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Subject: Technical Letter 26  
Removal of Water Supply Contaminants - Chlorophenoxy Acid Herbicides

This is the twelfth in a series of Technical Letters dealing with state of the art methods for removal of contaminants from water supplies so that the supply will be in compliance with state and federal drinking water standards.

## Contaminant

This Technical Letter is concerned with chlorophenoxy acid herbicides as contaminants of drinking water supplies. In 1976 there were no water supplies in Illinois known to exceed the new federal drinking water standards for the chlorophenoxy acid herbicides 2,4D and 2,4,5TP (silvex).

## Prevalence and Uses

Chlorophenoxy acid herbicides are man-made compounds and are not found in the environment naturally. These compounds can contaminate water supplies as a result of runoff from or percolation through agricultural land, from manufacture or formulation, improper disposal of herbicide containers, and drift from aerial spraying. These compounds can also appear in surface water supplies if used in aquatic weed control. Water supplies may also be contaminated if backsiphoning occurs during dilution of these compounds.

These compounds have been used as the acids, as the ester (methyl and octyl), as water soluble amine salts, and as sodium or potassium salts.

These herbicides have been used for weed control in some grain crops and in pastures. They have been used extensively for weed and brush control along power line and railroad rights-of-way, and along stream and river banks. They have been used widely for aquatic weed control particularly in irrigation ditches. These herbicides have also been used for weed control in lawns and in forest management for weed and brush control.

## Health Effects

Only limited health problems have been associated with these compounds. Acute toxicities require ingestion of relatively large amounts of these herbicides. An acute dose will affect the central nervous system with possible collapse of the

respiratory or cardiovascular system. Subacute doses may cause some kidney or liver damage. There have been no reported adverse health effects as a result of long-term exposure to low levels. These compounds are eliminated rapidly from the body so they do not accumulate in the body tissues.

#### Maximum Levels

The maximum levels for the chlorophenoxy acid herbicides are:

2,4D (2,4- dichlorophenoxyacetic acid) 0.1 µg/l

2,4,5TP (silvex) (2,4,5 trichlorophenoxypropionic acid) 0.01 µg/l

#### Removal

The solubility of these compounds depends on the pH. As the pH decreases the solubility decreases since the undissociated acids show limited water solubility. As the pH is increased the solubility will increase because of the formation of water soluble salt forms. The acid will be completely undissociated at a pH below about 7 while complete dissociation will occur at a pH above about 10. The efficiency of various removal processes is dependent on the pH.

#### *A. Activated Carbon Adsorption*

Activated carbon adsorption has been effective in removing chlorophenoxy acid herbicides from water. Both the acid and salt forms are removed with carbon. The undissociated acid form is expected to be removed more efficiently than the salt form, so a lower pH will provide best results. The process involves contact of the water and activated carbon to achieve removal by means of adsorption of the material onto active sites on the carbon. Both granular carbon in a column and powder carbon added directly to the water have been used. The granular activated carbon is somewhat more expensive at the present time but it can be regenerated by thermal methods. Continuous counter-current systems have been used which provide for maximum removal efficiency without the need for shutdown to regenerate the carbon.

Powdered activated carbon is mixed directly with the water and is removed by filtration. Under normal operation the carbon is used on a once-through basis as a disposable item, which provides easier operation than with the granular carbon beds. Also, the required dosage is somewhat lower than for granular carbon because of more efficient contact and mixing. Systems for using powdered carbon with regeneration are under development. At the present time losses during regeneration offset any cost savings between granular and powdered carbon. Because the costs of powdered and granular carbon are continually fluctuating, the price advantage of one over the other is uncertain.

Granular carbon can also be used in a conventional filter bed. Eighteen to twenty-four inches of sand can be replaced by carbon. Simple backwashing does not regenerate the carbon relative to herbicide removal so it must be replaced periodically or regenerated by thermal methods. If the carbon is not replaced or regenerated, it serves only as a filtering media in removing suspended material rather than as adsorption media removing the herbicides in solution. Some means of monitoring would be required to determine when the carbon needed to be changed or regenerated. This makes this system somewhat impractical for routine use. The lifetime of activated carbon for removal of single contaminants is on the order of several months compared with several years for taste and odor removal. This requires careful monitoring of treated water in a fixed bed system.

### *B. Porous Resin Adsorption*

Several years ago ion exchange resins with well-characterized pore structures were prepared. Unlike previous gel-type resins the new materials have a definite pore structure and porosity similar to the classical adsorbents such as aluminas, silicas, and carbons. These porous structured resins were found to be effective in removing organics from water without the problem of clogging as observed with the gel-type resins. In addition regeneration was possible with sodium hydroxide. Although weakly basic anion exchange resins were found to be the most effective for removing organics, the removal is not an ion exchange process but an adsorption process. The resins have primarily been used for treatment of boiler feed waters for organic removals and other water treatment processes. The resins have also been used for concentrating pesticides from water prior to analysis, and for removing pesticides from waste streams in the manufacture of pesticides. These resins should be effective in treating drinking water. Some ion-exchange removal in addition to adsorption for the acid herbicides might occur if weak anion resins are used. An effect of pH on removal efficiency for this process is expected although the exact nature of the effect is unknown.

For water with high organic content and high suspended solids it may be necessary to treat the water before it passes through the resin. Coagulation and sedimentation can be used to reduce the amount of suspended material to be removed by the resins. This will increase the run time of the resin between regenerations.

### *C. Coagulation, Sedimentation, and Filtration*

Coagulation is the removal of material from solution by precipitation. Either iron or aluminum salts are added to the water and the pH raised by the addition of lime. The iron or aluminum added precipitate as the insoluble hydrated oxides. The precipitate carries down suspended matter and some soluble material as it settles. The compound removed may be occluded in the precipitate or adsorbed onto the surface. The process has been effective in the removal of organics from water where the organics were present as suspended solids or adsorbed onto suspended solids. Since chlorophenoxy

acid herbicides can be adsorbed onto suspended solids, this process should be effective in reducing the level of pesticides. Since the aluminum or iron salts of these compounds are insoluble, soluble salts of these compounds should also be removed. It is unlikely that the process alone will be able to reduce the pesticides to the level required. Improved removal efficiencies have been obtained by the addition of powdered activated carbon. Whether this process will be sufficient to achieve reductions to the maximum allowed levels will have to be evaluated on a given water by pilot studies.

#### *D. Polyurethane Foam Plug Adsorption*

Plugs of polyurethane foam have been used for collecting various pesticides from water for the purpose of analysis. It is possible that a somewhat similar water system might be useful for treatment of contaminated waters. The removal process is based on the adsorption of the pesticides onto the surface of the polyurethane. Some limited studies have been carried out with polyurethane foam for removal of organics from water. Only limited information is available on their practicality and utility.

Since removal of adsorbed material from the polyurethane requires rinsing with alcohol or another organic solvent, it is unlikely that a convenient regeneration scheme can be developed. The plugs would have to be used on a throwaway basis. The plugs may be of use for fine polishing of water, after other treatment methods have reduced the levels of pesticides to near the allowable level. In waters with high suspended solids, pretreatment would be necessary to prevent clogging of the plugs and excessive replacement of the adsorption media.

#### *E. Ion Exchange*

Since under certain conditions the chlorophenoxy acid herbicides will exist as ionic species in water, removal by ion exchange may be possible. In the ion exchange process the herbicides in solution will exchange with ions from the resin. An anion exchange resin will be necessary since the herbicides will exist as anionic species. There is no resin which will selectively remove the herbicides so there will be competition from other anions such as chloride, sulfate, carbonate, etc. Careful pH control will also be necessary to insure that the herbicides are dissociated ions. It is expected that this will be a relatively poor and costly method for removal of the herbicides, requiring very careful control of conditions and close monitoring of the effluent.

#### *F. Reverse Osmosis*

Reverse osmosis involves the removal of soluble materials by passage of water through a semipermeable membrane. To get water to pass through the membrane it is necessary to apply pressure to the water containing the

dissolved materials to overcome the natural direction of flow which would be for pure water to diffuse into the water containing dissolved material. The amount of pressure necessary depends on the mineral content of the raw water. For waters with high suspended solids, pretreatment is necessary to prevent clogging of the membrane. Although reverse osmosis can be used to reduce the chlorophenoxy acid herbicide level, its application is impractical and costly unless it is already in use for the treatment of brackish water, it is reported by the Federal Environmental Protection Agency that 99 percent or better removal efficiencies can be obtained for the chlorophenoxy acid herbicides for which limits are established. The most significant cost is plant construction. For a 1000 m<sup>3</sup>/day plant (183 gpm), construction costs will be about \$250,000 based on 1976 costs. This cost does not include costs for any interest during construction, site and site improvement, discharge facilities, storage and delivery facilities, or special treatment. Operating costs are about \$18,000 for a plant of that capacity.

#### General Comments

All of the removal techniques discussed above require pilot-scale testing for a specific application to determine their efficiency. Pilot-scale studies are also needed to determine what, if any, pretreatment is necessary to insure good operating efficiency.

Technical Letters are issued as part of the Water Survey's continuing service to citizens of Illinois. Should you need further clarification, please let us know.

Very truly yours,



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Associate Professional Scientist

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