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Northern River Basins Study

NORTHERN RIVER BASINS STUDY PROJECT REPORT NO. 87

A REVIEW OF LITERATURE ON THE REMOVAL OF ORGANIC CHEMICALS FROM DRINKING WATER

Prepared for the
Northern River Basins Study
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by

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PREFACE:

The Northern River Basins Study was initiated through the "Canada-Alberta-Northwest Territories Agreement Respecting the Peace-Athabasca-Slave River Basin Study, Phase II - Technical Studies" which was signed September 27, 1991. The purpose of the Study is to understand and characterize the cumulative effects of development on the water and aquatic environment of the Study Area by coordinating with existing programs and undertaking appropriate new technical studies.

This publication reports the method and findings of particular work conducted as part of the Northern River Basins Study. As such, the work was governed by a specific terms of reference and is expected to contribute information about the Study Area within the context of the overall study as described by the Study Final Report. This report has been reviewed by the Study Science Advisory Committee in regards to scientific content and has been approved by the Study Board of Directors for public release.

It is explicit in the objectives of the Study to report the results of technical work regularly to the public. This objective is served by distributing project reports to an extensive network of libraries, agencies, organizations and interested individuals and by granting universal permission to reproduce the material.

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Whereas the above publication is the result of a project conducted under the Northern River Basins Study and the terms of reference for that project are deemed to be fulfilled,
IT IS THEREFORE REQUESTED BY THE STUDY OFFICE THAT;
this publication be subjected to proper and responsible review and be considered for release to the public.

F. C. Wrona
(Dr. Fred J. Wrona, Science Director)

14 Feb 96
(Date)

Whereas it is an explicit term of reference of the Science Advisory Committee "to review, for scientific content, material for publication by the Board",
IT IS HERE ADVISED BY THE SCIENCE ADVISORY COMMITTEE THAT;
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P. A. Larkin
(Dr. P. A. Larkin, Ph.D., Chair)

14 Feb 1996
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Lucille Partington
(Lucille Partington, Co-chair)

14/02/96
(Date)

Robert McLeod
(Robert McLeod, Co-chair)

14/02/96
(Date)

A REVIEW OF LITERATURE ON THE REMOVAL OF ORGANIC CONTAMINANTS FROM DRINKING WATER

STUDY PERSPECTIVE

Water is essential to life and it can be an important vector for conveying contaminants into humans. To assist the Northern River Basins Study (NRBS) Board in making recommendations about the safety of drinking water supplies, the Drinking Water component designed a five-step program of studies. The steps included:

1. synthesis of existing data on water use and water quality;
2. investigation of odour in water and tainting in fish;
3. review of health records for water borne diseases;
4. assessment of conventionally treated and non-conventional water; and
5. preparation of a synthesis report.

Related Study Questions

2) What is the current state of water quality in the Peace, Athabasca and Slave River basins, including the Peace-Athabasca Delta?

8) Recognizing that people drink water and eat fish from these river systems, what is the current concentration of contaminants in water and edible fish tissue and how are these levels changing through time and by location?

This report deals with step four and provides a literature review of the current state of knowledge in the area of inorganic chemical removal from drinking water. The review considered inorganic contaminant parameters that include arsenic, barium, boron, cadmium, chloride, chromium, copper, cyanide, fluoride, iron, lead, manganese, mercury, nitrate, selenium, sodium, sulphide, total dissolved solids, uranium and zinc. Sources of inorganic chemicals include industrial and municipal effluent, agricultural runoff, and natural sources. The effects of high concentrations of inorganic chemicals range from aesthetic problems to toxic effects. Some inorganic chemicals are required for good health although in high doses they can be toxic. Also they can exist in a relatively safe form that is not toxic and then change into a toxic form due to a chemical reaction that may be natural or due to industrial processes or other human intervention. The review revealed that conventional water treatment processes such as coagulation/flocculation, water softening and filtration, can effectively remove many of the inorganic contaminants. Advanced processes such as ion exchange and membrane exchange processes were found to be very effective at removing inorganics" but are also very expensive to apply.

A previous report "Independent Assessment of Drinking Water Quality in the Northern River Basins" (NRBS Report Number 115) determined that, in general, the raw water sources of drinking water in the Northern River Basins had low concentrations of inorganic chemicals and that microbiological contamination was more of a concern. In general, the main effect that inorganic chemicals have is related to the aesthetics of the drinking water.

The information from this report and its companions surveys, "A Review of Literature on the removal of Organic Chemicals from Drinking Water", and "A Review of Literature on the Removal of Microbial Contaminants from Drinking" (NRBS Report Numbers 87 and 132) provide an overview of the current state of knowledge in drinking water treatment. These and other drinking water projects will form the basis for the Drinking Water Synthesis report. This report will also support a companion study, "Human Health Monitoring Program" that will be examining human health issues in Northern Alberta.

REPORT SUMMARY

This report provides a review of the literature concerning the current state of knowledge for removing organic chemicals from drinking water. Sources of organic chemicals include humic substances (products form the natural degradation of plant and animal matter), municipal and industrial effluent, agricultural runoff (pesticides, fertilizer and manure), contaminated leachate from landfill sites and lagoons, and accidental and illegal dumping. Humic substances are the products of natural processes and are the most significant class of organics in terms of volume. Because the humic substances are natural, little can be done to prevent them from entering the water, as opposed to other sources that are a result of human activity. Although treatment processes can significantly improve water quality, the cleaner the raw water supply, the simpler and more economical the water treatment is. The effect of organic chemicals on drinking water quality ranges from aesthetic (taste, odour, colour) to threats to human health (carcinogens).

Virtually all organic chemicals can be reduced in concentration by the appropriate water treatment processes. The amount of reduction is a function of the parameters of the chemical of interest, the water treatment process used and the other materials present in the raw water. Coagulation and flocculation, softening, sedimentation, filtration, chlorine, activated carbon (GAC and PAC), resin adsorption, air stripping, reverse osmosis, chlorine dioxide, ozone and UV radiation were evaluated as to their effectiveness in removing organic chemicals from water.

As may be expected, no one process is capable of treating the whole range of organic chemicals. The effectiveness of a treatment process is a function of the characteristics of the organic chemical in question. For example, physical processes such as coagulation and flocculation can be effective in removing organic chemicals that associate with the organic material in the water.

When designing a water treatment facility extensive testing may be necessary to determine the appropriate processes for treating the raw water. Bench top and pilot plant testing will likely be necessary to estimate the effectiveness of the design treatment processes on treating the water.

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1. Foreword

Due to ever-increasing numbers and quantities of organic chemicals in our environment, and public concern as to the adverse health effects of these compounds, the treatment of water to remove organic contaminants has become important for the protection of public health. This literature review was compiled with the intent that it be used as a guide, outlining processes that might be implemented and the removal efficiencies that may be observed during water treatment for the removal of organic compounds. These unit processes are generally not intended to be used on their own, but rather as single elements in a series of processes. This concept is commonly known as the multiple barrier treatment approach, and is necessary to obtain high quality water.

It must be emphasized that while treatment processes can significantly improve water quality, there is no substitute for source water purity. The task of removing contaminants from a clean supply is far simpler and economical than for a heavily contaminated source. Thus, every effort should be made to draw water from as unpolluted a source as possible. Very few sources, however, will provide clean enough water that no treatment is necessary, and therefore, it is in every community's interests to investigate the characteristics of their water supplies and the technologies that are available to help remediate any problems encountered. This review should therefore provide a starting point, after which testing must be done to determine how individually selected processes and combinations will function to treat the water at a specific location.

This review is part of a series of studies by the Drinking Water Component of the Northern River Basin Study (NRBS), whose overall task is to assess the quality of drinking water in the NRBS area. Analysis of existing water quality has found that generally raw water sources in the NRBS area have low concentrations of health related organic contaminants based on comparisons to the Guidelines for Canadian Drinking Water Quality (Prince et al 1994). The only health related organic contaminant which was found to exceed guideline values at some sites was trihalomethanes (THM). THMs are generally produced in the treatment process by the reaction of chlorine, used as a disinfectant, and certain organic material from the water. Concentrations of THMs in the finished water can generally be lowered to acceptable levels by ensuring effective removal of organic material from the water prior to the addition of chlorine.

The goal of water treatment is to reduce possible risk associated with drinking water to an acceptable level. Risk to public health may be posed by various organic and inorganic chemicals, microbiological contaminants and radiological contaminants. In addition, the aesthetic quality of the water can be very important to the consumer. This report makes up one of three literature reviews completed as part of the NRBS. The other two review removal of inorganic and microbiological contaminants. Although this report only considers organic contaminants, in making decisions on treatment requirements it is important to consider all types of contaminants as trying to minimize concentrations of one type of contaminant may actually negatively impact the removal of other contaminants.

2. Introduction

2.1 Significance of Organic Chemicals in Drinking Water

Public awareness of organic chemicals in our environment, both synthetic and natural, and their possible effects on organisms which contact them have increased. The avenues by which we, as humans, come into contact with these substances are numerous, but one route of particular importance is via our drinking water. Canadian adults, on average, ingest 1.5 litres per day (Curry et al 1991), and hence the potential for exposure to contaminants is great.

Perhaps the compounds that cause the most concern are those which fall into the *carcinogen* or *suspected carcinogen* category. These would include such compounds as some of the halogenated hydrocarbons, carbamates, nitrosamines, azocompounds, and many aromatic compounds (Rodricks 1993). In fact, it was relatively recently discovered that the chlorine used to disinfect water can actually react with many naturally occurring organics to produce trihalomethanes (THMs), which are now known to be carcinogenic in laboratory animals. Compounds that are believed to initiate cancer are given special treatment in regulations, because there is thought to be no dose below which there exists no risk to an exposed individual.

In addition to health effects, many organic compounds produce disagreeable tastes or odours in our drinking water, often at extremely low concentrations. For example, 1,4-dichlorobenzene has an odour threshold as low as 0.0003 mg/L (Pontius 1990). While taste and odour merely constitute aesthetic problems, their detection does indicate the presence of contaminants and hence possible health risks, and thus they are often used as indicators of treatment efficiency. In addition, consumers often judge the quality of a drinking water based on its aesthetic characteristics.

In regions where agricultural practices dictate that pesticides be used, the risk of contamination with these compounds is high. While health effects are certainly the most important fear, frequent watering of gardens and lawns with water containing high concentrations of pesticides has been shown to damage plants (Aly & Faust 1965).

Conventional water treatment, consisting of screening, coagulation, flocculation, sedimentation, filtration and disinfection, has been demonstrated to be ineffective at removing some organic chemicals. Hence, advanced treatment processes such as air stripping, activated carbon adsorption, and membrane processes may be required. The interrelated nature of unit processes must also be accounted for when designing a treatment scheme, as changes to one process can significantly affect other processes. Extensive testing is therefore required, on a case-by-case basis, in order to determine which processes are needed and can be afforded at the necessary scale by a given community.

2.2 Classification of Organic Chemicals in Drinking Water

Rather than attempting to provide removal efficiencies for every organic chemical in common use, this review will instead classify chemicals into categories based on a number of properties. Trends will be noted and differences pointed out, so that a user may form a broad understanding of how groups of chemicals are removed. Specific chemicals can then be fitted into categories to obtain some estimate of how a process may perform.

Molecular weight is a frequently used means of classifying organic materials. It is usually used as a surrogate measure of molecular size. Typically, the useful range of molecular weights in water treatment extends from very low values in the vicinity of 16 g/mol (eg. methane), right up to tens of thousands of grams per mole (naturally occuring humic substances). Molecular size becomes important in processes such as reverse osmosis and activated carbon adsorption, where whether a molecule is larger or smaller than a certain pore size will determine whether it may be removed or not.

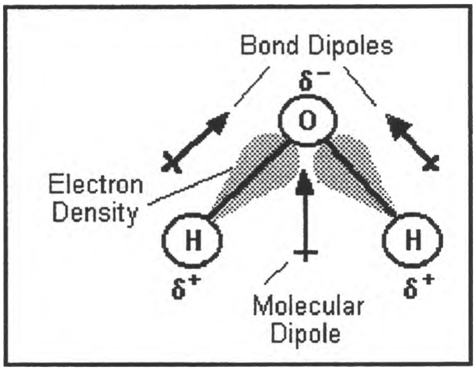

Figure 1. Bond and molecular dipoles of a water molecule.

Another frequently used classification system is molecular polarity. Polarity is a function of how different atoms attract the electron density between them (bonds). Bonds in which the electrons are equally shared will have polarities of zero. This is usually only found between atoms of the same type (eg. a bond between two carbon atoms). However, in the case of bonds between different atoms (eg. a bond between a carbon and a chlorine atom), the two atoms will have different affinities for the electrons, and the charge density between them will be more concentrated at one end of the bond. The result of this is a small net charge at each end of the bond - negative (δ^-) at the end with the higher electron density and positive (δ^+) at the other. The vector that describes the magnitude and direction of this polarity is called a dipole moment, and the sum of all the dipole moments in a molecule yields a net molecular dipole. The magnitude and direction of this molecular dipole dictates how the molecule will interact with other molecules, especially water which has a very large molecular dipole. Molecules with large dipoles will often attract one another, whereas a highly polar molecule will generally not interact closely with non-polar molecules.

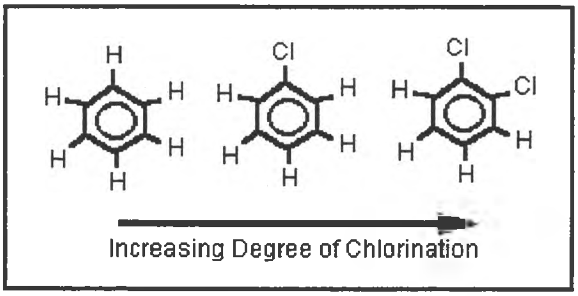

Figure 2. Degree of halogenation.

The degree of halogenation, especially chlorination, of a compound is often used to differentiate classes. The degree of halogenation refers to the number of halogen atoms present in the molecular structure of the compound, with more halogens giving a higher degree of halogenation. Halogenation is important in water treatment, as certain processes do not remove highly halogenated compounds effectively. An example of this would be biological degradation, in which the more highly chlorinated a compound is, the harder it is to degrade in general (Manahan 1991).

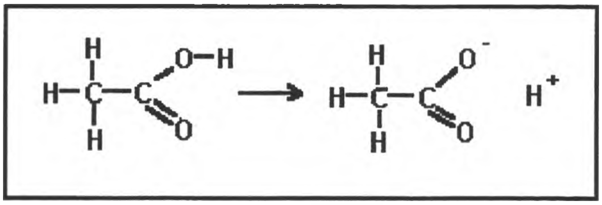

Figure 3. A deprotonation reaction example.

Acidity or basicity is another means of classifying compounds. This refers to their ability to donate or accept protons (positively charged H^+ ions), respectively. Highly acidic compounds will undergo deprotonation under a very wide range of conditions, while weakly acidic ones will only lose protons under more strict conditions, usually at high pH. Highly basic compounds are those which will accept protons under most conditions, while weakly basic ones will only do so under a narrower range, usually at low pH.

The final characteristic that will often be used to group chemicals is solubility. This refers to the amount of a compound that can dissolve in solution. While the solution is usually water, it is not limited to water alone, as substances can dissolve in other liquids, such as liquid organics, or even in other phases, such as the membranes used in reverse osmosis.

2.3 Common Sources of Organic Chemicals in Water

There are many sources of organic compounds that affect our water supplies. Perhaps the most significant class of organics, in terms of volume, is humic substances. These are generally the result of the degradation of natural materials such as plant and animal matter. There is thus very little that can be done to prevent these substances from accumulating in our water sources, and so instead, there must be a heavy reliance on treatment processes to reduce their concentrations.

Another major source of pollution in our rivers and lakes is municipal effluent. Storm sewers can transport a large number of organics from our streets to their receiving waters, while treated sanitary sewage still contains large quantities of organic material, including refractory organics, detergents, greases and oils (Manahan 1991).

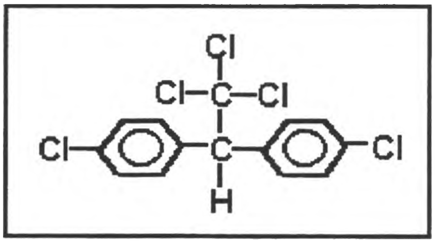

Figure 4. Structure of DDT.

Agricultural land use leads to the input of a wide range of organic pollutants into water systems. Runoffs contain fertilizers and pesticides that eventually find their way into drinking water supplies downstream, and aerial spraying can lead to direct input of chemicals into water bodies. Due to the heavily chlorinated nature of many pesticides, they are often highly persistent in the environment. DDT, for example, was banned in the United States in 1972, but it can still be found in some water sources (Manahan 1991).

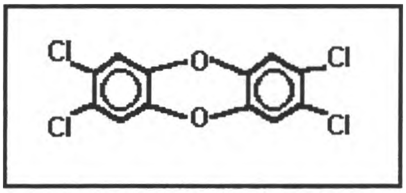

Figure 5. Structure of 2,3,7,8-tetrachlorodibenzo-p-dioxin

Several industrial processes are known to be significant contributors to organic loads. Pulp mills are known to discharge dioxins due to the chlorinated bleaching processes used. In fact, one dioxin, 2,3,7,8-tetrachlorodibenzo-p-dioxin, is one of the most toxic synthetic substances known (Manahan 1991), and its tendency to concentrate in fatty tissues can lead to higher concentrations in fish than are found in the water.

Illegal and accidental dumping can play a significant role in increasing the organics concentration of a source water, especially over a short time period, after which levels may drop back to their original values. However, these shock inputs can be extremely hazardous, as treatments may not be able to accommodate unexpected peaks. Frequent testing of source and product water, and/or large safety factors are therefore required to attempt to identify shock loadings.

Finally, contaminated groundwater can be a source of organic pollutants, especially volatile organic compounds (VOC's). Groundwater baseflow comprises a significant portion of the water content of lakes and rivers. Facilities such as landfills and lagoons can provide leachate which percolates down to the water table and eventually travels via aquifers to point source springs or seepage zones, where the water emerges to run off along the surface, thus transporting contaminants to potential drinking water source bodies.

3. Overview of Water Treatment

3.1 Conventional Processes

Conventional water treatment is generally defined as coagulation, flocculation, sedimentation, filtration and disinfection. Figure 6 is a representation of the normal order of these processes.

While these processes do remove significant amounts of debris and dissolved chemical matter, in the cases of many organic chemicals, these conventional processes may not be adequate to remove sufficient quantities of the contaminant if high concentrations are present in the raw water source. However, as first stages in the removal scheme they do serve to make the job of removing the remaining contaminants easier by either partially removing the compounds of interest or by removing other material that could interfere with the removal by another process.

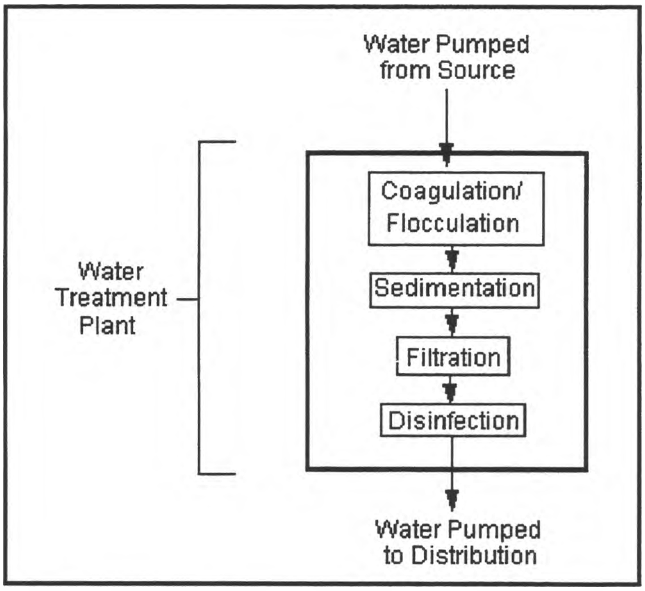

Figure 6. Treatment Sequence

3.2 Advanced Treatment Processes

For the many organic chemicals that are not removed satisfactorily by conventional treatment processes alone, there are numerous advanced processes that can be employed to improve the overall removal. These processes include: activated carbon adsorption, air stripping, reverse osmosis, chlorine dioxide oxidation, ozonation, and ultra-violet light treatment. Each of these have been shown to be effective at removing at least one category of chemicals, whether that be volatile organic compounds (VOC's), highly chlorinated organics, or some other class.

The processes which are needed at any one given site will be a function of the organics present in the water supply, the water demand of the community, and the financial viability of buying, operating and maintaining such a system.

3.3 Multiple Barrier Treatment Approach

While individual unit processes may be seen as removing adequate amounts of organic material, performance consistency, safety, and financial considerations make it important that a multiple barrier treatment scheme be implemented. Some conventional processes may be able to remove large quantities of material, but then a finishing step required in order to reduce the contaminant level to acceptable levels. This approach often makes it possible to reduce the costs associated with an advanced process by utilizing a conventional, less expensive process to perform the bulk removals and hence reduce the loads placed on the advanced process.

Also, due to the specificity of some unit processes for certain classes of organic compounds, it is unlikely that one process will be able to remove all of the compounds present in a water supply. Therefore, in order to include a margin of safety in the treatment system, multiple processes should be included. This becomes especially important when the water supply is vulnerable to accidental spills or shock loadings, and monitoring of the supply is performed infrequently.

4. Mechanisms of Organics Removal

4.1 Adsorption

Simply put, adsorption is a process in which a contaminant in solution changes from the solution phase to the solid phase by attaching to the surface of another particle which can then be removed from the system, thus removing the impurity from solution. The attachment can either occur at the outer surface of the adsorbent particle, or the impurity may penetrate the adsorbent and attach to an inner surface by means of travelling through the pore spaces found in the adsorbent particle.

In general, the smaller a contaminant is, the deeper it will be able to penetrate into the adsorbent by means of the pore system. This is referred to as molecular screening, with large molecules being limited to the surface due to their minimal pore penetration, and smaller molecules being more evenly distributed across the total surface area of the adsorbent, both on the outer surface and within the pores.

Adsorption can be described thermodynamically, and the most convenient method of doing so is via adsorption isotherm equations. Isotherm equations relate the equilibrium concentration in the solution to the amount adsorbed per weight of adsorbent. The two most frequently used relationships describing adsorption equilibria are the Langmuir and Fruendlich equations:

Freundlich Equation

$$q_e = KC_e^{1/n} \qquad \text{Equation 1}$$

Linearized Freundlich

$$\log q_e = \log K + \frac{1}{n}\log C_e \qquad \text{Equation 2}$$

Langmuir Equation

$$q_e = \frac{q_{max} b C_e}{1 + bC_e} \qquad \text{Equation 3}$$

Linearized Langmuir

$$\frac{1}{q_e} = \frac{1}{q_{max} b C_e} + \frac{1}{q_{max}} \qquad \text{Equation 4}$$

where q_e is the mass of compound adsorbed per unit adsorbent, C_e is the equilibrium concentration of compound in solution, q_{max} is the maximum value of q_e that can be obtained by increasing C_e, and K, n, and b are constants (Pontius 1990).

4.2 Precipitation

Precipitation is the mechanism whereby compounds in solution are reacted with another chemical to produce an insoluble product which can then be removed either by sedimentation or filtration. The most common scenario is that of a charged particle in solution which is reacted with a chemical species of opposite charge to form an insoluble complex, or precipitate. Figure 7 represents a generic precipitation reaction.

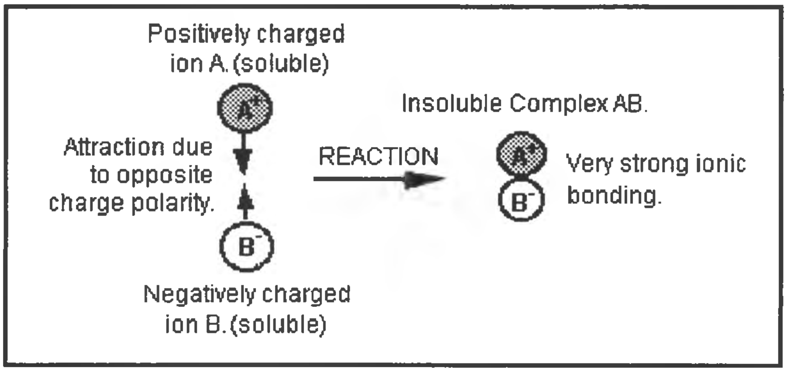

Figure 7. Generic Precipitation Reaction.

The degree to which any complex will be soluble can be determined by its solubility product constant, K_{sp} (see Equations 5 and 6)

$$A_nB_m \leftrightarrow nA^{a+} + mB^{b-} \qquad \text{Equation 5}$$

$$K_{sp} = \left[A^{a+}\right]^n \cdot \left[B^{b-}\right]^m \qquad \text{Equation 6}$$

The value of the solubility product constant cannot be exceeded without precipitation occuring to compensate and return the product to the constant value.

4.3 Gas Transfer

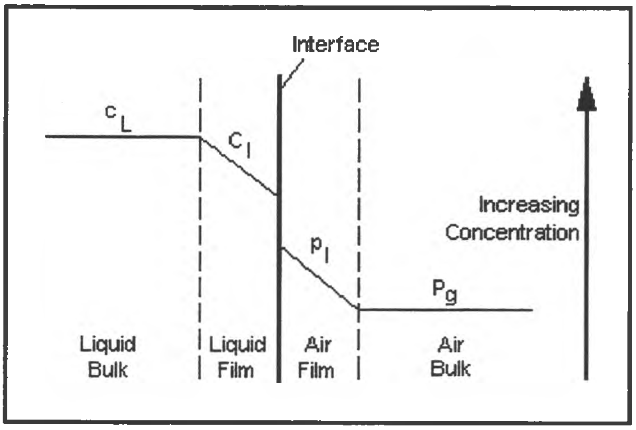

Figure 8. Gas stripping concentration gradient (Pontius 1990).

Gas transfer involves the transfer of a gas between the aqueous and gaseous phases. By bringing air into contact with the aqueous solution, dissolved gases may be permitted to transfer to the air phase and hence bubble out. However, a concentration gradient must exist between the air and the water, meaning that the concentration of the gas in question must be lower in the air than in the water, otherwise no net transfer out of solution can occur. If the liquid concentration is lower than the related gas concentration, transfer into the solution will occur. A gas stripping situation is illustrated in Figure 8, where the concentration gradient between the bulk liquid and air phases is represented. It can be shown that the rate of change of concentration of gas in the bulk water phase is approximated by Equation 7, in which c is the concentration in the bulk water phase, K_L is the overall transfer coefficient in a liquid film controlled situation, A is the interfacial area, V is the volume of liquid containing the interfacial area, c_t is the concentration in the liquid bulk phase at time t, and c_S is the concentration in equilibrium with gas at time t.

$$\frac{dc}{dt} = K_L \frac{A}{V}(c_t - c_s)$$ Equation 7

4.4 Filtration

Filtration is the mechanism whereby molecules and particles are excluded from passing through a given medium. This exclusion can be a result of molecular or particle size, or polarity or solubility incompatibilities between the molecules and the filter. This would apply to operations such as sand filtration and membrane filtration. Water, being a relatively small molecule, can generally fit through small pores, while larger organic molecules often cannot, thus removing them from the filtrate.

4.5 Biodegradation

Biodegradation is an important aspect of water treatment and must be controlled rigidly in order to avoid contamination of the water supply. Microorganisms consume certain organic materials and degrade them in order to obtain energy which can then be used for life processes. Often, specialized enzymes are needed for the degradation, and thus degradation works best with common compounds to which the bacteria are acclimated. If an unfamiliar organic chemical is encountered, enzymes may be developed eventually by the bacterial population to allow them to degrade it.

4.6 Oxidation

Oxidation reactions involve the loss of electrons by the compound being oxidized by the oxidizing agent (which gains the electrons). Oxygen itself is not needed, although in most water treatment oxidation reactions, oxygen in some form is present. The ability of a compound to oxidize another is expressed as its standard potential, E^o, in volts. This merely determines whether or not the oxidation reaction can proceed. The initiation of the reaction may require a threshold energy input. The rate of reaction is not related to the standard potential, and in the case of most oxidation reactions, the rate is slow enough to make the reaction of very little use in water treatment. Hence, under some conditions the complete oxidation of organic compounds to carbon dioxide is not possible. Often, only partial oxidation is possible via chemical reaction in the time available, leading to the production of organic by-products, some of which may be removed more easily than the original compound by other treatment processes, while others may be more difficult to remove, and still others are possibly more toxic. In the example below, oxalic acid is fully oxidized to carbon dioxide, with the formal oxidation state of the carbon atoms increasing from +3 in the oxalic acid to +4 in the carbon dioxide (Glaze 1987).

$$H_2C_2O_4 \xrightarrow[\text{agent}]{\text{oxidizing}} 2CO_2 + 2H^+ + 2e^-$$ Equation 8 (Glaze 1987)

5. Coagulation and Flocculation

5.1 Unit Process Description

5.1.1 Physical Characteristics

Colloidal particles in water supplies are often the result of electrostatic repulsive forces due to positive or negative surface charges, hydrophilic interactions due to bound water on the particles' surface, and steric effects due to adsorbed macromolecules which prevent the colloidal particles from contacting one another. Coagulation and flocculation are the processes by which these particles are destabilized, and brought into contact so that they might form larger aggregates which can be more easily removed. The coagulation process is generally performed in a rapid-mix tank, where a coagulant such as alum (aluminum sulphate) ($Al_2(SO_4)_3 \cdot 14(H_2O)$) or iron (ferric) chloride ($FeCl_3$) and often a coagulant aid (usually a polymer) are added and dispersed. Particles can be removed either by charge neutralization followed by flocculation, or by the formation of a sweep floc consisting of $Al(OH)_{3(s)}$, which is formed via the simplified Equation 9, and enmeshes colloidal particles as it settles.

$$Al_2(SO_4)_3 \cdot 14H_2O + 3Ca(HCO_3)_2 \leftrightarrow 2Al(OH)_{3(s)} + 3CaCO_4 + 6CO_2 + 14H_2O \qquad \text{Equation 9}$$

In the process of alum coagulation, the limited case of charge neutralization is believed to be caused by positively charged aluminum species which are intermediates in Equation 9. Therefore, the steps involved in the actual coagulation phase are the addition and reaction of coagulant, and the rapid mixing which facilitates colloid stabilization.

The second phase, flocculation, is performed in a large, slowly mixed tank. It is during this process that the destabilized particles are brought together in collisions, causing them to aggregate and form larger particles known as floc which can then settle.

5.1.2 Factors Affecting Efficiency

There are numerous factors which affect how well the coagulation and flocculation processes occur. First, the coagulant dose is very important. Underdosing may lead to much of the colloidal material maintaining its stability, whereas overdosing may lead to restabilization due to an excess of positive charge.

Second, the degree of mixing will affect the efficiency of both coagulation and flocculation. The mean velocity gradient, G, is a commonly used method of quantifying mixing, and is calculated as in Equation 10:

$$G = \sqrt{\frac{P}{\mu V}} \qquad \text{Equation 10}$$

where: G = velocity gradient (s^{-1})
P = power input (Watts)
μ = dynamic viscosity (Ns/m^2)
V = mixing tank volume (m^3)

Coagulation is usually performed at G values of up to $1000s^{-1}$, while flocculation is generally done with velocity gradients of between 20 and $70s^{-1}$. Flocculation is performed at these low G values in order to avoid shearing the floc particles apart once collisions have taken place. In addition to the power applied, the temperature of the water can have a significant effect on the efficiency of mixing, because of the temperature dependence of dynamic viscosity. The viscosity of water decreases by a factor of 6.4 between 0 and 100°C (Weast 1985).

5.2 Mechanisms of Organics Removal

There are three mechanisms by which organic chemicals are removed from water during the coagulation and flocculation processes. First, some organic matter may be removed by direct precipitation (Edzwald 1993, Rebhun & Lurie 1993, Amirtharajah et al 1993, AWWA 1979). The precipitation reaction of natural humic acids (HA) with alum can be represented by (Rebhun & Lurie 1993):

$$\text{HA} + \text{Monomeric Al} \rightarrow [\text{HA} \cdot \text{Monomeric Al}]_{(s)} \qquad \text{Equation 11}$$

or

$$\text{HA} + \text{Polymeric Al} \rightarrow [\text{HA} \cdot \text{Polymeric Al}]_{(s)} \qquad \text{Equation 12}$$

where bracketed species represent complexes. Second, some organic material may be removed by adsorption onto metal hydroxide precipitates (Edzwald 1993, Rebhun & Lurie 1993, Amirtharajah et al 1993), which may then be separated from the water. Third, if sweep floc blankets are produced during coagulation, then some organic material may become enmeshed within the blanket's matrix and settle out (Rebhun & Lurie 1993).

5.3 Organics Removals Efficiency

It has been found that coagulation can be instrumental in removing significant amounts of certain classes of organic chemicals (Amirtharajah et al 1993, AWWA 1979, Reckhow & Singer 1984). Edzwald's results are summarized below (Edzwald 1993):

Table 1. Organics removal effectiveness of coagulation.

SUVA*	% Removal		
m^{-1}/mg/L	UV	DOC	TTHMFP
4.5	90	70	not measured
4.6	80	70	72
2.5	56	23	not measured
2.1	30-60	22	45

*Note: SUVA = Specific UV Absorbance = a measure of the amount of DOC that is humic material (4-5 is largely humic, <3 is predominantly non-humic)

Similarly, Babcock and Singer found that total chloroform (THM) formation potential decreased by 70% when humic acid samples were coagulated before chlorination (Babcock & Singer 1979), indicating a decrease in the amount of natural organic material. The AWWA Research Committee on Coagulation found that alum coagulation removes most THM precursors to some extent (AWWA 1979). As most trihalomethane precursors are humic materials and thus have relatively high molecular weights, these findings agree with those of Amirtharajah et al (1993) who found that dissolved organic carbon can be removed by coagulation to a degree that is proportional to the molecular weight and inversely proportional to the solubility of the material.

A large amount of work has been done on the removals of pesticides from drinking water. Robeck et al (1965) determined that less soluble materials, such as DDT, are removed much more easily by coagulation than are more soluble materials, such as lindane and parathion. The results indicating that DDT can be removed very well agree with those of Sigworth (1965), and with the AWWA Research Committee on Coagulation who found that 97% removals of DDT could be obtained with coagulation and sedimentation (AWWA 1979). However, the solubility argument failed when Cohen et al (1960) found that alum coagulation was completely ineffective for the removal of rotenone and toxaphene, two pesticides that are practically insoluble in water. This was confirmed by the AWWA Research Committee on Coagulation who determined that alum is ineffective at removing cyclodiene-based pesticides such as aldrin, endrin, dieldrin and toxaphene, as well as lindane, parathion, malathion, 2,4-D and rotenone. It was postulated that the removal of pesticides relies heavily on their degree of association with natural organic material found in the water (AWWA 1979).

Love and Eilers (1982) studied the removals of several volatile organic solvents. Their conclusions were that coagulation was an ineffective means of their removal, except for the small amounts lost due to incidental evaporation. No reasons were given for their poor removals.

5.4 Recommended Design and Operating Parameters for Organics Removal

Much of the literature indicates that pH and coagulant dosage are the two primary factors in determining how much of the organic matter in water can be removed by coagulation and flocculation. The AWWA Committee Report states that coagulant dose and pH are extremely important parameters in trihalomethane precursor removal, and that a stoichiometric relationship exists between raw water colour and optimum coagulant dosage (AWWA 1979). The optimum pH for coagulation of organic matter is reported by Amirtharajah et al (1993) as being 5 for alum, and 4 for iron (III) salts. This is supported by the work of Babcock and Singer (1979), who found that colour and humic acid removals are high at pH 5.0 and with an alum dose of 50 mg/L. Edzwald's (1993) research showed that for highly coloured waters, ideal coagulant dosages were 0.5 mg of aluminum per mg of dissolved organic carbon (DOC) at pH 5.5, and 1.0 mg aluminum per mg DOC at pH 7.0. Also, it has been shown that the conditions at which colour removal is optimized are almost identical to those at which trihalomethane formation potential removals are best (Amirtharajah et al 1993).

6. Softening

6.1 Unit Process Description

6.1.1 Physical Characteristics

The lime softening process consists of chemical addition, rapid mix, flocculation and sedimentation. Chemicals are dispersed rapidly into the flow stream, with the correct dosages of lime and soda ash (for non-carbonate hardness). The rapid mix process then violently agitates the solution to provide adequate contact between the chemicals for all the water. If the lime is added as a powder then care must be taken in the design of the rapid mix basin to allow sufficient time in the rapid mix for all of the lime to dissolve, as it does so relatively slowly (Pontius 1990).

The flocculation step provides the retention time and contact opportunities needed for the precipitate to grow large enough that it can be separated relatively quickly by gravity settling. The flocculation basin is mixed, but with much lower force than the rapid mix tank, in order to promote collisions but not be powerful enough to shear floc particles apart. Current designs tend to provide a series of flocculation basins, each with a slightly lower velocity gradient (G) than the previous one (Pontius 1990).

Clarification consists of providing an unmixed basin, in which the precipitated and flocculated particles are able to settle out of suspension to the bottom of the tank where they are removed by scrapers. The softened water is then removed from the basin for further treatment (Pontius 1990).

Settling velocities are a function of particle size and density, and can proceed by discrete (Equation 13), flocculant, hindered (or zone), or compression settling. These differ in the amount of interaction between particles (Pontius 1990).

Stokes' Equation

$$U_t = \frac{g(\rho_s - \rho)d^2}{18\mu}$$

Equation 13 (Pontius 1990)

U_t = settling velocity (cm/s)
g = gravity (cm/s^2)
ρ_s = density of the particle (g/cm^3)
ρ = density of the liquid (g/cm^3)
d = diameter of the spherical particle (cm)
μ = dynamic viscosity of liquid (g·cm^{-1}·s^{-1})

6.1.2 Factors Affecting Efficiency

The temperature will play and important role in determining the efficiency of softening. First, it will affect the dissolution of the chemicals in the water, probably increasing the rate with increasing temperature. Second, in the mixing phases (rapid mix and flocculation) the amount of energy input required to obtain the same velocity gradient will be lowered with increasing temperature, due to the decrease in viscosity of the water. Finally, as can be seen in Stokes' Law (Equation 13), the viscosity will also affect the rate of settling of the particles, with a higher temperature leading to faster settling (Pontius 1990).

Other factors affecting efficiency include the pH, the hardness and the alkalinity of the water, along with the concentrations and types of organics present.

6.2 Mechanisms of Organics Removal

Softening produces crystals of $CaCO_3$ and $Mg(OH)_2$. As these solids are formed, they may trap fractions of the organic material present in the water within their structure. This is known as coprecipitation (Liao & Randtke 1985). The calcium ions present in the water can also bind with negatively charged fulvic acids to cause the direct precipitation of calcium fulvate (Liao & Randtke 1985). Adsorption of humic substances by calcium carbonate can also occur, as can coagulation and flocculation of very large humic molecules, which can act like colloidal particles (Liao & Randtke 1985). Of these four mechanisms, Liao and Randtke observed that coprecipitation appeared to be the most effective mechanism, at least for the removal of humic substances.

6.3 Organics Removal Efficiency

The removal of pesticides by lime softening has been consistently found to be insignificant. Robeck et al (1965) stated that no removals were obtained, while Miltner et al (1989) found that all of the pesticides they studied passed through the softening process relatively untouched. The reason suggested for this is the hydrophilic, highly soluble nature of these compounds.

Love & Eilers (1982) found that lime does not remove trichloroethylene or related solvents.

McCarty et al (1979), however, found that lime is an effective treatment for the removal of both suspended and dissolved organic compounds from water. Much of the work has been based on the reduction of total organic carbon (TOC) concentrations. Semmens & Staples (1986) found that lime and recarbonation reduced the TOC content of Mississippi River water by 33%. Weber & Jodellah (1985) studied the effectiveness of lime in removing TOC from Hudson River water, and found that the maximum removal obtainable was approximately 50% of the original 5.5 to 6.5

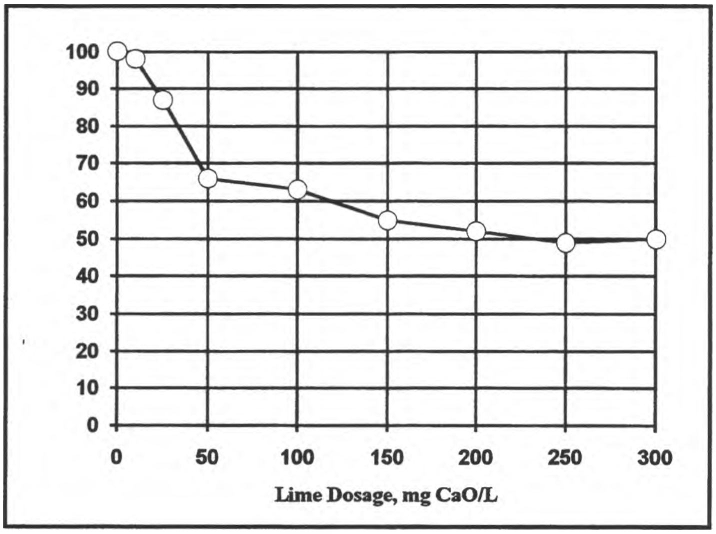

Figure 9. TOC Remaining vs. Lime Dosage (Weber & Jodellah 1985).

mg/L (see Figure 9). Liao & Randtke (1985) found that lime softening removed, on average, 40% of the fulvic acid content of a surface water, and that pH adjustment could significantly improve the TOC removal without hindering softening (Table 2).

Table 2. pH influence on TOC removal by lime softening.

pH	TOC % Removal
9	28
11	35
12	44

Note: Initial TOC = 3 mg/L fulvic acid

Johnson & Randtke (1983) published the results found in Table 3 on the removals of TOC and non-purgeable organic chlorine (NPOCl) using lime and post-chlorination.

Table 3. Lime and postchlorination reductions of TOC and NPOCl (Johnson & Randtke 1983).

Treatment	Calcium Hardness mg $CaCO_3$/L	Magnesium Hardness mg $CaCO_3$/L	Lime Dose mg $CaCO_3$/L	TOC Final mg/L	TOC Removal %	NPOCl Final µg/L	NPOCl Removal %
None	0	0	0	3.00	0	696.0	0
Lime and postchlor.	100	0	100	1.61	46	388.5	45
	200	0	200	0.46	85	127.2	82
	200	100	300	0.23	92	69.6	90

6.4 Recommended Design and Operating Parameters for Organics Removal

According to Liao and Randtke (1985), the ideal water conditions consist of a high pH, high hardness, and low alkalinity. Weber and Jodellah (1985) recommend a lime dosage of 150 to 160 mg CaO/L, but this is based on the results presented in Figure 9, and therefore will probably differ, depending on the water used. Johnson and Randtke (1983) demonstrated a significant reduction in organics removal efficiency if pre-chlorination is used, but recommend only the use of post-chlorination to reduce the formation of halogenated organics.

In terms of the physical dimensions and configuration used, Pontius provides recommended specifications. The use of three flocculation basins with velocity gradients decreasing from 50 s^{-1} in the first to 1 s^{-1} in the third, with a combined hydraulic detention time of at least 30 minutes should be used. Also, for the sedimentation basin, 1.5 to 3 hours settling time are generally required, and thus the basin should be sized accordingly, based on the design flow (Pontius 1990).

7. Sedimentation

7.1 Unit Process Description

7.1.1 Physical Characteristics

Sedimentation is the unit process designed to remove particulate matter in order to lessen the loading on filter beds. This is the stage where solids formed during coagulation/flocculation and softening are removed. In all cases, water flows into a sedimentation basin, remains there for a certain period of time during which particles settle out of suspension, and then flows out for further treatment. Often inclined plates or angled tubes are used to improve particulate removals, and flow geometries available include cocurrent, countercurrent, and crossflow. Removals will generally improve as the flow through the basin approaches plug flow, as this reduces turbulence and short-circuiting (Pontius 1990).

Tank designs include rectangular and cylindrical forms, as well as more unconventional shapes, such as large hoppers with cone shaped bottoms. In all cases, however, there must be some mechanism for the removal of sludge from the bottom of the basin. Commonly, this will take the form of a scraper that moves sludge to a removal hopper (Pontius 1990).

7.1.2 Factors Affecting Efficiency

The factors which affect the removal of solids in sedimentation include the surface loading rate, the residence time, the size and shape of the tank, the inlet distribution, and the water quality. Also, the size and density of the particles present in the water will play a significant role in determining the efficiency.

7.2 Mechanisms of Organics Removal

Organics may be removed indirectly during sedimentation. If they have been incorporated into the particles formed during coagulation/flocculation and softening, through adsorption, precipitation or co-precipitation, then sedimentation is the process where they will actually be removed from the system.

Particles settle under the influence of gravity by one or a combination of settling types. These types are:

- Type 1: low concentration of particles, interparticle effects are negligible
- Type 2: low concentration of particles, particles flocculate during sedimentation, increasing their rate of settling
- Type 3: hindered (zone) settling, rates of settling depend on particle concentration
- Type 4: compression settling, layers of sediment above compress those underneath

7.3 Organics Removal Efficiency

Robeck et al (1965) studied the removals of pesticides in various treatment processes. They determined that less soluble materials, such as DDT, may be removed more easily during coagulation and sedimentation than more soluble materials such as lindane and parathion.

Buhler et al (1973)studied the removals of hexachlorophene and pentachlorophenol during water treatment. They found that sedimentation removed none of the hexachlorophene remaining after flocculation, and 31% of the pentachlorophenol.

7.4 Recommended Design and Operating Parameters for Organics Removal

To optimize the sedimentation process, settling column tests must be performed to determine the necessary tank size for the given flow rate and solids loading (Pontius 1990). It should also be noted that coagulation, flocculation, sedimentation, and filtration all depend on each other for optimum turbidity and organics removal. For example, an insufficient coagulant dose can lead to excessive particle carryover from the sedimentation basin and poor filter performance (McGuire et al 1978).

8. Filtration

8.1 Unit Process Description

8.1.1 Physical Characteristics

Filter beds are composed of porous, granular material called media. Common media types include silica sand, anthracite coal, garnet and ilmenite. Water is usually applied to the top of the bed (although upflow configurations can be used), from where it moves down through the bed either due to gravity or applied pressure, and is removed from the filter through the underdrains at the bottom of the bed (Pontius 1990).

Filters can be classified based on the driving force (pressure or gravity), the rate of filtration (rapid or slow), whether depth or cake filtration is used, and on the number of media types present in layers (1, 2 or 3).

Filters can only perform for a limited length of time before the accumulated material either clogs the pores, leading to excessive head-loss, or the effluent quality begins to deteriorate. At this time, the filter must be cleaned by backwashing. This consists of forcing water back up through the filter bed, expanding the bed and causing attached material to be dislodged. The backwash water is collected and usually sent to waste. A number of different backwash procedures are in use, including water-only, water with air scour in which bubbles of air are also used to help shear off attached material, and a combination of water, air and mechanical agitation.

8.1.2 Factors Affecting Efficiency

Several characteristics of the media will help determine the efficiency of filtration. These include size, shape, density and porosity. Other factors that will affect particulate removals will be the filter rate, the influent water quality, and whether a filter aid polymer is used to strengthen the attachment of particles to the media.

8.2 Mechanisms of Organics Removal

As in sedimentation, there is very little direct removal of organic compounds during filtration. However, some organic material will be removed as particulate material. Precipitated or colloidal humic materials may be removed, organics trapped in coagulation and softening precipitates can be removed, as can organic material adsorbed onto clay and silt particles.

One mechanism operating in filtration is physical straining of larger particles in the interstices of the media grains. For smaller particles, a transport mechanism is needed to bring the material near the media. These transport mechanisms can include gravity settling, diffusion and interception. Once the particles are close to the media, if they have been destabilized by coagulation, collisions may occur, resulting in attachment via van der Waals forces (Pontius 1990).

Filtered material will gradually penetrate deeper and deeper into the bed until eventually a deterioration in the effluent quality is observed. This rapid deterioration is known as breakthrough (Pontius 1990).

8.3 Organics Removal Efficiency

Miltner et al (1989) studied the removal of pesticides during drinking water treatment processes. Their research showed that none of the pesticides studied were reduced during filtration. Robeck et al (1965) also studied pesticide removals, and found that less soluble compounds such as DDT may be removed more easily during filtration.

Buhler et al (1973) studied the removals of hexachlorophene and pentachlorophenol during conventional treatment. They found that filtration removed 50% of the hexachlorophene and none of the pentachlorophenol remaining in solution after sedimentation.

8.4 Recommended Design and Operating Parameters for Organics Removal

Typical sand filtration rates are from 5 to 25 m/hr, while the normal run length is between 12 and 96 hours (between backwashings). If improved organics removals are desired, some portion of the filter bed may be replaced with GAC media, allowing adsorption of many compounds during the filtration process (Pontius 1990).

The degree of interaction between coagulation, sedimentation and filtration must be remembered in the operation of filters. Particle carryover due to poor coagulation can greatly affect the efficiencies and run-lengths of filters.

9. Chlorine

9.1 Unit Process Description

9.1.1 Physical Characteristics

Chlorine treatment of drinking water supplies can be performed in a number of ways. Chlorine itself is available in a number of different forms. It may be purchased as a gas or a liquid in pressurized metal tanks, as a concentrated solution of sodium hypochlorite, or as solid calcium hypochlorite. If liquid chlorine is used, it is usually administered by first evaporating the liquid to a gas, and then metering it into water to form a solution, and finally adding the solution to the untreated water at the determined point of addition. Gas may also be dissolved directly in the main treatment stream, or, more commonly, into a sidestream which then rejoins the main flow. Sodium hypochlorite solution is generally added directly to the main flow. Its use is more common in smaller plants. Solid granules of calcium hypochlorite are either added directly to the solution, or by first dissolving them into a concentrated solution that can then be added (Pontius 1990).

9.1.2 Factors Affecting Efficiency

The effectiveness of chlorine oxidation of organic material is affected by temperature, total chlorine concentration, pH, and the types and concentrations of organic materials found in the water. The pH is a significant factor, in that it determines which forms of chlorine are present, as shown below in Figure 10.

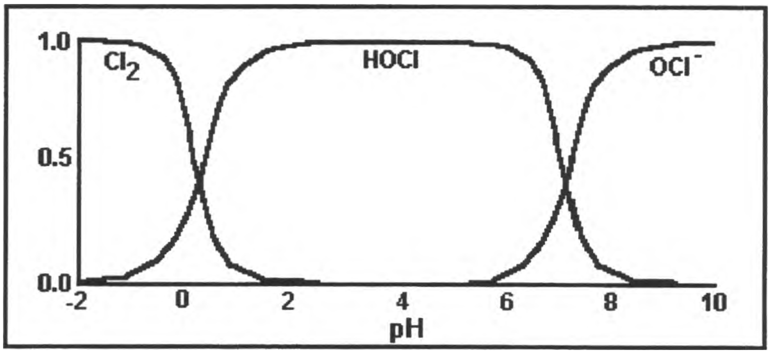

Figure 10. Chlorine species fractions with pH (Pontius 1990).

9.2 Mechanisms of Organics Removal

The only mechanism of organics removal during chlorination is oxidation. On the addition of chlorine to the water, the following reactions take place.

$$Cl_2 + H_2O \leftrightarrow HOCl + H^+ + Cl^- \quad \text{Equation 14}$$

$$HOCl \leftrightarrow H^+ + OCl^- \quad \text{Equation 15}$$

Chlorine, hypochlorite ion and hypochlorous acid are all powerful oxidizing agents, although due to the limited pH range of molecular chlorine, hypochlorite and hypochlorous acid will be dominant. Which species predominates at the given conditions of pH can be determined from Figure 10.

While complete oxidation of organics is desired, substitution reactions are also common when chlorine is used. These are the reactions which produce chlorinated organics, a large class of compounds that includes trihalomethanes (see Figure 11) which are presently of concern due to their possibly toxic effects on humans (Glaze 1987).

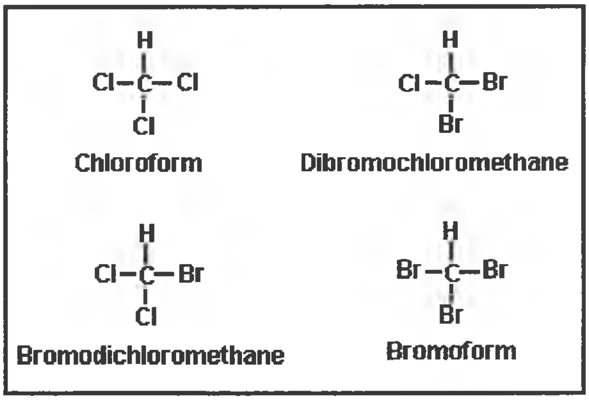

Figure 11. Trihalomethane structures.

Glaze reports that the earliest discovery that chlorine can substitute for hydrogen atoms in organic molecules was with the chlorination of phenols to produce chlorophenols. This reaction is still relevant to modern treatment, as 2,6-dichlorophenol still constitutes one of the more common taste-causing compounds in treated water (Glaze 1987).

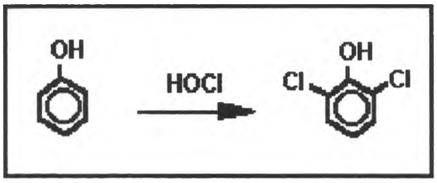

Figure 12. Chlorine substitution in phenol.

9.3 Organics Removal Efficiency

Much of the literature encountered that dealt with chlorine oxidation of organic compounds was focussed on pesticides. Sigworth (1965) found that chlorination of pesticides gave very poor removals. This finding was corroborated by Robeck et al (1965), whose study of pesticide chlorination led them to state that chlorine is ineffective against chlorinated hydrocarbon pesticides, and that in the case of parathion, chlorination oxidized it to paraoxon, which is far more toxic than the original compound. El-Dib & Aly (1977) studied the oxidation of phenylamide pesticides with chlorine, and found that 15 minutes contact time at the doses given in Table 4 was sufficient to acheive the maximum removals.

Table 4. Phenylamide pesticide removals by chlorination (El-Dib & Aly 1977).

Compound	**% Removal 50 mg/L Cl_2**	**% Removal 50 mg/L Cl_2**
IPC	0.0	5.0
CIPC	10.0	21.0
Monouron	5.0	15.0
Diuron	8.0	20.0
Linuron	10.0	30.0
Neburon	11.0	22.0
Stam	0.0	8.6
Karsil	10.0	20.0
Dicryl	0.0	5.0
Vitavax	10.0	20.0

Miltner et al (1989) studied the removals of pesticides via conventional treatment and found that all of the pesticides studied passed through clarification, filtration, softening and recarbonation relatively untouched. Only metribuzin was removed by chlorination, where it was reduced below the detection limit in typical detention times.

Kuhn et al (1978) studied the chlorination of surface waters and found that the process led to the formation of several specific chlorinated organic compounds, including tetrachloroethylene, chloroform, chlorobenzenes, dichlorobenzenes and chlorotoluenes. Also, chlorination was found to form bromoorganics, due to the common contamination of chlorine with bromine.

Glaze (1987) states that prechlorination can enhance the coagulation-flocculation process. This statement is agreed with by Pontius (1990). However, prechlorination is often avoided to to an increased potential to form THMs.

Pontius (1990) states that chlorine can remove colour-, taste-, and odour-causing compounds from drinking water. Glaze et al (1990) studied the oxidation of taste- and odour-causing compounds by chlorine, and found the following removals of compounds, using a reaction time of 120 minutes, and a chlorine dose of 3 mg/L. Their conclusion stated that the data demonstrated that chlorine could not be used to remove taste and odour caused by geosmin and methylisoborneol (MIB).

Table 5. Taste and odour compound chlorine removals (Glaze et al 1990).

Compound	**% Removal**
1-hexanal	5
1-heptanal	-79
dimethyltrisulfide	>99
2,4-decadienal	54
MIB	10
Geosmin	16

9.4 Recommended Design and Operating Parameters for Organics Removal

Due to the potential for the formation of chlorinated organic compounds, especially trihalomethanes, the use of chlorine as a preoxidant is not recommended, especially in waters with high humic material content. However, if chlorine oxidation is used, El-Dib and Aly (1977) found that a pH of 7.0 was the optimum for pesticides removal. Pontius (1990), however, points out the hypochlorous acid is the species with the largest redox potential, and thus the pH should be kept low to maximize its proportion of the total chlorine concentration.

Chlorine is still useful as a disinfectant, as it does provide a lasting residual. Some oxidation processes (such as ozonation) tend to convert non-biodegradable compounds into biodegradable ones, and therefore a disinfection residual, such as that provided by postchlorination, is necessary in order to prevent microorganism growth within the distribution system (Kuhn et al 1978). As long as the chemical chlorine demand has been largely satisfied by previous treatment processes, chlorinated organics formation in the distribution system should not be of great concern. This would require some degree of monitoring of the trihalomethane formation potential to determine whether preceeding unit processes are removing enough organic material to keep THM formation to a minimum.

10. Granular Activated Carbon

10.1 Unit Process Description

10.1.1 Physical Characteristics

Granular activated carbon (GAC) treatment of drinking water involves the passing of water through a column or columns containing GAC. The design of the process can take any of a number of forms, as there are many options available. The system can be driven by pressure or gravity, upflow or downflow configurations can be used, single columns or multiple columns in series or parallel are effective (Figure 13), and the bed can either comprise part of the filtering process or it can follow the filter. All of these configurations have their place in different treatment plants. The decision as to which configuration to use will depend on any of a number of factors, including capital and maintenance costs, the amount of water needed, which other unit processes are in use, and the types of organic compounds present in the water supply.

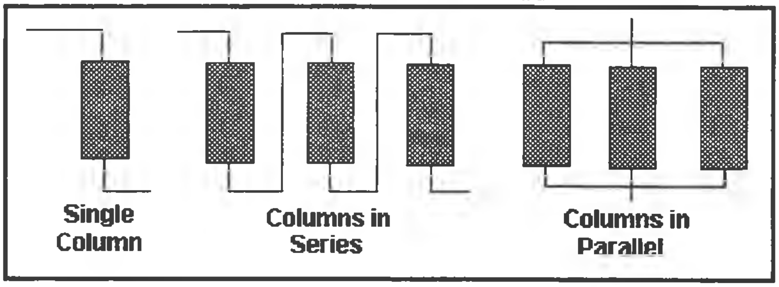

Figure 13. GAC column arrangements.

The three configurations shown in Figure 13 are all in common use. Single column contactors are generally used in smaller plants. Sets of columns in series or in parallel are usually used in larger plants. The benefits of these two arrangements are that when one column is exhausted, treatment can continue while it is replaced or regenerated, and that there is no wasting of carbon. Wasting occurs in a single column because the mass transfer zone gradually moves down the column, with all the carbon above the zone being exhausted. When the zone reaches the bottom of the column, breakthrough will be observed before the carbon at the very bottom of the column has been completely exhausted.

Whatever the configuration of the GAC system, there must be some means of removing the carbon once it has been exhausted so that it can be replaced or reactivated. Depending on the organics present and the purpose for which the process is used, the GAC may need replacement often (eg. once per month) or very infrequently (eg. once every five years).

One factor limiting the placement of GAC in the treatment process is its ability to remove all free chlorine. Therefore, in order to maintain a disinfectant residual in the distribution system, chlorination must be performed on the carbon effluent (Wood & DeMarco 1979).

10.1.2 Factors Affecting Efficiency

The primary factors which influence the effectiveness of GAC adsorption are: molecular weight, polarity, polarizability, concentration and solubility of the compounds, the pore size distribution, surface area, particle sizes and degree of activation of the carbon, and the temperature and pH of the water (Weber & van Vliet 1981). Also, factors such as the polarity of the surface of the carbon particles can affect adsorption. For instance, if the carbon's surface becomes oxidized (by chlorine, ozone, permanganate, or oxygen) then it becomes polarized, and once the surface contains polarized functional groups, water molecules may hydrogen bond to the surface, decreasing the capacity of the carbon for organic material (McGuire & Suffet 1978, McGuire et al 1978). The particle size distribution has been shown to affect the rate of adsorption, with the rate being inversely proportional to the square of the particle's diameter (McGuire & Suffet 1978). The pH is an important factor as it will determine whether the organic compounds are in their neutral or charged form, and as adsorption works best with neutral species, the charged forms are disadvantageous. It has been shown that, due to the exothermic nature of the adsorption process, an increase in temperature will decrease the capacity of a carbon bed (McGuire & Suffet 1978).

10.2 Mechanisms of Organics Removal

There are three main mechanisms involved in the removal of organic material in a granular activated carbon bed: adsorption, filtration, and biodegradation. In adsorption, the bonding of the adsorbate to the adsorbent particles is due to hydrogen bonds, dipole-dipole interactions, or van der Waals forces (Pontius 1990). Adsorption takes place either on the carbon surface or within the pore structure of carbon particles, the pore size determining which organic molecules can penetrate and hence have an increased adsorption capacity over those compounds which cannot penetrate, due to the larger number of adsorption sites available.

The degree to which filtration plays a role in organics removal will vary considerably, depending on the configuration used. If the GAC is placed in the sand filter, the expectation will be for the GAC to perform a considerable amount of the filtration. If, however, the GAC is in a post-filter position on its own, the sand filter should be expected to perform the majority of filtration. This configuration is likely superior, as it decreases the frequency of backwashing of the GAC bed that is required and should lead to lower organic loading, hence increasing the life of the carbon.

Biodegradation may or may not play a significant role in GAC treatment at any given facility. There is always a risk of increased microorganism levels in the effluent water (Wood & DeMarco 1979). Thus, some facilities will choose to chlorinate their backwash water as a disinfection measure, and simply rely on the filtration and adsorption mechanisms. On the other hand, if adequate chlorination is performed after GAC contact, then this may not be of concern. In this case, biodegradation can account for up to 40% of the total organics removal (Pontius 1990). The amount of removal due to biodegradation has been found to be extremely susceptible to temperature, however, with greatly reduced levels of biological activity taking place at colder temperatures. Biodegradation can be greatly enhanced with the correct pre-treatment as well. For example, ozonation has been shown to break down humics into smaller, more biodegradable organic acids (McCreary & Snoeyink 1977), and with the associated increase in biological activity, bed life can be extended from weeks to months in some cases (McGuire & Suffet 1978; Kuhn et al 1978).

10.3 Organics Removal Efficiency

Granular activated carbon is an extremely effective means of removing organic compounds from water supplies (Kuhn et al 1978; Suffet 1980). Research has shown extensive removal capabilities for hydrocarbons, polycyclic aromatic hydrocarbons (PAHs) and chlorinated aromatic compounds (McCreary & Snoeyink 1977), pesticides (Miltner et al 1989), and for many taste and odour causing compounds (Crittenden et al 1987). Some of the experimental results have been summarized in Table 6, below.

Table 6. Reported organics removals using GAC.

Compound Class	Influent Conc. (μg/L)	Effluent Conc. (μg/L)	Removal %	Reference
Pesticides	4.3 0.39 to 6.39	0.05 not given	98.8 47 to 72	McCreary & Snoeyink 1977 Miltner et al 1989
PAHs	not given	not given	99	McCreary & Snoeyink 1977
High mol. wt.	not given	not given	> 90	Pontius 1990
THMs	not given 8.2	not given not given	36 to 78 21	Pontius 1990 McCarty et al 1979
THMFP	not given	not given	9 to 54	Pontius 1990
Chlorinated Aromatics	.02 to .07	not given	>90	McCarty et al 1979
Chlorinated Hydrocarbons	825 to 1367	<0.1 to 2.8	>99	Love & Eilers 1982

One aspect that these data do not take into account, however, is the expected bed-life of GAC processes removing these substances. For instance, Wood and DeMarco (1979) determined that chlorinated pesticides exhibited an early breakthrough tendency, and McCreary and Snoeyink (1977) found that in severely industrially polluted waters, GAC beds may be exhausted in periods as short as one month, leading to high replacement and regeneration costs. Just because a bed has been exhausted of its capacity to adsorb one compound, however, does not mean that it is useless. Miltner et al (1989)suggested that even a shallow GAC bed could reduce pesticide concentrations by over 50% for several years. GAC beds tend to last significantly longer for taste and odour removal than they do for total organic matter reduction. This, of course, also means that odour threshold numbers cannot be relied upon for bed life monitoring purposes (McCreary & Snoeyink 1977).

Competetive adsorption can cause problems when dealing with GAC beds. This refers to the preference of the carbon adsorption sites for one compound over another, and can often lead to poor adsorption of some compounds, while others are removed very well. Also, if the influent composition is variable, new organics can displace previously adsorbed material, causing higher effluent concentrations of a compound than were ever found in the influent (Suffet 1980).

It is possible that while the capacity of a carbon bed has not been exhausted for one compound, it is not removed. This may be the case when, for example, a pesticide adsorbs to a humic molecule, the carbon's capacity for which has been exhausted. The pesticide may then travel through the carbon bed without being adsorbed (McCreary & Snoeyink 1977).

One measure of efficiency of a unit process is how it can handle shock loads of contaminants. Robeck et al (1965) determined that GAC maintains good performance standards, even when abnormally high COD loads are encountered.

With regulations regarding trihalomethanes currently becoming more stringent, there will likely be an increased interest in processes capable of removing significant quantities of halogenated organic compounds. One trend that has been observed with regard to THM removal in GAC beds is the improved removals with increasing degrees of bromination (ie. bromoform removal is better than dibromochloromethane, etc.) (McCarty et al 1979). It was hypothesized that this may be due to increasing hydrophobicity.

10.4 Recommended Design and Operating Parameters for Organics Removal

In order to obtain the best organics removal efficiencies, testing will need to be performed for each individual situation. However, the following tables (7 & 8) present common ranges for parameters based on whether biodegradation is being practiced or not (Pontius 1990).

Table 7. Common parameter ranges for activated carbon adsorption with biological activity.

Parameter	Range
Ozone Dosage	0.5 to 1.0 g O_3 / g DOC
Biological Degradation	~ 100 g DOC / m^3 / day
O_2 Demand	~ 200 g O_2 / m^3 / day
Empty Bed Contact Time	15 - 30 min

Table 8. Parameter ranges for GAC contactors.

Parameter	Median	Typical
Empty Bed Contact Time (min)	10	5 to 24
Bed Depth (m)	1.0	0.5 to 4
Hydraulic Loading (m/hr)	6	2.6 to 17
Influent Concentration (as mg/L TOC)	3.5	2 to 6

The empty bed contact time (EBCT) may be defined as the average residence time of influent water if there were no media in the contactor, and can be calculated from Equation 16,

$$EBCT = \frac{V_R}{Q_F}$$

Equation 16

where Q_F is the volumetric flow rate in cubic metres per minute, and V_R is the total bed volume, including the void spaces, in cubic metres (Pontius 1990).

As mentioned previously, the best performance and lowest operational costs will be obtained if previous treatment steps are optimized for organics removal, thus lowering the organics loading rate on the carbon and leaving the GAC bed to remove compounds which evade other processes and polish others. The presence of other organics will almost invariably reduce the capacity of carbon for a particular organic of interest. If softening is performed prior to carbon filtration, however, the softened water must be stabilized before contacting the carbon, otherwise precipitates may be deposited on the carbon surface, greatly reducing efficiency (McCreary & Snoeyink 1977).

In general, it has been shown that lower filter rates and smaller GAC particles will improve efficiency, while temperature and pH ranges that can be accommodated may be narrow. The pH may be very important in determining the extent of competition between species, especially where humic materials are involved (McCreary & Snoeyink 1977).

The choice of which carbon type to use will depend on the organics of interest in a particular water supply. Tests to determine the iodine number, methylene blue number, modified phenol value, and tannin value are just a few of the tools available to help make this decision. These tests are indicators of a carbon's ability to adsorb high molecular weight compounds, polar compounds, etc., and the results are generally available from the carbon manufacturer (Troxler et al 1989).

A design process has been formulated by Crittenden et al (1987), which takes into account the isotherms of individually targeted organic compounds and their desired removals. The process determines how much water can be treated by a bed before replacement or regeneration is required, empty bed contact times, mass transfer zone heights, and the configuration of beds that might be used.

It is highly recommended that a monitoring program be maintained on the bed effluent. Parameters such as COD, TOC and UV absorbance are generally of use when determining bed performance.

11. Powdered Activated Carbon

11.1 Unit Process Description

11.1.1 Physical Characteristics

The process of adding powdered activated carbon (PAC) to drinking water during treatment is commonly practiced as a means of removing organic compounds. However, rather than removing these compounds for the purpose of meeting effluent concentration requirements, PAC is more often used as a means of improving the aesthetic quality of the product, namely the taste and odour. There are cases where PAC can be used as a means of adhering to imposed standards.

The process involves the addition and mixing of powdered carbon in the water, and then allowing the carbon to adsorb organic material before being removed by some other unit process, such as sedimentation or filtration. Capital investment often only requires the purchase of powder addition equipment or a slurry contactor. If the carbon is added in its powdered form, there are a number of sites where it may be introduced, each of which will have its own advantages and disadvantages. Common points of addition include the plant intake, rapid mix, flocculation basin influent and filter influent (Pontius 1990). The selection of which site to use should be based on the contact time needed, the ability to thoroughly mix the PAC with the water, the potential for interference due to other treatment chemicals and the potential for finished water quality reduction due to carbon fines which may elude subsequent unit processes (Pontius 1990). The benefits and disadvantages of using each addition point are summarized in Table 9.

Table 9. Advantages and disadvantages of different PAC addition points (Pontius 1990).

Point of Addition	Advantages	Disadvantages
Intake	Long contact time, good mixing	Some substances may adsorb that otherwise would be removed by coagulation, thus increasing the activated carbon usage rate.
Rapid Mix	Good mixing during rapid mix and flocculation; reasonable contact time	Possible reduction in rate of adsorption because of interference by coagulants. Contact time may be too short for equilibrium to be reached for some contaminants. Some competition may occur from molecules that otherwise would be removed by coagulation.
Filter Inlet	Efficient use of PAC	Possible loss of PAC to the clear well and distribution system. Increased rate of filter headloss.
Slurry Contactor Preceding Rapid Mix	Excellent mixing for the design contact time, no interference by coagulants, additional contact time possible during flocculation and sedimentation	A new basin and mixer may have to be installed. Some competition may occur from molecules that otherwise would be removed by coagulants.

11.1.2 Factors Affecting Efficiency

The factors which affect the removal efficiency of PAC are similar to those which affect GAC. These include the carbon's surface area, pore structure, surface polarity, particle size, and hardness, the water's temperature, pH and other chemical loads, and the chemicals' molecular weight, polarity, polarizability, concentration, and solubility (McGuire et al 1978, Weber & van Vliet 1981). Other factors that will affect the efficiency are the contact time and the possibility of interference due to other chemicals such as coagulants.

A number of studies have found that PAC can be incorporated into floc particles if added before the flocculation basin. This leads to lower organic removal rates and capacities as the chemicals must penetrate the floc particle before adsorption can occur (Pontius 1990, Najm et al 1990). Also, the presence of humic materials can greatly affect the efficiency of PAC adsorption. Humics tend not to be able to penetrate the pores of carbon particles due to their large size, and hence adsorb to the surface, blocking pores and preventing smaller organics from penetrating. In general, the presence of other organics will usually lead to lower capacities for the organics of interest due to competitive adsorption on available sites (McGuire et al 1978, Suffet 1980, Weber & Pirbazari 1982).

Care must be taken not to oxidize the surface of the carbon particles. This can occur through contact with chlorine, ozone or permanganate and leads to hydrogen bonding of water molecules on the surface and a decreased capacity for organics (McGuire et al 1978).

With PAC there is no need to attempt to keep the water temperature up to maintain organic growth as in GAC. Therefore, lower temperatures are better due to the exothermic nature of the adsorption reaction and thus the increased capacity at lower temperature (McGuire et al 1978).

In locations where the quality of influent water can change significantly, PAC may be a more favourable choice of process over GAC. GAC can concentrate large amounts of contaminants over a period of time. If the influent water then changes, new organics may quickly displace large quantities of previously adsorbed compounds due to preferential adsorption of the new compounds (Love & Eilers 1982). As PAC is generally added for a relatively short contact time (hours) before it is removed from the system, there is relatively little chance of such an incident occuring on the same scale.

11.2 Mechanisms of Organics Removal

Unlike the granular activated carbon process, there is only one mechanism of organics removal at work in powdered activated carbon addition. There is no opportunity for bacterial degradation to occur due to the relatively short period for which any given carbon sample is in contact with the water. Thus, adsorption is the only mechanism acting to remove organic material. The adsorption reaction bonds organics to the carbon particles via van der Waals or dispersion forces, thus removing the impurity from the system entirely, instead of simply changing its nature as some processes do (Hyndshaw 1972).

It has been found that indirect adsorption may also play a significant role in organics removal. For instance, Weber and Pirbazari (1982) state that while direct PCB adsorbance capacities were reduced by the presence of humic substances, humics may adsorb PCBs, thus removing PCBs by the adsorption of humic material.

11.3 Organics Removal Efficiency

Powdered activated carbon has been shown to be very effective at removing many types of organic impurities from water supplies (Suffet 1980, Kuhn et al 1978, Licsko 1993, Sigworth 1965). A large volume of work has been published on the ability of PAC to remove pesticides. Sigworth (1965) performed much of the early work on pesticide removal and found that PAC was effective on many pesticides, although the required doses for removals varied widely. Overall, however, he did conclude that 10 ppm PAC could reduce most extensively used pesticides from their likely concentrations by 90%. Work by Robeck et al (1965) demonstrated that some pesticides do not exhibit competition for PAC adsorption sites, but instead have adsorption capacities that are independent of each other. Najm et al (1990) concluded from their studies that activated carbon is in fact necessary for pesticide removal, and that 6 mg/L PAC can lead to a 50% reduction in most pesticide concentrations. Miltner et al (1989) studied a wide range of pesticides, and found that all were adsorbed on PAC, and developed the following generalized data on PAC requirements, based on their observed removals of atrazine:

Table 10. PAC estimates for pesticide control (Miltner et al 1989).

Influent Concentration µg/L	Effluent Concentration µg/L	Removal %	PAC Requirement mg/L
5	1	80	21
10	1	90	46
10	5	50	6
20	1	95	97
20	5	75	18
20	10	50	6
50	1	98	251
50	10	80	26
50	25	50	7

Hyndshaw (1972) demonstrated that using PAC can help to reduce the chlorine demand necessary to obtain a free chlorine residual by reducing the organic load of the water.

Table 11. Example chlorine demand reduction due to PAC (Hyndshaw 1972).

PAC Dose (ppm)	Cl_2 Required to Observe Free Residual (ppm)
0	1.5
4	1
8	< 0.5

Hyndshaw also determined that PAC generally has a higher attraction for high molecular weight, non-polar molecules than for low molecular weight, polar molecules, as long as the molecules are small enough to penetrate the pore structure of the carbon particles (Hyndshaw 1972, McGuire et al 1978).

The chemical oxygen demand (COD) of a water supply can be reduced by the application of PAC. Licsko (1993) states that the following removals were obtained in full scale testing, although no dosages are given.

Table 12. COD removals by PAC (Licsko 1993).

Raw Water COD mg/L	PAC Treated Water COD mg/L
5.0	2.3
3.5	2.5
12.0	3.2
11.2	3.0

Najm et al (1990) state that the removals of synthetic organic chemicals can be very good, as they found that chlorobenzene and polycyclic aromatic hydrocarbons (PAHs) were reduced by up to 90% by administering PAC doses of between 10 and 15 mg/L.

Not everything is removed well by PAC treatment. Love and Eilers (1982) state that PAC is poor at removing chlorinated solvents, and McGuire et al (1978) found that highly polar, highly soluble organics are removed very poorly, if at all, by PAC. Also, the following removals are given as examples of compounds poorly adsorbed.

Table 13. Removals of compounds by PAC (McGuire et al 1978).

Compound	Removal % After 5 hours @ 50 mg/L PAC
Nitromethane	3
Methyl Ethyl Ketone	3
n-Butanol	4
1,4-Dioxane	0

Najm et al (1990)found that removal of volatile organics with PAC is not efficient. They found that 70 μg/L of CCl_4 was only reduced by 20% by 30 mg/L PAC, and that 60 μg/L $CHCl_3$ was only reduced by 50% at a PAC dose of over 100 mg/L.

It has been demonstrated that PAC does not remove materials contributing to the THMFP well, either. One study showed that the addition of up to 40 mg/L PAC had no effect on the formation potential (Pontius 1990).

11.4 Recommended Design and Operating Parameters for Organics Removal

The advantages and disadvantages of each addition point should be considered before a decision is made regarding the location of PAC injection. Adequate contact time must be allowed for in order for the system to come to equilibrium, although if equilibrium cannot be achieved, an increase in carbon dose may be able to compensate. It has been found that adding the PAC in two stages dramatically reduces the total dose required in order to obtain the same removal (Robeck et al 1965). For example, PAC might be added in the rapid mix, where most would be incorporated into the floc and removed, and then again adding it just before filtration. By cutting down on the dose required at this point, the filter headloss rate would not be as great a problem, and if correctly selected polymers are added as well, the amount of carbon that might evade the filter and contaminate the clearwell could be minimized. The major benefit of adding PAC before filtration is the greater time that the carbon will be in contact with the water, thus increasing efficiency.

Licsko (1993) determined that the most efficient location to add carbon was 3 to 5 minutes prior to the addition of coagulant. This period allows the PAC to begin some adsorption, and also to become part of the suspended particulate content of the water.

In addition to the point of addition, the type of carbon used is of great importance. Troxler et al (1989) devised a carbon selection protocol for the task of determining which carbon type will perform best on a specific source water.

Even in facilities where GAC adsorption is currently practiced, Suffet (1990) recommends that PAC be kept on hand in case of spills. If added to the water before the GAC bed, the PAC can reduce the loading on the GAC bed, allowing it to perform better.

In summary, small-scale tests need to be performed at each site in order to determine the needed dose of PAC, and the optimum addition point. Raw water quality varies to such a degree that no one configuration can possibly be adequate at all sites.

12. Resin Adsorption

12.1 Unit Process Description

12.1.1 Physical Characteristics

The adsorption of organic compounds using synthetic resins has received mixed reviews in the literature on whether it is a viable treatment option. Resins consist of highly cross-linked copolymers that form rigid, spherical, opaque beads (McGuire & Suffet 1978). Some common matrices are pictured in Figure 14.

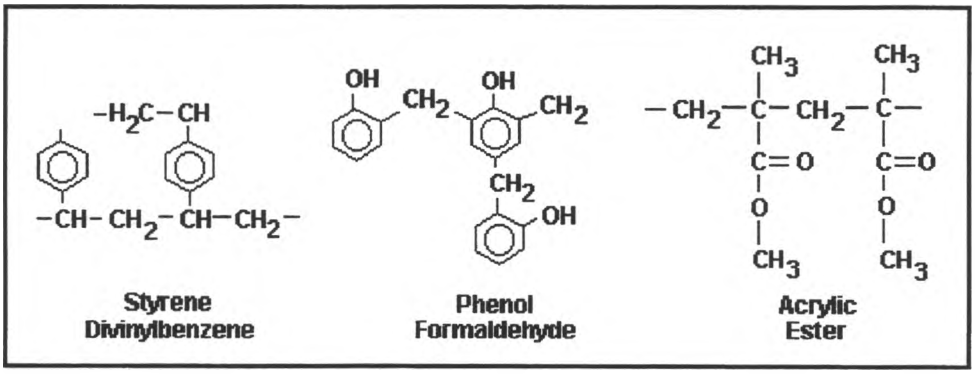

Figure 14. Common resin matrices (Pontius 1990, Chudyk et al 1979).

In order to give the resin specifically desired characteristics, different functional groups can be added to the surface (Cook & Hartz 1983). Some of the commonly used groups are shown in Figure 15.

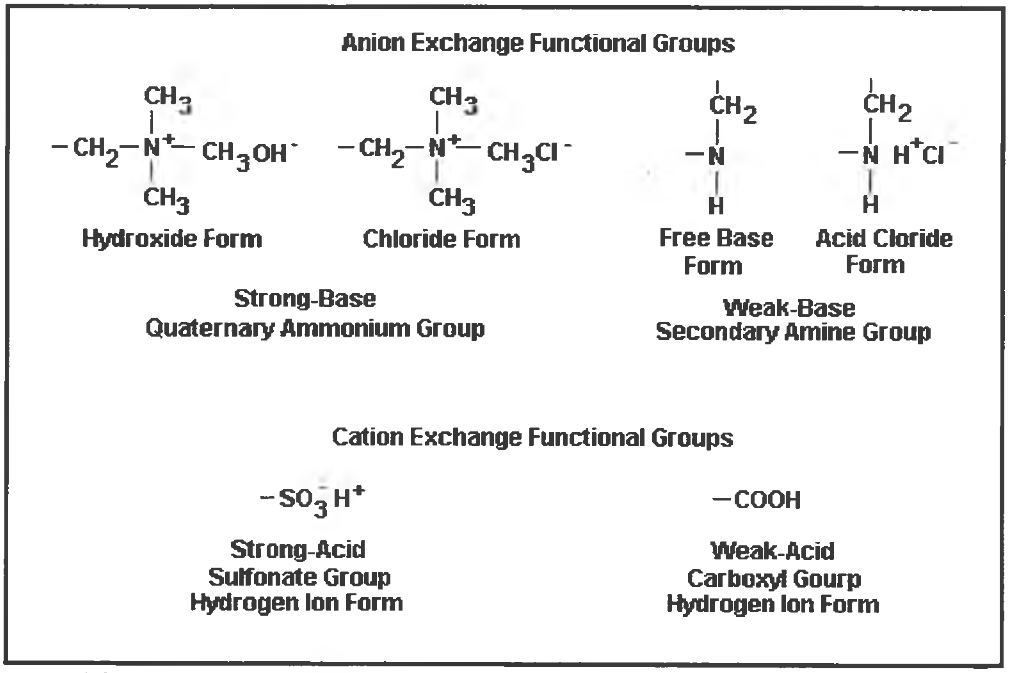

Figure 15. Common functional groups (Pontius 1990, Chudyk et al 1979).

Beads of adsorbent are usually placed in a contactor, similar to those used in granular activated carbon treatment, such that water may be passed through the vessel and contact made with the resin. One benefit of using resins for organics adsorption is that the regeneration process is easily carried out on-site with the appropriate basic, acidic or salt solution (Cook & Hartz 1983).

12.1.2 Factors Affecting Efficiency

As in the case of carbon adsorption, resin adsorption is also affected by the molecular weights of the compounds in solution, their sizes, polarity, polarizability, concentration, solubility, the pore size distribution and surface area of the resin, and the temperature and pH of the water (Weber & van Vliet 1981). One major benefit of using resins is the ability to control the pore sizes. This is accomplished by controlling the degree of cross-linking between molecules in the matrix structure of the resin (Pontius 1990, Chudyk et al 1979).

In general, the colder the water, the higher the capacity of the resin due to the exothermicity of the adsorption reaction (McGuire & Suffet 1978). Also, the lower the solubility of the compounds present in the water, the more easily they may be removed by resin adsorption. Trends affecting other controlling factors cannot be as easily generalized, as they are more specific to the actual compounds in question. For instance, most compounds will have an optimum pH at which they are adsorbed most effectively, but this may be completely different from the pH necessary for another compound.

12.2 Mechanisms of Organics Removal

There are two primary mechanisms by which resin contactors remove organic material. One is by filtration. Some organic molecules may be removed in this manner is they have adsorbed to larger particles that are filtered out during the passage through the resin bed. The major mechanism, however, is adsorption. Polymeric adsorbents function primarily by hydrophobic bonding and dispersion force interactions (weber & van Vliet 1981). However, if appropriate functional groups are present on the surface of the resin beads, many organics may be removed by ion exchange (Pontius 1990).

12.3 Organics Removal Efficiency

Synthetic resins can be used to remove certain organic compounds in water treatment (Cook & Hartz 1983). However, most studies seem to indicate that resins are highly selective in which classes of compounds they can remove.

Cook and Hartz (1983) compared the abilities of several resin types (polyethylene, neoprene, polyvinyl chloride and polyurethane) with GAC to remove chloroform, methyl chloride and carbon tetrachloride. It was determined that the GAC had a higher capacity than the synthetic resins in every case, and that the solubilities and concentrations of the contaminants were significant in determining adsorption efficiency.

On the other hand, Boening et al (1980) compared carbons and resins for their abilities to remove humic substances. They found that a styrene-divinylbenzene strong-base resin had an excellent humics capacity that did not vary widely with pH. In fact, the resin had a better humics capacity than any carbon tested. This statement is in agreement with Pontius (1990), who states that strong-base resins and GAC have comparable capacities for humics.

Suffet (1980) states that it is possible to reduce the THM formation potential by the use of an anion exchange resin, and that in general, synthetic carbonaceous polymers tend to selectively adsorb low molecular weight compounds.

Love and Eilers (1982) determined that an Ambersorb® resin exhibited a lower slope on a breakthrough curve for volatile organic compounds than GAC. Also, they determined that the capacity of the resin may be up to three times that of the. Their data are summarized in Table 14.

Table 14. Removal of VOCs by Ambersorb® resin (Love & Eilers 1982).

Time in Operation (weeks)	Cumulative Bed Volumes (m^3 water/m^3 adsorbent)	Influent Average Concentration (µg/L)	Effluent Average Concentration (µg/L)
4	4700	1367	< 0.1
8	9400	1984	0.1
12	14100	1950	< 0.1
16	18800	906	0.2
20	23500	825	0.4

In Pontius' (1990) study of strong-base styrene-divinylbenzene (SDVB) resins, it was determined that while good TOC removals are possible, they are not as efficient as GAC, and they were eventually discarded due to very low capacities. However, the SDVB resin without any functional groups was found to adsorb chlorinated pesticides very well, and it also adsorbed phenols. Pontius also states that a phenol-formaldehyde weak-base resin removed colour very well.

12.4 Recommended Design and Operating Parameters for Organics Removal

Resins are generally not applicable as general adsorbents in water treatment due to their highly selective nature. Activated carbon adsorbent tends to adsorb a much wider range of organic material (Pontius 1990, Chudyk et al 1979). However, resins may be useful in situations where specific compounds need removal (Pontius 1990).

Acid resins have been found to be of little use in organics removal. This is presumably to the neutral or negative charge carried by most organics in water (Pontius 1990, Chudyk et al 1979). Acid resins, upon deprotonation, would carry a negative charge and hence would repel negatively charged organics electrostatically.

One major problem with using resins for adsorption is the disposal of used regenerant, as these solutions tend to carry very high concentrations of contaminants

(Boening et al 1980). In general, therefore, it is beneficial to produce as little spent regenerant as possible. Pontius describes a study which used a SDVB resin which required only 1 unit of regenerant for every 25,000 units of water treated (Pontius 1990). Of course, this will very depending on the concentrations and types of contaminants present in the water. It may be recommended that weak-base resins be used, if possible, as they tend to be regenerated more easily than those with strong-base functional groups (Pontius 1990, Chudyk et al 1979).

13. Air Stripping

13.1 Unit Process Description

13.1.1 Physical Characteristics

Air stripping involves the intimate contact between air and water, so that volatile contaminants present in the water may volatilize and be removed in the gas phase. There are a number of different configurations that are used to achieve this. Packed towers are probably the most extensively studied method. Water is distributed at the top of a tower that is packed with some regularly or randomly packed media, and is allowed to trickle down, while air is pumped into the bottom of the tower and out the top. The media allows for a thin film of water, maximizing the surface area between the liquid and gas phases, and hence maximizing gas transfer (Pontius 1990, Environmental Science and Engineering, Inc. 1986, McCarty 1987).

Diffused aeration consists of fine bubbles of air, pumped into the bottom of a chamber filled with water. The diffusers distribute the air uniformly through the chamber cross-section, and are designed to produce bubbles of the desired size (Pontius 1990, Environmental Science and Engineering, Inc. 1986, McCarty 1987).

In spray aeration, water is sprayed into the air by nozzles. It divides into small droplets, thus increasing its surface area, and providing the opportunity for gas exchange to occur (Pontius 1990, Environmental Science and Engineering, Inc. 1986, McCarty 1987).

Fleming (1989) itemizes the advantages and disadvantages of each of these configurations in the following tables.

Table 15. Diffused aeration advantages and disadvantages (Fleming 1989).

Advantages	**Disadvantages**
• high potential liquid throughput • high liquid turndown ratio • wide range of air:water ratios • low potential for fouling • low liquid pressure drop • simple device, low maintenance • adaptability to field situations • short setup time • adaptable to available tankage and equipment	• surfactants in water limit flow rate • single stage device, low removal percentage • high gas pressure drop, high pump power

Table 16. Spray aeration advantages and disadvantages (Fleming 1989).

Advantages	**Disadvantages**
• low pressure drop for gas • simple operation • low fouling and channeling potential • short setup time • design adaptable to available equipment	• high pressure drop for liquid • gas flow limited by liquid entrainment • limited number of stages, low removal % • number of stages not proportional to height • possibility of fouling in nozzles • low turndown ratio (unless nozzles changed)

Table 17. Packed column aeration advantages and disadvantages (Fleming 1989).

Advantages	**Disadvantages**
• excellent removal efficiency (multistage device) • high rate mass flow • high turndown potential • large range of air:water ratios • low liquid pressure drop	• potential for fouling (depends on column design) • difficult to set up • significant gas pressure drop • difficult to adapt to available equipment

Mechanical aeration is also used in some cases. It involves the beating of the surface with some mechanical device, causing water to form into droplets as they are propelled into the air, and forming air bubbles in the water vessel. Gas transfer can occur by both processes (McCarty 1987).

In all of these design configurations, the contaminated air is generally vented out through the top of the vessel into the atmosphere (Environmental Science and Engineering, Inc. 1986). The volume of air used and the amount of material stripped from the water will determine whether or not some form of emissions control must be performed on the off-gas.

13.1.2 Factors Affecting Efficiency

The primary factor which affects how well a compound may be stripped from water is the compound's Henry's Law constant. This value is an expression of how easily separable from water a compound is. A higher constant indicates more effective stripping (Environmental Science and Engineering, Inc. 1986, McCarty 1987, Love & Eilers 1982, Amy et al 1987). Also, as the Henry's Law constant increases with increasing temperature, an increase in temperature will lead to more effective removals (Environmental Science and Engineering, Inc. 1986).

In all designs, the air:water ratio will play a role. The more uncontaminated air is introduced to the system, the better the removals will be (Environmental Science and Engineering, Inc. 1986, McCarty 1987). Also, the diffusivity of the compounds in water will play an important role. Compounds can only be volatilized from the surface film, and hence the rate at which they can diffuse through the water will dictate the rate at which the compound can volatilize (Environmental Science and Engineering, Inc. 1986).

Due to differences between configurations, there exist factors that are specific to a particular configurations. In packed tower aeration, the packing media, and the tower height will influence the organics removals (Amy et al 1987). For diffused air stripping, removals will be influenced by the diffuser type, the bubble size, the water depth, and the detention time (Environmental Science and Engineering, Inc. 1986). In spray aeration, the size of the droplets and the height of the spray (which determines the contact time) will be important (Environmental Science and Engineering, Inc. 1986).

13.2 Mechanisms of Organics Removal

Gas transfer is the major mechanism of organics removal in the process of air stripping. However, the possibility does exist for some degree of oxidation to take place as well, due to the large quantities of air involved.

13.3 Organics Removal Efficiency

Air stripping is an effective treatment method for the control of volatile organic compounds. Amy et al performed experiments investigating the removals of carbon tetrachloride and 1,1,2-trichloroethene with different depths of packing material in a packed column. The data are summarized in Table 18 (Amy et al 1987).

Table 18. Removals vs. bed depth. (Amy et al 1987)

Experiment	Loading	Air:Water	Compound	Percent Removal Using Indicated Bed Depth				
	$L / m^2 / s$	vol : vol		0 m	1.22 m	2.44 m	3.65 m	4.57 m
1	13.8	30:1	CT	0	50.9	91.3	98.3	99.6
			TCE	0	45.2	85.9	95.6	98.2
2	13.8	60:1	CT	0	74.0	92.5	97.5	99.8
			TCE	0	70.8	89.9	95.6	98.9
3	13.8	100:1	CT	0	76.3	94.4	99.3	99.9
			TCE	0	74.5	93.2	98.2	99.3
4	20.7	30:1	CT	0	68.8	92.5	97.6	99.3
			TCE	0	63.9	88.4	92.5	96.3
5	20.7	60:1	CT	0	68.6	95.1	99.6	99.9
			TCE	0	65.7	91.4	98.2	98.9
6	28.0	35:1	CT	0	70.7	94.6	99.2	99.8
			TCE	0	65.7	90.3	97.3	98.3

Using an air:water ratio of 22:1, McCarty studied the removals of trihalomethanes by packed tower aeration. The results are presented below, in Table 19.

Table 19. Trihalomethane removals by packed tower aeration (McCarty 1987).

Trihalomethane	Influent Concentration mg / m^3	Average % Removal
chloroform	10.4	79
bromodichloromethane	4.1	85
dibromochloromethane	1.7	71

Using a full-scale packed column aeration system with a 200:1 air:water ratio, McKinnon & Dyksen (1984) studied the removals of three compounds found in the water supply of Rockaway Township, New Jersey. The system was found to remove 99.9% of diisopropyl ether, greater than 95% of methyltertiary butyl ether, and virtually all trichloroethylene.

Love & Eilers (1982) studied the effects of diffused air aeration with an air:water ratio of 4:1 (vol:vol) and a water depth of 0.8 m on a solvent-contaminated groundwater, and presented the following data:

Table 20. Effects of diffused air aeration on contaminated groundwater (Love & Eilers 1982)

Contaminant	**Average Concentration**		**Removal %**	**Henry's Law Constant**
	Before (mg/L)	**After (mg/L)**		
1,1-Dichloroethylene	122	4	97	6.3
1,1,1-Trichloroethane	237	23	90	1.2
Tetrachloroethylene	94	9	90	1.1
Trichloroethylene	3	0.4	87	0.5
cis-1,2-Dichloroethylene	0.5	< 0.1	> 80	0.31
1,1-Dichloroethane	6	1	83	0.24
1,2-Dichloroethane	1.4	0.8	42	0.05

Using different air:water ratios, Environmental Science and Engineering, Inc. (1986) demonstrated that VOC removals of greater than 99% can be obtained.

Table 21. Pilot study packed tower VOC removals (Environmental Science and Engineering, Inc. 1986).

Compound	Temp.	Average % Reduction at Air:Water Ratio Shown					
	°C	80	45	25	15	8	5
trichloroethylene	10 - 16	99.7	99.3	97.2	91.4	75	55
trichloroethylene	26	>99.99	>99.99	99.3	99.7	91.0	86
tetrachloroethylene	11 - 16	99.8	99.5	98.3	96.1	86	72
1,2-dichloroethane	16	-	98.5	93.0	87	77	85
1,1-dichloroethylene	12 - 24	99.99	99.7	99.3	98.8	95.4	90.6
benzene	20	99.98	99.8	98.6	94.8	82	-
1,1,1-trichloroethylene	11 - 14	99.92	99.4	98.2	95.7	86	77
p-dichlorobenzene	26	99.9*	90.8	98.5	85	-	57

* Air:Water = 100:1

13.4 Recommended Design and Operating Parameters for Organics Removal

Air stripping has been demonstrated to be very effective at removing volatile organics in water. However, its use is limited to compounds with high Henry's Law values. Therefore, in most cases, its use will be coupled with other processes. For instance, Amy et al (1987) state that stripping may be good to use as a pretreatment step for adsorption, as substantial reductions in carbon requirements can be obtained. McKinnon & Dyksen (1984) agree with this, as they found that preaeration can reduce the frequency of the costly process of GAC bed replacement by decreasing the volatile organics loading to the adsorption step. By adding preaeration, their carbon usage rates dropped from 0.12 to 0.24 kg of carbon per cubic metre treated, to less than 0.01 kg / cubic metre. Of course, this decrease is heavily dependent upon the compounds present in the water.

A current concern with aeration techniques is the emission of volatile organics into the atmosphere (McCarty 1987, Love & Eilers 1982). In addition to air quality concerns, this can be a safety concern too, due to the risk of explosion. Currently, the U. S.

Environmental Protection Agency standards require that flammable VOCs be kept at concentrations below 25% of their lower flammability limits in the air emissions (Fleming 1989).

14. Reverse Osmosis

14.1 Unit Process Description

14.1.1 Physical Characteristics

The reverse osmosis unit process consists of a selectively permeable membrane, through which water is pumped, removing some of the organic impurities. The process is called reverse osmosis because the osmotic pressure would cause water to flow from the pure side to the contaminated side of the membrane, but the applied pressure, which is larger than the osmotic pressure, is applied in the opposite direction. The formula used to calculate the osmotic pressure is given below.

$$\pi = 1.12(T + 273)\sum \overline{mi}$$

Equation 17 (Pontius 1990)

where: π = osmotic pressure, psi
T = temperature, °C
$\Sigma \overline{mi}$ = summation of molalities of all ionic and nonionic constituents in solution

The passage of water and contaminants through the membrane can be approximated using Equations 18 and 19, respectively:

$$F_w = A(\Delta p - \Delta \Pi)$$

Equation 18 (Pontius 1990)

$$F_s = B(C_1 - C_2)$$

Equation 19 (Pontius 1990)

where: F_W = water flux, g/cm²/s
A = water permeability constant, g/cm²/s/atm
Δp = pressure differential applied across membrane, atm
$\Delta \pi$ = osmotic pressure differential across membrane, atm
F_S = salt flux, g/cm²/s
B = salt permeability constant, cm/s
$C_1 - C_2$ = concentration gradient across membrane, g/cm³

The membranes are generally made of synthetic polymers such as cellulose acetate and polyamide (Weber & Smith 1986). Reverse osmosis is a higher pressure process than the similar ultrafiltration (Weber & Smith 1986), and uses a membrane with a smaller pore size (expressed as a molecular cutoff weight).

Different configurations of membranes are available. The four most common configurations are spiral wound, hollow fibre, tubular and plate and frame (Weber & Smith 1986). Each configuration has advantages and disadvantages.

14.1.2 Factors Affecting Efficiency

The effectiveness of reverse osmosis depends on the chemical characteristics of the membrane and the contaminants (Alsaygh et al 1993). The level of rejection of any given compound will be a function of its concentration, molecular shape, flexibility, size, ionic charge, and solubility, along with the type of membrane used and the concentrations and types of other compounds present in the water (Weber & Smith 1986).

The quality and quantity of the product water are vulnerable to water pressure changes, temperature changes, total dissolved solids concentration changes and pre-filter clogging. Increases in temperature will generally lead to an increase in product yield due to a decrease in the viscosity of the water, and hence an increase in the rate of passage across the membrane (Darcy's Law) (Bader & Jennings 1992).

The product yield will decrease very, very slightly due to an increase in feed concentration. This occurs due to a small increase in osmotic pressure (relative to the applied feed pressure) as seen in Equation 20

$$Q_w = (\Delta P - \Delta\pi) K_w A / \delta$$

Equation 20 (Bader & Jennings 1992)

where: Q_W = product flow rate, cm^3/s
ΔP = applied pressure difference across membrane, atm
$\Delta\pi$ = osmotic pressure difference across membrane, atm
K_W = membrane permeability constant for water, cm^2/atm/s
A = membrane area, cm^2
δ = membrane thickness, cm

Increasing the feed concentration will also lead to a decrease in organics rejection percentage (Bader & Jennings 1992).

The organics' molecular structures influence permeability in a number of ways. Firstly, rejection generally increases with an increasing number of carbon atoms in the structure. Secondly, the more highly branched a structure is, the greater its rejection (Alsaygh et al 1993).

14.2 Mechanisms of Organics Removal

The mechanisms which affect the removals of organic contaminants during reverse osmosis are selective sieving, selective solubilities, and adsorption. The sieving mechanism functions to physically exclude molecules larger than a certain size, known as the molecular weight cutoff. Some molecules, however, can dissolve in the membrane and diffuse through it before emerging in the effluent. This is due to the selective solubility of the membrane for some compounds (Weber & Smith 1986).

Adsorption of compounds onto the surface of the membrane can account for some organics removals. However, as more material accumulates on the membrane's surface, the number of sites available for adsorption decreases, reducing the effectiveness of this mechanism. Also, pores can be blocked by adsorbed molecules, making the membrane less permeable to water and hence reducing the product yield (Weber & Smith 1986).

Another way in which the effectiveness of the rejection can be reduced is by a mechanism known as concentration polarization. As more organics are rejected at the surface of the membrane, their concentrations there increase above those of the bulk solution. As can be deduced from Equation 19, this leads to an increase in the concentration gradient across the membrane, and hence an increase in the flux of organic components, and a decrease in the rejection percentages of the compounds (Bader & Jennings 1992).

14.3 Efficiency of Organics Removal

McCarty et al (1979) state that reverse osmosis is a very effective means of removing high molecular weight organics. Reinhard et al (1986) suggested that reverse osmosis, along with activated carbon and air stripping, are the most effective means of reducing the concentrations of organic compounds in drinking water.

Reinhard et al (1986) studied a full scale reverse osmosis operation using a cellulose acetate membrane. They found that reverse osmosis removed 83% of the organic material from the effluent of an activated carbon column. When operated on its own, the membrane managed to remove 89% of the TOC and from 50 to 90% of the trihalomethanes present, while recovering 84% of the water (ie. 16% of the water was sent to waste with the concentrated rejected compounds). They postulated that the good removals of TOC were due to steric hindrance and charge rejection, as the TOC consisted mainly of highly complex, negatively charged molecules. Charge was found to play an important role in the rejection of organics, as benzoic acid, a relatively small molecule, was reduced by 73%. In non-charged molecules, however, they found that one- and two-carbon chlorinated solvents and one ring aromatics were poorly removed.

Clark et al (1988) found that reverse osmosis removes volatile and synthetic organic compounds, and that it reduced the THM formation potential by over 75%, from 400 to less than 100 μg/L. They also demonstrated that reverse osmosis can be used to effectively remove alkanes and pesticides. Chlorinated pesticide removals were also investigated by Weber & Smith (1986), who found that many are rejected at levels of up to 98%. In bench-scale tests, Edwards and Schubert (1974) found rejections of 2,4-D to be between 52 and 65%, although they quote reported values of up to 99%. They also state that low to intermediate weight organic compounds are not always effectively remove by reverse osmosis, but that nearly all high molecular weight compounds (>2000) are removed very well.

In order to demonstrate the effect of structure on membrane rejections, Alsaygh et al (1993) tested 5 similar compounds. The results are summarized in Table 22.

Table 22. % removals of different structures (Alsaygh et al 1993).

Compound	% Removal
1-propanol	43.77 - 44.90
1-butanol	72.65 - 74.62
2-butanol	75.38 - 81.54
2-methyl-1-propanol	83.80 - 89.76
2-methyl-2-propanol	> 90.0

Bader & Jennings (1992) tested a low pressure membrane, and found that high molecular weight, low solubility, highly branched structures have the highest rejections. In general, they also found that higher polarity yields lower rejection due to better incorporation in the water matrix. They also presented the following data to demonstrate the effect of changing the feed pressure on the removals of compounds of different types.

Table 23. Compound rejection differences with varying feed pressure (Bader & Jennings 1992).

Pressure	% Average Rejection of			
(kPa)	TDS	Benzene	Chloroform	PCP
551.6	98.4	87.1	88.9	94.1
689.5	98.4	78.6	60.5	94.3
827.4	98.4	76.4	51.3	94.5
965.3	98.5	76.2	49.5	94.5
1103.2	98.5	77.1	53.2	93.5
1241.1	98.4	77.6	50.4	95.0
1344.5	98.4	83.5	-	-

Baier et al (1987) studied different membranes and their abilities to remove 1,2-dichloropropane, a compound considered to be of a relatively low molecular weight (112.99 amu). It was found that the thin-film composite membrane consistently removed 91% of the compound, while the polyamide membrane removed 61%. A cellulose acetate membrane was determined to be ineffective at removing the compound. Weber & Smith (1986) also found that reverse osmosis can remove some low molecular weight compounds, and that membranes are excellent for the removal of humics and fulvics.

14.4 Recommended Design and Operating Parameters for Organics Removal

It has been stated that reverse osmosis membranes are applicable to the reduction of organic contaminants in large volumes of drinking water (Deinzer et al 1975). They have also been found to require minimal maintenance, consisting of a periodic cleaning with 2% citric acid and two daily water rinse cycles to remove growth and sediment (Baier et al 1987).

Bader & Jennings (1992) stated that the feed pressure over the membrane is the major operational parameter that can affect performance. A pressure somewhere in the range of 690 to 1380 kPa will likely be optimal, but specific testing would be required. Alsaygh et al (1993) found that the rejection of organics was best at approximately 1100 kPa for most of the compounds studied. This will vary depending on the organics present, the type of membrane used and the configuration.

The correct pre-treatment processes are essential to maximize membrane life and reduce the cost of operation. Weber & Smith (1986) found that conventional treatment, consisting of coagulation, sedimentation, and filtration is usually enough to remove excess turbidity and suspended solids that can clog membrane pores. This is corroborated by Baier et al (1987). GAC may be required to remove some organics that can otherwise degrade the membrane, and it has been found that a low level of chlorination can help prevent the buildup of a biofilm on the membrane surface (Weber & Smith 1986).

One final factor that must be accounted for is the disposal of the concentrate. This solution can contain very high concentrations of toxic compounds, and thus may be difficult and expensive to dispose of.

15. Chlorine Dioxide

15.1 Unit Process Description

15.1.1 Physical Characteristics

Chlorine dioxide has been demonstrated to be an effective oxidizing agent in water treatment. It is always made on site due to its explosive nature, but is stable once dissolved in water. Its production can be extremely efficient, with percent efficiencies as high as 95% reported (Walker et al 1986). The two different processes for the production of ClO_2 are given below in Equations 21 and 22.

$$5NaClO_2 + 4HCl \rightarrow 4ClO_2 + 5NaCl + 2H_2O$$ Equation 21 (Glaze 1987, Pontius 1990)

$$2NaClO_2 + Cl_2 \rightarrow 2ClO_2 + 2NaCl$$ Equation 22 (Glaze 1987, Pontius 1990)

Due to the lack of a sustainable effective residual concentration of chlorine dioxide, it is generally used as a preoxidant. Walker et al (1986) found that the optimum addition points for the chemical were at the plant headworks, and after the softening process, preceding filtration.

15.1.2 Factors Affecting Efficiency

One benefit of chlorine dioxide over chlorine for oxidation, is that its reactivity is not as dependent upon pH due to the lack of reaction with the water itself (Rav-Acha et al 1983). While the pH of the water does not directly affect the reaction of chlorine dioxide with organic compounds, it does have an effect on the stability of the oxidant. The disproportionation reaction is given in Equation 23.

$$2ClO_2 + 2OH^- \rightarrow ClO_2^- + ClO_3^- + H_2O$$ Equation 23 (Pontius 1990)

The types of organics present in the water supply will be the major determinant of how effective the process is. Highly oxidizable compounds such as phenols, aldehydes, and aromatic amines are removed very well, while waters high in halogenated hydrocarbons, saturated aliphatic compounds, and benzene may not see the same quality improvement. Compounds of intermediate oxidizability include alcohols, alkyl substituted aromatics, nitro substituted aromatics, unsaturated alkyl groups, carbohydrates, aliphatic ketones, acids, esters and amines (Weber & Smith 1986).

15.2 Mechanisms of Organics Removal

The removal of organic material during the application of chlorine dioxide is via oxidation only (Pontius 1990, Weber & Smith 1986, Aieta & Berg 1986). A major benefit of chlorine dioxide over chlorine oxidation is that chlorine dioxide produces almost no trihalomethanes (Glaze 1987, Pontius 1990, Malley et al 1988). This is because in addition to oxidation, chlorine also reacts with natural organic materials by electrophilic substitution, yielding chlorinated products (Aieta & Berg 1986). Generally, the oxidation products when chlorine dioxide is used are aldehydes, ketones, quinones and low molecular weight carboxylic acids (Rav-Acha et al 1983).

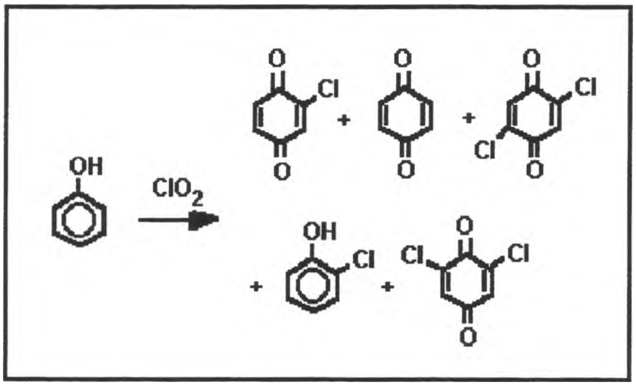

Figure 16. ClO_2 oxidation of phenol (Glaze 1987).

15.3 Organics Removal Efficiency

A number of studies have found that chlorine dioxide is an excellent means of removing colour, taste and odour causing compounds from drinking water (Walker et al 1986, Pontius 1990, Weber & Smith 1986, Aieta & Berg 1986, Glaze et al 1990), and unlike chlorine treatment, the oxidation of phenolic material does not lead to the production of the unpleasant chlorophenol taste and odour (Rav-Acha et al 1983, Aieta & Berg 1986). A study by Walker et al (1986) demonstrated, through the use of public complaints, that chlorine dioxide as a preoxidant at doses ranging between 0.15 and 1.20 mg/L eliminated tastes and odours in Edmonton city water supplies due to natural organic material, although some synthetics were still a problem. Glaze et al (1990) evaluated a number of oxidants for their abilities to remove taste and odour causing compounds and found that while chlorine dioxide is effective for most compounds, it cannot remove tastes and odours due to the compounds methylisoborneol and geosmin.

Chlorine dioxide is listed by the U.S. EPA as one of the most effective methods for controlling THMs. Walker et al (1986) found that once ClO_2 replaced chlorine as the preoxidant used, trihalomethane concentrations in the finished water were observed to decrease. Similar decreases in THM formation have been found in many studies (Rav-Acha et al 1983, Aieta & Berg 1986, Malley et al 1988, Lykins & Griese 1986). This decrease in THM formation is due to two factors. First, the reaction of ClO_2 with natural organics has been shown not to produce trihalomethanes (Glaze 1987, Pontius 1990, Aieta & Berg 1986, Malley et al 1988), and second, the ClO_2 oxidizes some of the THM precursors. Precursor oxidation was demonstrated by Malley et al (1988) who found that pretreatment with chlorine dioxide reduced the THM formation potential by up to 30%, and by Aieta & Berg (1986), who found that pretreatment reduced the THMFP by as much as 50%. Lykins & Griese (1986) found precursor reductions of 32% with chlorine dioxide oxidation, and that by substituting chlorine dioxide for chlorine as a pretreatment step, total THM reductions of 60% were attainable.

The oxidation of pesticides is generally not very effective due to their highly chlorinated natures. Miltner et al (1986) found that while some degree of oxidation was achieved with many pesticides using chlorine dioxide, it did not react with others (see Table 24).

Table 24. ClO_2 removals of selected pesticides.

Pesticide	Concentration µg/L	ClO_2 - mg/L Dose	ClO_2 - mg/L Residual	Time hours	Percent Removal %
alachlor	61.0	3.0	1.9	2.5	9
metolachlor	32.4	2.0	1.4	5.33	-4
atrazine	65.8	6.0	3.6	6.25	10
simazine	43.0	1.5	1.0	6	7
linuron	51.8	6.0	3.6	6.25	16
carbofuran	50.0	1.5	1.0	6	-3
metribuzin	34.4	2.0	0.4	2.6	60
metribuzin	60.1	5.9	3.8	6	100

One final benefit of chlorine dioxide oxidation is its effect on later treatment processes, especially activated carbon adsorption. First, the partial oxidation of many compounds can lead to improved adsorbability (Malley et al 1988), and second, oxidation can improve the biodegradability of many compounds, as they are broken into smaller fractions (Weber & Smith 1986).

15.4 Recommended Design and Operating Parameters for Organics Removal

When setting up a chlorine dioxide oxidation/disinfection system, there are a number of factors to be aware of. Possibly the most important is a knowledge of the chemical composition of the water to be treated. Partial oxidation of some compounds can lead to products which are more toxic than their parent compounds (Weber & Smith 1986). Gas chromatography can be used to help identify such compounds, as was done by Lykins & Griese (1986), although in their study, no hazardous organic by-products were found. Also of importance is the pH of the water to be treated. As shown in Equation 23, highly basic solutions will be unstable environments for chlorine dioxide due to disproportionation. The chlorite and chlorate ions that result from this reaction are very strong oxidants, and thus concerns exist regarding their presence in drinking water, although evidence does exist that there are no acute or chronic health risks with exposure (Aieta & Berg 1986). The U.S. EPA recommends that the combined residual concentrations of ClO_2, ClO_2^-, and ClO_3^- be less than 1.0 mg/L (Pontius 1990, Aieta & Berg 1986). Therefore, basic solutions should be avoided.

It is recommended that chlorine dioxide be used as a preoxidant and as the primary disinfectant, but that chlorine should still be added to provide the residual disinfection power. Difficulty has been encountered in maintaining a chlorine dioxide residual, possibly leaving the distribution system vulnerable to microbial contamination, and therefore enough postchlorination is recommended to provide adequate protection. This combination has been tested and has proven effective for the reduction of THMs and other organic compounds, as well as providing residual disinfection (Aieta & Berg 1986, Lykins & Griese 1986).

16. Ozone

16.1 Unit Process Description

16.1.1 Physical Characteristics

Ozone can be added to drinking water as an oxidant to help remove organic material. A common point of addition is just prior to filtration, as it can help in the biodegradation process, as will be discussed later.

The ozone unit process is expensive when compared to chlorination (Pontius 1990). Due to the highly unstable nature of ozone gas, it must be generated on-site. The loss of ozone is due to its reactivity with compounds in the water, and its decomposition (Pontius 1990). The instability of the gas leads to a lack of a residual ozone concentration, and thus the ozone application cannot be relied upon for maintaining the disinfected condition in the distribution system. A small chlorine dose is usually added as a final treatment step to provide some degree of residual disinfection.

Water may be treated either in a co-current bubble contactor or a countercurrent contactor. If the contactor is made of metal, 304 stainless steel is the recommended material, otherwise concrete may be used if the joints are caulked with an inert material (Pontius 1990).

The design of the contactor must be such that unused ozone in the off-gas can be collected. This is due to the hazardous nature of ozone (Pontius 1990).

16.1.2 Factors Affecting Efficiency

Factors which affect the efficiency of ozone oxidation are the concentrations and types of organic materials present, the temperature and pH of the water, and the dose and contact time of the ozone.

Trussell and Umphres (1978) determined that the time between ozonation and chlorination may be significant in determining THM reduction.

16.2 Mechanisms of Organics Removal

Ozone is a very powerful oxidant, with an oxidation potential of 2.07V (Rice et al 1981, Weast 1985). It is, however, very unstable in aqueous solution, due to its high reactivity and tendency to spontaneously degrade in the presence of basic solutions, as shown in Equations 24 to 29 (Pontius 1990).

$$HO^- + O_3 \rightarrow HO_2 + O_2^- \qquad \text{Equation 24}$$

$$HO_2 \leftrightarrow H^+ + O_2^- \qquad \text{Equation 25}$$

$$O_2^- + O_3 \rightarrow O_2 + O_3^- \qquad \text{Equation 26}$$

$$O_3^- + H^+ \rightarrow HO_3 \qquad \text{Equation 27}$$

$$HO_3 \rightarrow O_2 + HO^{\bullet}$$ Equation 28

$$HO^{\bullet} + O_3 \rightarrow HO_2 + O_2$$ Equation 29

It can be seen from these equations that the decomposition mechanism is initiated by hydroxide, and hence is more pronounced in waters with high pH. This decomposition is not without benefit, however. The HO radical intermediate species is one of the most powerful oxidizing agents known, and therefore, the rate of oxidation of some species will be seen to increase at pH values above 8 (Pontius 1990). The chain reaction leading to decomposition may be halted by the bicarbonate ion found in waters with high bicarbonate alkalinity, as shown in Equation 30 (Pontius 1990).

$$HO^{\bullet} + HCO_3^- \rightarrow OH^- + HCO_3$$ Equation 30

Colour in water is generally caused by unsaturated humics known as chromophores. Ozone is very reactive with the double bonds found in these molecules. Rice et al (1981) have stated that via oxidation, ozone cleaves these humics into ketones, aldehydes and acids. This is corroborated by the work of Edwards et al (1993) who state that ozone reacts with natural organic material to yield smaller molecules with increased acidity.

Edwards et al (1993) also determined that stripping is a mechanism of action during ozonation. In fact, stripping removed more organics than oxidation in their study.

16.3 Organics Removal Efficiency

Ozone has been shown to be effective at removing various types of organics to different degrees. In addition to actually oxidizing some organics to water and carbon dioxide, ozone can alter some organics making them easier (or more difficult in some cases) to remove with other unit processes.

Ozone has been shown to be very effective at removing taste- and odour-causing chemicals (Rice et al 1981). In fact, studies have shown ozone to be more effective at destroying taste and odour than any other oxidant (Pontius 1990).

Humic materials are very reactive with ozone, hence reducing the THM formation potential of some waters. Trussell and Umphres (1978) stated that ozonation prior to chlorination can reduce the production of trihalomethanes, while another study found that 2.5 mg/L ozone removed 10 to 15% of the THMFP on its own, and ozonation helps further by increasing GAC biodegradation reductions in THMFP (Pontius 1990, Rice et al 1981). This is accomplished by breaking humics into aldehydes and carboxylic acids which are more readily degraded (Pontius 1990, Tobiason et al 1993).

Some synthetic organic compounds are oxidized well by ozone. These include benzopyrenes, benzene, toluene, xylenes, styrene, chlorophenol and the pesticide aldrin. Other synthetics, however, are not oxidized at all. These include the more heavily chlorinated compounds such as DDT, heptachlorepoxide, dieldrin, chlordane and lindane.

Trihalomethanes also tend to be quite resistant to ozone oxidation (Rice et al 1981). This same study found that pesticides vary in their reactivity with ozone, and therefore it is essential that the pesticides present be identified. Also, this is important as the products of oxidation of some pesticides can be more toxic than the original compounds (Rice et al 1981). Robeck et al (1965) studied the removal of pesticides and found that ozone was only slightly better than chlorine oxidation.

Tobiason et al (1993) found that 1.5 mg/L of ozone reduced the UV absorbance reading at 254nm by 30 to 40% on its own. They also studied the effects of pre-ozonation on filter performance. Firstly, they determined that the pre-ozonation does not hurt the filter performance, based on effluent turbidity and rate of headloss. It was found that pre-ozonation increases the assimilable organic carbon content (a measure of the biodegradable organic matter) by a factor of 1.5 to 4. Therefore, better removals are obtained by filters that do not chlorinate their backwash due to the increased biological degradation. In fact, a reduction in the THMFP of the filter effluent of 15 to 40% was observed, and on some occasions the filter run length was increased due to later organic breakthroughs. These results were corroborated by McGuire and Suffet (1978), who found that ozone can extend the life of a GAC bed via increased biodegradability.

Two studies investigated the effect of pre-ozonation on coagulation processes. Reckhow and Singer (1984) found that ozone could improve the coagulation of turbidity, while Edwards et al (1993) found that ozone had no impact on turbidity after coagulation. Edwards et al (1993) also determined that pre-ozonation may cause an increase in the coagulant metal residual concentration. This is of concern due to the toxicity of aluminum.

Three studies were encountered that investigated the combination of ozone and UV light for organics removal. Gurol and Vatistas (1987) investigated the claim that UV light can increase the effectiveness of ozone, but found that the cumulative effect of the two processes was nothing more than an additive relationship. Two other studies examined ozone/UV systems and found substantial organics removals. Their results are summarized below in Table 25.

Table 25. Ozone/UV process data (Anonymous 1987, Anonymous 1989).

Compounds	Influent Concentration (μg/L)	Effluent Concentration (μg/L)
TCE, PCE	170, 16	below detection
TCE	5,000	< 2
benzene, toluene, xylene, ethyl benzene mixture	10,750 (total)	4
TCE, CCl_4, PCE	16, 9.6, 1.2	0.2, 3, below detection

On the downside of ozone treatment, ozone may decrease the adsorbability of some organics (Suffet 1980), and due to the increased biodegradability of its effluent, extra care must be taken to ensure that disinfection is adequate (Kuhn et al 1978). Also, ozonation can result in increased concentrations of low molecular weight chlorinated organic compounds due to the cleaving of larger ones (Kuhn et al 1978). If ozone is used as a carbon filter pretreatment process, McGuire and Suffet (1978) found that pretreating with ozone can lead to oxidation of the carbon's surface, increasing the polarity and causing a decrease in organics capacity.

16.4 Recommended Design and Operating Parameters for Organics Removal

In view of the weight of the evidence presented here, ozone is recommended as a pre-treatment process for filtration, preferably with granular activated carbon. The combined effect of direct oxidation of some organics and the increased biological degradation of others makes this a good treatment option. Optimum doses would need to be determined for each site individually, due to the differences in water quality between sites.

17. Ultraviolet Radiation

17.1 Unit Process Description

17.1.1 Physical Description

Although more commonly used as a disinfectant, ultraviolet radiation has been shown to have some effect at removing organic materials through oxidation. It can be produced effectively through the use of mercury vapour or antimony vapour lamps. The lights can either be immersed in the main stream if protected by a sheath, or the water can be passed through UV-transparent tubes near an ultraviolet source (Pontius 1990). For disinfection purposes, contact times are generally low (under one minute) but for good organics removals, considerably longer contact times may be required (up to 100 minutes) (Gurol & Vatistas 1987), although by increasing the light intensity, shorter times may be used.

UV radiation on its own is not a common treatment practice for organics removal. However, more common is the use of so-called "advanced oxidation processes", in which UV light acts as a catalyst to the improve oxidation properties of another oxidant, such as chlorine, ozone or hydrogen peroxide.

17.1.2 Factors Affecting Efficiency

One major parameter affecting the efficiency of processes utilizing UV is the bicarbonate alkalinity. Bicarbonate ions can reduce the efficiency of reaction by stopping radical chain reactions.

17.2 Mechanisms of Organics Removal

UV radiation can be absorbed directly by some compounds, causing them to undergo photolysis (Johnson & Gurol 1990). More common, however, is the interaction of light with water or other oxidants present to form highly reactive radicals, primarily hydroxyl radicals. These radicals react rapidly and non-selectively with organic (and inorganic) materials present in the water, oxidizing them (Johnson & Gurol 1990, El-Dib & Aly 1977). Ozone and UV light react to form hydrogen peroxide, which then degrades and reacts with ozone to give hydroxyl radicals faster than they are produced by just UV or ozone alone via the mechanism shown below (Johnson & Gurol 1990).

$$O_3 + H_2O + UV \rightarrow H_2O_2 + O_2$$ Equation 31

$$H_2O_2 \rightarrow HO_2^- + H^+$$ Equation 32

$$HO_2^- + O_3 \rightarrow HO_2 + O_3^-$$ Equation 33

$$O_3^- + H^+ \rightarrow HO_3$$ Equation 34

$$HO_3 \rightarrow O_2 + HO^\bullet$$ Equation 35

The problem with alkalinity in processes that utilize radicals, is due to the following reaction by which hydroxyl radicals are removed from the environment (Pontius 1990):

$$HO^{\bullet} + HCO_3^- \rightarrow OH^- + HCO_3 \qquad \text{Equation 36}$$

17.3 Organics Removal Efficiency

El-Dib & Aly (1977) compared the efficiency of phenylamide pesticide removals due to UV with and without chlorine. Their results are summarized in Table 26.

Table 26. Phenylamide pesticide removals with UV and UV + Cl_2 (El-Dib & Aly 1977).

Compound	% Removal with UV	% Removal with UV + Cl_2
IPC	5	20
Stam	35	50
Neburon	35	47
Vitavax	32	50

Their study also demonstrated that these removals may take up to 30 minutes to achieve. Gurol & Vatistas (1987) found that ultraviolet light, on its own, could reduce the concentration in a mixture of phenols by 30% in 100 minutes. Glaze (1987) presented the following data on the removals of three organic compounds by UV oxidation:

Table 27. UV removals of 3,4-benzopyrene, chloroform, and bromodichloromethane (Glaze 1987).

Period of UV radiation (min)	% Removal of 3,4-benzopyrene	% Removal of chloroform	% Removal of bromodichloromethane
0	0	0	9
60	-	8	9
120	29	58	25

When tested in conjunction with 35 mg/L hydrogen peroxide, the following results were obtained:

Table 28. Removals of 3,4-benzopyrene, chloroform and bromodichloromethane with UV and H_2O_2 (Glaze 1987).

Period of UV Radiation (min)	% Removal of 3,4-benzopyrene	% Removal of chloroform	% Removal of bromodichloromethane
0	0	0	0
30	-	25	42
60	72	32	56
120	91	91	91
240	98	-	-

Johnson & Gurol (1990) investigated the rates and mechanisms in the UV-catalyzed destruction of pentachlorophenol and toluene by ozone. They determined that the combination of the two processes oxidized the compounds faster than either one alone, and that compounds that were otherwise resistant to ozone oxidation were degradable. Two other studies on the use of ozone and UV light found that the combination can drastically reduce the concentrations of volatile organics. The first took an influent water containing 16 μg/L TCE, 9.6 μg/L CCl_4 and 1.2 μg/L PCE, treated it with ozone and UV, and produced an effluent with concentrations of 0.2 μg/L, 3 μg/L, and a concentration below the detection limit, respectively (Anonymous 1987). The second study used the same system on a number of other compounds and mixtures, and produced the following results:

Table 29. Ozone + UV removals of VOCs (Anonymous 1989).

Influent	**Effluent**
170 mg/L TCE, 16 mg/L PCE	both below detection limit
200 mg/L TCE	< 5 mg/L
benzene, toluene, xylene, ethyl benzene: total concentration 10750 mg/L	4 mg/L
5000 mg/L TCE	< 2mg/L

Both of these two studies found that economically, this system is cheaper than air stripping or granular activated carbon filtration (Anonymous 1987 and 1989). Pontius (1990) states that the combination of UV and ozone does show promise in the removal of refractory taste- and odour-causing compounds such as geosmin and methylisoborneol.

Gurol & Vatistas (1987), however, found that the efficiency of ozone and UV in combination was no greater than an additive effect of the two individual efficiencies.

17.4 Recommended Design and Operating Parameters for Organics Removal

While factors such as light intensity, contact time, turbidity, pH and temperature may affect the removal of organic materials by processes utilizing ultraviolet light, bench and pilot-scale experiments are needed to determine the optimum conditions for any given water supply. In the case of alkalinity, due to the quenching action of bicarbonate, lower alkalinities will generally lead to more efficient removals.

18. Summary

Below is a listing of the processes that may be used for organics reduction in domestic water treatment. A range and expected performance value is provided based on the literature that has been cited.

Table 30. Summary of Organics Removal by Water Treatment Processes

Process	Parameters	Range of Reduction	Likely Performance	Comments
Coagulation & Flocculation	coagulant dose mixing intensity	0 to 97%	20 to 70%	good removals of humic material
Softening	temperature pH hardness alkalinity	0 to 92%	30 to 50%	poor pesticide reductions
Sedimentation	loading rate residence time particle geometry	0 to 40%		less soluble materials removed more easily
Filtration	media type filter rate filter aids used	0 to 50%		less soluble materials removed more easily
Chlorine	temperature pH Cl_2 concentration	0 to 30%		very poor pesticide removals
GAC	compound chemistry media type pretreatment	9 to >99%	20 to 90%	very good chlorinated organics removals
PAC	point of addition carbon type water chemistry	0 to 98 %	50 to 90%	very good pesticide removals
Resin Adsorption	water chemistry resin chemistry temperature & pH		similar to carbon	highly selective
Air Stripping	Henry's Law air:water ratio process configuration	50 to 99%	70%	very good for volatile organics
Reverse Osmosis	membrane type water chemistry	40 to 98%	70%	
Chlorine Dioxide	water chemistry	0 to 100%	30 to 60%	excellent for colour, taste & odour
Ozone	water chemistry ozone dose ozone contact time	15 to 40%		excellent for taste & odour
UV Radiation	water chemistry	0 to 60%	5 to 30%	better when combined with O_3 or H_2O_2

19. Conclusions

The information presented shows that virtually all organic compounds can be reduced in concentration by selected water treatment processes. The degree of reduction is a function of the compound of interest and the other materials in the water being treated. There is not a universal method for predicting the performance of a process in removing a particular organic compound, and therefore bench and pilot plant testing is highly recommended where there is concern about the removal of an organic chemical. Effective processes must be matched with the chemical species present, and then optimized for the specific water to be treated.

References

Aieta, E.M. & Berg, J.D. 1986. A review of chlorine dioxide in drinking water treatment. *Journal AWWA*, *78*(6), p. 62.

Alsaygh, A.A., Jennings, P.A. & Bader, M.S.H. 1993. Separation of organic solutes from water by low pressure reverse osmosis. *J. Environ. Sci. Health, A28*(8), p. 1669.

Aly, O.M. & Faust, S.D. 1965. Removal of 2,4-Dichlorophenoxyacetic acid derivatives from natural waters. *Journal AWWA*, *57*(2), p. 221.

American Water Works Association (AWWA) Committee, 1979. Organics removal by coagulation: A review and research needs. *Journal AWWA, 71*(10), p. 588.

Amirtharajah, A., Dennett, K.E. & Studstill, A. 1993. Ferric chloride coagulation for removal of dissolved organic matter and trihalomethane precursors. *Wat Sci. Tech. 27*(11), p. 113.

Amy, G.L., Narbaitz, R.M. & Cooper, W.J. 1987. Removing VOCs from groundwater containing humic substances by means of coupled air stripping and adsorption. *Journal AWWA, 79*(8), p. 49.

Anonymous. 1987. Pilot studies show new cleanup technique effective for VOC cleanup. *Journal AWWA, 79*(1), p. 84.

Anonymous. 1989. Ozone technology removes organics from groundwater. *Journal AWWA, 81*(6), p. 124.

Babcock, D.B. & Singer, P.C. 1979. Chlorination and coagulation of humic and fulvic acids. *Journal AWWA*, *71*(3), p. 149.

Bader, M.S.H. & Jennings, P.A. 1992. Separation of priority organic pollutants from tap water by low pressure composite membrane. *J. Environ. Sci. Health*, *A27*(1), p. 117.

Baier, J.H., Lykins, B.W., Jr., Fronk, C.A. & Kramer, S.J. 1987. Using reverse osmosis to remove agricultural chemicals from groundwater. *Journal AWWA, 79*(8), p. 55.

Boening, P.H., Beckmann, D.D. & Snoeyink, V.L. 1980. Activated carbon adsorption versus resin adsorption of humic substances. *Journal AWWA*, *72*(1), p. 54.

Buhler, D.R., Rasmusson, M.E. & Nakaue, H.S. 1973. Occurrence of hexachlorophene and pentachlorophenol in sewage and water. *Environ. Sci. Technol.*, *7*(10), p. 929.

Chudyk, W.A., Snoeyink, V.L., Beckmann, D. & Temperly, T.J. 1979. Activated carbon versus resin adsorption of 2-methylisoborneol and chloroform. *Journal AWWA*, *71*(9), p. 529.

Clark, R.M., Fronk, C.A. & Lykins, B.W., Jr. 1988. Removing organic contaminants from groundwater: a cost and performance evaluation. *Environ. Sci. Technol., 22*(10), p. 1126.

Cohen, J.M., Kamphake, L.J., Lemke, A.E., Henderson, C. & Woodward, R.L. 1960. Effects of fish poison on water supplies. Part 1, Removal of toxic materials. *Journal AWWA*, *52*(12), p. 1551.

Cook, F.C., Jr. & Hartz, K.E. 1983. Adsorption of chlorinated methanes from aqueous solution on selected plastic adsorbents. *Journal AWWA*, *75*(8), p. 423.

Crittenden, J.C., Hand, D.W., Arora, H. & Lykins, B.W., Jr. 1987. Design considerations for GAC treatment of organic chemicals. *Journal AWWA, 79*(1), p. 75.

Curry, P., Kramer, G., Newhook, R., Sitwell, J., Somers, D., Bliss, T. & Van Oostdam, J. 1991. Reference Values for Canadian Populations (Draft). Environmental Health Directorate.

Deinzer, M., Melton, R. & Mitchell, D. 1975. Trace organic contaminants in drinking water; their concentration by reverse osmosis. *Water Research, 9*(9), p. 799.

Edwards, V.H. & Schubert, P.F. 1974. Removal of 2,4-D and other persistent organic molecules from water supplies by reverse osmosis. *Journal AWWA*, *66*(10), p. 610.

Edwards, M., Boller, M. & Benjamin, M.M. 1993. Effect of pre-ozonation on removal of organic matter during water treatment plant operations. *Wat. Sci. Tech.*, *27*(11), p. 37.

Edzwald, J.K. 1993. Coagulation in drinking water treatment: particles, organics and coagulants. *Wat. Sci. Tech. 27*(11), p. 21.

El-Dib, M.A. & Aly, O.A. 1977. Removal of phenylamide pesticides from drinking waters - I. Effect of chemical coagulation and oxidants. *Wat. Res.*, *11*, p. 611.

Environmental Science and Engineering, Inc. 1986. Removal of Volatile Organic Chemicals from Potable Water: Technologies and Costs. Pollution Technology Review No. 134. Noyes Data Corporation, Park Ridge.

Fleming, J.L. 1989. Volatilization Technologies for Removing Organics from Water. Pollution Technology Review No. 164. Noyes Data Corporation, Park Ridge.

Glaze, W.H. 1987. Oxidation of organic substances in drinking water. In Berger, Bernhard B., ed., *Control of Organic Substances in Water and Wastewater: Pollution Technology Review No. 140.*, Noyes data Corporation, Park Ridge.

Glaze, W.H., Schep, R., Chauncey, W., Ruth, E.C., Zarnoch, J.J., Aieta, E.M., Tate, C.H. & McGuire, M.J. 1990. Evaluating oxidants for the removal of model taste and odor compounds from a municipal water supply. *Journal AWWA*, *82*(8), p. 79.

Gurol, M.D. & Vatistas, R. 1987. Photolytic ozonation of phenols. *Wat. Sci. Tech.*, *19*(7), p. 1177.

Hyndshaw, A.H. 1972. Activated carbon to remove organic contaminants from water. *Journal AWWA*, *64*(5), p. 309.

Johnson, D.E. & Randtke, S.J. 1983. Removing nonvolatile organic chlorine and its precursors by coagulation and softening. *Journal AWWA*, *75*(5), p. 249.

Johnson, J.L. & Gurol, M.D. 1990. Removal of trace organic chemicals from water by ozone, UV and ozone + UV. *Proceedings of the 1988 Joint CSCE-ASCE National Conference on Environmental Engineering, July 13-15, 1988. Vancouver, BC, Canada.* p. 447.

Kuhn, W., Sontheimer, H., Steiglitz, L., Maier, D. & Kurz, R. 1978. Use of ozone and chlorine in water utilities in the Federal Republic of Germany. *Journal AWWA*, *70*(6), p. 326.

Liao, M.Y. & Randtke, S.J. 1985. Removing fulvic acid by lime softening. *Journal AWWA*, *77*(8), p. 78.

Licsko, I. 1993. Dissolved organics removal by solid-liquid phase separation (adsorption and coagulation). *Wat. Sci. Tech.*, *27*(11), p. 245.

Love, O.J., Jr. & Eilers, R.G. 1982. Treatment of drinking water containing trichloroethylene and related industrial solvents. *Journal AWWA*, *74*(8), p. 413.

Lykins, B.W., Jr. & Griese, M.H. 1986. Using chlorine dioxide for trihalomethane control. *Journal AWWA*, *78*(6), p. 88.

Malley, J.P., Jr., Edzwald, J.K. & Ram, N.M. 1988. Preoxidant effects on organic halide formation and removal of organic halide precursors. *Environmental Technology Letters, 9*, p. 1089.

Manahan, S.E. 1991. Environmental Chemistry. Fifth Edition. Lewis Publishers, Chelsea.

McCarty, P.L., Argo, D. & Reinhard, M. 1979. Operational experiences with activated carbon adsorbers at Water Factory 21. *Journal AWWA*, *71*(11), p. 683.

McCarty, P.L. 1987. Removal of organic substances from water by air stripping, in Berger, Bernard B., ed., *Control of Organic Substances in Water and Wastewater. Pollution Technology Review No. 140.* Noyes Data Corporation, Park Ridge.

McCreary, J.L. & Snoeyink, V. 1977. Granular activated carbon in water treatment. *Journal AWWA*, *68*(8), p. 437.

McGuire, M.J., Suffet, I.H. & Radziul, J.V. 1978. Assessment of unit processes for the removal of trace organic compounds from drinking water. *Journal AWWA*, *70*(10), p. 565.

McGuire, M.J. & Suffet, I.H. 1978. Adsorption of organics from domestic water supplies. *Journal AWWA*, *70*(11), p. 621.

McKinnon, R.J. & Dyksen, J.E. 1984. Removing organics from groundwater through aeration plus GAC. *Journal AWWA*, *76*(5), p. 42.

Miltner, R.J., Baker, D.B., Speth, T.F. & Fronk, C.A. 1989. Treatment of seasonal pesticides in surface waters. *Journal AWWA*, *81*(1), p. 43.

Najm, I.N., Snoeyink, V.L., Suidan, M.T., Lee, C.H. & Richard, Y. 1990. Effect of particle size and background natural organics on the adsorption efficiency of PAC. *Journal AWWA*, *82*(1), p. 65.

Pontius, F.W., ed. 1990. Water Quality and Treatment: A handbook of community water supplies, Fourth ed., McGraw-Hill, Inc., Toronto.

Prince, D.S., Smith, D.W. & Stanley, S.J. 1994. Review and Synthesis of Existing Information on Consumptive use of Drinking Water and Available Drinking Water Quality Data.

Rav-Acha, C., Blits, R., Choshen, E., Serri, A. & Limoni, B. 1983. The action of chlorine dioxide on aquatic organic materials during the disinfection of drinking water. *J. Environ. Sci. Health*, *A18*(5), p. 651.

Rebhun, M. & Lurie, M. 1993. Control of organic matter by coagulation and floc separation. *Wat. Sci. Tech.* *27*(11), p. 1.

Reckhow, D.A. & Singer, P.C. 1984. The removal of organic halide precursors by preozonation and alum coagulation. *Journal AWWA*, *76*(4), p. 151.

Reinhard, M., Goodman, N.L., McCarty, P.L. & Argo, D.G. 1986. Removing trace organics by reverse osmosis using cellulose acetate and polyamide membranes. *Journal AWWA*, *78*(4), p. 163.

Rice, R.G., Robson, C.M., Miller, G.W. & Hill, A.G. 1981. Uses of ozone in drinking water treatment. *Journal AWWA*, *73*(1), p. 44.

Robeck, G.G., Dostal, K.A., Cohen, J.M. & Kreissl, J.F. 1965. Effectiveness of water treatment processes in pesticide removal, *Journal AWWA*, *57*(2), p. 181.

Rodricks, J.V. 1993. Calculated Risks: The toxicity and human health risks of chemicals in our environment. Cambridge University Press, Cambridge.

Semmens, M.J. & Staples, A.B. 1986. The nature of organics removed during the treatment of Mississippi River Water. *Journal AWWA*, *78*(2), p. 76.

Sigworth, E.A. 1965. Identification and removal of herbicides and pesticides. *Journal AWWA*, *57*(8), p. 284.

Suffet, I.H. 1980. An evaluation of activated carbon for drinking water treatment: A National Academy of Science Report. *Journal AWWA*, *72*(1), p. 41.

Tobiason, J.E., Edzwald, J.K., Reckhow, D.A. & Switzenbaum, M.S. 1993. Effect of pre-ozonation on organics removal by in-line direct filtration. *Wat. Sci. Tech.*, *27*(11), p. 81.

Troxler, S., Smith, D.W. & Knettig, E. 1989. Powdered activated carbon selection for water treatment. Can. J. Civ. Eng., *16*, pp. 743-752.

Trussell, R.R. & Umphres, M.D. 1978. The formation of trihalomethanes. *Journal AWWA, 70*(11), p. 604.

Walker, G.S., Lee, F.P. & Aieta, E.M. 1986. Chlorine dioxide for taste and odor control. *Journal AWWA*, *78*(3), p. 84.

Weast, R.C. 1985. Editor-in-Chief, CRC Handbook of Chemistry and Physics, 66th Edition. CRC Press, Inc., Boca Raton.

Weber, W.J. & Jodellah, A.M. 1985. Removing humic substances by chemical treatment and adsorption. *Journal AWWA*, *77*(4), p. 132.

Weber, W.J., Jr. & van Vliet, B.M. 1981. Synthetic adsorbents and activated carbons for water treatment: Statistical analyses and interpretations. *Journal AWWA*, *73*(8), p. 203.

Weber, W.J., Jr. & Pirbazari, M. 1982. Adsorption of toxic and carcinogenic compounds from water. *Journal AWWA*, *74*(4), p. 203.

Weber, W.J., Jr. & Smith, E.H. 1986. Removing dissolved organic contaminants from water. *Environ. Sci. Technol.*, *20*(10), p. 970.

Wood, P.R. & DeMarco, J. 1979. Treatment of groundwater with activated carbon. *Journal AWWA*, *71*(11), p. 674.

APPENDIX A

NORTHERN RIVER BASINS STUDY

APPENDIX A - TERMS OF REFERENCE

Project 4402-Do: Literature Reviews on Treatment Efficiencies

I. BACKGROUND AND OBJECTIVES

The quality of drinking water is based both on the quality of the source water and the treatment processes used. The methods used and proposed for the treatment of drinking water are many and varied. A great deal of information is available in the literature on the performance, advantages and disadvantages of the various processes. A detailed critical review of this information will be performed in this proposed project. The reviews will concentrate on processes that are appropriate for use and contaminants that are of special concern in the study area. This information will be used for a general assessment on drinking water quality in the basins. This will be completed by assessing the raw water quality and treatment systems that various communities use (Project 4422-Do). In addition the reviews will be valuable information for communities in the study area for selection and assessment of treatment processes that are in use or are proposed.

Objectives

1. Review and assess existing water quality data for raw and treated water in the study area.

2. Critically review the available literature on the performance, advantages, disadvantages and appropriateness of drinking water treatment processes for organic and inorganic chemical and bacterial contaminant removal applicable to the study area.

II. REQUIREMENTS

The completion of three literature reviews on the efficiency of drinking water treatment processes is proposed for 1994/95. The reviews will include: assessment of inorganic chemical removal efficiencies; assessment of organic chemical removal efficiencies; and assessment of microbial contaminants removal efficiencies. Each review will involve:

1. Assessment of existing water quality data for the study area (inorganic, organic and microbial). Most of this information will be obtained from provincial, federal and NRBS studies (4401-C1, 4421-C1).

2. Thorough review of pertinent literature. Extensive use will be made of the University of Alberta Library that is the second largest library in Canada. Information obtained from various suppliers, past unpublished research projects, and personal contacts will also be incorporated in the review. The following will be completed as part of the review:
   o A literature search carried out using facilities at the U of A Library.
   o Review of literature found.

o Review of information from suppliers, personal contacts and other unpublished research reports.
o Summarizing available information in a concise form.

3. Evaluation of process alternatives. Treatment methods found in (II.2) will be evaluated for use in the study area. Evaluation will include factors such as:
o Effectiveness of the treatment process
o The degree of control, skill and supervision needed to achieve good performance.
o Technical support required for operation - special skills needed for maintenance and repair.
o Safety and handling precautions required.
o Process reliability
o Climatic effects (water temperatures)
o Effect of different water quantities and qualities.
o Level of development of current technology.
o Public acceptance.
o Economic considerations.

4. Write three reports outlining the results of the investigation of II.1-3 for organic and inorganic chemicals, and microbial contaminants.

III. DELIVERABLES

1. Critical Review of Organic Treatment Efficiencies - 10 copies due March 31, 1995

2. Critical Review of Inorganic Treatment Efficiencies - 10 copies due March 31, 1995

3. Critical Review of Bacterial Treatment Efficiencies - 10 copies due March 31, 1995

4. Prepare 35 mm slides for use in presentations. These would include photographs of relevant items such as field work (if appropriate) and a summary of the main findings of your investigation. due March 31, 1995

III. REPORTING REQUIREMENTS

1) The Contractor is to provide draft and final reports in the style and format outlined in the NRBS Style Manual. A copy of the Style Manual entitled "A Guide for the Preparation of Reports" will be supplied to the contractor by the NRBS.

2) Ten copies of the Draft Report along with an electronic disk copy are to be submitted to the Project Liaison Officer by March 31, 1995.

Three weeks after the receipt of review comments on the draft report, the Contractor is to provide the Project Liaison Officer with two unbound, camera ready copies and ten cerlox bound copies of the final report along with an electronic version.

3) The final report is to include the following: an acknowledgement section that indicates any local involvement in the project, Project Summary, Table of Contents, List of Tables, List of Figures and an Appendix with the Terms of Reference for this project.

Text for the report should be set up in the following format:

a) Times Roman 12 point (Pro) or Times New Roman (WPWIN60) font.
b) Margins; are 1" at top and bottom, 7/8" on left and right.
c) Headings; in the report body are labelled with hierarchical decimal Arabic numbers.
d) Text; is presented with full justification; that is, the text aligns on both left and right margins.
e) Page numbers; are Arabic numerals for the body of the report, centred at the bottom of each page and bold.

- If photographs are to be included in the report text they should be high contrast black and white.
- All tables and figures in the report should be clearly reproducible by a black and white photocopier.
- Along with copies of the final report, the Contractor is to supply an electronic version of the report in Word Perfect 5.1 or Word Perfect for Windows Version 6.0 format.
- Electronic copies of tables, figures and data appendices in the report are also to be submitted to the Project Liaison Officer along with the final report. These should be submitted in a spreadsheet (Quattro Pro preferred, but also Excel or Lotus) or database (dBase IV) format. Where appropriate, data in tables, figures and appendices should be geo-referenced (latitude and longitude).

4. All figures and maps are to be delivered in both hard copy (paper) and digital formats. Acceptable formats include: DXF, uncompressed E00, VEC/VEH, Atlas and ISIF. All digital maps must be properly geo-referenced (latitude and longitude).

5. All sampling locations presented in report and electronic format should be geo-referenced. This is to include decimal latitudes and longitudes (to six decimal places) and UTM coordinates. The first field for decimal latitudes / longitudes should be latitudes (10 spaces wide). The second field should be longitude (11 spaces wide).

V. CONTRACT ADMINISTRATION

The Project Liaison Officer (Component Coordinator) for this project is:

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