
- Evaporation/distillation is not economically feasible for the removal of dissolved solids from groundwater. However, this technology could be used for concentration of the RO reject stream residues having TDS concentrations of 10,000 mg/L or more.
- The biological GAC-FBR treatment system should be capable of removing metals, chlorinated hydrocarbons and PAHs from groundwater.
- UV/ozone/H_2O_2 oxidation of groundwater should be capable of degrading PAHs with no residue generation. Oxidation pretreatment of iron in the groundwater should precede the UV/ozone/H_2O_2 treatment.
- Electrochemical treatment of spiked groundwater samples (at neutral pH) was not capable of removing nickel to concentrations lower than the San Pablo Bay discharge limits.
- The evaporation/distillation-carbon adsorption, reverse osmosis and lime precipitation-biological GAC-FBR treatment alternatives should be capable of producing effluents that meet both the San Pablo Bay and the Novato district POTW discharge limits. Cost-effectiveness is lowest for the first treatment alternative and is highest for the third alternative. Reverse osmosis treatment is expected to consistently meet the San Pablo Bay or the Novato district POTW discharge limitations and is thus recommended for conceptual design.

ACKNOWLEDGEMENT

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