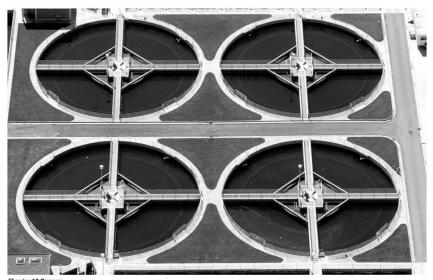
Environmental Chemistry

Chapter 11:

The Pollution and Purification of Water

Contents

- Treatment Processes
- Disinfection of Water
- Clean Water Act
- Chemical Contamination



Chapter 10 Opener

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- The quality of surface and ground water varies widely
- Need to be treated before it can be used for human consumption
- The purification of water involves:

Non-disinfection

- 1. Aeration of water
- 2. Removal of Ca²⁺ and Mg²⁺
- 3. Removal of colloidal particles by precipitation
- 4. Settling & Filtering of water

Disinfection

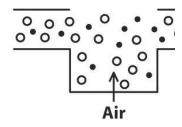
- 1. Disinfection by membranes
- 2. Ultraviolet Radiation
- 3. Ozone and chlorine dioxide

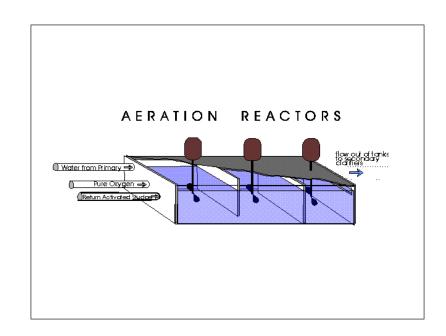
Aeration

1. Aeration of water

Removal of dissolved gases (e.g. H₂S) and organosulfur compounds Removal of volatile organic compounds Oxidation of Fe²⁺ to Fe³⁺ and precipitation as insoluble Fe(OH)₃

Aeration

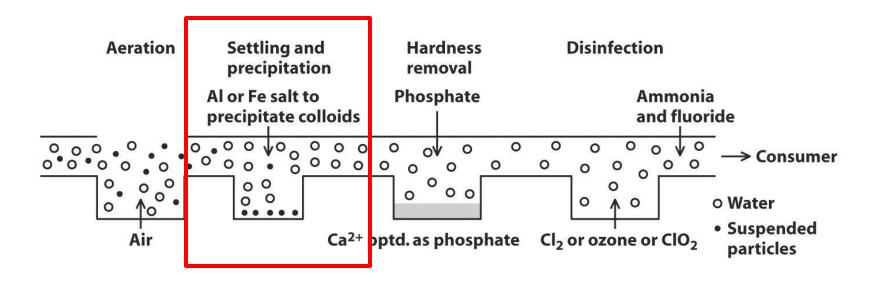




Removal of Ca²⁺ and Mg²⁺

2. Removal of colloidal particles by Precipitation

Particle of diameter less than 1µm diameter – referred as colloidal particles - suspend in water Weakly bound molecules and ions Charge neutralization by the addition of Fe₂(SO₄)₃ and Al₂(SO₄)₃ (alum) causes coagulation and form removable precipitate



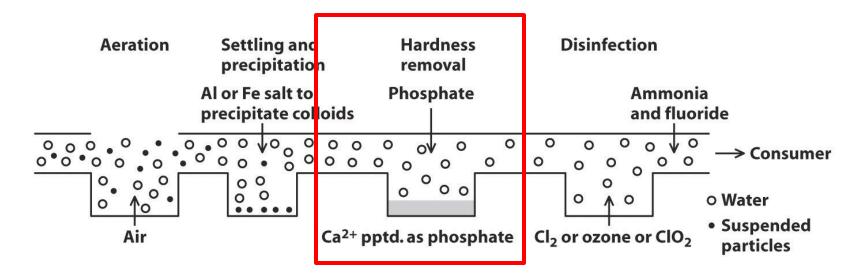
Removal of Ca²⁺ and Mg²⁺

3. These ions can be removed by precipitation following addition of phosphate and filtration

Ca²⁺ ions are also more commonly removed by the addition of soluble carbonate (Na₂CO₃)

$$Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3(s)$$

Mg²⁺ is precipitated as Mg(OH)₂ under alkaline conditions



- Removal of biological contaminants is equally important
- Microorganisms in raw water include
 - Bacteria Salmonella genus ..E coli O157:H7 responsible for typhoid
 - Viruses polio, Hepatitus-A
 - Protozoans (single celled species) Cryptosporidium, Giardia



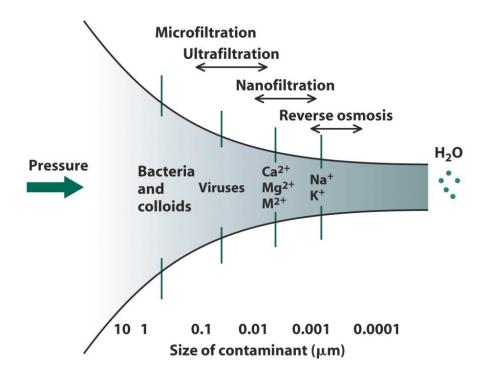
Filtering

- Micro-organisms commonly attach to particles
- Large particles may be easily removed by filtration
- Filtering through sand is the oldest known form of water purification

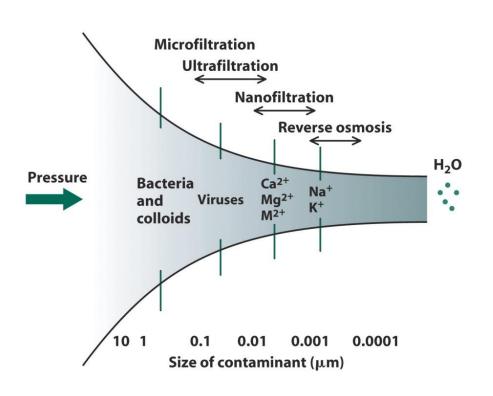
http://www.ars.usda.gov/is/video/vnr/grassbuffers.htm

Membrane Technology

- Must be pre-treated to remove larger particles
- Membranes of pores 0.002 -10 mm diameter facilitates microfiltration and ultrafiltration
- When pumped under pressure nanofilters allow removal of Ca²⁺ and Mg²⁺ ions



Membrane Technology



Reverse Osmosis

Semipermeable membrane composed of cellulose acetate or triacetate allows only water molecules to pass through

Effective in removal of particles, organic molecules and biological species.

Process is widely used in desalination of water

Small units are available for household use

UV-irradiation

- 10s exposure of UV-C light (254 nm) is sufficient to eliminate the toxic microorganisms (including cryptosporidium)
- Absorption of UV-C results in the formation of new covalent bonds between nearby thiamine units on the same DNA strand
- Germicidal action of UV-light thus disrupts the DNA activity and prevents subsequent replication
- Dissolved iron and other UV-absorbing compounds make this treatment less effective



Chemical Methods

- Ozone Treatment (Los Angeles and Montreal)
 - Ozone cannot be stored or shipped
 - It is produced by electrical discharge (2000 V)
 - Ozone is short-lived, hence no long-term residual effects
 - If Br is present it generates bromate ion

$$Br^{-} + 3O_{3} \rightarrow BrO_{3}^{-} + 3O_{2}$$

- Bromate ions react with organic moleules (if present) and produce toxic organobromine compounds
- Chlorine Dioxide, CIO₂ Treatment (more than 300 North American cities)
 - Readily oxidize molecules by extracting electrons

$$CIO_2 + 4H^+ + 5e^- \rightarrow Cl^- + 2H_2O$$

- Much smaller amounts of toxic organic by-products
- Usually stored in the reduced form as chlorite (Sodium chlorite)

$$ClO_2^- \rightarrow ClO_2 + e^-$$

Leaves residual chlorite and chlorate ions have raised some concerns

Chlorination: Production of Hypochlorous Acid

- Most common purification agent used in North America
- Like ozone, HOCl cannot be stored
- Generated by dissolving Cl₂

$$Cl_2(g) + H_2O(aq) \rightleftharpoons HOCl(aq) + H^+ + Cl^-$$

In swimming pools hypochlorite salt, NaOCl or Ca(OCl)₂ is used

$$OCI^- + H_2O \rightleftharpoons HOCI + OH^-$$

 Close control of the pH is crucial to avoid corrosion (acidic) or formation of chloroamines, NH₂Cl, NHCl₂ and NCl₃ (alkaline)

$$NH_3 + 3HOCI \rightarrow NCI_3 + 3H_2O$$

 pH in swimming pools (slightly above pH 7) is controlled by NaHSO₄ and Na₂CO₃

Chlorination: Production of Hypochlorous Acid

Advantages:

- Proved important in protecting human health (eradicated typhoid & cholera)
- Since some chlorine remains in water, it prevents subsequent bacterial contamination
- Chloramines or combined chlorine provide longer residual protection
- EPA has set MRDLs of 4 ppm for both chlorine and chloramine in drinking water

Disadvantages:

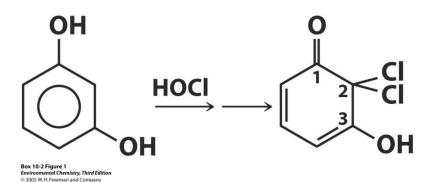
- Pathazonic bacteria called Cryptospordium is resistant to common chemical treatment procedures.
- HOCl is not only an oxidizing agent but also a chlorinating agent
 - Formation haloacetic acids (EPA restriction of <60 ppb)
 - phenols are converted into more toxic chlrinated phenols
 - Reaction of HOCI with organic matter (humic acid) produces trihalomethanes CHX3 (EPA limit 80 ppb)

THM

Chlorination By-Products

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- Humic acids react with HOCl to form chlorinated phenols
- Ring cleaves at C-2 and C-3
- Terminal C is chlorinated
- -CCl₃ group is displaced by OH⁻
- Trihalomethanes are suspected carcinogens



Clean Water Act

- Growing public awareness and concern for controlling water pollution led to enactment of the Federal Water Pollution Control Act Amendments of 1972.
- As amended in 1977, this law became commonly known as the Clean Water Act.
- The Act established the basic structure for regulating discharges of pollutants into the waters of the United States. It gave EPA the authority to implement pollution control programs such as setting wastewater standards for industry.
- The Clean Water Act also continued requirements to set water quality standards for all contaminants in surface waters.
- The Act made it unlawful for any person to discharge any pollutant from a point source into navigable waters, unless a permit was obtained under its provisions.
- It also funded the construction of sewage treatment plants under the construction grants program and recognized the need for planning

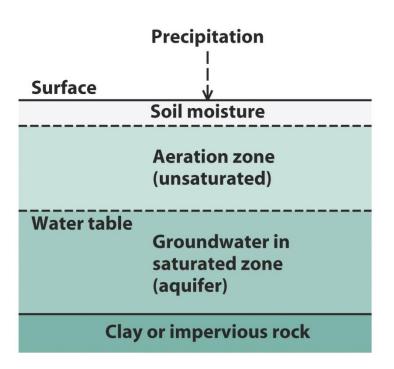
Point-Of-Use Water-Disinfection

• P474-477

Ground Water

Supply, Contamination, Remediation

Ground water refers to water in the saturated zone -0.6% of the world'stotal water supply



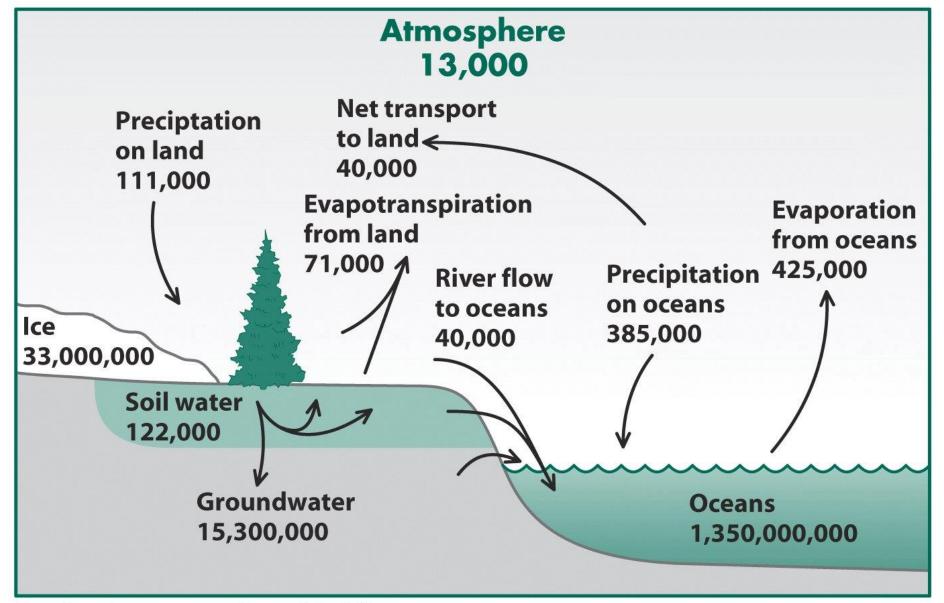
Water table near the surface - swamps

Water table above the surface - lakes

Majority of ground water use in the US is for irrigation water resources are depleting rapidly in some places

In the US about 39% of the of the water used for public supplies are extracted from wells



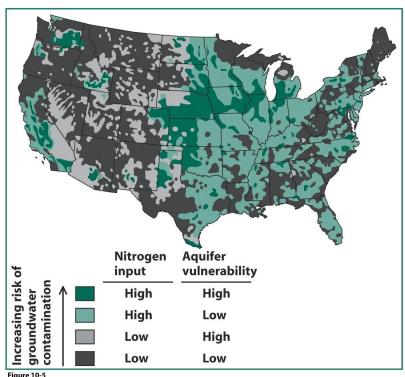


Pool volumes are in cubic kilometers. Fluxes are in cubic kilometers per year.

Ground Water

Contamination of Ground Water

 Although concerned about pollution of surface water in rivers and lakes for a long time, the contamination of ground water was not recognized until 1980s!



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Nitrates and nitrosamines

Nitrates in water originates mainly from 4 sources

Application of nitrogen fertilizers and animal manure

Atmospheric deposition

Human sewage deposited in setic systems

Cultivation of the soil

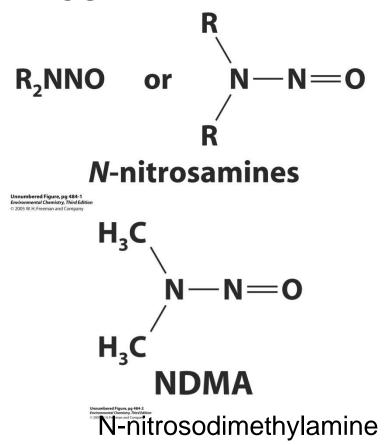
Ground Water

Nitrates in Water and Health Hazards

- The natural concentration in the US is ~2 ppm. (US-EPA standard for MCL is 10 ppm)
- The main source of nitrate is runoff from agricultural lands
- Rural areas with high nitrogen input, well drained soil and little woodland are at greater risk
- Methemoglobinemia in infants –blue-baby syndrome
 - Nitrate is reduced nitrite (NO₂-) by bacteria in the stomach Nitrite then combines and oxidizes the hemoglobin in blood thereby preventing oxygen supply
- Potential risk of stomach and bladder cancer in adults

Nitrosamines

- Excess nitrate ions in drinking water can cause increase incidence of stomach cancer
- Conversion of nitrate to nitrite in the stomach
- Reaction between nitrite and amines can result in the formation of nitrosamines – a known carcinogen



NDMA can transfer methyl group to N- or O- group of DNA base and alter the instructional code for protein synthesis in the cell – In 1980s the commercial beer had 3000 ppt, reduced now to 70 ppt

Ground Water

Contamination by Organic Chemicals

 Municipal landfills and industrial waste disposal sites are often the sources of contaminants

Typical organic contaminants include:

- Chlorinated solvents such as trichloroethylene
- Hydrocarbons from gasoline and other petroleum products (benzene, toluene, xylene)
- MTBE

Nonpoint Source (NPS) Pollution

Unlike pollution from industrial and sewage treatment plants, comes from many diffuse sources. NPS pollution is caused by rainfall or snowmelt moving over and through the ground.

As the runoff moves, it picks up and carries away natural and humanmade pollutants, finally depositing them into lakes, rivers, wetlands, coastal waters, and even our underground sources of drinking water.

These pollutants include:

- Excess fertilizers, herbicides, and insecticides from agricultural lands and residential areas;
- Oil, grease, and toxic chemicals from urban runoff and energy production;
- Sediment from improperly managed construction sites, crop and forest lands, and eroding streambanks;
- Salt from irrigation practices and acid drainage from abandoned mines;
- Bacteria and nutrients from livestock, pet wastes, and faulty septicsystems;

TABLE 10-1

Organic Compounds Commonly Found in U.S. Groundwater-Based Community Water Supplies and Their Properties

Chemical	Density (g/mL)	Water solubility (g/L)
(1907) 146 (4-700) W		
Present at $25-50\%$ of sites:		
Chloroform (trichloromethane)	1.48	8.2
Bromodichloromethane	1.98	4.4
Dibromochloromethane	2.45	2.7
Bromoform (tribromomethane)	2.89	3.0
Present at a smaller fraction of sites:		
Trichloroethene	1.46	1.1
Tetrachloroethene (perchloroethene)	1.62	0.15
1,1,1-Trichloroethane	1.34	1.5
1,2-Dichloroethenes	1.26, 1.28	3.5, 6.3
1,1-Dichloroethane	1.18	5.5
Carbon tetrachloride	1.46	0.76
Dichloroiodomethane	1.58	
Xylenes	0.86 - 0.88	0.18 (0)
1,2-Dichloropropane	1.16	2.8
Benzene	0.88	1.8
Toluene	0.87	0.54

Source: Based on U.S. EPA surveys of about 2% of U.S. water supplies.

Table 10-1 part 1 *Environmental Chemistry, Third Edition*© 2005 W. H. Freeman and Company

and Their Properties						
Chemical	Density (g/mL)	Water solubility (g/L)				
Also commonly present at wells close to						
hazardous waste sites:						
Methylene chloride	1.33	20				
Ethylbenzene	0.87	0.15				
Acetone	0.79	sol				
1,1-Dichloroethene	1.22	2.3				
1,2-Dichloroethane	1.24	8.5				
Vinyl chloride (chloroethene)	gas	8.8				
Methyl ethyl ketone	0.80	268				
Chlorobenzene	1.11	0.47				
1,1,2-Trichloroethane	1.44	4.5				
Chloroethane	0.90	5.7				
Fluorotrichloromethane	gas	1.1				
1,1,2,2-Tetrachloroethane	1.60	2.7				
Methyl isobutyl ketone	0.80	19				

Organic Compounds Commonly Found in U.S.
Groundwater-Based Community Water Supplies

Source: Based on U.S. EPA surveys of about 2% of U.S. water supplies.

Table 10-1 part 2 *Environmental Chemistry, Third Edition*© 2005 W.H. Freeman and Company

Ground Water

The Ultimate sink for Organic Contaminants

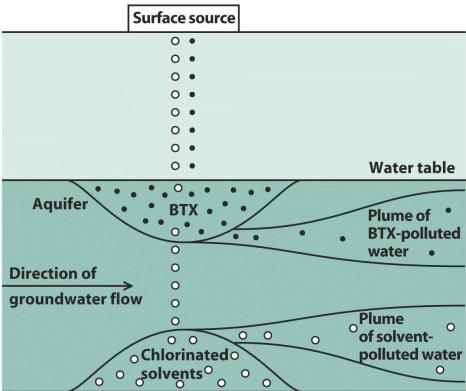


Figure 10-6 Environmental Chemistry, Third Edition © 2005 W. H. Freeman and Company

EPA Issues Approval to Dispose of PCBs Onboard Oriskany

Release date: 02/15/2006

Contact Information: Laura Niles,

(404) 562-8353,

niles.laura@epa.gov

(ATLANTA -February 15, 2006)
Today, EPA issued to the U.S. Navy and the state of Florida an Approval to Dispose of Polychlorinated Biphenyls (PCBs) contained in electrical cable and other non-liquid materials and equipment onboard the decommissioned USS Oriskany.

This approval allows the Navy to deploy the ex-Oriskany as an artificial reef in the East Escambia Large Area Artificial Reef Site, located in the Gulf of Mexico, approximately 23 miles south of Pensacola, Fla.

http://www.epa.gov/pcb/

Pump and Treat

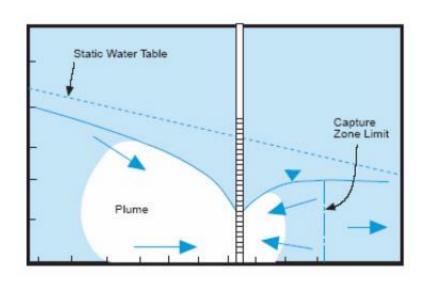
The pump and treat remediation approach is used at about three-quarters of the Superfund sites where ground water is contaminated and at most sites where cleanup is required

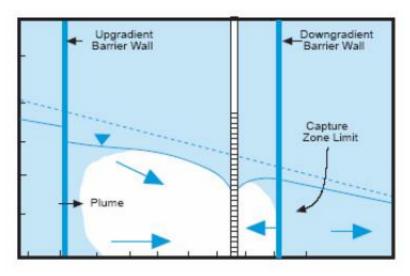
This method relies on pumping the contaminated groundwater to the surface using a series of extraction wells, treating it at the surface to remove the contaminants, and then either reinjecting the water underground or disposing of it off site.

The difficulties encountered with contaminant chemistry and subsurface geology often increase the cost and time required to adequately remediate the site.



Pump-and-Treat Technology





Examples of hydraulic containment in a plan view and cross section using pump-and-treat technology: (a) a pumping well alone, and (b) a well within a barrier wall system

In situ Remediation

The *in-situ* chemical oxidation process is designed to destroy organic contaminants either dissolved in groundwater, sorbed to the aquifer material, or present in their free phase (for examples, as gasoline).

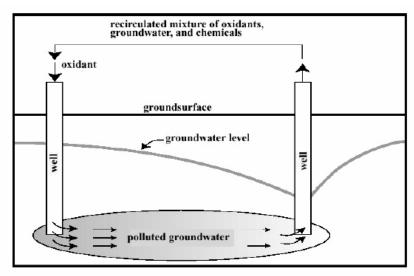


Fig. 1 — In-situ chemical oxidation system diagram. (http://clu-in.org/download/citizens/oxidation.pdf)

Oxidants most frequently used in chemical oxidation include hydrogen peroxide (H_2O_2) , potassium permanganate $(KMnO_4)$, persulfate $(Na_2S_2O_8)$ and ozone (O_3) .

What contaminants can be treated with chemical oxidation?

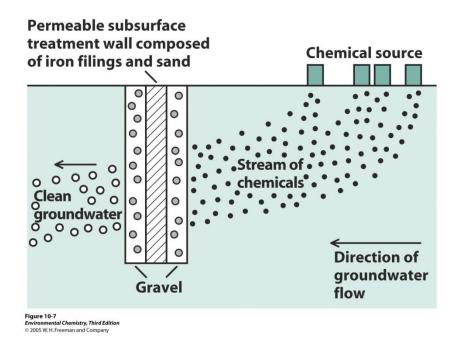
Common contaminants treated by chemical oxidation are amines, phenols, chlorophenols, cyanides, halogenated aliphatic compounds, mercaptans, and certain pesticides in liquid waste streams (for more on these particular contaminants, see the website www.envirotools.org). Soil slurries and sludge can also be treated. Oxidation effectiveness depends on the organic compound

In situ Remediation

- Fe0 granules and sand placed within barrier cleans the water as it passes through.
- Effective for the reductive degradation of chlorinated organics such as trichloroethylene

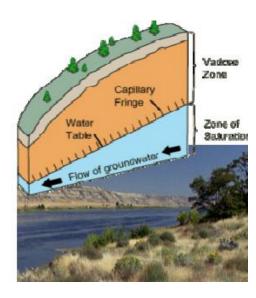
$$Fe(s) \rightarrow Fe^{2+} (aq) + 2e^{-}$$

$$C_2HCl_3 + 3H_2O + 6e^- \rightarrow C_2H_4 + 3Cl^- + 3OH^- After$$



Hanford Vadose Zone – A case study

After 50 years of nuclear materials production, 1.7 trillion liters (450 billion gallons) of liquid waste had been released to the ground at the Hanford Site. Many contaminants remain in the "vadose zone," the area between the top of the water table and the surface of the ground. Some of those contaminants have reached groundwater and some have reached the river.



http://www.hanford.gov/information/sitetours/?tour=virtual

Types of Groundwater Contaminants

The major chemical contaminants present in Hanford groundwater include carbon tetrachloride, chromium and nitrate. Major radioactive contaminants include **iodine-129**, **strontium-90**, **technetium-99**, **tritium and uranium**.

http://www.ci.richland.wa.us/RICHLAND/Hanford/

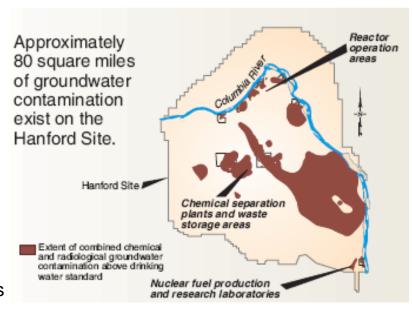
Sources of Groundwater Contamination

During the 1940's and 1950's, liquid wastes were disposed into the ground because it was assumed that the arid desert soil would trap contaminants, preventing them from entering the groundwater.

Disposal sites include:

Reverse wells where liquid contaminants were pumped directly into the soil;
Pits, burial trenches and landfills where solid and liquid wastes in barrels and boxes were buried:

Underground storage tanks where 67 single shell tanks are known or suspected to have leaked about one million gallons of liquid wastes; Cribs, ponds trenches and French Drains for disposal of reactor cooling and wastewater; and Plant waste discharge where wastes were disposed directly to the soil outside the plant.



http://vadose.pnl.gov/characterization.stm

http://www.ci.richland.wa.us/RICHLAND/Hanford/

Groundwater Remediation Project Mission:

In-Situ Redox Manipulation uses a 2,230-foot permeable barrier to treat groundwater changing toxic chromium in a migrating, underground plume to a less mobile, non-toxic form.

Pump-and-treat, another technique, pumps contaminated groundwater from an extraction well to the surface where contaminants are removed.

Monitoring Groundwater – The project has an extensive monitoring network (more than 1,100 wells) providing data for remediation and compliance.

To protect the Columbia River from contaminated groundwater resulting from past, present, and future operations at the Hanford Site and to protect and restore groundwater.



http://www.hanford.gov/cp/gpp/

Bioremediation

Chemical class	Dominant attenuation processes	Likelihood of success given current level of understandin
	Organic Compounds	
Hydrocarbons	•	
BTEX	Biotransformation	High
Gasoline, fuel oil	Biotransformation	Moderate
Nonvolatile aliphatic	Biotransformation,	
compounds	immobilization	Low
PAHs	Biotransformation,	
	immobilization	Low
Creosote	Biotransformation,	
	immobilization	Low
Oxygenated hydrocarbons		
Low-molecular-weight alcohols, ketones, esters	Biotransformation	High
MTBE	Biotransformation	Low
Halogenated aliphatics		
PCE, TCE, carbon tetrachloride	Biotransformation	Low
TCA	Biotransformation,	
	abiotic transformation	Low
Methylene chloride	Biotransformation	High
Vinyl chloride	Biotransformation	Low
Dichloroethylene	Biotransformation	Low

Likelihood of Success of Groundwater Remediation by Natural Attenuation for Various Substances			
Chemical class	Dominant attenuation processes	Likelihood of success given current level of understanding	
Halogenated aromatics			
Highly chlorinated PCBs, tetrachlorodibenzofuran, pentachlorophenol, multichlorinated benzenes	Biotransformation, immobilization	Low	
Less chlorinated PCBs, dioxins	Biotransformation	Low	
Monochlorobenzene	Biotransformation	Moderate	
	Inorganic Substances		
Metals			
Ni	Immobilization	Moderate	
Cu, Zn	Immobilization	Moderate	
Cd	Immobilization	Low	
Pb	Immobilization	Moderate	

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Likelihood of Success of Groundwater Remediation by Natural Attenuation for Various Substances (continued)			
Chemical class	Dominant attenuation processes	Likelihood of success given current level of understanding	
Cr	Biotransformation,		
	immobilization	Low to moderate	
Hg	Biotransformation,		
	immobilization	Low	
Nonmetals			
As	Biotransformation,		
	immobilization	Low	
Se	Biotransformation,		
	immobilization	Low	
Oxyanions			
Nitrate	Biotransformation	Moderate	
Perchlorate	Biotransformation	Low	

Source: Adapted from J. A. Macdonald, "Evaluating Natural Attenuation for Groundwater Cleanup," Environmental Science & Technology (1 August 2000): 346A.

Table 10-2 part 3 Environmental Chemistry, Third Edition

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http://www.epa.gov/safewater/publicoutreach/posters_vids.html

Impact of Pollution on Human Health

Chemical Contamination and Treatment of Wastewater and Sewage

- Sewage treatment
- Phosphate
- Salt
- Biological Treatment
- Cyanides

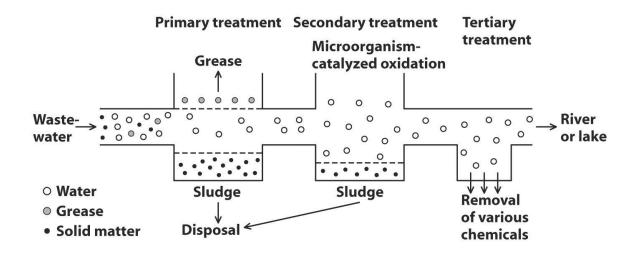






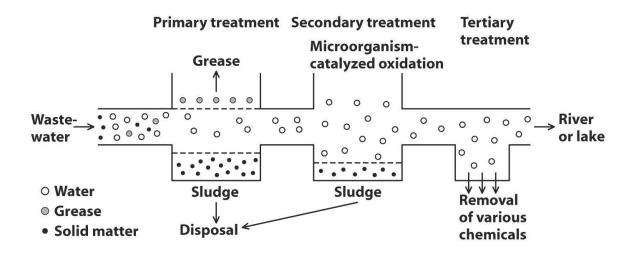
Sewage Treatment

- Primary/mechanical
 - Removal of large particles via settling
 - Produce sludge and grease, lowers BOD by 30 %



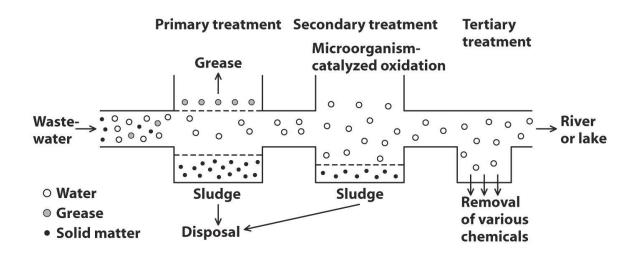
Sewage Treatment

- Secondary/biological
 - Removal of organic matter via oxidation
 - Aeration reactor simple agitation may be enhanced via bacteria
 - Further reduces BOD



Sewage Treatment

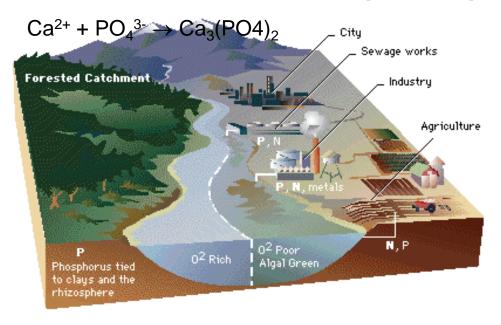
- Tertiary (advanced chemical)
 - Removal of specific chemicals (BOD, organics, P, metals, anions)
 - e.g. simply adjusting pH to 11 converts NH₄⁺ to NH₃
 - May be used as drinking water after treatment or mixed with river water



Phosphate

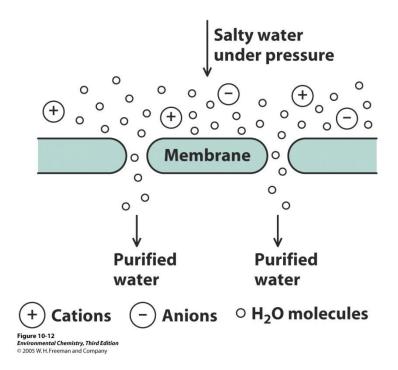
- Phosphates from detergents, fertilizer runoff from farms cause eutrophication
- PO₄³⁻ is a nutrient for algae which deplete O₂ on decomposition
- \$8 billion used to remove phosphates from Lake Erie
- Precipitation with slaked lime, Ca(OH)₂

Catchment Altered by Human Activity



Reducing Salt Concentration

- Decomposition of OM results in high salt concentrations
- Reverse osmosis
- Electrodialysis
- Ion Exchange



Reverse osmosis

Biological Treatment

- Constructed wetland 'natures kidneys'
 - bullrushes and weeds
- Natural microorganisms decontaminate water
- Plants concentrate metals via phytoaccumulation



Olentangy River Wetland Research Park

Chemical Contamination and Treatment Cyanides

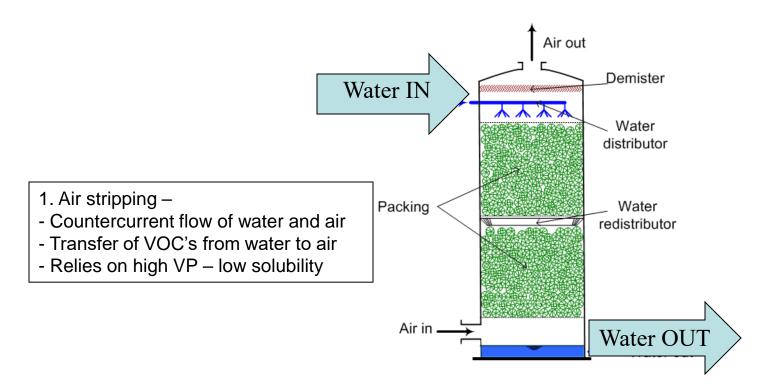
• A

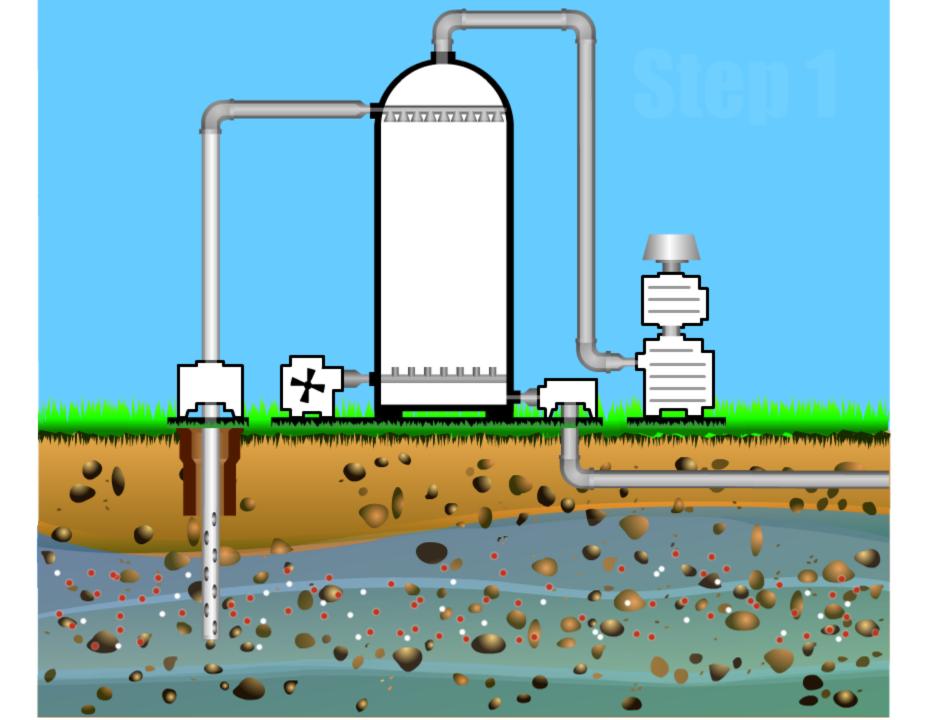
Chlororganics, phenols, cyanides and heavy metals

- · Antibiotics
- · Hormones
- · Chlorinated intermediates
- · Organic poly-Phosphonates
- · Organic acids (z.B.: EDTA, NTA, ...)
- · Hetero- cyclo- aliphatics (e.g.: 1,4-Dioxan)
- · N-organics
- · Aromatics and hetero aromatics
- · Hetero- cyclo- aliphatics (e.g.: 1,4-Dioxan)
- · Aromatics and hetero aromatics

Destruction of VOC's

- 2. Emitted VOCs either:
- absorbed on activated carbon
- oxidized by passing over a heated Pt catalyst





Advanced Oxidation Methods (AOMs)

- All use oxidation by OH· radical
 - abstraction of H or addition to double bond
- For low concentrations of compounds resistant to air stripping, e.g. trichloromethane

Table 1.10. Oxidizable compouns by hydroxyl radicals (Bigda, 1995)

Compounds			
Acids	Formic, gluconic, lactic, malic, propionic, tartaric		
Alcohols	Benzyl, tert-butyl, ethanol, ethylene glycol, glycerol, isopropanol, methanol, propenediol		
Aldehydes	Acetaldehyde, benzaldehyde, formaldehyde, glyoxal, isobutyraldehyde, trichloroacetaldehyde		
Aromatics	Benzene, chlorobenzene, chlorophenol, creosote, dichlorophenol, hydroquinone, p-nitrophenol, phenol, toluene, trichlorophenol, xylene, trinitrotoluene		
Amines	Aniline, cyclic amines, diethylamine, dimethylformamide, EDTA, propanediamine, n-propylamine		
Dyes	Anthraquinone, diazo, monoazo		
Ethers	tetrahydrofuran		
Ketones	Dihydroxyacetone, methyl ethyl ketone		

Table 1.11. Reaction rate constant (k, L mol⁻¹ s⁻¹)

Compounds	OH•	
Chlorinated alkenes	10 ⁹ to 10 ¹¹	
Phenols	10 ⁹ to 10 ¹⁰	
N-containing organics	10 ⁸ to 10 ¹⁰	
Aromatics	10 ⁸ to 10 ¹⁰	
Ketones	10 ⁹ to 10 ¹⁰	
Alcohols	10 ⁸ to 10 ⁹	
Alkanes	10 ⁶ to 10 ⁹	

Modern Wastewater Purification Techniques UV based AOMs

UV light and H₂O₂

$$H_2O_2 \rightarrow 2OH^{\cdot}$$

UV light and O₃

$$O_3 \rightarrow O_2 + O$$

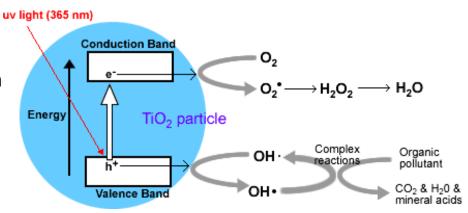
O + H₂O \rightarrow H₂O₂ \rightarrow 2OH·



Completely oxidizes VOCs: $VOCs + OH \rightarrow CO_2 + H_2O + HC$

UV based AOMs

- UV action on semiconductor photocatalytic TiO₂
- Thin films of TiO₂ now being used to coat interior and exterior buildin materials and paints
 - Deodorizes offices
 - Removes condensation
 - Defogs mirrors
 - Kills bacteria in hospitals



UV excites TiO₂ particles creating a photo-generated e⁻ and a highly oxidizing hole in the conduction and valence band of the semiconductor

The e⁻ can be scavenged by O₂ and the hole can react with surface bound OH⁻ on the TiO₂, creating a highly reactive OH• radical that can completely mineralise organic component

Modern Wastewater Purification Techniques H₂O₂ based AOMs

• H_2O_2/O_3 process

$$H_2O_2 + 2O_3 \rightarrow 2 \text{ HO} \cdot + 3 O_2$$

Fenton Reaction

Fe²⁺ + H₂O₂
$$\rightarrow$$
 OH· + Fe³⁺ + OH·
$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + OOH· + H^+$$
Net: $2H_2O_2 \rightarrow 2OH· + H_2O$