

CONTAMINATED GROUNDWATER: ABOVE-GROUND TREATMENT ALTERNATIVES

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Summary

Treatment of contaminated groundwater has become increasingly important as contamination incidents are discovered with greater frequency and as increased public and regulatory pressure for corrective action is exerted. This paper examines the differences between treatment of contaminated groundwater and conventional wastewaters. The need for treatability studies and pilot testing, use of adaptable equipment configurations, and importance of operating considerations are discussed. Contaminated groundwater treatment technologies currently employed most frequently for removal of organic contaminants — activated carbon adsorption, air stripping and biological treatment — are then reviewed. Applications and economic considerations, when data are available, are discussed for each process. Finally, several unique or experimental treatment technologies are presented.

Introduction

Cleanup of contaminated groundwater is becoming of greater concern due to the large number of uninvestigated potential sources, increased groundwater usage and additional regulatory focus. It has been estimated that tens of thousands of hazardous waste dumps, hundreds of thousands of surface impoundments, and millions of underground tanks may be affecting groundwater quality [1]. Usage of groundwater is estimated to have increased from 35 billion gallons per day in 1950 to 90 billion gallons per day in 1980 [2]. In addition, while RCRA interim status regulations for land disposal hazardous waste management facilities require only groundwater monitoring and groundwater quality assessments, final permit standards require a corrective action plan (such as groundwater treatment) if a contamination problem is revealed.

Treatment of groundwater may require removal of organic contaminants, such as solvents or fuels, inorganic contaminants, such as metals, or both. Because removal of inorganic species can generally be handled by conventional methods, this paper focuses on removal of organic contaminants.

Groundwater treatment can be achieved through use of in-situ techniques, above-ground treatment technologies, or combinations thereof. In-situ methods essentially involve treatment of groundwater in place, while above-

ground methods generally involve three elements — collection of groundwater, treatment through unit processes, and subsequent disposal. This paper considers only above-ground treatment systems and, accordingly, discusses these three elements with particular detail to the unit processes currently used or under development for groundwater treatment. Prior to the discussion of treatment systems, however, a brief discussion of the special considerations in groundwater treatment is warranted.

Special considerations in groundwater treatment

Treating contaminated groundwater differs substantially from conventional wastewater and leachate treatment, even though the same constituents may be involved. Prior to discussing treatment systems, therefore, it is important to consider several factors which make groundwater treatment system selection and design elusive.

Contaminants involved. Because of the varying and, sometimes, unknown sources of groundwater contamination, a variety of constituents can be involved for which little treatability information is available. Accordingly, waste-specific laboratory and/or pilot-scale treatability studies are often a prerequisite to system selection and design.

Levels of contamination. Groundwater treatment can necessitate removal of contaminants at microgram-per-liter levels to levels below the limit of detection; extending theoretical removal levels to situations involving low initial concentrations and high removal efficiencies is questionable and often necessitates waste-specific bench and pilot scale treatability studies. Moreover, because analytical determinations of low concentrations are often subject to high relative error values (particularly if a non-standard compound or complicated matrix is involved), the interpretation of such results can be difficult.

Fluctuations in flow. Seasonal variations and delay factors in the collection system (such as cycling of collection pumps) cause contaminated groundwater flows to vary greatly, especially if a shallow aquifer is involved. The selected treatment process must be able to accommodate fluctuating flows; this can be accomplished by use of conservative design factors for worst-case (highest) flow rates, and by using modular equipment that can be brought on- and off-stream as required.

Fluctuations in contaminant levels. Groundwater contaminant concentrations fluctuate owing to seasonal changes, the effect of removal and treatment, and concentration gradients within the contamination plume. The treatment system must be able to handle the anticipated range of groundwater contamination concentrations. Use of modular equipment that permits expansion or reduction of the system when warranted often is appropriate.

System life. Because the extent of groundwater contamination often is not known, the amount of time the system must remain in operation typically is uncertain at the time of equipment design and selection. Depending on

the degree of aquifer decontamination required, the treatment system life may range from a few months to several years. For this reason, use of leased, mobile or modular equipment generally is worthy of consideration.

Operating constraints. Groundwater treatment systems usually are subject to operating constraints owing to area limitations, remote site location, the possible need to limit exposure of personnel to hazardous materials, and, often, lack of sufficient operating funds. For these reasons, use of automated processes or unit operations that by nature are not operator-intensive is advantageous.

Discharge options. Effluent disposal options vary depending on the quantity of treated effluent and the degree of treatment provided. Options include groundwater recharge for disposal or controlled contaminant flushing, discharge to an existing treatment plant, collection for off-site disposal, or direct discharge to surface water.

The factors discussed above illustrate some of the differences between groundwater and traditional wastewater treatment design considerations. These factors necessitate consideration of the following when selecting a groundwater treatment system:

- waste-specific treatability studies;
- modular or mobile process equipment; and
- equipment requiring minimal operator attention.

Groundwater treatment systems

At a groundwater contamination problem site, remedial measure selection must focus on more than the actual treatment technology to be applied. In addition to treatment technology, consideration must be given to:

1. methods for groundwater containment and withdrawal;
2. methods for addressing contaminants not in solution but associated with subsurface materials;
3. degree of groundwater decontamination required;
4. time required to achieve desired degree of aquifer decontamination;
5. management of treated process effluent; and
6. management of treatment process by-products (i.e., sludges, spent treatment media, contaminated air streams).

Thus, a comprehensive approach must be taken when developing a groundwater treatment system. Groundwater treatment systems include three elements — (1) groundwater collection, (2) groundwater treatment, and (3) effluent disposal. While the main focus of this paper is on groundwater treatment, the other elements must first be considered because they can effect the degree of treatment required.

Groundwater collection

Collection of groundwater for above-ground treatment frequently is accomplished by well point pumping and interceptor drains. Groundwater

withdrawal often is combined with some form of subsurface barrier to create hydrologic conditions which direct groundwater flows to a withdrawal point, minimize groundwater intrusion through a zone of contaminated subsurface materials, or confine the contamination plume. Barriers most frequently used include the following:

- upgradient or downgradient interceptor trenches,
- underdrains,
- slurry walls,
- grout curtains,
- sheet piling,
- upgradient groundwater drawdown wells, and
- upgradient injection wells.

Selection and design of a groundwater collection system depends on the particular situation. Site geology, subsurface behavior of contaminants (e.g., whether they sink, float or are adsorbed), and physical/chemical properties of contaminants in solution (e.g., solubility, miscibility) must be considered.

Effluent disposal

Effluent disposal is an important consideration in treatment system selection because it often influences the degree of treatment (effluent quality) required. For this reason, a brief examination of disposal options is in order before reviewing treatment alternatives.

Groundwater recharge by injection wells or spray irrigation can be conducted in several locations:

- upgradient of the contamination plume to create a barrier to minimize further groundwater intrusion,
- within the zone of subsurface contamination to flush the soils and groundwater, to maintain a “closed system”, or to introduce subsequent in-situ treatment, or
- downgradient of the contamination plume for disposal purposes.

Disposal by *discharge to surface water* generally is employed when treatment objectives have been achieved or where further effluent dilution is possible without adversely affecting water quality and downgradient uses.

Routing of effluent to a POTW (publicly-owned treatment works) is practical if a facility with sufficient hydraulic capacity and appropriate treatment processes is located in economically reasonable proximity, and may allow on-site treatment objectives to be limited to pretreatment for removal of particular contaminants or for attainment of gross removal levels. Consideration must be given to potential effects on POTW treatment process performance, permit conditions and sludge management practices.

Disposal offsite is employed primarily in situations where smaller quantities of contaminated groundwater are encountered and economics do not justify construction of an on-site facility (i.e., short term remediation). Off-site disposal also may be attractive if highly sensitive contaminants are involved or if an off-site facility is located nearby.

Groundwater treatment alternatives

As discussed previously, design of a groundwater treatment system frequently is complicated by the presence of "unconventional" contaminants, low-level concentrations, fluctuations in flow and contaminant concentrations, uncertainty of system life, and operating/maintenance constraints. Moreover, the degree of treatment required is dependent, in part, on effluent disposal options.

Treatment process selection involves consideration of objective and subjective criteria including the following:

1. groundwater constituents and concentrations, including variations with time and location in the aquifer (actual contaminated water may account for less than 20% of the water pumped from the aquifer) [3];
2. required effluent quality and ability to achieve desired treatment objective;
3. process economics (capital, operating and maintenance);
4. ease of implementation;
5. ease of operation and maintenance;
6. reliability;
7. flexibility/adaptability to changing loading conditions;
8. nature of treatment by-products;
9. duration of operation (volume of groundwater to be treated);
10. requirement for ancillary pre- or post-treatment operations;
11. process monitoring requirements; and
12. process performance demonstrations.

Selection of treatment techniques often is skewed toward technologies with demonstrated performance records. Consequently, in spite of the differences pointed out earlier, current practice for removal of organic contaminants primarily involves use of technologies commonly applied for industrial wastewater and drinking water treatment. Technologies most widely applied are activated carbon adsorption, air stripping, and biological treatment. A discussion of these groundwater treatment technologies follows.

Activated carbon adsorption

Use of activated carbon, alone or in combination with other processes, typically is the most frequently applied technology when removal of organic constituents is required. In general, activated carbon is effective on non-polar compounds of mid-level (four to 20 carbon atoms) molecular weight. Table 1 lists the classes of compounds that are readily adsorbed on activated carbon [4]. Low and very high molecular weight compounds are not good candidates for adsorption.

Activated carbon can be applied in granular form in contact beds and in powdered form in aerobic biological treatment processes. The process has been used alone as well as following air stripping to remove non-volatile compounds; it also can be used prior to biological treatment to remove toxic or inhibitory compounds.

TABLE 1

Compounds readily adsorbed on activated carbon [4]

Class	Compounds
Aromatic hydrocarbons	Benzene, toluene, xylene
Polynuclear aromatics	Naphthalene, anthracene, biphenyls
Chlorinated aromatics	Chlorobenzene, PCBs, aldrin, endrin, taxophene, DDT
Phenolics	Phenol, cresol, resorcinol, tannin, and lignin derivatives
Chlorinated phenolics	Trichlorophenol, pentachlorophenol
High molecular weight aliphatic and branch chain hydrocarbons	Gasoline, kerosene
Chlorinated aliphatic hydrocarbons	Carbon tetrachloride, perchloroethylene
High molecular weight aliphatic acids and aromatic acids	Tar acids, 2,4-dichlorobenzoic acid, sulfonated lignins, benzoic acid
High molecular weight aliphatic amines and aromatic amines	Aniline, toluene diamine
High molecular weight ketones, esters, ethers and alcohols	Hydroquinone, polyethylene glycol
Surfactants	Alkyl benzene sulfonates, linear alcohol sulfates
Soluble organic dyes	Methylene blue, indigo carmine, benzopurpurin 4B phthalocyanines

Design and operating considerations for use of granular activated carbon (GAC) beds are discussed in detail in the literature [5–7]. Key parameters include the following:

Adsorber design configuration. The most popular configurations include downflow-fixed beds, upflow-pulsed beds, and upflow-expanded beds [8]. Often, fixed-bed systems can be designed and operated at carbon use rates similar to pulsed beds and generally at less cost [9]. Several manufacturers offer mobile adsorption services.

Contact time. The most important design parameter is contact time. Hydraulic loading rate, within the ranges normally used, is reported to have little effect on adsorption [6]. One system supplier has reported contact times of less than 60 min in more than half of the reported projects, minimum contact times of 12 to 15 min, and hydraulic loading rates ranging from 0.25 to 9.6 gal/min ft.² (10.2 to 391 l/min m²) [9].

Carbon usage. Carbon usage rates from 0.10 to 7.7 lb per 1,000 gallons (0.012 to 0.92 kg per 1,000 l) have been reported for treatment of microgram-per-liter influent levels with median usage of 0.35 lb per 1,000 gallons (0.042 kg per 1,000 l). At milligram-per-liter influent levels, usage rates of 0.45 to 13.5 lb per 1,000 gallons (0.054 to 1.62 kg per 1,000 l) with median usage of 1.54 lb per 1,000 gallons (0.185 kg per 1,000 l) have been reported [9].

Pretreatment requirements. Suspended solids can foul activated carbon and decrease the available surface area on which contaminants are adsorbed.

For this reason, filtration for removal of suspended solids may be required. The use of air stripping as pretreatment has been reported in cases where compounds not amenable to activated carbon treatment were present or as a means of lowering carbon usage by effecting gross removal of volatile organics prior to activated carbon treatment [10,11]. In many cases, pretreatment may not be necessary.

Costs. Treatment costs (including annualized capital and operating and maintenance costs in August, 1983 dollars) for 99% removal of volatile organics at microgram-per-liter influent levels have been reported as follows [12]:

Capacity (mgd)	0.037	0.95	36.8
Capacity (mld)	0.140	3.60	1.39
Total cost/1,000 gallons	\$0.45—\$1.50	\$0.15—\$0.83	\$0.07—\$0.38
Total cost/1,000 liters	\$0.12—\$0.40	\$0.04—\$0.22	\$0.018—\$0.10

GAC performance is dependent on the theoretical adsorptive characteristics of the contaminant(s) to be removed, the existing and desired contaminant concentration and the overall contaminated groundwater composition matrix. The latter is especially important as constituents other than the contaminant(s) of concern (including solids, inorganics and other organics) will “compete” for activated carbon adsorption sites. Literature describing GAC performance is available, including a compendium of adsorption isotherms for 128 compounds [13]. Performance and system design are highly waste-stream specific, however. Because of this, treatability tests should be conducted to assure that performance objectives can be achieved in a cost-effective manner. Typically, these tests entail batch isotherm studies and continuous flow column studies at bench or pilot scale.

Activated carbon adsorption applications

GAC has been applied to a wide variety of groundwater contamination problems ranging from individual household water wells to extensive aquifer restoration. Selected specific applications are summarized below.

1. Household water wells [14]

Groundwater contaminated with trichloroethylene (TCE) affected both the local public water supply and numerous individual household wells in Olean, New York. Although the public water supply problem was solved through relocation of the well field, groundwater treatment was employed for the affected individual wells. Individual GAC treatment packages, consisting of 1 to 2 cubic foot adsorbers and water meters, were installed at each well. At household water use rates of 50 to 60 gpcd (189 to 227 lpcd) and TCE concentrations ranging from a few hundred $\mu\text{g/l}$ to 12 mg/l and TOC concentrations up to 10 mg/l, the GAC units have had service lives of less than three months to greater than six months. For a three-year period, the cost per treatment unit has been about \$1,400 (excluding monitoring).

A local public agency was responsible for maintaining the units.

Observations made regarding this case included:

- Individual unit performance was greatly affected by varying groundwater constituent matrix.
- Backwashing of the GAC units was required because there was no filtration pretreatment. Because single beds were used, raw groundwater had to be used for backwashing, resulting in TCE loading at the “clean” end of the bed.
- Because of the institutional problems of carbon replacement frequency, system maintenance responsibility, monitoring procedures, and funding limitations, it is believed that it may have been more cost-effective in the long-term to have provided public water to affected households.

2. Air-stripping pretreatment [11]

The groundwater treatment system employed at the Rockaway Township, New Jersey groundwater supply system illustrates the potential advantages of using air stripping pretreatment. Approximately half of the township's population of 20,000 is served by three groundwater wells which were found to contain 50 to 220 $\mu\text{g/l}$ TCE. Concentrations of diisopropylether (DIPE) from 70 to 100 $\mu\text{g/l}$ and methyltertiary butyl ether (MTBE) from 25 to 40 $\mu\text{g/l}$ also were detected.

A GAC adsorption system was installed expeditiously at a cost of about \$200,000. At the time of installation, influent levels were about 10 $\mu\text{g/l}$ of TCE, 70–80 $\mu\text{g/l}$ of DIPE, and 25–35 $\mu\text{g/l}$ of MTBE. While it was anticipated that carbon replacement would be required every six to eight months, replacement was necessary every four to six weeks. A packed column aeration system was added prior to GAC adsorption at a cost of about \$375,000. The aeration system, designed after conducting treatability studies, provided removal efficiencies greater than 99% for DIPE, 95% for MTBE and essentially 100% for TCE.

It was found that 1.0 to 2.0 pounds of GAC per 1,000 gallons (0.12 to 0.24 kg per 1,000 l) of water treated was required without aeration, and that less than 0.1 pound per 1,000 gallons (0.012 kg per 1,000 l) was required with aeration. Thus, the aeration system significantly reduced the organic loading to the GAC system; ultimately, the GAC system was taken off-stream because the aeration system alone was found to be adequate. Installation of the aeration system was judged to have reduced GAC-only operating costs by one-third to one-half. The operating cost of the system is estimated at \$0.40 to \$0.48 per 1,000 gallons (\$0.106 to \$0.127 per 1,000 l).

3. Short-term application [15]

Groundwater was found to contain organics (primarily TCE and 1,1,1-trichloroethane) ranging up to 1,400 $\mu\text{g/l}$ at an upstate New York industrial facility. Until the plant's wastewater treatment facility could be upgraded to treat the contaminated groundwater to organic concentration levels of

less than 10 $\mu\text{g/l}$, a temporary organic treatment system utilizing activated carbon was developed. The temporary system also was used to treat water generated during installation of the groundwater collection system.

During construction of the groundwater collection system, the temporary treatment system initially was capable of treating up to 70 gal/min (265 l/min), and consisted of prefiltration followed by seven package GAC units in parallel; effluent was discharged into a local storm sewer. If flows greater than 70 gal/min were encountered during construction, tank trucks were used to transport contaminated groundwater to an offsite facility.

After construction of the collection system, the state environmental agency required placement of two units in series to provide redundancy. As a result, the system capacity was reduced to 30 gal/min (114 l/min); effluent is discharged to the facility's wastewater treatment plant for removal of inorganics. Process monitoring reportedly indicated that total volatile organics exceeding 300 $\mu\text{g/l}$ in the influent were reduced to 1 $\mu\text{g/l}$ in the effluent.

4. Process train incorporating GAC [16]

A more complicated groundwater treatment system relying on several unit operations preceding and following GAC treatment was employed at the Goose Farm Site in Plumstead, New Jersey. Groundwater organic contaminant concentrations as high as 134 mg/l methylene chloride, 106 mg/l benzene and 88 mg/l toluene were reported with TOC levels ranging from 1,600 to 17,000 mg/l. The treatment system consisted of the following:

- well point withdrawal system,
- vacuum receiving vessels (with vapors passed through a carbon adsorber),
- clarification for solids and metals removal with pH adjusted to 6.0 using sodium hydroxide,
- GAC contact beds,
- spray aeration to remove methylene chloride breaking through the GAC unit, and
- spray irrigation to form a groundwater mound to control groundwater hydraulics.

The GAC contact beds reduced TOC from 125 mg/l to 54 mg/l (66% removal). Costs to install, operate and dismantle the system were two to three million dollars. Approximately 7.8 million gallons (29.5 million liters) were processed at a cost of \$0.26 to \$0.40 per gallon (\$0.069 to \$0.106 per liter) or \$343 to \$1,300 per pound (\$156 to \$590 per kg) of TOC removed.

Air stripping

Air stripping frequently has been applied for removal of volatile organic compounds. The literature reports successful air stripping treatment of contaminants including trichloroethylene, benzene, toluene, xylene, methylene chloride, and many other volatile organic compounds. Amenability of contaminant removal by air stripping is dependent on the ease of transfer of the contaminant from liquid phase to gas phase.

TABLE 2

Henry's law constants of selected organic compounds [34]

	Henry's law constant at 25° C (atm m ³ /mol)
Carbon tetrachloride	3.08×10^{-2}
Tetrachloroethylene	2.93×10^{-2}
Trichloroethylene	1.20×10^{-2}
Toluene	6.11×10^{-3}
Benzene	5.62×10^{-3}
1,1,1-Trichloroethane	5.13×10^{-3}
Chlorobenzene	3.91×10^{-3}
Chloroform	3.42×10^{-3}
1,2-Dichlorobenzene	1.98×10^{-3}
1,2,4-Trichlorobenzene	1.44×10^{-3}
1,2-Dichloroethane	1.12×10^{-3}
1,1,2-Trichloroethane	9.04×10^{-4}
Bromoform	5.38×10^{-4}
Di-n-butyl phthalate	7.33×10^{-5}
Phenol	1.47×10^{-6}

Although there is no simple way to model interactions of numerous organic species in water, the Henry's law constant (H) is an excellent indicator of the contaminant's liquid-to-gas transfer characteristics for dilute binary solutions. A contaminant with high Henry's law constant is generally more "stripable" than one with a low constant. Henry's law constants are determined experimentally and can be difficult to find in the literature or unavailable for a particular contaminant. Table 2 lists Henry's law constants and boiling points for selected contaminants of environmental interest in order of decreasing "stripability". It should be noted, however, that the contaminant matrix, temperature, pressure, and concentration greatly affect stripability. For these reasons, treatability studies are recommended prior to design.

Air stripping can be effected using countercurrent contact of air and water in a packed tower, cocurrent or countercurrent contact in a tray tower (such as a cooling tower with redwood or PVC slats), diffused aeration, spray irrigation, and in-well diffused aeration. An induced-draft air stripping chamber, said to have lower capital and operating costs than conventional packed towers but with some loss in removal efficiency, has been reported [10]. Use of packed or tray towers is generally the most common configuration.

The design of air stripping towers and modeling of their performance is based upon liquid-gas mass transfer dynamics, which are discussed in detail in the chemical engineering literature [17-19] as well as in several recent groundwater treatment application articles [20-22]. Equipment generally includes: (1) the tower(s); (2) tower packing, usually rings, saddles or slats which provide a contacting arrangement for effective liquid-to-gas mass

transfer; (3) pumping and distribution equipment to transfer water through the tower; and (4) fans or blowers to provide the air stream. The number and height of towers required to effect a specific removal is dependent on the air/water flow rate ratio, packing type, tower cross-sectional area (hydraulic loading), operating temperature, and heat and mass transfer coefficients, as well as the contaminated groundwater's pH and volatile constituent concentrations.

EPA recently published cost data for 99 percent removal of nine volatile organic compounds at microgram-per-liter levels [15]. Total treatment costs (including annualized capital and operating and maintenance costs in August 1983 dollars) were reported as follows:

Capacity (mgd)	0.037	0.95	36.8
Capacity (mld)	0.14	3.60	139
Total cost/1,000 gallons	\$0.71—\$1.01	\$0.081—\$0.285	\$0.046—\$0.187
Total cost/1,000 liters	\$0.19—\$0.27	\$0.021—\$0.075	\$0.012—\$0.049

The prime advantages of air stripping are low capital and operating cost, simplicity of operation, and relatively low maintenance costs relative to other treatment technologies.

The major disadvantage is generation of air emissions. Increasingly strict new source performance standards for volatile organic compound emissions may require emissions control measures such as activated carbon treatment of the exhaust stream. Operating simplicity and cost advantages of air stripping are likely to be reduced greatly if vapor phase adsorption is required; in such cases, costs could increase by a factor of two or more [15,23]. The literature describes a proposed air stripping application in which air emissions are routed to an on-site commercial process boiler [24].

Other disadvantages of air stripping include applicability only to volatile compounds, temperature sensitivity, and scale build up. High temperature stripping has been employed to effect removal of less volatile compounds [25]. In some situations, dilute acid has been added to mitigate scaling problems.

Air stripping applications

Air stripping has been used alone to remove selected volatile contaminants to below detection levels as well as for pretreatment to reduce gross contaminant levels prior to GAC adsorption (see Application 2 under activated carbon adsorption). Selected applications are discussed below.

1. Drinking water supply [21,26]

Air stripping treatment of contaminated groundwater was implemented at the City of Tacoma, Washington, where contaminants included 1,1,2,2-tetrachloroethane (300 $\mu\text{g/l}$), trans-1,2-dichloroethylene (100 $\mu\text{g/l}$), trichloroethylene (130 $\mu\text{g/l}$) and tetrachloroethylene (5 $\mu\text{g/l}$). Pilot studies revealed that much higher air/water ratios were required to remove

1,1,2,2-tetrachloroethane than the other compounds. Based on extensive pilot work and modelling of mass transfer characteristics, a system of five 12 ft. (3.77 m) diameter towers was selected. Each tower was designed to handle 3,500 gal/min (13,250 l/min) with 310:1 volumetric air/water ratio and packing depth of 20 ft. (6.10 m) of 1 in. (2.54 cm) polypropylene saddles for an expected 1,1,2,2-tetrachloroethane removal of 89%. The system, put into operation in July 1983, consistently yielded 94% to 98% 1,1,2,2-tetrachloroethane removal and achieved nondetectable levels of the other volatile organic compounds. Installed cost was approximately \$750,000.

2. Air stripping versus activated carbon [20]

One of several references comparing use of air stripping in lieu of or prior to activated carbon adsorption discusses laboratory studies and full-scale design of an air stripping system to remove TCE from drinking water at the Wurtsmith Air Force Base (Oscoda, Michigan). Based on 1.44 mgd (5.45 mld) flow, 2,000 $\mu\text{g/l}$ TCE influent concentration, and 5 $\mu\text{g/l}$ TCE treatment objective, it previously was estimated that GAC treatment would require three 40,000 lb (18,200 kg) units in parallel. Projected carbon usage for each unit was 13,800 lb/y (6270 kg/y). Treatability studies were conducted to determine if air stripping could provide a less costly alternative to GAC adsorption. Based on treatability study results, a stripping system was designed using two 30.2 ft. (9.2 m) high, 4.9 ft. (1.5 m) diameter towers, each with 18 ft. (5.5 m) beds. Target efficiency of the system was greater than 90% TCE removal in parallel and greater than 99% TCE removal in series. Stripper effluent was fed to a small activated carbon system for polishing prior to discharge to a small creek. Estimated costs for activated carbon alone and air stripping with GAC polishing were as follows for 1.44 mgd (5.45 mld) influent:

	<u>GAC</u>	<u>Air stripping/GAC polishing</u>
Capital	\$1,552,000	\$200,000
O&M	\$264,000	\$30,000
Ammortized capital	\$204,000	\$26,300
Total annual cost	\$468,000	\$56,300
Treatment cost/1,000 gallons	\$0.98	\$0.11
Treatment cost/1,000 liters	\$0.26	\$0.03

Air stripping was shown to reduce per gallon treatment costs by one order of magnitude; however, no provisions were made for treatment of air emissions and continuous chlorination was required to control biological growth.

3. Elevated stripping temperature [25]

A Long Island, New York site required design of a system to treat groundwater contaminated with methyl ethyl ketone (MEK). Reduction of the

MEK concentration from 1,000 mg/l to 0.050 mg/l (99.995% removal) at a flow rate of 100 gal/min (378 l/min) was required. Pilot tests of ambient-temperature air stripping resulted in only 25% MEK removal. Laboratory pilot tests were conducted using a 21 ft. (6.4 m), 10 in. (0.25 m) diameter tower packed with 15 ft. (4.57 m) of polypropylene Pall rings. Tests conducted at temperatures from 120°F to 180°F (50–80°C) over air/water ratios from 75:1 to 300:1 resulted in MEK removal efficiencies ranging from 85% to greater than 99.995%. A design operating temperature of 140°F (60.0°C) and air/water ratio of 200:1 were selected. Final design utilized a modular approach allowing modification of system operation to accommodate increases in throughput as influent MEK concentrations decreased in later stages of cleanup. The initial configuration consisted of three 25 ft. (7.62 m) high, 3.5 ft. (1.07 m) diameter towers in series with a fourth back-up tower of identical size. The system also permits configurations of two parallel trains of two towers in series for treatment of 200 gal/min (756 l/min) as well as, ultimately, four towers in parallel for treatment of 400 gal/min (1512 l/min).

4. Pressurized gas stripping [27]

Pressurized gas stripping (similar to dissolved air flotation) using air or CO₂ followed by incineration of the organics-rich off-gas was tested at laboratory scale using contaminated groundwater at the Rocky Mountain Arsenal. The process was found to be less efficient than conventional packed tower stripping. Volatile organic compound removal efficiencies for the pressurized gas stripping process ranged from 51 to 73%, while packed column stripping provided greater than 90% removal. The pressurized gas stripping process, however, used air/water ratios of 0.006 and 0.3 scf/gal (0.168 and 8.71 standard liters/liter) compared to 6.67 to 13.13 scf/gal (187.1 to 368.3 standard liters/liter) for the packed tower.

Biological treatment

Even though many organic compounds frequently associated with groundwater contamination are biodegradable, biological processes have not been applied as extensively as activated carbon adsorption or air stripping for on-site groundwater treatment. This is largely because steady-state, effective performance cannot be attained as rapidly as for physical and chemical processes. In addition, the degree of operator attention required, susceptibility to loading fluctuations, and generation of a high moisture content sludge requiring further management are notable disadvantages, especially at abandoned sites.

The following approaches incorporating biological treatment have been used:

- activated sludge in concert with powdered activated carbon, and
- fixed-film and suspended-growth aerobic processes inoculated with com-

mercially available biological cultures or organisms cultured from the mixed microbial populations occurring at the problem site.

Both approaches involve groundwater withdrawal, processing through an aeration system, and effluent clarification; reinjection of treated effluent to flush subsurface contaminants and discharge to a POTW are reported [14]. In some cases, biomass is permitted to carry over in the final effluent to promote continued in-situ biological treatment of the groundwater.

Biological treatment applications

On-site biological treatment applications have shown high degrees of organic contaminant removals. The applications have involved equipment typical for aerobic biological processes, with suspended growth or fixed film reactors being used. Available performance data do not clearly distinguish between constituent removals attributed to biodegradation and that resulting from stripping. Selected specific applications are summarized below.

1. Activated sludge/powdered activated carbon [28]

An example incorporating activated sludge enhanced with powdered activated carbon is the system developed by Environmental Systems Corporation (ESC, a joint venture of Bofore—Nobel, Zimpro Inc., and Chemical Waste Management). For groundwater treatment at a site near Muskegon, Michigan, the PACT[®] system is used for groundwater and process wastewater treatment and Zimpro[®] wet air oxidation is used to regenerate powdered activated carbon. ESC reports the PACT[™] system treats about 1.475 mgd (5.58 mld) of contaminated groundwater along with 0.025 mgd (0.095 mld) of process wastewater and has reduced orthochloroaniline from 6,500 $\mu\text{g/l}$ to less than 10 $\mu\text{g/l}$ (99.89%) and dichlorobenzidine from 400 $\mu\text{g/l}$ to less than 2 $\mu\text{g/l}$ (99.5%). PACT[™] system effluent is discharged to the local POTW.

2. Aeration/GAC/reinjection [16,29]

At the Biocraft site in Warwick, New Jersey, a biological-based groundwater treatment system has been operating since 1981. Groundwater is collected via an interceptor trench and conveyed to an aeration tank containing a biomass cultured from a mixed microbial population found to proliferate naturally in the contaminated groundwater. A nutrient solution also is added. Air sparged from the aeration tanks is passed through activated carbon adsorbers. Treated effluent is passed through a clarifier and then pumped to upgradient reinjection trenches to flush contaminants from site soils. Biomass is allowed to be carried over in the effluent to promote in-situ treatment. Groundwater aeration wells were installed between the reinjection and interceptor trenches. The process has been patented by Biocraft and Ground Water Decontamination Systems. System flow has averaged about 13,700 gal/day (51,850 l/day) and the aeration tank hydraulic retention time is 17.5 h. Average performance over the initial 1.5 y of operation is summa-

rized below:

Specific constituents	Average concentration (mg/l)		
	Influent	Effluent	Percent removal
Isopropyl alcohol	52	<1	>98
Methylene chloride	98	<2.2	>98
Acetone	47	<5.6	>88
Butyl alcohol	43	<1.4	>97
Dimethylaniline	23	<8.3	>64

It should be noted that removal due to stripping was not differentiated from biodegradation.

More recent data indicate that the system has been effective in reducing the contaminant plume by approximately 90% [29]. To demonstrate that aerobic biological degradation is occurring, the production of carbon dioxide gas in the contaminated zone has been measured. The results showed that the production of CO₂ is greater (by tenfold) in the plume area than measurements taken in background areas. Soil core samples collected over time from contaminated areas exhibited a decrease in COD concentrations. Complete removal of the organic compounds of concern has been reported (i.e., to below detection limits) throughout much of the original plume (between the effluent reinjection trenches and the collection trenches). Downgradient of the collection trenches, contaminants remain present at high levels, although CO₂ production indicates that biodegradation continues to be active.

Total plant design and construction cost was reported to be \$221,000. O&M costs, as provided in 1983, were \$0.0165/gal (\$0.00436/l) at a flow of 13,700 gal/day (51,850 l/day).

3. Fixed-film [14]

Polybac Corporation has reported success in treating groundwater containing phenol at 70 to 265 mg/l. The system entails a recovery well and pumping system, an equalization impoundment, two "Biotreaters" tanks (fixed film reactors with diffused aeration) inoculated with biomass cultured to degrade phenols, a clarifier, and effluent disposal by direct discharge to surface waters (although spray irrigation and injection well system options are provided). Although the system was designed to process 50,000 gal/day (189,000 l/day), the well recovery system typically has yielded flows as low as 15,000 gal/day (57,000 l/day). Therefore, the second "biotreater" has not been used. After about two years of operation, effluent phenol levels less than 0.5 mg/l (the desired objective) consistently have been achieved. Groundwater phenol concentrations approaching detection limits have been reported and it is anticipated that the system will be removed after 26 months of operation. Equipment cost was about \$250,000.

4. *Bacterial inoculum [14]*

Polybac Corporation also has reported use of a bacterial inoculum to treat shallow groundwater and soil containing trichloroethylene; benzene; toluene; xylene; chloroform; ethylbenzene; 1,1,1-trichloroethane; pentachlorophenol; 2-butanone; 1,1-dichloroethane; anthracene; di-n-butylphthalate; fluorene; and phenanthrene. At this site groundwater seepage is collected in a pond equipped with an aerator. At the pond, pH is adjusted and bacterial inoculum and nutrients are added. Effluent is pumped from the pond to an up-gradient site, sprayed to air strip volatile organics, and then allowed to recharge to flush solvents from site soils. This recharge water is intercepted by the perched water table and is collected at a downgradient seep, thus, providing a "semi-closed" system. Organic levels in the pond decreased from 600 $\mu\text{g/l}$ to 7 $\mu\text{g/l}$ in about five months; organic levels in contaminated soils decreased from 22,000 $\mu\text{g/l}$ to 8 $\mu\text{g/l}$. Total system cost including pond construction, aeration system, pumps, and spray system was about \$50,000. O&M costs including Polybac Corporation professional services and bacterial inoculum were about \$20,000 over six months.

5. *Activated sludge/filtration/GAC [30]*

Detox, Inc., has developed a system incorporating an activated sludge process for removal of phenol and gross TOC levels from a brine aquifer contaminated from a Gulf Coast hazardous waste management site. The contaminated groundwater has an average concentration of 15,000 mg/l total dissolved solids, 1,300 mg/l TOC, and 400 mg/l phenol. Required operating duration was estimated to be ten years based on a flow rate of 23,000 gal/day (87,000 l/day). A preliminary economic comparison of GAC alone versus biological treatment resulted in the conclusion that GAC would cost at least 16 times the cost of biological treatment. However, because of uncertainty that biological treatment alone could produce the 18 mg/l TOC treatment requirement, it was decided to employ GAC polishing. Based upon laboratory and pilot testing, a final system was developed using the following sequence of unit operations:

- first-stage activated sludge system consisting of two 20,000 gallon (76,000 liter) aeration basins in series;
- hopper bottom clarifier;
- second stage complete mix biological reactor, 10 ft. \times 10 ft. \times 28 ft. long (3 m \times 3 m \times 8.5 m), that combines activated sludge and fixed film technologies (plastic media submerged in the water for film attachment) to produce an activated sludge system that is not limited by sludge age considerations;
- dual media filter providing 10 ft.² (0.93 m²) area with 1 ft. (0.30 m) anthracite coal and 1 ft. (0.30 m) sand; and
- two GAC columns in series, each with 30 min retention time.

The system has been designed to respond to changes in influent concentrations, one of the key considerations in groundwater treatment. At influ-

ent TOC concentrations of 1,300 mg/l and above, all of the process equipment above are used. Below 900 mg/l, one of the first stage aeration basins is taken off-line. Below 300 mg/l, the entire first stage is eliminated. At 100 mg/l, only GAC is employed.

The system has been in operation for approximately two years. The biological treatment process consistently has provided 75% to 85% TOC reductions and greater than 99% phenol removal, resulting in pre-carbon concentrations of about 260 mg/l TOC and 4 mg/l phenol. Two 4-foot GAC units in series provide the additional TOC removal required to meet the 18 mg/l effluent objective. Although the biological component of the system provides acceptable removal levels, efforts are currently underway to develop a bacteria that will provide additional TOC removal and, as a result, reduce carbon usage.

System capital cost (uninstalled) was approximately \$120,000 in 1983 dollars. In spite of an automated filtration and GAC system, manpower requirements are estimated at 12–20 hours per week, which may limit applications.

Other technologies

Although air stripping, activated carbon and biological treatment are the most common above-ground treatment technologies for removal of organics, several others of note have been reported. These processes are discussed below.

Ozonation was employed at a drinking water supply in West Germany to treat dissolved organic carbon (DOC) levels greater than 5 mg/l and cyanide levels greater than 0.11 mg/l by oxidation [31]. Organic contaminants were determined to be petroleum hydrocarbons. A treatment objective of 1 mg/l DOC and less than 0.05 mg/l cyanide at 1,780 gal/min (6,740 l/min) was required. Groundwater was withdrawn, ozonated, and reinjected to effect treatment. The system reportedly has reduced DOC levels to just over 1 mg/l and has removed petroleum hydrocarbons to levels below detection. Cyanide levels are reported to have dropped below the 0.1 mg/l detection limit. In addition, iron and manganese, previously at levels of 0.07 and 0.04 mg/l, respectively, also were reduced to levels below detection.

Scholze et al. have conducted pilot studies of the ULTROX process, which utilizes ozone and ultraviolet light to treat volatile halogenated organics. Reductions of 90 to 93% were reported [32].

Groundwater recirculation (i.e., recovery and recharge) systems with and without treatment have also been reported [33]. At one site, groundwater contaminated with greater than 100 mg/l chlorinated and aromatic solvents and over 800 mg/l water soluble organics was addressed by pumping from one withdrawal well to five recharge wells to contain contaminant migration without treatment. After 2 y of operation, the system is reported to have reduced offsite migration from 7.5 to 2 lb. (3.4 to 0.91 kg) of volatile organics per day.

Conclusions

Treatment of contaminated groundwater requires strategies different from those employed in conventional wastewater treatment because of: (1) the nonconventional contaminants involved, (2) low contaminant concentrations, (3) fluctuations in flow, (4) variability of influent concentration, (5) unpredictable system life, and (6) site and operating limitations. For most situations, these factors necessitate conduct of treatability studies, use of modular equipment, and consideration of low-maintenance processes, regardless of the selected treatment technology.

In developing a system for treatment of contaminated groundwater, a comprehensive, site-specific approach must be employed. Consideration must be given to groundwater collection and effluent disposal requirements as both can greatly affect the degree of treatment attainable or required. Other important factors include process economics, nature of treatment by-products, requirement for ancillary operations, and ease of implementation, operation and maintenance.

The most common above-ground technologies employed for removal of organics from contaminated groundwater are activated carbon adsorption, air stripping and biological treatment. Activated carbon adsorption is effective on a variety of organic contaminants, including aromatic hydrocarbons, polynuclear and chlorinated aromatics, and phenolics. Air stripping, while generally lower in capital and operating costs, is effective primarily for volatile compounds and may have minimal advantages if treatment of air emissions is required.

Biological treatment processes have not been applied as extensively as air stripping and activated carbon adsorption because steady-state performance cannot be achieved as rapidly and a greater amount of operator attention is generally required. Other technologies currently are employed on a limited basis, or only at the bench or pilot scale level.

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