

The Removal of Organics from Municipal
Wastewaters by Lime-Magnesium Coagulation

by

LEUNG YUK-CHING

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Department of Civil Engineering

The University of British Columbia
2075 Wesbrook Place
Vancouver, Canada
V6T 1W5

Date 16th June, 1978

ABSTRACT

In view of a potentially hazardous problem existing in municipal wastewater due to heavy metals and trace organics, this research attempted to find the removal efficiency of trace organics that could be achieved by chemical treatment (lime-magnesium coagulation) instead of by conventional biological treatment.

Pesticides, polychlorinated biphenyls (PCB's) and phenols were chosen because of their high toxicity, existence in significant quantities, and ubiquitous nature. Extraction, concentration, derivatization and gas liquid chromatography (GLC) were employed to detect these compounds. Jar tests at pH 10.0, 10.7 and 11.4 with magnesium (Mg^{2+}) dosages of 0, 8, 17, 33 and 50 mg/l were carried out to find the optimum removal condition.

Very high removal of each from an initial concentration of 250 $\mu g/l$ could be obtained, although not under the same experimental conditions. The highest removal efficiencies of Dieldrin, Aroclor 1254, Dichlorvos and Pentachlorophenol were 88.1%, over 95%, over 80% and 73.5% respectively. The two optimum dosages found were 8 mg/l Mg^{2+} at pH 10.7 and 33 mg/l Mg^{2+} at pH 11.4. The former combination of conditions is worthy of consideration when magnesium and lime recycle are not practised, especially with regard to sludge handling, chemicals used and final pH adjustment. The latter set of conditions gives the highest average removal and is worthy

of consideration when lime and magnesium recycle are included. Whether lime-magnesium coagulation can be a cost-effective treatment process for municipal wastewater, and how it can be instituted within existing treatment plants, still requires further investigation.

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GC = Gas Chromatography

PPE = Prechlorinated Primary Effluent

PCP = Pentachlorophenol

PCBs = Polychlorinated biphenyls

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CHAPTER I

1. INTRODUCTION

1.1 Research Rationale

Entering into an era of energy crisis, resource recycle is becoming an economically attractive process. Lime-magnesium coagulation for the removal of impurities in water and wastewater with the potential of recycling both magnesium and lime, and reducing the amount of sludge at the same time, merits consideration under such a rationale.

Chemical coagulation employing magnesium in conjunction with lime is the subject of recent research. Its application to municipal wastewaters and kraft mill effluents in the pulp and paper industry has been investigated (7,43). Superior effluent quality in comparison to wastewater treated with lime coagulation alone was reported by Black et al (7) with respect to several parameters: COD, TOC, BOD and total phosphorus. Rush (43) found that over 90% colour removal in kraft mill effluent was obtained.

Greater Vancouver Regional District is looking at the possibility of installing secondary biological treatment in its sewage treatment plants which only offer primary treatment at the present. However, the main concern in the receiving waters is the toxicity of heavy metals and trace organics, for which only unpredictable removal can be achieved by secondary biological treatment. One potential alternatives

may be the use of chemical treatment, for example, the lime-magnesium coagulation process.

Maclean (30) looked at the removal efficiencies of five heavy metals (Cr^{3+} , Cu^{2+} , Pb^{2+} , Ni^{2+} and Zn^{2+}) by such a process. Results indicated that removal efficiency was enhanced by the presence of magnesium. This research, which is a continuation of that investigation, looks into the removal of trace organics (especially those of primary concern such as organochlorine pesticides and polychlorinated biphenyls) by application of the lime-magnesium coagulation to municipal wastewater.

1.2 Selection of Effluent and Nature of Effluent

Greater Vancouver Regional District has four sewage treatment plants. The Annacis Island Sewage Treatment Plant, is located on Annacis Island, 3 miles downstream of New Westminster on the south arm of the Fraser River.

The prechlorinated primary effluent (PPE) and raw sewage for this treatment plant was selected in this research for three reasons:

a) it contributes a significant portion of the total wastewater flow entering the Fraser River estuary (16% by volume).

b) it contains a number of industrial waste streams, since Annacis Island is an industrial area that contains varied industries such as automobile undercoating, food processing,

steel products manufacture, chemical and solvent processing.

c) it is a potential concern to aquatic species in the Fraser River at the plant outfall.

Annacis Island Sewage Treatment Plant provides primary treatment including: influent and effluent sampling; prechlorination; mechanical screening; pumping, pre-aeration and grit removal; sedimentation; scum removal; sludge removal, thickening and digestion; post-chlorination and dechlorination.

Average characteristics of PPE and raw sewage are listed as follows:

Table 1. Sewage Characteristics, Annacis Island Treatment Plant

Flow	Raw Sewage	PPE
	75 cfs/40 Imgpd	75 cfs/40 Imgpd
Temperature	21°C	21°C
pH	6.8	6.8
Suspended Solids (mg/l)	230	60
BOD ₅ (mg/l)	200	130
COD (mg/l)	530	300
Phenols (mg/l)	0.13	0.13
Mg ²⁺ (mg/l)	8.5	8.5
Alkalinity (mg/l as CaCO ₃)	-	145
Pentachlorophenol (µg/l)	under 10	under 10
Polychlorinated-biphenyls (µg/l)	0.05	0.05
Organochlorine-pesticides (ng/l)	Trace Amounts	Trace Amounts

Table 1 (cont'd)

Note: According to Standard Methods (2), pentachlorophenol cannot be detected during detection of phenols, therefore the phenol concentration of 0.13 mg/l does not include pentachlorophenol. Data on pentachlorophenol and alkalinity were measured during this research on grab samples while information on polychlorinated biphenyls was obtained from Environmental Protection Service (Environment Canada), organochlorine pesticides from the Provincial Water Quality Laboratory and the rest from Greater Vancouver Regional District Office (using composite samples).

1.3 Review of Removal Technology

1.3.1. Chemical Treatment by Coagulation

Water clarification or water reclamation by chemical coagulation was started in 1910 (53) in the U.S. Extensive theoretical and practical work has been developed. The use of polyelectrolytes as a coagulant aid stimulated new interest in chemical treatment. Today, many full-scale plants are in operation and satisfactory results can be obtained by careful control.

The A.W.W.A. publication (3) presents a very complete chapter on chemical coagulation of water. Conventional coagulants include alum, ferric salts and lime. The low solubility of metallic hydroxides and/or carbonates has been noted and used through adjusting the pH and adding the appropriate chemicals. However, wastewaters usually have an intermediate buffering capacity and this factor plus other factors such as alkalinity and turbidity, will affect the coagulation process.

The wide application and increased use of chemical coagulation are due to its many advantages: it provides an intermediate degree of treatment between primary and secondary treatment, it is not sensitive to flow variation, it is not susceptible to industrial wastes as is biological treatment and it requires a relatively inexpensive capital investment. For effective removal of impurities, an understanding of their properties and behaviour, the chemical mixing time, peripheral speed of mixers, time of slow mix and settling time is necessary. Standard jar tests can be used to determine the range of optimum dosage and evaluate other required conditions. Filtration is usually employed after clarification. Recent practice uses chemical precipitation in conjunction with other advanced treatment processes such as activated carbon adsorption, reverse osmosis, ion exchange, etc. Chemical conditioning of sludge is often used as it can improve sludge filtering properties and make dewatering easier.

BOD removal of 65-85% has been reported (16) while S.S. removal up to 90% can be obtained with just chemical coagulation and sedimentation. Soluble organics are only slightly affected by coagulation. Pesticide and p lychlorinated biphenyl removal of over 25% and 40% respectively are expected. Common heavy metals such as Zn, Pb, Ni, Cu, Fe, Cr, Cd, Hg, and As can be substantially removed by using hydroxide precipitation. Even uncommon metals such as Ag, Co, Bi, Sb, Se, Sn, Ti, Be were found to be removed effectively by chemical

clarification (12). Carbonate precipitation for these metals has been investigated but it was found that no benefit could be obtained; neither denser sludges nor better filtration were observed (45).

1.3.2. Advanced Treatment

Advanced waste treatment processes are used to remove pollutants in secondary effluents such as phosphorus, nitrogen and nondegradable organics which are not removed by conventional secondary treatment. There are many available advanced processes such as ammonia stripping for the removal of nitrogen, electrodialysis and ion exchange for the removal of inorganic ions, recarbonation for pH adjustment, freezing, distillation, and chemical oxidation. Only activated carbon adsorption and reverse osmosis will be mentioned briefly with respect to trace organics removal.

Adsorption of trace organics by activated carbon is becoming practical, reliable and economical. It is based on the very great adsorptive capacity provided by a large surface area for contact between the carbon and the organics. Of course, pH, size of carbon medium, turbidity, packing of column, carbon regeneration, etc have to be taken into design consideration. Carbon adsorption is often used after chemical clarification and filtration, otherwise the carbon beds would be quickly saturated with suspended solids. Effluent BOD concentration under 10 mg/l can easily be obtained. Phenol

reduction from 0.17 mg/l to 0.005 mg/l was found using chemical clarification and carbon adsorption (10) on a pilot scale, while the phenol concentration in the clarified effluent was 0.055 mg/l. Even though very effective removal can be achieved by this process, it has seldom been used as an intermediate treatment step.

Reverse osmosis removes impurities when the treated water is forced through a semipermeable membrane at high pressure. It is used as a polishing step for upgrading water quality for recycle purposes. Therefore, it is often used to treat secondary effluents or perhaps even effluents from the carbon column. There are presently many types of membranes available and future development should make this process economically feasible. Fouling of the membrane is still a problem area. BOD and COD removal of over 95% can usually be achieved on secondary effluents. Refractory organic materials such as odour and colour producing organics, herbicides and pesticides can be removed.

1.3.3. Other Methods

Primary treatment including screens, grit removal and sedimentation would have very little effect on phenol, pesticide and polychlorinated biphenyl removal. Their persistent nature makes secondary biological treatment ineffective against them and even exerts adverse effects on these processes through their toxic effects on the micro-

organisms. Although bacteria may be acclimatized to wastes containing these pollutants (e.g. the Dow Chemical Manufacturing Plant in Vancouver, B.C. has successfully acclimatized bacteria to treat phenolic wastes) variations in concentration and flow are an operational difficulty to be overcome and removal is unpredictable. So, biological treatment is usually not recommended for achieving consistent removals of heavy metals and trace organics.

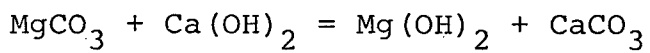
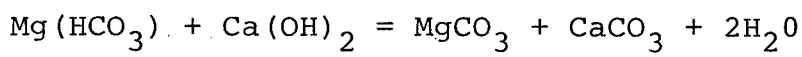
1.3.4. The Lime-Magnesium Process

The lime-magnesium process is an application of chemical coagulation which removes dissolved, colloidal and suspended materials (organic and inorganic) from wastewaters by many mechanisms including precipitation, adsorption, complexation, chelation, flocculation and entrapment. For heavy metal removal, effective results are chiefly due to direct precipitation of insoluble metallic hydroxides (40). For trace organics removal, adsorption, flocculation and entrapment seem to be the important mechanisms.

This process utilizes a magnesium salt as the coagulant. The preferred use of magnesium carbonate is discussed later. With the addition of significant lime slurry to wastewaters containing magnesium bicarbonate, or to which magnesium carbonate has been added, magnesium hydroxide and calcium carbonate will precipitate out. Carbonation of the sludge selectively redissolves the magnesium which can be

recovered by vacuum filtration. Then, the filter cake of CaCO_3 may be recalcined to recover lime. The many advantages of this process are as follows:

(1) There is no hardness added to the wastewaters because magnesium bicarbonate is converted to magnesium carbonate and then to magnesium hydroxide on further addition of lime according to the following equations:



(2) If the magnesium concentration naturally present in the wastewaters is high, the optimum dosage for impurities removal in wastewaters can be economically achieved as the added magnesium required can be reduced. Also, recycle of magnesium and lime is an important economic factor affecting both chemical costs and sludge handling costs.

(3) Recarbonation of treated effluents recovers magnesium and at the same time adjusts the pH downwards to a more acceptable level.

From a review of magnesium chemistry, it is found that maximum magnesium solubility is nearly constant below pH 10, then rapidly decreases at higher pH values. For example, increasing phosphate removal (31) was found between pH 9 and 11 and little effect was noted above pH 11.5. On the other hand, a sufficient carbonate alkalinity in the wastewaters would be necessary for a satisfactory CaCO_3 precipitate

to be formed. If disposal of sludge on land is preferred to recycling of magnesium and lime, magnesium hydroxide may present a problem in dewatering because of its gelatinous nature. In this case, the use of polyelectrolytes may be helpful in improving sludge characteristics for good settling and consolidation.

CHAPTER 2

EXPERIMENTAL METHODS AND MATERIALS

2.1. Selection of Organic Parameters

Organics such as phenols, pesticides and polychlorinated biphenyls (PCBs) are commonly used in industry. The potential for environmental damage, especially due to toxic effects is the main reason for their selection for this research. Their common usage, their presence in significant quantities and their detection methods are also important in deciding which test substances to use.

These organics can enter into wastewaters in many ways such as direct application, percolation, run-off, entrapment in aerosols and return from sediments. Possible effects on wildlife, aquatic creatures and even man include toxicity, synergistic effects on toxicity, and taste and odour problems. Most of these compounds are only slightly soluble in water, so lime-magnesium coagulation may offer a good treatment both in terms of removal efficiency and cost effectiveness.

At the present time, concentrations of phenols, pesticides and PCBs found in river water (Fraser River) are generally below detection limits. Pesticides that have been found in river sediments (19) include p,p'-DDT and its degradation products p,p'-DDE and p,p'-DDD, α -chlordane and γ -chlordane. PCBs are also present and most chromatograms compared favourably with Aroclor 1254, with concentrations ranging from

10 µg/Kg to 780 µg/Kg.

Because DDT has been banned for use for many years in Canada, it was not considered for testing in this research. The chosen impurities were: Dieldrin (an organochlorine pesticide), Aroclor 1254 (a PCB), Pentachlorophenol (PCP, a phenol) and Dichlorvos (an organophosphate pesticide). Originally, 2,4-D (a herbicide) was also chosen as one of the testing parameters. Its use was subsequently abandoned, as discussed in Appendix C. The first three are very common and very persistent in nature. Organophosphorus compounds (e.g. Dichlorvos) generally have less problems to non-target organisms than organochlorine compounds (e.g. Dieldrin) and are more easily degraded. The most common organophosphorus insecticides are Parathion and Malathion. They were not selected because of less convenient detection techniques. As a result, Dichlorvos was chosen since it could be detected in conjunction with the other parameters by Gas Liquid Chromatography using an electron capture detector. Besides, it is a very popular pesticide, although not the most commonly used one.

Drinking water standards usually limit phenols and pesticides to less than 50 µg/l (61). The Greater Vancouver Regional District limits phenol discharges to sewers to 1 mg/l at the entrance to the sewer system (51). The difference between drinking water standards and sewer discharge levels is obviously due to treatment in sewage treatment plants, which may remove some quantities of the pollutants, and to dilution

in the receiving water. Consequently, "spiking" of the selected parameters in sewage to a concentration of 250 $\mu\text{g/l}$ was decided upon, as it would allow meaningful comparisons on removal efficiency. However, since there might be a difference in removal efficiency because of different initial concentrations, 50 $\mu\text{g/l}$ spikes of Dieldrin and Aroclor 1254 were also undertaken. Each of the organic parameters was measured individually and mixed in PPE and in raw sewage before and after chemical treatment. Vancouver has a low alkalinity water, so an elevated alkalinity was investigated by spiking sewage with sodium bicarbonate solution with Dieldrin to detect any difference in removal efficiency. From Maclean's work (30), there was no significant increase in removal after filtration. Only 1-2% was achieved, so no observations were made for filtered samples in this work.

BOD removal was also measured to give a comprehensive idea of (biodegradable) organics removal by this process. Visual observations of the floc properties and settling rate were also included. A sludge recovery test was performed with Dieldrin in order to calculate the mass balance. Table 2 summarizes the experimental program.

Table 2. Summary of Experimental Program

Test Conditions	pH 10.0	pH 10.7	pH 11.4
	Natural Alkalinity		
Dieldrin 250 $\mu\text{g/l}$ in PPE	✓	✓	✓
Dieldrin 50 $\mu\text{g/l}$ in PPE	✓	✓	✓
Aroclor 1254 250 $\mu\text{g/l}$ in PPE	✓	✓	✓
Aroclor 1254 50 $\mu\text{g/l}$ in PPE	✓	✓	✓
Dichloros 250 $\mu\text{g/l}$ in PPE	✓	✓	✓
PCP 250 $\mu\text{g/l}$ in PPE	✓	✓	✓
BOD in PPE	✓	✓	✓
Σ in PPE	✓	✓	✓
Σ in RS	✓	✓	✓
Dieldrin sludge recovery	✓		
Dieldrin 250 $\mu\text{g/l}$ in PPE	✓	✓	✓
Elevated Alkalinity			

Notes for Table 2:

- (1) Mg^{2+} dosage: 0, 8, 17, 33, 50 mg/l. (over 50 mg/l of Mg^{2+} dosage would not be considered practical or economically attractive)
- (2) RS - Raw Sewage
- (3) Natural Alkalinity: 120 - 130 mg/l as $CaCO_3$
Elevated Alkalinity: 180 - 200 mg/l as $CaCO_3$
- (4) Σ indicates a combination of four organic parameters each with initial concentration of $250 \mu g/l$.

2.2. Ubiquitous Nature of Chosen Organics

2.2.1. General

The use of pesticides and PCBs is unquestionably wide and extensive. For the last two decades, pesticides have been produced in very large quantities, e.g. in 1965 there were 140 million pounds of DDT and 133 million pounds of other organo-chlorine pesticides manufactured in the U.S.A. Considering their persistent nature in the environment, minimal removal in water systems, easy adsorption in soils, and their ability to accumulate in plants and animal body fats, they are excellent candidates for biological magnification. Dispersal in air, water and soil often leads to hazardous effects on non-target organisms and even human beings. In Clear Lake, California, 46000 acres of the lake area was sprayed with DDD, for gnats in 1949, 1954, and 1957 with 250 times of the applied dosage being subsequently found in plankton, 2000 times in frogs, 12000 times in sunfish and 80000 times in grebes (48). For ten years, there were no grebes in the area and the first

nestling appeared in 1962. Also, edible fish flesh contained up to 7 mg/l of DDD which was above the tolerance level set by the Food and Drug Administration Act.

The effective toxicity of a pesticide is usually described by the percentage reduction of numbers in a pest population. The most reliable figure is the amount of chemical formulation that will kill one-half of a test population. This value is called the LD₅₀, i.e. lethal dosage. In fish, the standard measurement of toxicity is the median tolerance limit following a 96-hr. exposure. This is symbolized 96-hr. TL_m which is roughly equivalent to the LD₅₀. The actual amounts of toxicants are normally as parts per million by weight or volume. Parts per billion (ppb) is the usual term in the analysis of aquatic environments where even the slightest traces of pesticides may have important biological effects. Acute toxicity is usually taken to mean immediate toxic reactions from a single exposure while chronic toxicity may appear either over or after a long period of time from single or continuous exposure.

There are many pesticides which are in common use. They can be classified into inorganics (arsenicals, mercurials, fluorides, borates), synthetic organics (chlorinated-hydrocarbons, organophosphates, thiocarbamates), and natural organics such as rotenone, pyrethrum and nicotine. According to their uses, they may be categorized as algicides, insecticides, ascaricides, fungicides, herbicides, etc. Common

examples are listed in Table 3.

Table 3. Commonly Used Pesticides (38)

Chemical group or action	Examples
Insecticides and Acaricides	
Inorganic	
Arsenicals	Lead arsenate
Copper-bearing	Copper sulfate
Organic, naturally occurring	
Nicotine alkaloids	Nicotine sulfate
Pyrethroids	Pyrethrum
Rotenoids	Rotenone
Organic, synthetic	
Chlorinated hydrocarbon compounds	Aldrin, benzene, hexachloride, DDD, DDT, endrin, heptachlor, methoxychlor, ovatran toxaphene
Organic phosphorus compounds	DDVP, malathion, parathion, Phosdrin, schradan, TEPP, Systox
Carbamates	Isodan, pyrolan, Sevin
Fungicides	
Mercurials	Mercuric chloride, "organics"
Dithiocarbamates	Nabam, ziram
Others	Captan
Herbicides	
Contact toxicity	Sodium arsenite, "oils"
Translocated (hormones)	2,4-D; 2,4,5-T, dalapon
Soil sterilants	Borates, chlorates
Soil fumigants	Methyl bromide, Vapam
Rodenticides (Mammal Poisons)	
Anticoagulants	Pival, warfarin
Immediate action	Endrin, phosphorus, sodium fluoroacetate ("1080"), strychnine, thallium
Other Vertebrate Targets	
Birds	Strychnine, TEPP
Fishes	Rotenone, toxaphene

Toxicities of these pesticides to non-target organisms are not always immediately evident, with several cases of poisoning being experienced before the dangers are fully recognized and effective counter measures implemented or enforced. Although many have been banned for use (e.g. DDT), they are still present due to storage and continuous use by some uninformed consumers.

2.2.2. Dieldrin (organochlorine)

Dieldrin is a white crystalline odourless solid with the elemental formula $C_{12}H_8Cl_6O$. Its common name, Dieldrin, is used rather than its long chemical name. It is stable to both acids and alkalis. To most insects, it is highly stomach toxic, but it is non-phytotoxic. Following are some of its effects on and toxicities to animals and aquatic life:

- LD₅₀ for rats 90 mg/Kg
 dogs 80 mg/Kg
- 96-hr. TL_m for most fishes such as gold fish,
 bluegills, trout, etc 10-50 µg/l
 striped Bass juvenile 2.5-29 µg/l
- Frogs: no effect when dosage is up to 5×10^{-4} M
 Mallard Ducks: 100 ppm causes egg shell thinning
- In Florida, 1117000 fish (20-30 tons) of 30
 species were killed when Dieldrin was applied to
 kill sand flies (1).

Since 1958, Dieldrin has been one of the most

commonly used pesticides. The U.S. National Food Regulation sets a tolerance level of 0.1 mg/l for Dieldrin in foods such as carrots, grapes, oats, potatoes, etc. Aly et al (1) found Dieldrin concentration ranged from 5 to 10 µg/Kg in surface sediments in Lake Michigan. Since many insects have acquired resistance to several insecticides, other measures such as improved sanitation may be more effective. Many non-target organisms such as marine organisms are extremely sensitive to minute amounts of insecticide. Delayed response in human beings may include risks of genetic defects. One report stated that chlorinated hydrocarbons, organophosphates and carbamates were able to disrupt DNA molecules and mutations might occur 40 generations later (38).

2.2.3. Aroclor 1254 (polychlorinated biphenyl)

Aroclor is the commercial name used in the United States. Aroclor 1254 is the most popular PCB used in industry for the production of electrical insulators, fire resistant materials, lubricants for high pressure and temperature use, paints, adhesives, waxes, etc. The last two digits in its name indicate the chlorine content of the compound, i.e. Aroclor 1254 contains up to 54% chlorine. It is a mobile, oily light-yellow liquid, inert, insoluble in water, but soluble in most organic solvents. It is non-flammable, non-drying, thermoplastic and it adheres strongly to smooth surfaces such as glass and metal.

It is quite toxic to liver cells. In the Hudson River (New York City), an average 15 mg/l concentration was found in the fish, but 350 mg/l was found in fish close to the outfall where electrical products manufacturing plants discharge their wastes (25). A 1 µg/Kg level was found in humans in 75% of the persons tested (26). A very recent publication in Japan (22) reviewed a detailed study on epidemiology, toxicology and pathology of PCB poisoning. The average levels found in air, water, soil and agricultural products, fish, birds and man are summarized in Table 4.

Table 4. PCB Levels in Japan

	PCB Level
Air (Electrical Appliance Factories)	12 µg/m ³
Water (Sewage Treatment Plants)	< 0.01 mg/l
Soil and Agricultural Products (Rice)	0.01-0.1 ppm in 20% of the samples
Fish (fresh edible parts)	> 1 ppm*
Birds (varies from specimen to specimen)	0.3-180 ppm
Man (fisherman, on fat basis)	7.5 µg/g

* in 16% of seawater samples and 18% of fresh water samples

The above concentrations are considerably higher than those measured in other places of the world. The principal target organs for PCB's in man appear to be the liver and skin. The LD₅₀ of Aroclor for rats is about 1-2.5 g/Kg. Highly chlorinated biphenyls seem to be less toxic than lower

chlorinated biphenyls. The reason for this may be accelerated intestinal absorption of low chlorinated biphenyls due to their greater solubility in water.

The feeding of Aroclor 1254 at 100 mg/Kg to dogs led to liver hypertrophy. Porphyria was observed in rats at a feed rate of 100 mg/Kg. Significantly higher mortality occurred in birds fed with 25-100 mg/Kg of Aroclor 1254, but no difference was noted at different dose levels. Also, with Aroclor 1254, there were reductions in number of offspring in rats and increase in the number of stillbirths at the 100 mg/Kg level. No effect was observed at 1 or 10 mg/Kg.

Similar to various chlorinated organic pesticides, PCBs are known to induce drug-metabolizing enzymes in the liver at a possible level of 20 mg/Kg in human tissues. Symptoms include increase discharge from the eye, swelling of the limbs, pigmentation of nails and lips, swelling of the eyelids, nausea and vomiting. In 1968, over 1000 persons in southwest Japan were affected by PCB poisoning. Up to September 1973, a total of 22 deaths had occurred among the patients. Although the potential interactions of low levels of PCB's and physiological functions in adult man remain uncertain, PCB's ubiquitous nature is obvious and they are surely very dangerous pollutants with regard to human health.

2.2.4. Dichlorvos (organophosphate)

Inorganic pesticides are toxic to plants, insects

and human beings, so they are rarely used today. Natural organic pesticides are in limited supply and are not in general use. Present trends seem to lean toward organochlorine pesticides and organophosphorus compounds. Of these two, preference favours the use of organophosphorus compounds as they degrade fairly rapidly. However, the acute toxicity of organophosphates is still a matter of some concern.

In Houston, August 6, 1977 (New York Times) there was a report on labourers working with leptophos (which is an organophosphate pesticide, brand name: phosvelat) in Velsicol Chemical Corporation. Exposure to the chemical led to nervous disorder and even partial paralysis (62). General symptoms of organophosphate poisoning are uncontrollable vomiting, nervous disorders and partial paralysis.

Dichlorvos, whose chemical name is 2,2-dichlorovinyl-dimethylphosphate, is a colourless to amber liquid with an aromatic odour and an elemental formula $C_4H_7Cl_2O_4P$. It is soluble in water up to 1% at room temperature, stable to heat, but hydrolyzes on exposure to air and does so rapidly at high pH. It is used as a stomach and contact insecticide with fumigant and penetrant action against diptera and mosquitoes. Toxicity levels are listed as follows:

- LD ₅₀ for rats	75-80 mg/Kg
bluegills	1000 mg/l (24 hr exposure)
- Striped Bass juvenile	100-140 µg/l (96 hr. TL _m)

Mammalian toxicity of organophosphate pesticides is due to phosphorylation of acetylcholinesterase (which is one of the enzymes related to nervous functions). However, Dichlorvos does not inhibit cholinesterase and is not toxic to phytoplankton.

2.2.5. Pentachlorophenol

Pentachlorophenol has a number of applications in industry and agriculture such as a fungicide and bactericide in cellulosic products, starches, and adhesives; in food processing to control mold and slime; in lumber industry to control mold and termite infestation; etc. It is a white solid with needle-like crystals, practically insoluble in water, stable to heat, nonflammable, non-corrosive to metals, but deteriorates rubber materials. With an elemental formula of C_6HCl_5O , it is a very toxic chemical, especially to phytoplankton. Toxicity levels and toxic effects are as follows:

(5)

- Lethal dose to man 18 gm/70 Kg
- Contact with more than 1% concentration produces dermatitis
- Maximum tolerated concentration of its sodium salt, sodium phenate to 19 different species of fish:
0.2-0.6 ppm
- LD_{50} for rats 78 mg/Kg
- 10 ppm level is lethal to 90% of snails

2.3. Sampling Procedure and Sample Storage

PPE and raw sewage were collected at Annacis Island Sewage Treatment Plant as samples for this research. PPE was obtained by sampling the overflow at the discharge end of the primary sedimentation basin using a plastic bucket on a rope. The samples was then poured into a plastic container and stoppered. Generally speaking, plastic containers should not be used for collecting samples in which trace organics such as organochlorine pesticides and PCBs are to be detected, as they are easily adsorbed onto the plastic walls. They were used in this instance because trace organics would be spiked in the samples before coagulation. A sample of about 5 gallons was obtained each week - this was usually adequate for one week of testing. Raw sewage was obtained at the sewer entrance to the treatment plant prior to the comminutors.

In order to eliminate dilution effects caused by stormwater flows, no sampling was done within eight hours of the completion of a rain storm within the sewer catchment area. This precaution is deemed necessary because Vancouver is a high-rainfall area and a large part of the sewage collection system is comprised of combined sewers. Dilution would lower the alkalinity concentration and incomplete precipitation of CaCO_3 might result.

All samples were transported to the laboratory and stored at 4°C within 2 hours of collection. Prior to the coagulation test, these samples were warmed to room temperature

(21°C) in a 35°C water bath - this usually took 45 minutes to 1 hour.

2.4. Coagulation Process Procedure

All the procedures were developed by Maclean (30). He used Rush's work (43) as a basis and investigated the time required for rapid mixing, flocculation, settling and pH stabilization; and also mixing speed; magnesium and lime addition; and alkalinity and initial concentration spike. The following procedures were exactly the same as those used in his research except that the PPE and raw sewage samples were spiked with trace organics instead of heavy metals. These procedures were quite close to the standard jar test procedures recommended (6,13).

The detailed test procedure consisted of the following steps:

- (1) For each test, a set of 7-600 ml samples were measured into 1 litre beakers using a 1 litre graduated cylinder. The samples were warmed to 20°C by placing them in the 35°C water bath for 45 minutes to 1 hour before they were poured into the beakers.

- (2) The samples were then spiked to the required initial trace organic concentrations using the prepared organic solutions.

- (3) For runs at elevated alkalinity, the samples were spiked with the alkalinity spike solution.

(4) One of the samples was set aside for initial trace organic concentration analysis.

(5) One of the samples was used to calculate the lime dosage. The sample was mixed at 100 rpm on a Phipps and Bird Laboratory stirrer and the pH was constantly monitored to pH 10.0, 10.7, or 11.4. The $\text{Ca}(\text{OH})_2$ requirement was calculated and five such doses were measured out.

(6) The five remaining samples were stirred on the laboratory stirrer at 100 rpm for 1 minute to disperse the trace organic and the alkalinity spike.

(7) With the stirrer off, the following conditions of the Mg^{2+} solution were pipetted into the samples: 0 ml, 0.5 ml, 1 ml, 2 ml and 3 ml. These additions correspond to 0, 8, 17, 33 and 50 mg/l Mg^{2+} respectively. (see Section 2.7 for details).

(8) The samples were stirred for 1 minute at 100 rpm and then the $\text{Ca}(\text{OH})_2$ addition was made.

(9) The samples were then given a 15 minute rapid mix (for pH stabilization), a 10 minute flocculation and a 30 minute settling period.

(10) After settlement, 200 ml of supernatant were drawn off when individual trace organics were tested alone. Two portions of 200 ml (i.e. 400 ml) of supernatant were drawn off when mixed trace organics were tested together - one portion for the detection of Dieldrin, Arclor 1254 and Dichlorvos and the other portion for PCP detection.

(11) The trace organic analyses were performed by Gas Liquid Chromatography as described in the following sections.

(12) The trace organic percent removals were calculated using the following formula:

$$\frac{\text{Initial Concentration} - \text{Final Concentration}}{\text{Initial Concentration}} \times 100$$

- Note: (a) All handling apparatus such as beakers, cylinders, pipettes, etc were glass. Such a procedure was necessary for organochlorine pesticide and PCB detection for minimizing their loss due to adsorption to container walls. See Appendix A for more detailed information which was obtained in the preliminary study.
- (b) Initial concentration spike, alkalinity spike and Mg^{2+} addition were accomplished without increasing the total volume by more than 1%, in order to minimize dilution error.

2.5. Detection of Dieldrin, Aroclor 1254, Dichlorvos

Gas Chromatography is the recommended method for analyzing pesticides and PCBs to achieve a reasonable determination time, good reproduction of results, wide range of sensitivity and reasonable cost. However, much effort is required to calibrate the results, select the correct liquid

phase, prepare the liquid phase, pack the column, choose the detector, optimize the conditions and operate the instrument properly. The theory and practice of gas chromatography are not simple or easy to understand and often skilled technicians have to be employed for such analyses.

Hext (21) did a very extensive study of detection of Dieldrin using a DC-11 column and a Hewlett-Packard 5750 Gas Chromatograph. Discussions of the following were contained in his report: stationary phase; purge flow; syringe injection; column specifications and efficiency; temperature of injection port, column, and detector; theory of electron capture detector operation; area calibration; sensitivity; optimum operating conditions; linear range; pulse interval and septum usage. The Provincial Water Quality Laboratory (34) has an internal publication on organochlorine pesticide and PCB detection. It contains information on sampling techniques, detection procedure, florisil column separation of some pesticides from PCBs, chemical requirements and glassware cleaning steps. Lee et al (24-27) did a very extensive study on PCBs in rivers and other natural water systems, treatment plant effluents and fish in the Milwaukee Region (Lake Michigan). According to this literature, some other references (14, 39, 42) and the Journal of Water Pollution Federation 1975, 1976 literature reviews, Gas Liquid Chromatography with electron capture detection is the most suitable device for detecting low concentrations of organochlorine pesticides and PCBs.

A preliminary study (details given in Appendix A) was carried out with a DC-11 column to determine optimum operating conditions, linear range, injection precision, purity of chemicals and solvents, cleanliness of apparatus, standards preparation and storage, extraction volume, concentration techniques and florisil column separation. Subsequent to this preliminary work, an OV-101 column * was installed, preconditioned and a leakage test was carried out. Also, detector cleanliness was checked by measuring the standing current. Detection procedure, gas liquid chromatography conditions and florisil column separation techniques used in this research are given below:

(1) Detection Procedure:

- (a) 6-200 ml samples (clarified supernatant) were poured into 6-250 ml separating funnels. Each was shaken

* DC-11 column was used for preliminary study because OV-101 column was not available at that time. Actually, according to McReynolds' constant (35), there is not much difference between the two columns except OV-101 selectively retards electron attractors such as alcohols, nitriles, acids, etc for longer periods. However, OV-101 seemed to be a more suitable column for PCB detection and this was the chief reason why it was finally chosen for the research.

vigorously with 2 portions of 25 ml hexane each for 1 minute. There was some emulsion formed but it was not significant (only 1-2% of the total volume). The concentrated extract was injected into the column for detection when Dieldrin, Aroclor 1254 and Dichlorvos were detected individually. One aliquot of the concentrated extract was directly injected for Dichlorvos quantification, another aliquot of the mixture was taken when these three were mixed together and Dieldrin and Aroclor 1254 were separated by the florisil column, then injected individually for quantification.

(b) All glassware was specially cleansed. It was flushed with solvents such as alcohol or hexane, washed with heavy-duty soap, flushed with hot water and then distilled water.

(c) Solvents such as petroleum ether, hexane and alcohol were either reagent grade or technical grade. Anhydrous sodium sulphate used for drying purposes was nearly 100% pure and never gave any base line interference in the detection.

(2) Gas Liquid Chromatography Conditions

Table 5. Conditions of GC Operations for Dieldrin, Aroclor 1254 and Dichlorvos.

	Dieldrin	Aroclor 1254	Dichlorvos [†]
Column	3% OV-101, 6' x 1/4" 80/1000 mesh on HP Chromo sorb W		
Rotameter Setting	3.2, i.e. carrier flow rate at 60 ml/min		
Purge gas flow	none		
Pulse interval	150 µsecs		
Temperature program	Isothermal		
Carrier gas inlet pressure	Argon with 5% methane at 40 psi		
Detector	Electron Capture - Ni ⁶³ cell		
Recorder chart speed	0.25 inches/min or 0.5 cm/min		
Range	10		
Attenuation	64	32	64
Detector temp.	230°C	230°C	225°C
Injection port temp	230°C	230°C	220°C
Lowest detection limit	0.05 ng	0.5 ng	0.5 ng
linear range	0.05-0.5 ng	0.5-2.5 ng	0.5-2.5 ng *
Retention time	6.45 min	14 main ° peaks in 16 min	1.21 min

- † Dichlorvos is a more polar compound than Dieldrin and Aroclor 1254. At the conditions where Dieldrin and Aroclor 1254 are detected, Dichlorvos comes out together with the solvent which makes quantification impossible. The column temperature was therefore lowered to separate Dichlorvos from the solvent. This procedure makes separate quantification of Dichlorvos easily achieved during the mixed trials.
- ‡ There were two recorders used in recording the peak areas. The first one was a normal built-in recorder which just recorded peak height and area. With this recorder, the chart speed was set at 0.25 inches/minute. The second recorder was a computer-integrator-recorder which could be connected with a cable to the detector. It possesses separate attenuation and range switches, can record the area and retention time, can calculate the area percentage and it can be set to calibrate the results. It was installed after this research began, so it was used in the later part of the work. With this computer-recorder, the chart speed was set at 0.5 cm/min.
- * The volume of injection was either 2 μ l or 10 μ l. For example, when Dieldrin was detected alone, the concentrated extract of the initial sample was 1000 μ g/l (4 times concentration from 250 μ g/l in 200 ml sample to 1000 μ g/l in 50 ml extract - 2 portions of 25 ml). It was diluted 5 times and 2 μ l was injected to give a total mass of 0.4

nanogram (ng) which was in the linear range. When PCB was detected alone, 2 μ l of the concentrated extract was injected directly to give a total mass of 2 ng whereas 10 μ l of the separated fraction from the florisil column had to be injected to give the same total mass. With this technique and extrapolation on the standardization curve, concentrations as low as 25 μ g/l can be detected, (i.e 90% removal at an initial concentration of 250 μ g/l).

- o PCBs are not simple compounds. Aroclor usually consists of over 10 peaks that can be easily identified on the chromatograms. Aroclor 1254 has 14 main peaks, the first of which appears after 1.5 minute, and the last appears after 15 minutes.

Therefore the presence of PCB will not affect Dichlorvos quantification from the combined aliquot, but it must be separated from Diêldrin on the florisil column as the latter has a retention time of 6.45 minutes, which is within the time range for PCB peak appearances.

(3) Florisil Column Separation Technique

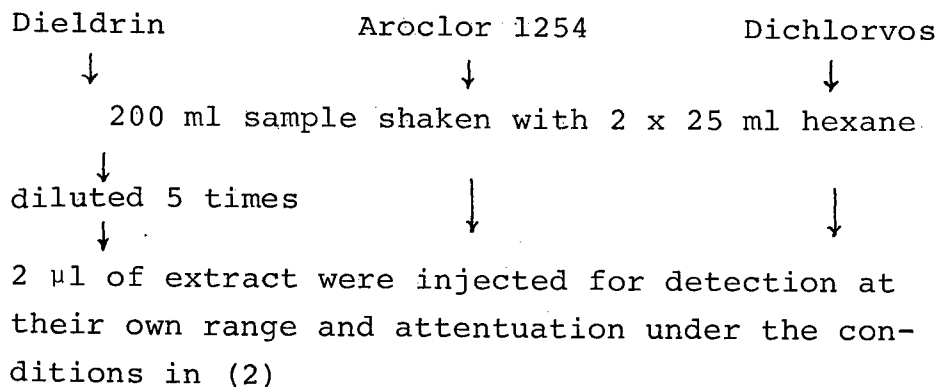
- (a) The florisil column was made by using a 15 mm internal diameter burette packed with glass wool at the bottom as a support for the florisil. Too little glass wool would lead to leakage of florisil and plug up the column. On the other hand, too much glass wool would make elution rate so slow that it would take a very

long time to complete elution and could lead to serious solvent evaporation loss, (i.e. there might be loss of materials to be detected and in any case evaporation loss would have to be accounted for in concentration calculations).

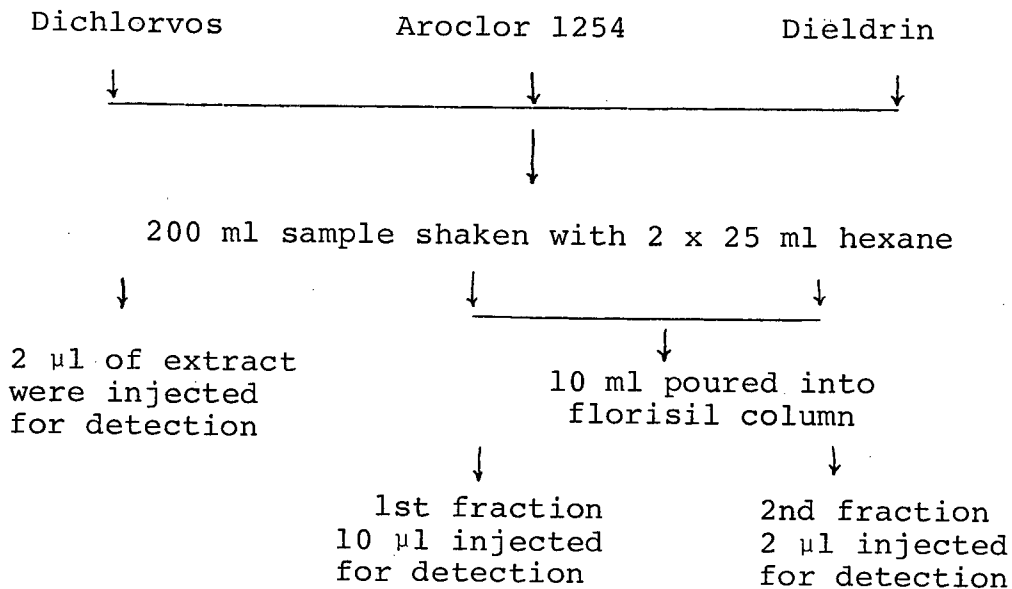
- (b) A 2 gm portion of anhydrous Na_2SO_4 was placed above and below 6 gm of 60-100 mesh florisil to prevent deactivation of the column by moisture and channelization in the florisil portion. After each sample run, the florisil and anhydrous Na_2SO_4 were completely replaced and repacked with new, dry material to avoid contamination.
- (c) After packing, the column was prewetted with 50 ml of hexane. Then 10 ml of the extract in the mixed trial samples were poured into the florisil column. Fifty ml of petroleum ether was applied to elute Aroclor 1254 out. Then 50 ml of 15% ethyl ether in petroleum ether was added to elute Dieldrin. The eluted solutions were injected for quantitative and qualitative analysis. The elution rate was adjusted to 3-6 ml/min. Under these conditions, complete separation was achieved and over 99% of both Aroclor 1254 and Dieldrin were recovered in the eluted portions.

A summary of the detection procedures is given below:

(i) Detection of individual impurities



(ii) Detection of combined impurities



2.6. Detection of Pentachlorophenol

Pentachlorophenol could not be directly chromatographed on the OV-101 column because of its high polarity and low volatility (b.p. 310°C). So other detection methods were investigated. Table 6 summarizes the results of the investigation, with method number 7 being chosen for the following reasons:

- (1) it is widely used in samples like sewage effluents, very dirty industrial waters and interferences can be avoided by this method.
- (2) it is simple, rapid and reproducible once the conditions are kept within a certain range.
- (3) it is a well documented method with available detailed information and it can be used down to very low detection limits, probably down to 1 µg/l or even lower depending on the size of the sample.

Table 6. Comparison of Different Methods for the Detection of Pentachlorophenol.

<u>Method</u>	<u>Comment</u>
(1) Titration with standard alkalis	(a) interference by other phenols (b) cannot be detected down to $\mu\text{g/l}$ level (58)
* (2) Colour development with phenazone, using ammonium persulphate as oxidizing agent	Used for 5 ml samples with the lowest detection limit at 6 mg/l. Specific for 2,3,5,6-tetrachlorophenol and pentachlorophenol detection in air (4)
* (3) Safranin-0 method	Too much background interference in sewage samples (32)
(4) Methylene Blue method	Interference from the presence of iron. (Annacis Island Sewage Treatment Plant has 1.5-2.0 mg/l of iron in its sewage) (52)
(5) Precipitate with CuSO_4	Interference from the phenols
(6) Infrared Spectroscopy	Detection limit, interference and detailed information are not available (59)
(7) Gas Chromatography	Advantages are listed as in Section 2.6. (59,23)

* These were tried several times without success.

Detection procedure, gas chromatography conditions, derivatization method and concentration technique are presented below.

- (l) Detection Procedure
- (a) 200 ml sample (clarified supernatant) was acidified with 6N-HCl to pH 2.
- (b) Extracted with 2 x 40 ml of CH_2Cl_2 (methylene chloride).
- (c) Extracts were combined, reextracted with 2 x 40 ml of 1N-NaOH and 20 ml of water.
- (d) Extracts were combined, acidified with 6N-HCl and re-extracted again with 2 x 40 ml of CH_2Cl_2 .
- (e) Extracts were combined, washed with water and drawn through filter funnel with anhydrous Na_2SO_4 on top of filter paper.
- (f) Filtrate was evaporated in rotary evaporator at room temperature (21°C) down to 2-5 ml.
- (g) Sample was derivatized for 7 minutes and covered for an hour for complete reaction in the fume cupboard.
- (h) Then sample was left uncovered overnight for evaporation to dryness.
- (i) Hexane was added to dissolve the residue and diluted to 200 times for detection.
- (j) 2 μl was injected for detection using gas liquid chromatography with electron capture detector and 3% OV-210 column.

(2) Gas Liquid Chromatography Conditions

Table 7. Conditions of GC Operation for PCP

Column	3% OV-210, 1.3m x 4 mm, 80/100 mesh on HP Chromo- sorb W
Carrier gas flowrate	50 ml/min
Purge gas flow	None
Temperature program	Isothermal
Carrier gas Inlet pressure	Argon with 5% methane at 40 psi.
Detector	Electron Capture - Ni ⁶³ cell
Recorder chart speed	0.25 inches/min.
Range	10
Attenuation	64
Detector Temperature	205°C
Injection port temperature	220°C
Column temperature	125°C
Lowest detection limit	0.05 ng
linear range	0.05-0.5 ng
Retention time	4.4 min
Pulse interval	150 µsecs

(3) Derivatization Method

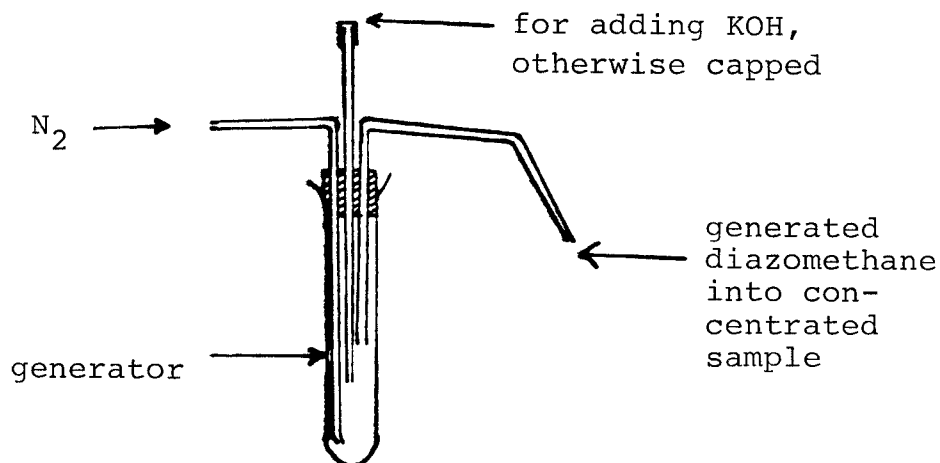


Figure 1 Diagram of the derivatization apparatus

- (a) 2 ml of ethyl ether was poured into the reaction vessel (see figure 1) then 2 ml of Carbitol (2 - (2-ethoxyethoxy) ethanol) was added. 190-200 mg of Diazald (N - methyl - N - nitroso - p - toluenesulphonamide) was weighed, added to the test tube and rinsed down with 3 ml of ethyl ether.
- (b) The test tube was stoppered and nitrogen was passed through for 30 sec. Then 1 ml of 60% KOH was added through the capped tube.
- (c) Nitrogen was added again at 1-3 bubbles/sec to a blank (pure CH_2Cl_2) until a yellow colour developed showing that diazomethane was present.

- (d) Then the samples were treated for 7 minutes one after another and left covered with a glass beaker to allow complete derivatization.

- Note:
1. Fresh KOH has to be used. It is recommended that it should be prepared within 12 hours of the derivatization.
 2. Amount of diazald added, bubbling rate of N_2 and generation time all have to be controlled in order to produce reproducible peaks. Incomplete derivatization or break down of the product leading to smaller peaks will result from variation of either one of the above conditions. See Appendix A for more detailed information.
 3. Solvent blank is used at the beginning and end of generation to check if excess diazomethane is present. A one hour reaction time to allow complete derivatization is also a required condition (23).
 4. After derivatization of the last sample, several mls of 10% acetic acid in ethyl ether should be added to stop the generation of diazomethane.

Furthermore, the toxic and potential explosive hazards of the diazolkanes warrant repeating the precautionary measures outlined by Bevenne (5) as follows:

1. Avoid breathing the vapors.
2. Use only in a well ventilated hood.
3. Use a safety screen.
4. Do not pipette the solution by mouth.
5. Avoid contact with the skin.
6. Do not heat solutions to 100°C (explosions).
7. Avoid use of rough or chipped glass (explosions).
8. Store solutions of the gas at low temperatures (freezer compartment of explosion-proof refrigerator).
9. Ground glass apparatus, glass stirrers, sleeve bearings where grinding may occur, should be avoided (explosions).
10. Keep solutions away from alkali metals (explosions).
11. Solid materials, such as copper powder, calcium chloride, boiling stones, etc., cause solutions of diazomethane to decompose rapidly; solid polymethylene and nitrogen gas are formed.

(4) Concentration Technique

The rotary evaporator is a simple device to allow quick evaporation of solvents under vacuum at temperatures much lower than their boiling points. The chief purpose is to prevent loss of materials in the solvents during evaporation which adversely affects quantitative analysis. For evaporating an 80 ml sample to 2-5 ml took about 15 min; this would be quite fast in comparison to evaporation at room

temperature without the evaporator.

2.7. Preparation of Chemicals

2.7.1. Organic Spike Solutions

The sewage samples only contain trace amounts of the several parameters chosen. In order to allow a meaningful comparison on the removal efficiencies, the samples were spiked with stock solutions of the chosen organics. Dieldrin, Aroclor 1254, Dichlorvos and Pentachlorophenol were obtained from the Pesticide Laboratory in the Provincial Department of Environment. Dieldrin had 15% impurities while Dichlorvos had 7%, but these would not interfere with either qualitative or quantitative analysis. The original compounds were weighed on a Mettler H54 balance (which was sensitive to 10^{-2} mg) and diluted with alcohol to prepare both 30 mg/l and 75 mg/l stock solutions. The reason for using alcohol was that it is soluble in the sewage samples and it is efficient for dissolving organic compounds. For a 250 μ g/l spike, 2 ml of the 75 mg/l stock solution were added to a 600 ml sample while 1 ml of the 30 mg/l stock solution was added for a 50 μ g/l spike. The stock solutions were checked by dilution with hexane followed by comparison with the standards. For each experiment, a spike sewage sample was analyzed to obtain an exact organic concentration. Recovery efficiency found in the preliminary study varied from 85.5% to 96.8%.

2.7.2. Lime

Maclean (30) found that dry reagent grade Ca(OH)_2 was better than 10 weight percent slurry in distilled water with respect to reproducibility. Therefore, lime was added in the powdered form after being weighed accurately on a Sartorius Model 2442 balance. The pH was measured on an Accumet Model 810 pH meter which was standardized at pH 10 before use.

2.7.3. Magnesium

A 10^4 mg/l Mg^{2+} solution was prepared from reagent grade $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ by weighing 1 gm on the balance and dissolving it in 100 ml of distilled water in a volumetric flask.

2.7.4. Sodium Bicarbonate

A 10^4 mg/l of NaHCO_3 solution was prepared to increase the alkalinity from the normal 120-130 mg/l to approximately 200 mg/l as CaCO_3 for the elevated alkalinity runs.

2.8. Gas Chromatography Standards.

2.8.1. Dieldrin, Aroclor 1254, Dichlorvos

The standard solutions were made by weighing the organic compounds accurately on the balance and dissolving them in hexane to concentrations of 250 $\mu\text{g/l}$, 200 $\mu\text{g/l}$, 150 $\mu\text{g/l}$, 100 $\mu\text{g/l}$, 50 $\mu\text{g/l}$ and 25 $\mu\text{g/l}$.

2.8.2. Pentachlorophenol

The standards were obtained by spiking distilled water at levels of 25 $\mu\text{g/l}$ to 250 $\mu\text{g/l}$. These standards were subsequently prepared for analysis by the extraction and derivatization procedure described previously.

2.9. BOD Test, Dieldrin Recovery from Sludge, Elevated Alkalinity.

2.9.1. BOD Test

BOD tests were performed on PPE as described in Standard Methods (2). Two dilutions were used for each sample and two bottles were prepared for each dilution. The sample (clarified supernatant after settling) was adjusted to the correct pH range. As the resident bacteria might be affected during the pH adjustment, all bottles were subsequently seeded with raw sewage.

2.9.2. Dieldrin Recovery from Sludge

If removal is really due to entrapment and/or adsorption during coagulation, Dieldrin should be present in the sludge which settles to the bottom after treatment. So Dieldrin recovery from the sludge was performed to check if the removal was actually due to coagulation. A mass balance was done for the supernatant and the sludge. The supernatant was withdrawn carefully in order not to disturb the sludge. It was analyzed for Dieldrin concentration in the

same way as described previously. Then the sludge was filtered and shaken with 3 x 25 ml portions of hexane. The extracts were combined and injected for detection.

2.9.3. Elevated Alkalinity

Samples were spiked with sodium bicarbonate solutions to an elevated alkalinity of approximately 200 mg/l as CaCO_3 . Alkalinity was measured by potentiometric titration method as described in Standard Methods (2).

CHAPTER 3

RESULTS AND DISCUSSIONS

3.1. The Removal Efficiency of Individual Organics from Prechlorinated Primary Effluent (PPE)

3.1.1. Dieldrin

Tables of experimental results are included in Appendix G. Figure G-1 shows the standardization curve of chromatogram peak areas at various Dieldrin doses. The chromatograms of the standards are shown in Appendix E. Figure 2 shows the percent removal at initial concentration of 250 $\mu\text{g/l}$ and 50 $\mu\text{g/l}$.

Five of the six initial concentration samples showed over 80% extraction efficiency which indicates that addition of organics in an alcohol base was appropriate. The low measured Dieldrin concentration in all the 250 $\mu\text{g/l}$ samples at pH 11.4 seems to indicate that there were some reactions between the spiked organic and the impurities in the wastewater. The precise reason for the low recovery efficiency is unknown, although adsorption by the container is an unlikely cause, as explained in Appendix A. However, the treatment removal efficiencies calculated relative to the initial measured concentration at that pH were comparable with results obtained in the mixed runs.

At 250 $\mu\text{g/l}$ spike, not much variation appeared over different Mg^{2+} dosages at a given pH, but there was a marked

difference in removal efficiency between each different pH. There was 20% increase in removal from pH 10.0 to pH 10.7 and about 30% increase from pH 10.7 to pH 11.4. The main reason for the improved efficiency may be more complete entrapment of the organic in the settling flocs, in view of the very clear supernatant that was noted at the highest pH. Also, a very dense layer of sludge was obtained. Removal efficiency seemed to rise with increasing Mg^{2+} dosages at pH 10.7 and 11.4. A potential optimum dosage of lime and Mg^{2+} exists at pH 10.7 and 8 mg/l of added Mg^{2+} , although not obvious with this information. It should also be remembered that the sewage had a natural Mg^{2+} content of about 8.5 mg/l.

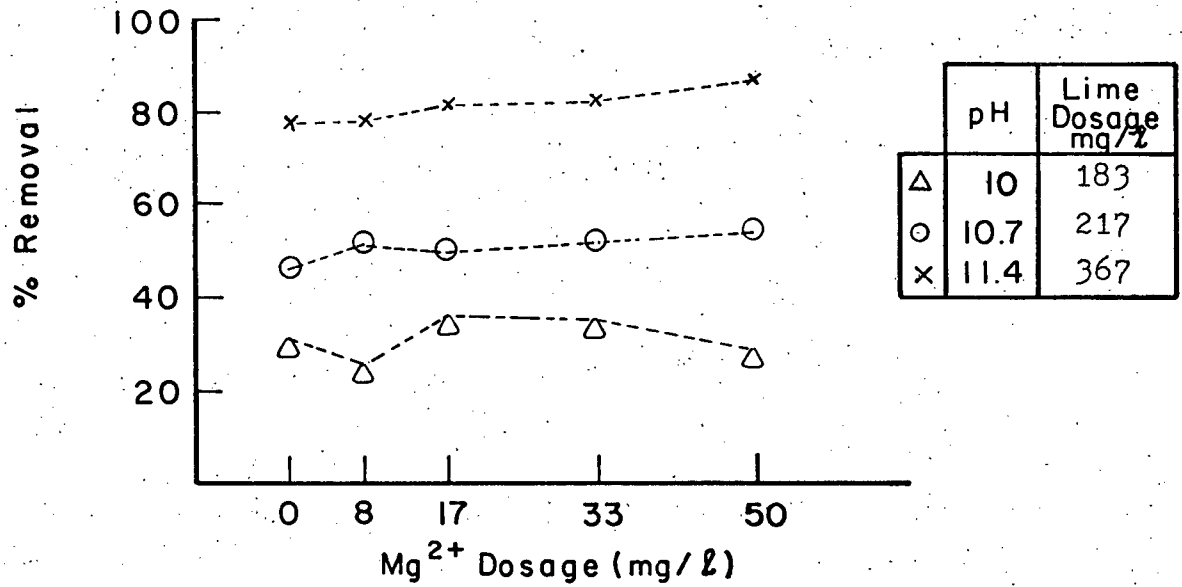
At 50 μ g/l spike, removal efficiencies at pH 10.0 and 10.7 were much lower than those at the 250 μ g/l spike. A logical explanation might be that the degree of adsorption on the settling flocs was decreased due to low initial concentration. At pH 11.4, removal efficiencies were comparable with the 250 μ g/l level and the trend over the different Mg^{2+} dosages was approximately the same. It would be important to compare the difference in the lime dosages required to achieve the same pH in the two different initial concentration. The change in buffering capacity of the wastewater samples was chiefly due to variation in flow and dilution by storm runoff. At pH 11.4, a very clear supernatant was obtained in all the runs in this research. However, there was a Brownish-yellow colour imparted by the ferrous and ferric ions

present in the wastewater (average total iron concentration: 1.6 mg/l) when the pH was raised. For pH 10.0 and 10.7, the final clarity varied between different samples even at the same pH. The more complete removal of suspended solids at pH 11.4 would be expected to provide a high removal of Dieldrin, independent of its initial concentration. This might be supported by the steep increase in removal efficiency at pH 10.7 as more precipitation of $\text{Mg}(\text{OH})_2$ occurred at higher Mg^{2+} dosages. The supernatant was clearer at higher Mg^{2+} dosages. At pH 10.0, the precipitation of $\text{Mg}(\text{OH})_2$ was so incomplete that there was not much difference in removal efficiency among the several Mg^{2+} dosages. The pH in the supernatant was also measured and there seemed to be no change before and after coagulation.

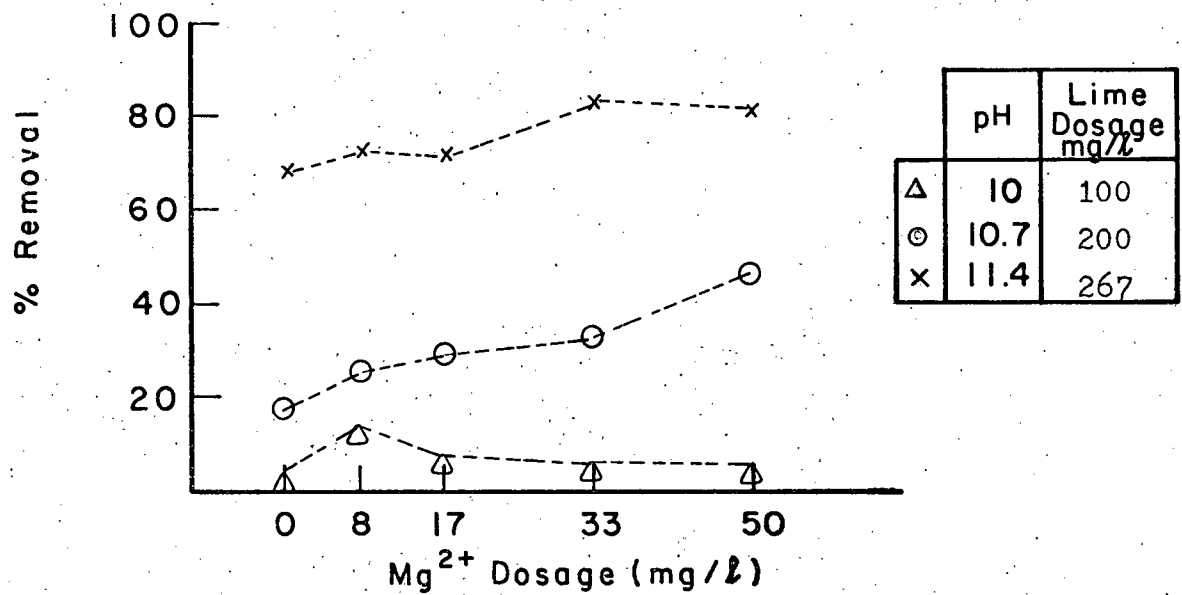
3.1.2. Aroclor 1254

Tables of experimental results are included in Appendix G. Figure G-1 shows the standardization curve for Aroclor 1254. The total area of all the peaks was used for standardization instead of using the area of a representative peak because no specific representative peak could be found. The area for any peak did not remain constant, but the total area did. The chromatograms of the standards are shown in Appendix E. Figure 3 shows the percent removal at initial concentration of 250 $\mu\text{g/l}$ and 50 $\mu\text{g/l}$.

The extraction efficiency was very high on all the



Dieldrin at 250 μ g/l



Dieldrin at 50 μ g/l

Figure 2 Percent Removal vs. Mg^{2+} Dosages

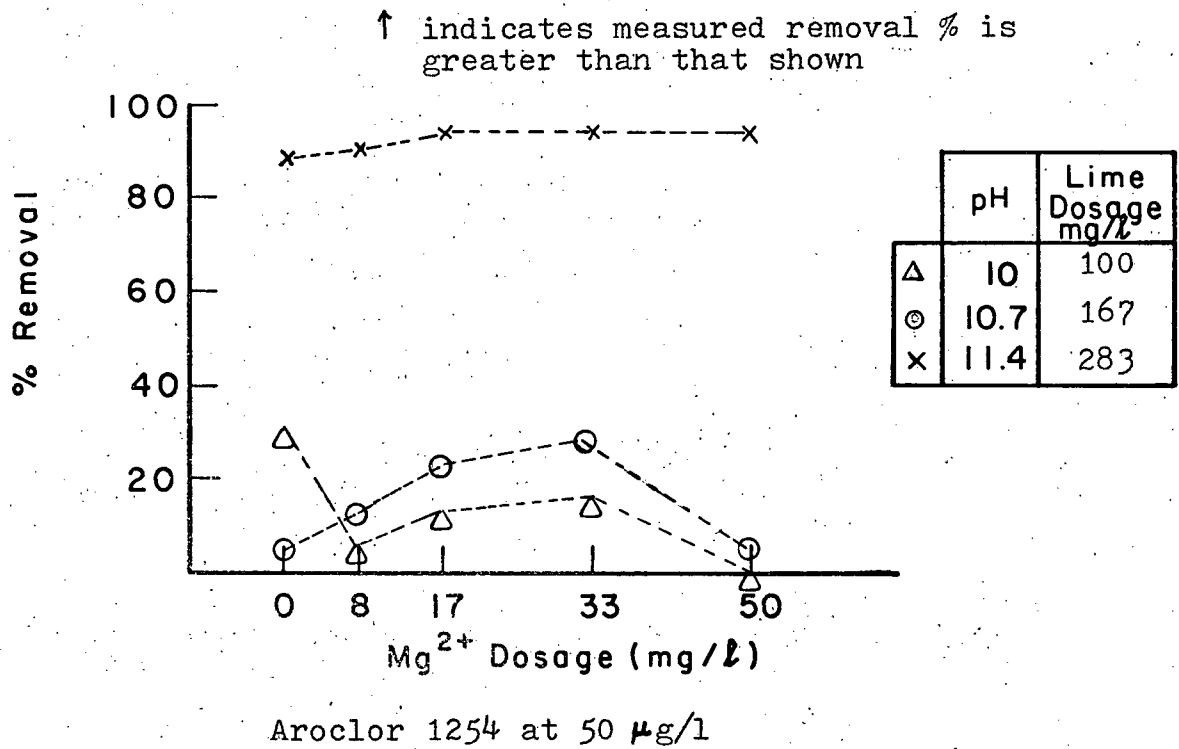
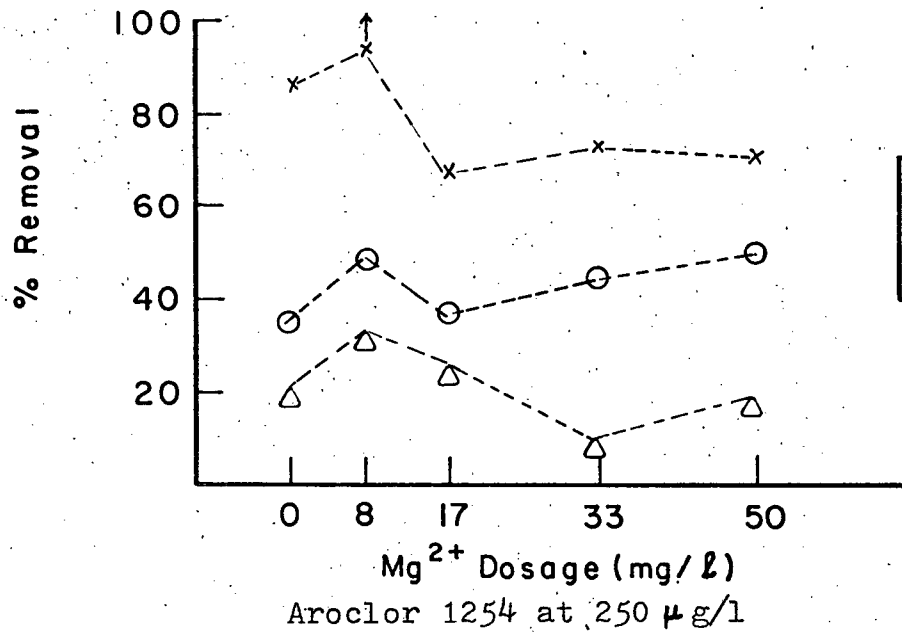


Figure 3 Percent Removal vs. Mg^{2+} Dosages

initial concentration samples, approaching 100% (see Tables G-3 and G4).. The many isomers of Aroclor 1254 may make it easier for adsorption onto the settling flocs and subject to more complete entrapment.

At 250 $\mu\text{g/l}$ spike, optimum dosage of Mg^{2+} occurred at 8 mg/l at all pH values tested. Increasing Mg^{2+} dosage even reduced removal although it seemed to rise again at the 50 mg/l level. The reason may be better settling of magnesium hydroxide precipitates which occurs at high Mg^{2+} dosage. The best settling characteristics (visually) were obtained at a dosage of 8 mg/l of Mg^{2+} at all the three pH values. This might account for the best PCB removal being obtained such a magnesium concentration. The increase in removal efficiency with increasing pH could obviously be due to more complete precipitation of $\text{Mg}(\text{OH})_2$ which enhanced adsorption and entrapment abilities.

At a 50 $\mu\text{g/l}$ spike, low removal was achieved at pH 10.0 and 10.7. The trends were not comparable with those at the 250 $\mu\text{g/l}$ level. The maximum occurred at 30 mg/l of Mg^{2+} at both pH 10.0 and 10.7. At pH 11.4, removal was high and was nearly constant irrespective of different Mg^{2+} dosages. The lime dosages required to achieve the different pH levels were approximately the same as those for Dieldrin.

3.1.3. Dichlorvos

The table of experimental results is included in

Appendix G. Figure G-2 shows the standardization curve with respect to peak height. There were two methods used to standardize Dichlorvos. Peak height was used with the recorder used during the early experimentation, while peak area was used with the second recorder because it could print out the area directly. The other standardization curve is given in Figure G-1. The chromatograms of the standards are shown in Appendix E. Figure 4 shows the percent removal at initial concentration of 250 µg/l.

Dichlorvos is fairly soluble in water. As a result, extraction efficiencies as low as 40% were obtained. The extraction efficiency was checked with a spike on distilled water and the results were the same as those on PPE; therefore the low extraction efficiency is not due to other factors such as adsorption, decomposition or reaction with impurities in the wastewater. However, Dichlorvos is not persistent in nature as Dieldrin or Aroclor 1254, because Dichlorvos is susceptible to hydrolysis. The half-life via hydrolysis in ethanol at pH 6.0 and temperature of 70°C was found to be 1.35 hr. Furthermore, the hydrolysis rate increases about 4 times with a 10°C temperature rise, and tenfold with each additional pH unit (17).

The hydrolysis rates of organophosphorus pesticides and their metabolites are of great importance because hydrolysis results in the detoxification of the pesticides; furthermore, the products of hydrolysis should be subject to

easier biodegradation. As recorded in the literature, Dichlorvos is hydrolysed in alkaline condition to dichloroacetaldehyde and dimethylphosphate (58). Further hydrolysis products are dichloroethanol, dichloroacetic acid and inorganic phosphate (47).

For Dichlorvos, alkaline hydrolysis could be regarded as one of the mechanisms of removal. From the results, the low removal at pH 10.0 might be due to the fairly soluble nature of Dichlorvos in water, with alkaline hydrolysis being slow at this pH. The great fluctuation in removal at pH 10.7 was difficult to explain, but more insights might be gained when compared to results in the mixed runs. The high removal at pH 11.4 was chiefly due to hydrolysis.

The hydrolysis rate was determined on a series of Dichlorvos spiked samples in distilled water with pH raised to 11.4 by NaOH. The samples were extracted at different intervals after spiking and detected for residue. The results and curves are shown in Figure 5. The half-life was found to be 28 minutes. It could be noticed that nearly 90% was hydrolysed after 1.5 hr. This was the time used in coagulation including adding chemicals, rapid mix, flocculation, settling, supernatant draw-off and extraction.

3.1.4. Pentachlorophenol

The table of experimental results is included in Appendix G. Figure G-1 shows the standardization curve. The

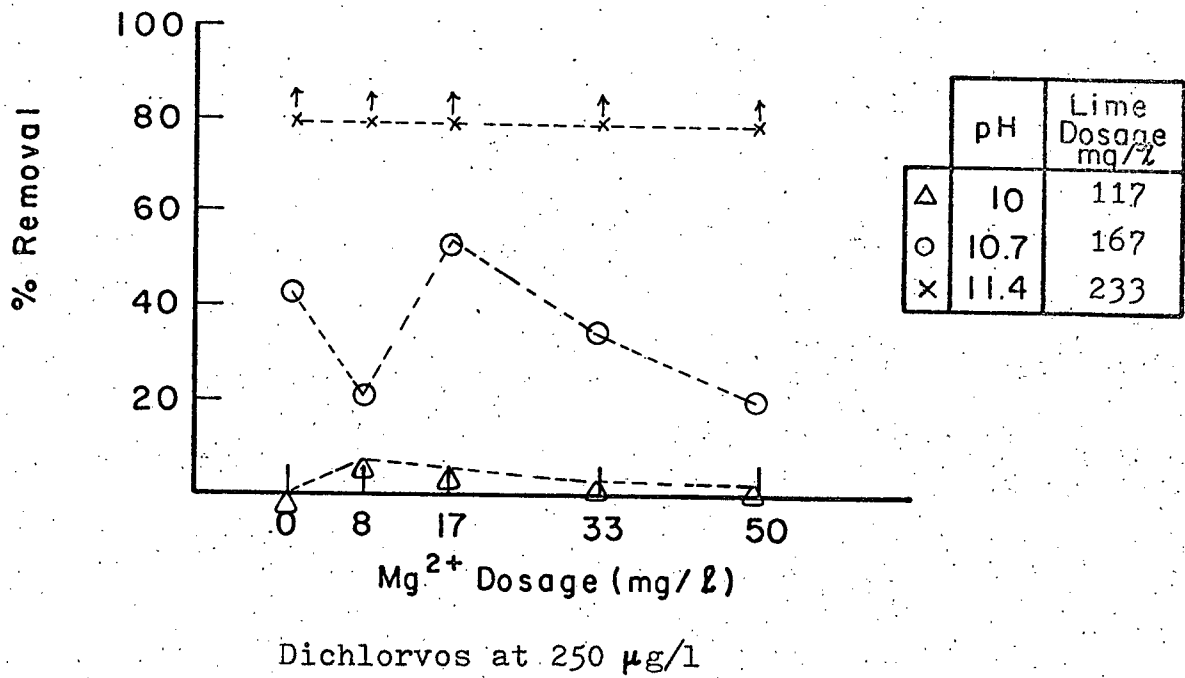


Figure 4 Percent Removal vs. Mg^{2+} Dosages

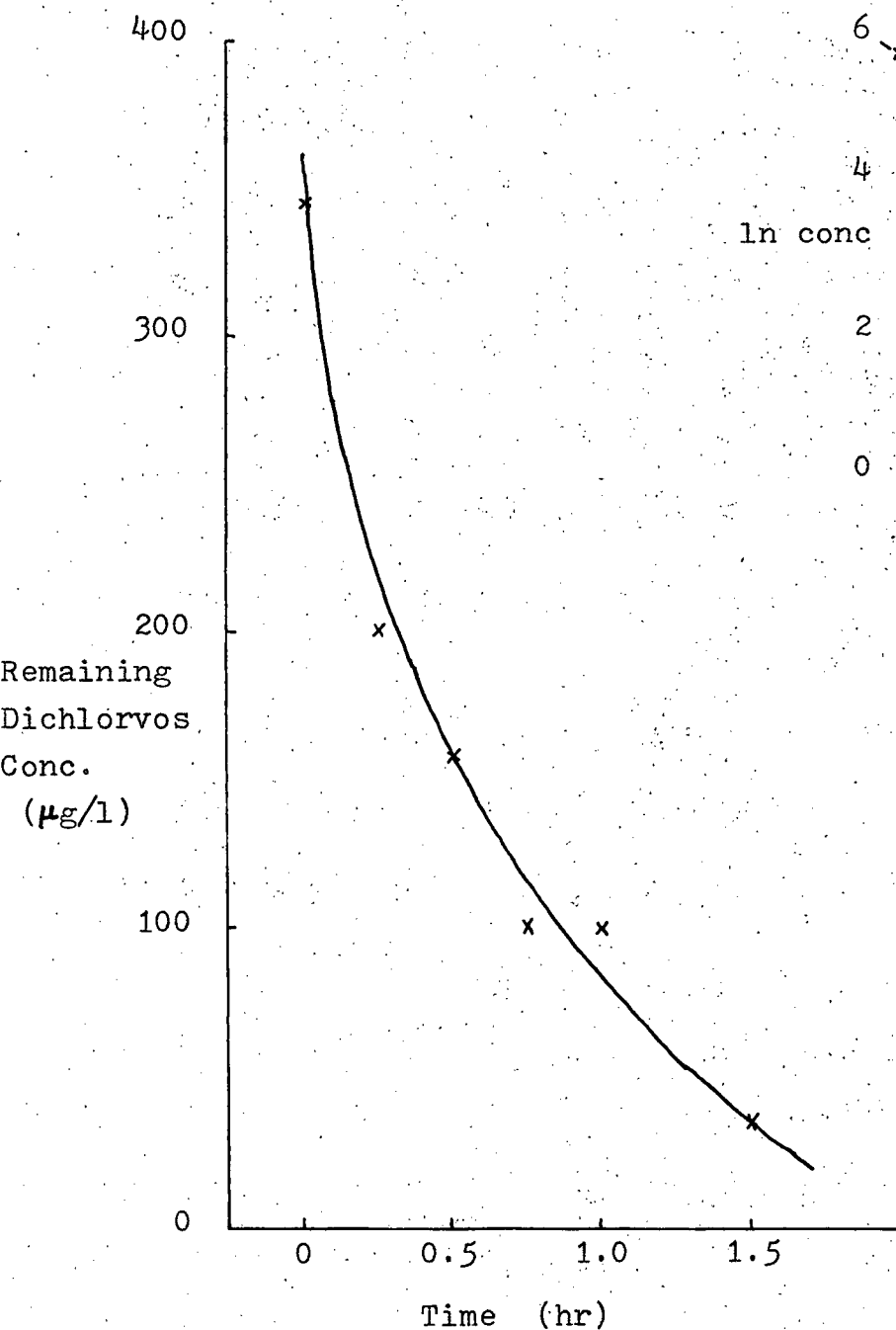


Figure 5a

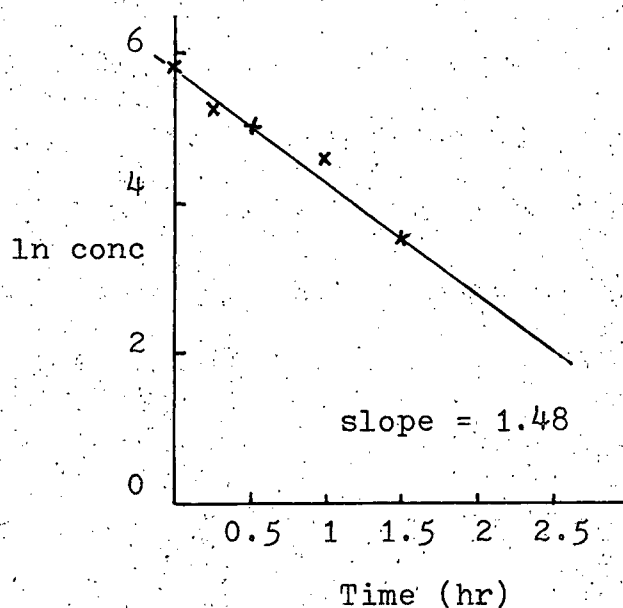


Figure 5b

Remaining Dichlorvos Conc. ($\mu\text{g/l}$)	Time from Start (hr)
345	0
200	0.25
157.5	0.5
100	0.75
100	1.0
35	1.5

Figure 5 Alkaline Hydrolysis of Dichlorvos

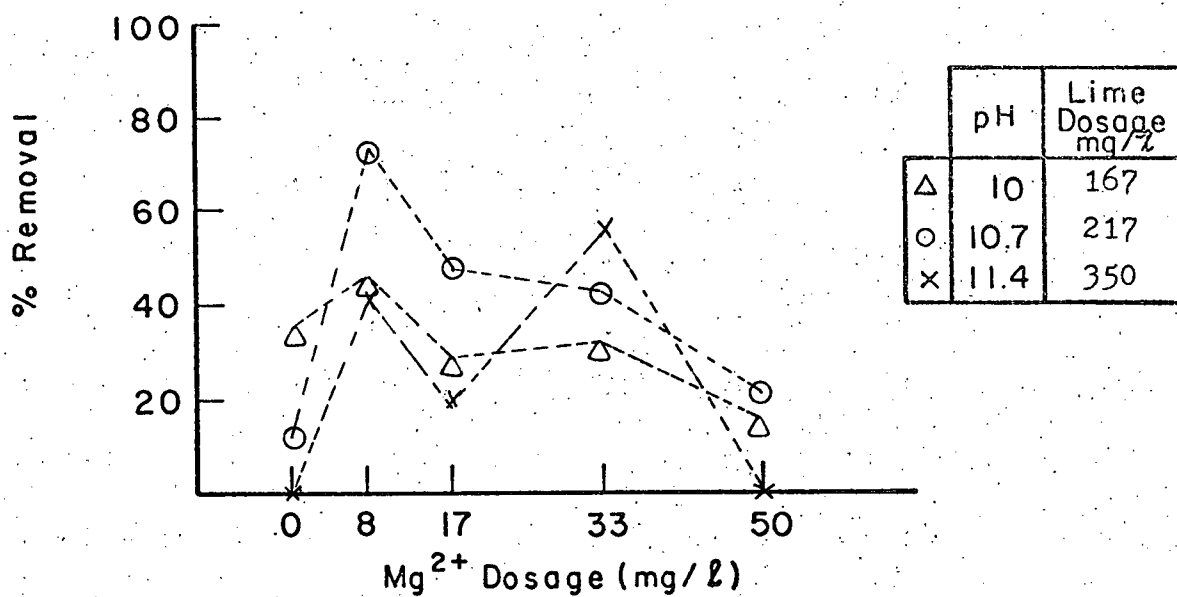
chromatograms of the standards are shown in Appendix E. Figure 5 shows the percent removal at initial concentration of 250 $\mu\text{g/l}$.

The derivatization process produced characteristic peak areas throughout the research. Although slight variations were noticed, they were not significant enough to cause concern about incomplete derivatization. The reasons for the relatively low peaks which were found at Ph 10.7 on Table G-6 are unknown; however, these did not affect the comparison of removal efficiencies.

Pentachlorophenol is slightly acidic. This causes the formation of calcium phenate during lime addition to raise the pH. The high solubility of the calcium salt makes removal efficiency unpredictable. Low removal would be expected and this phenomenon may be further illustrated by the BOD removal discussion on Section 3.6.

From Figure 6, two maximum removals are indicated at Mg^{2+} dosages of 8 mg/l and 33 mg/l respectively, at all pH values, with the maxima being very noticeable at pH 11.4. Increasing the pH did not necessarily enhance removal efficiency as occurred in the previous organic parameters. There was about 15% increase in removal efficiency from pH 10.0 to 10.7, but a 25% decrease from pH 10.7 to 11.4 except at 33 mg/l of Mg^{2+} . Two 0% removals appeared at pH 11.4 and more could be seen in the mixed runs.

These data indicate that the removal of pentachloro-



Pentachlorophenol at 250 µg/l

Figure 6 Percent Removal vs. Mg²⁺ Dosages

phenol is unpredictable because of the possible formation of highly soluble calcium salt.

3.2. The Removal Efficiency of Mixed Organics from PPE

Tables of experimental results are included in Appendix G. Figure 7 and 8 are results of the percent removal of each organic parameter in the mixed test in PPE. The initial concentration of each organic parameter was 250 µg/l. The recovery of Dieldrin and Aroclor 1254 in the initial concentration samples was low and irregular. The reasons are essentially unknown, but might be due to some reactions between the organics themselves. Such irregularity was not observed when the mixed trial was carried out with distilled water. The extract, the spike solutions and the fractions obtained after separation on the florisil column were carefully checked and there were no errors in method. Therefore an average mass of 0.35 ng of Dieldrin and 1.98 ng of Aroclor 1254 were used to calculate the removal efficiency. The lime dosages required to raise the pH were low in comparison with the individual runs which indicates that the sample was a dilute one, and hence had lower buffer capacity.

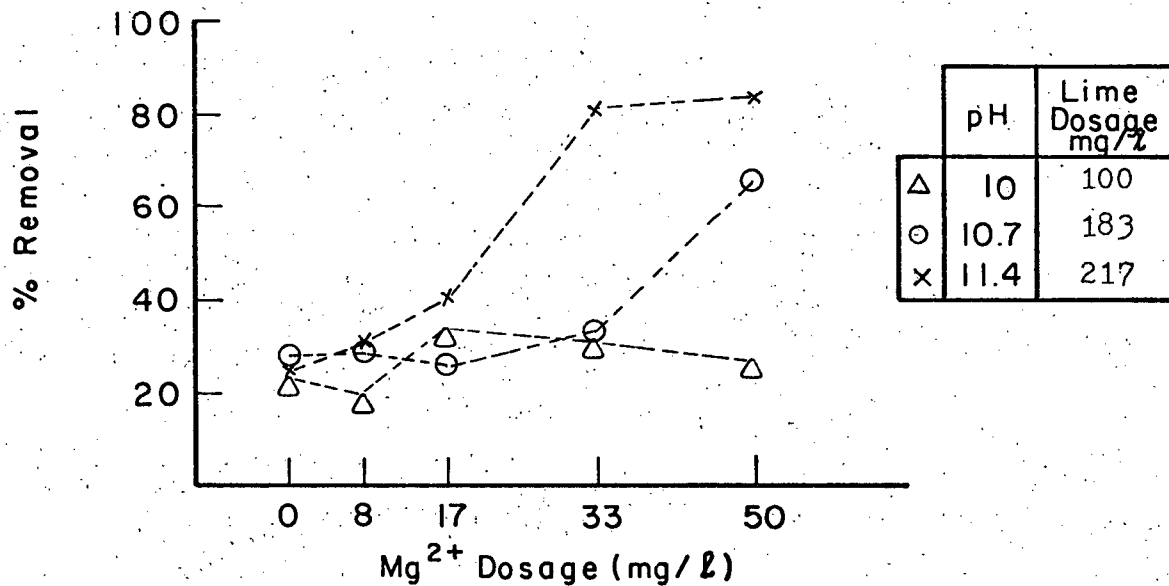
From Figure 7, the removal trends for Dieldrin and Aroclor 1254 over the different Mg^{2+} dosages at all the pH were very similar. This may be due to the chemical similarities of organochlorines and PCBs. Higher removal of Aroclor 1254 than Dieldrin may again be due to the existence of many

isomers, which are perhaps more easily adsorbed and entrapped. Both curves still showed that increasing pH enhanced removal, especially at higher Mg^{2+} dosages.

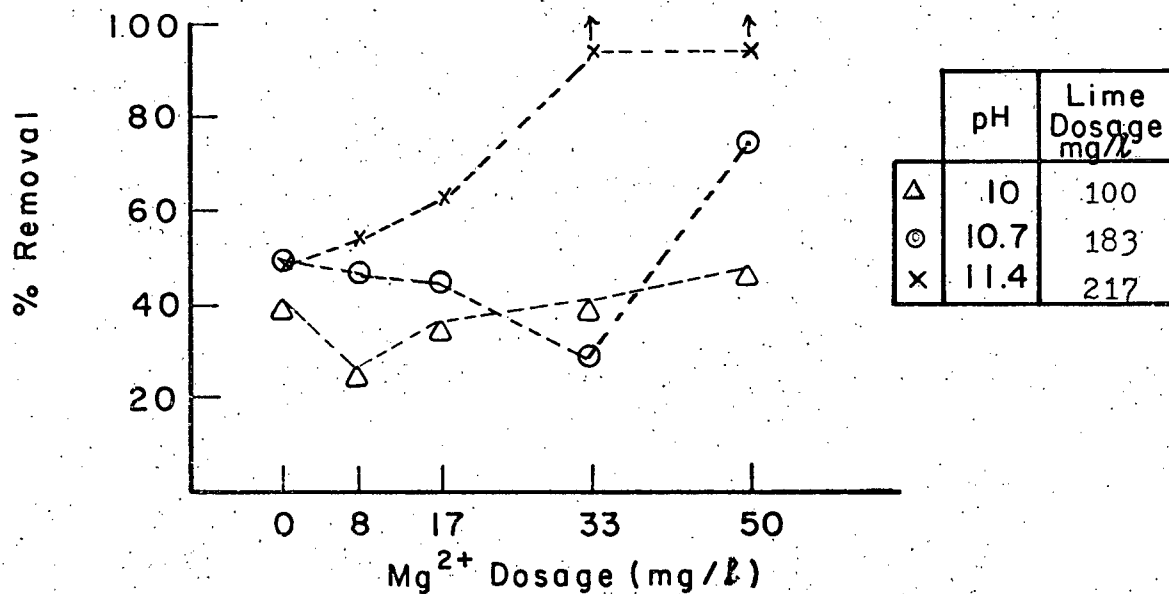
When compared to the individual runs, Dieldrin removals showed similar trends at pH 10.0 and 10.7 at various Mg^{2+} dosages (judged from the shapes of the curves) and at pH 11.4 with 33 mg/l and 50 mg/l of Mg^{2+} . The results for Aroclor 1254 were not comparable in the individual and mixed runs. Only at pH 10.7 at 8 mg/l of Mg^{2+} and pH 11.4 at 17 mg/l of Mg^{2+} were the removal efficiencies quite similar.

From Figure 8, the removal efficiency curves of Dichlorvos in the mixed runs were comparable to its individual runs, with especially similar trends appearing at pH 10.0 and 11.4. However, they were quite different from those of Dieldrin and Aroclor 1254.

From Figure 8, the two optimum Mg^{2+} dosages of 8 mg/l and 33 mg/l at all tested pH levels, as predicted by the individual runs on Figure 6, became more obvious. The enhanced effect from pH 10.0 to 10.7 was about 11%, which was very close to the 15% increase in removal efficiency in the individual runs. But from pH 10.7 to 11.4, there was a decrease of removal efficiency at low Mg^{2+} concentration and an increase of removal efficiency at 33 mg/l Mg^{2+} level. There were four 0% removals of Pentachlorophenol in this mixed run and no comparable results for Dieldrin and Aroclor 1254 could be observed. This supports the unpredictable and



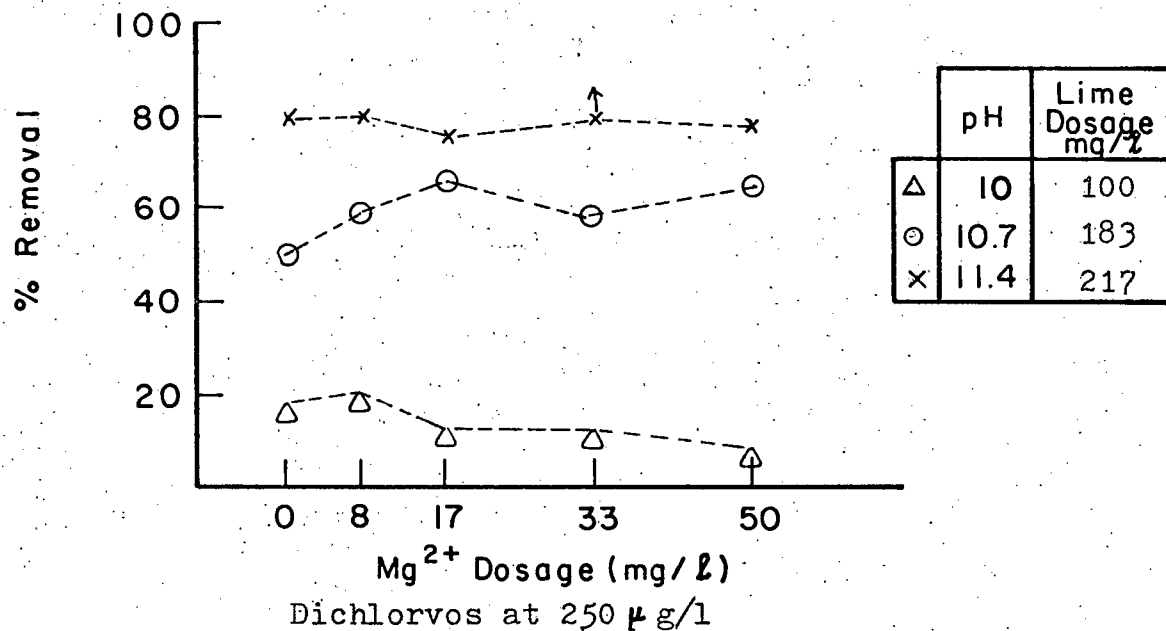
Dieldrin at 250 $\mu g/l$



Aroclor 1254 at 250 $\mu g/l$

↑ indicates measured removal % is greater than that shown

Figure 7 Percent Removal vs. Mg^{2+} Dosages (mixed in PPE)



↑ indicates measured removal % is greater than that shown

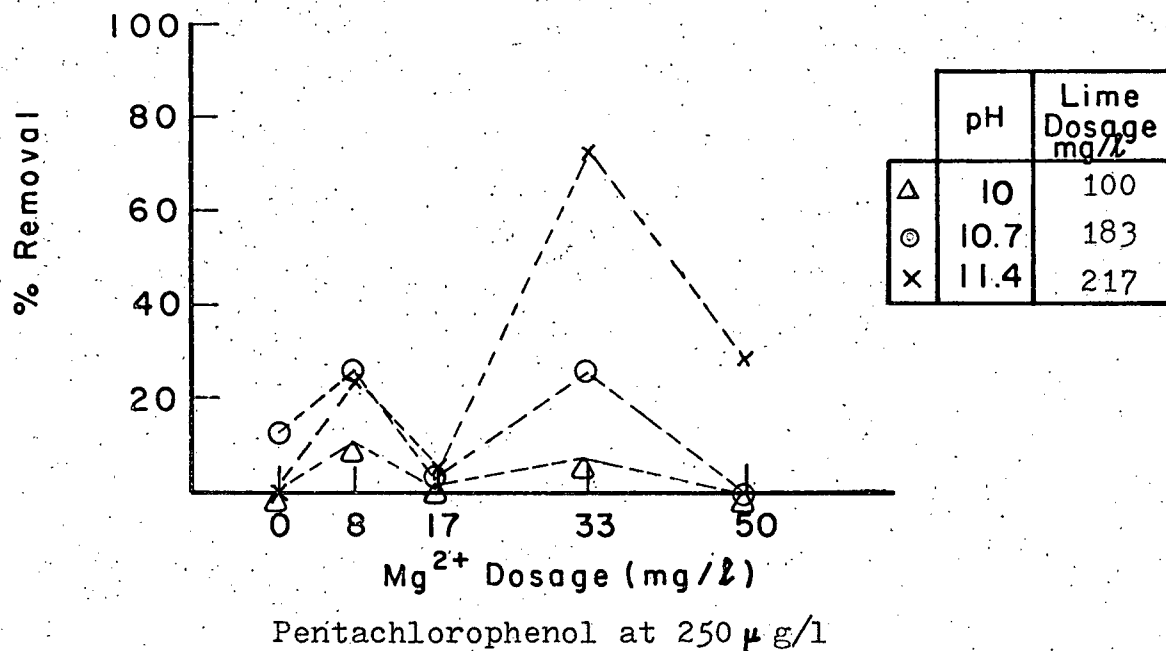


Figure 8 Percent Removal vs. Mg^{2+} Dosages (mixed in PPE)

low removal of Pentachlorophenol by coagulation (mentioned in Section 3.1.4.)

Recently the possible formation of organochlorines and PCBs after the chlorination of wastewaters has been investigated (see Appendix B for details) (28). This is a matter that should be cleared up before applying a removal process of trace organics to wastewaters: where should such a process be installed, before chlorination or after chlorination or after dechlorination?

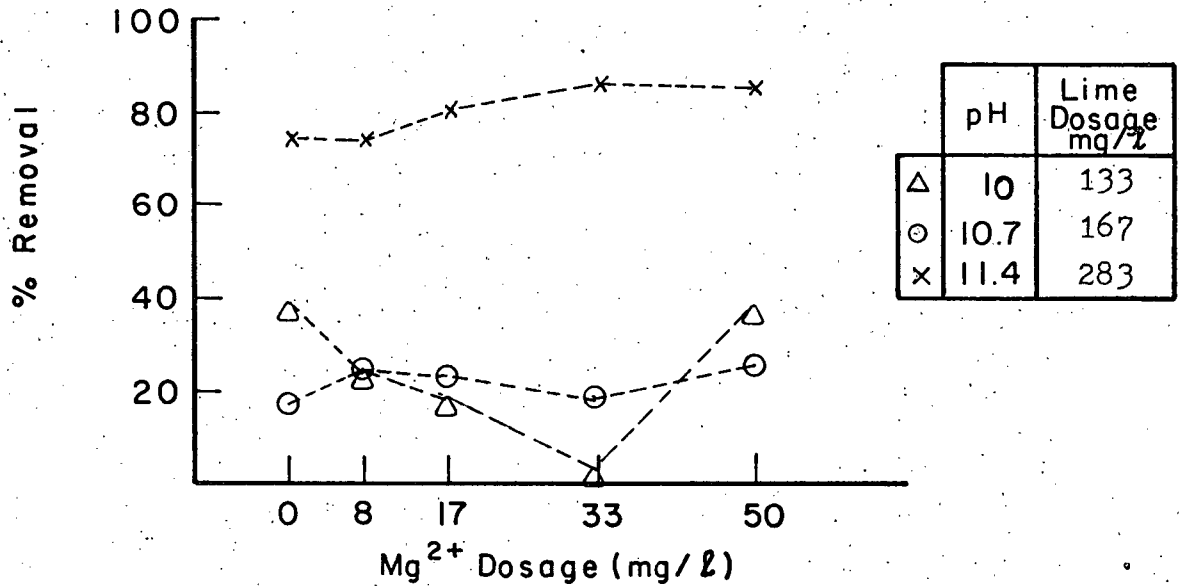
3.3. The Removal of Mixed Organics from Raw Sewage

Tables of experimental results are included in Appendix G. Figure 9 and 10 are results of the percent removal of each organic parameter in the mixed run in raw sewage. The initial concentration of each organic parameter was 250 µg/l. The recovery of Dieldrin and Aroclor 1254 in the initial concentration samples was low and irregular as were those in PPE samples. One of the reasons might be adsorption of some of the organics by the impurities in the wastewater since the total concentration of organics was so high. An average measured initial concentration of Dieldrin and Aroclor 1254 was therefore used to calculate the removal efficiency. The lime dosages required to raise the pH were roughly the same as in the mixed runs in PPE.

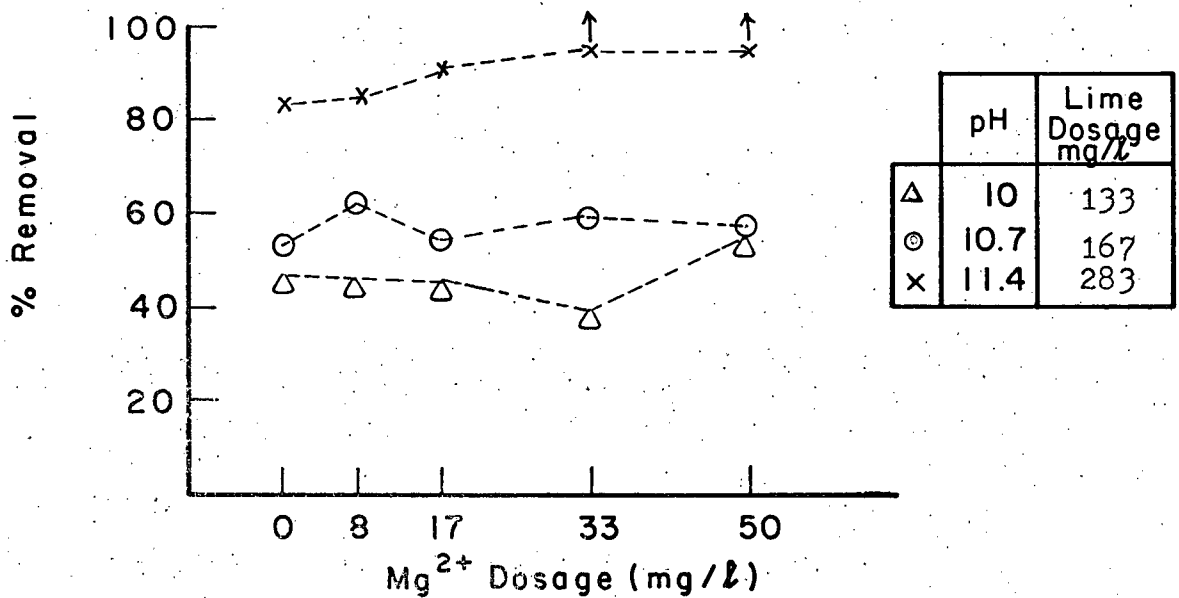
As the concentration of suspended solids in raw sewage is about four times that in PPE, higher removal due to

better opportunity for adsorption and entrapment is expected. This was obvious in Aroclor 1254 removal at all pH values and in Dieldrin removal at pH 11.4. The two optimum removals for all the organics appeared at pH 10.7 with 8 mg/l of Mg^{2+} and at pH 11.4 with 33 mg/l of Mg^{2+} . The former optimum removal could be considered as such because only intermediate lime and magnesium dosages were used and a relative high removal was obtained. The latter optimum removal was considered as optimum because the average highest removal existed at that condition, but high lime and magnesium dosages were required.

When compared to removal in the mixed runs in PPE, Dieldrin removal at pH 10.7 showed similar trends over the different Mg^{2+} dosages. Also, removals at pH 11.4 with Mg^{2+} dosages of 33 mg/l and 50 mg/l were comparable in both mixed runs. With regard to Aroclor 1254 removal, the mixed run in PPE at pH 10.7 showed similar trends over the various Mg^{2+} dosages in comparison to the mixed run in raw sewage at pH 10.0. As with Dieldrin removal, Aroclor 1254 removals at pH 11.4 with Mg^{2+} dosages of 33 mg/l and 50 mg/l were the same in both mixed runs. Dichlorvos removals were under 20% at pH 10.0 in both mixed runs at various Mg^{2+} dosages. Results at intermediate pH varied from 50-70% in the mixed run in PPE and 40-60% in the mixed run in raw sewage. High removal of over 80% was obtained in both mixed runs at the highest pH. Generally, the results could be said to be comparable to those obtained in PPE. For Pentachlorophenol,



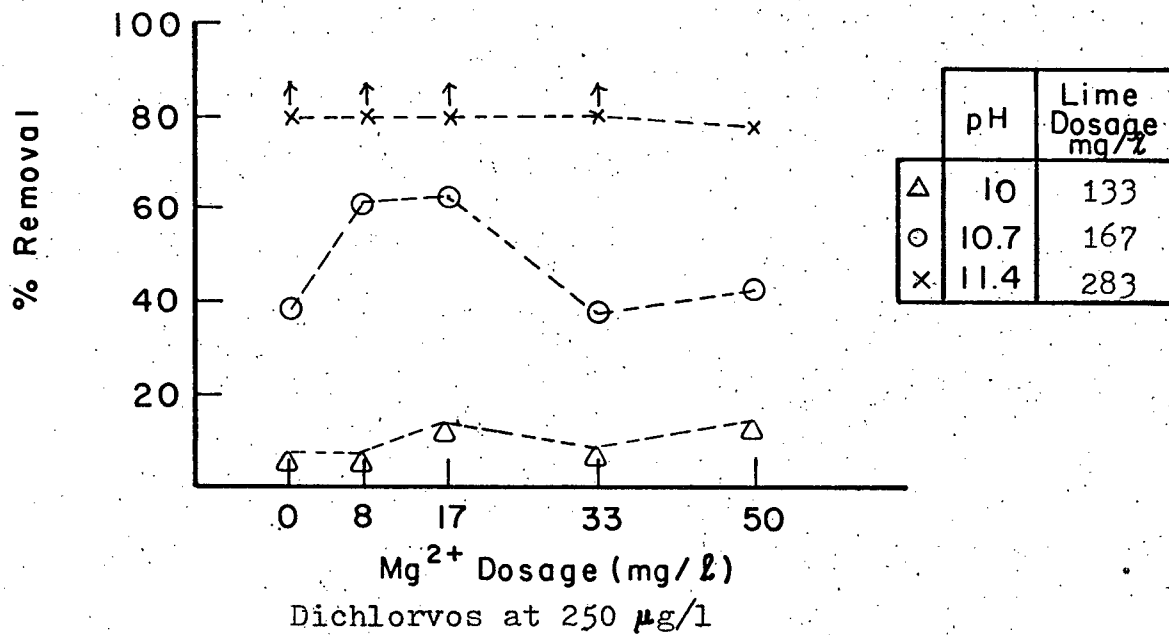
Dieldrin at 250 $\mu g/l$



Aroclor 1254 at 250 $\mu g/l$

↑ indicates measured removal % is greater than that shown

Figure 9 Percent Removal vs. Mg^{2+} Dosages (mixed in Raw Sewage)



↑ indicates measured removal % is greater than that shown

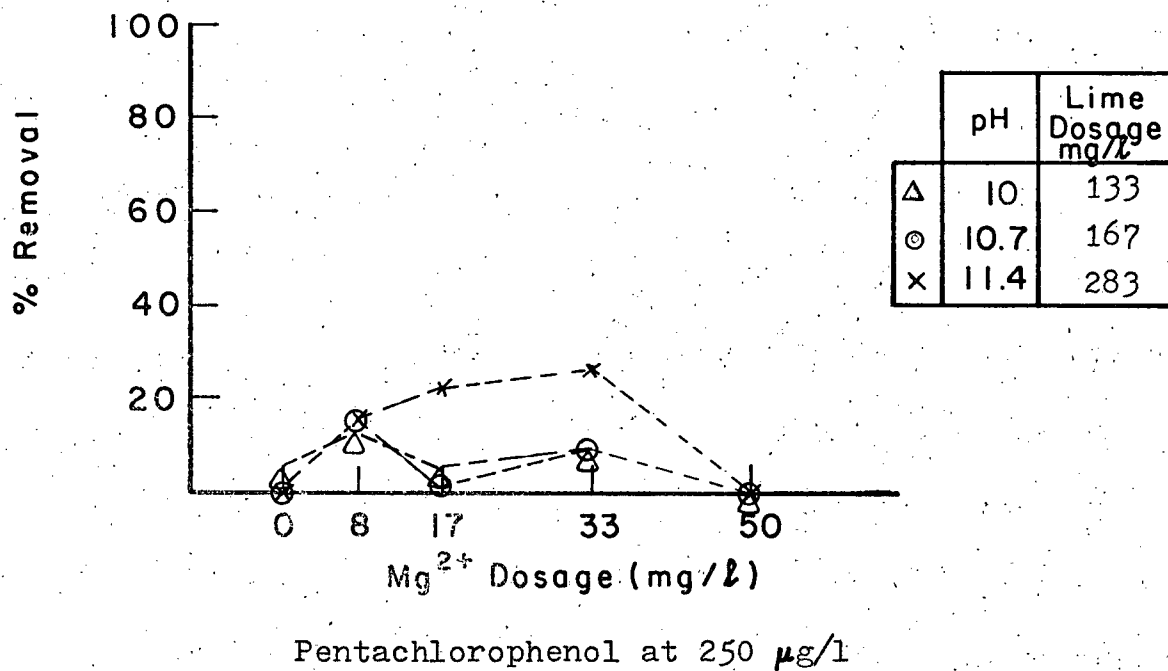


Figure 10 Percent Removal vs. Mg^{2+} Dosages (mixed in Raw Sewage)

very similar shaped removal curves were observed in raw sewage and PPE tests, but the measured removal efficiencies in raw sewage were generally lower. Thus, the highest removal in PPE was 72.5% and the highest removal in raw sewage was only 25.9%.

3.4. The Removal Efficiency of Dieldrin from PPE at Elevated Alkalinity

The table of experimental results is included in Appendix G. Figure 11 gives the results for percent removal of Dieldrin at an elevated alkalinity. The natural alkalinity of the sample was found to be 153 mg/l. The final elevated alkalinity was measured after adding 5 ml of 10^4 mg/l NaHCO_3 solution. Theoretically it should be 202.6 mg/l. The measured result was 199.5 mg/l.

In this run, the ratios of the equivalents of lime dosage to natural alkalinity were 1.6:1, 2.1:1, 3.2:1 where as the ratios of lime dosage to the elevated alkalinity were 1.2:1, 1.6:1, 2.5:1, to reach pH values of 10.0, 10.7 and 11.4 respectively. When comparing Figure 2 and Figure 11, the lime dosages were very similar. The removal efficiency was somewhat higher at the natural alkalinity at all the pH levels. The highest removal occurred at pH 11.4 and 50 mg/l Mg^{2+} , and was the same in both cases. This removal is attributed to high pH and high Mg^{2+} dosage only, since it is indicated that no enhanced removal was achieved by elevating the alkalinity.

3.5. The Recovery of Dieldrin from Sludge

Table 8 shows the results of the mass recovery of Dieldrin from the sludge. The recovery was carried out only at one pH because it would give sufficient information to do a mass balance, and thus determine if all the added pesticide can be found in one or the other phase of treated sewage.

Table 8 shows that over 93% of the Dieldrin was recovered from the supernatant and the sludge. Because of low removal at pH 10.0, most of the spiked Dieldrin still remained in the supernatant. However, the removed portion was found mostly in the sludge. This confirms that removal during coagulation is chiefly due to adsorption and entrapment. Note also, that the persistent nature of organochlorines makes it likely that they remain unchanged in the sludge. Sludge handling would therefore give rise to more problems because of their presence.

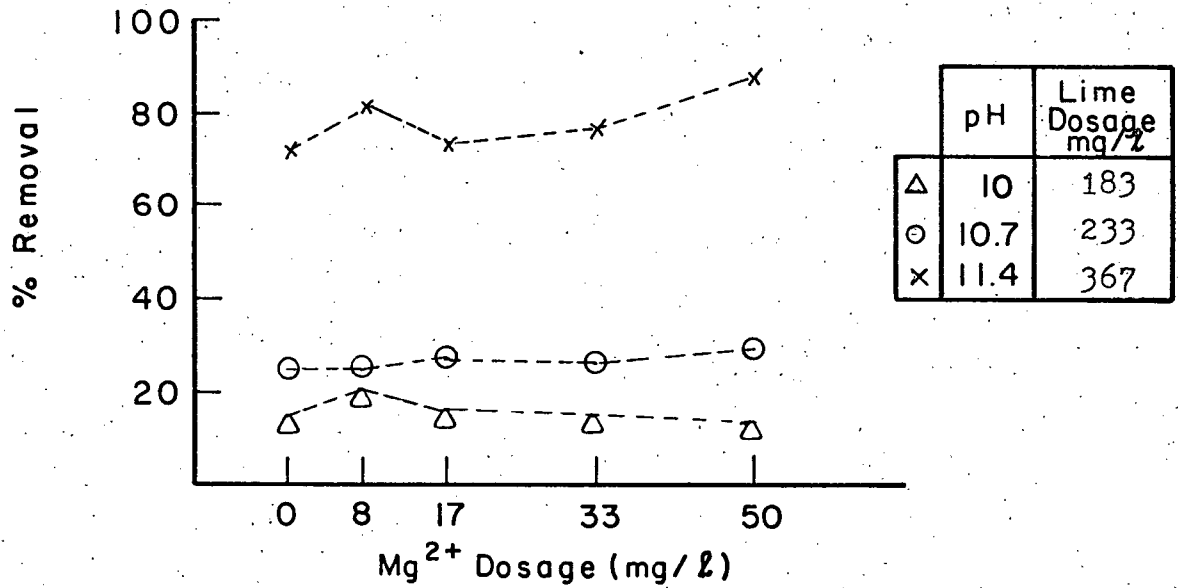
3.6. The Removal Efficiency of BOD from PPE

The table of experimental results is included in Appendix G. Figure 11 shows the results of the percent removal of BOD in PPE. For the determination of BOD, the sample was collected one hour just before coagulation to minimize biodegradation. The BOD_5 of this sample of PPE was found to be less than half of the average value (Table 1), indicating a very dilute sample. The raw sewage which was

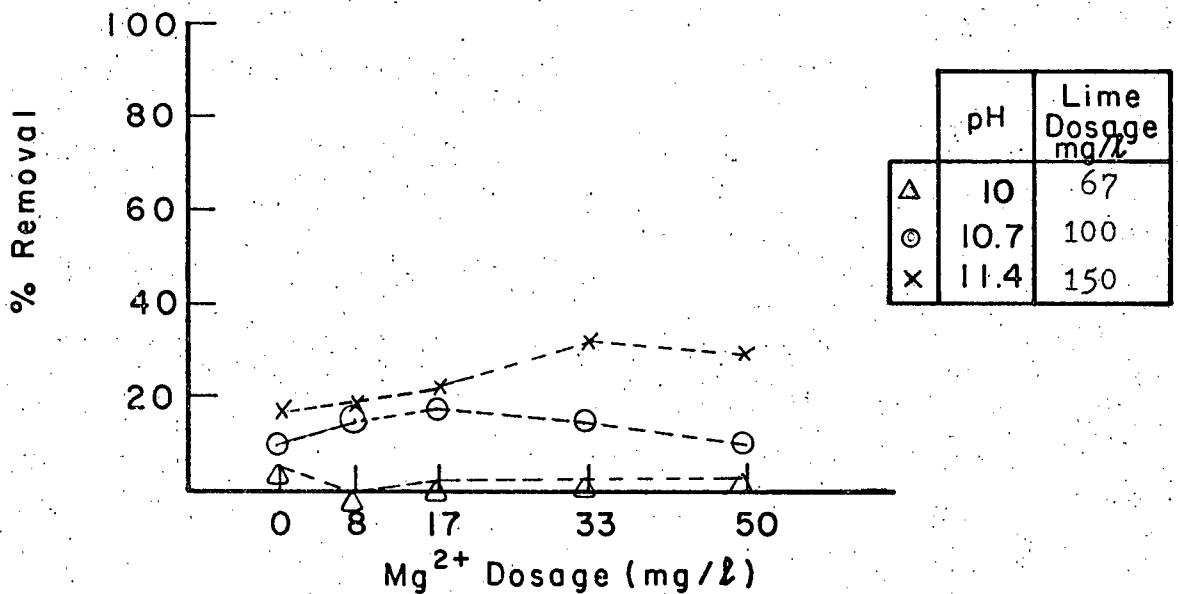
collected at the same time for use as seed also had a very low BOD₅. The results were calculated on a complete mass balance on dissolved oxygen in the sample, dilution water and seeding (see Appendix F).

A comparison of the average suspended solids concentration and BOD₅ in raw sewage and PPE indicates that a major portion of the BOD₅ is in the dissolved form. As adsorption and entrapment are not effective in removing dissolved materials, low removal would be expected. The highest BOD removal was only 32%. Again, removal was enhanced by an increase in pH. Optimum removal existed at pH 10.7 at 17 mg/l Mg²⁺ and pH 11.4 at 33 mg/l Mg²⁺, but removal at pH 10.7 at 8 mg/l Mg²⁺ was only 2.5 percentage points lower than the former optimum.

Table 9 shows the observed settling rate, floc size and final clarity in the supernatant for different conditions used. Along with Table 10, 11, 12 (summaries of the removal efficiencies), these tables present a more complete comparison of the research. The conclusions in the next chapter are drawn from these tables and the discussion given in Section 3.3.



Dieldrin at Elevated Alkalinity



BOD in PPE

Figure 11 Percent Removal vs. Mg^{2+} Dosages

Table 8. Data Sheet: Sludge Recovery for Dieldrin at pH = 10^Δ and Initial Concentration = 250 μg/l[†]

Mg ²⁺ Dosage (mg/l)	Average Peak Area	Conc. in the Extract μg/l	Conc. in [°] the 600 ml supernatant μg/l	(a) Total Mass in Supernatant (ng)	(c) (a) + (b) (ng)	Recovery % [⊗]
I.C.*	494	172.5	215.5	129.3	129.3	-
0	432	150	187.5	112.5	121.3	93.8
8	430	150	187.5	112.5	120.8	93.4
17	450	157.5	196.9	118.1	127.7	98.8
33	440	152.5	190.6	114.4	121.9	94.3
50	468	162.5	203.1	121.9	130.2	100.7

Mg ²⁺ Dosage	Average Peak Area	Conc. in the 75 ml Extract μg/l	(b) Total Mass in Sludge (ng)
I.C.	Negligible amount in the sludge		
0	344	117.5	8.81
8	325	110	8.25
17	370	127.5	9.56
33	295	100	7.50
50	322	110	8.25

*I.C. = see footnote on Table G-1

Δ Lime dosage = 167 mg/l

† 250 μg/l in 600 ml sample = 150 μg

⊗ Recovery % = $\frac{a+b}{c}$

° conc in the supernatant = 5/4
conc in the extract

Table 9. Comparison of Floc Size, Final Clarity and Settling Rate at Different pH and Mg^{2+} Dosages.

pH	Mg^{2+} Dosage (g/l)	Floc* Size	Final* Clarity	Settling Rate
10	0	✓	✓	2
	8	✓	✓	1
	17	✓	✓	3
	33	✓	✓	2
	50	✓	✓	3
10.7	0	2	✓	2
	8	2	✓	1
	17	1	✓	1
	33	2	✓	2
	50	2	✓	3
11.4	0	✓	✓	2
	8	✓	✓	1
	17	✓	✓	1
	33	✓	✓	1
	50	✓	✓	1

✓ No apparent difference between samples at the same pH. However, higher pH samples provided better clarity.

* Results were rated relative to each other, within the same pH. 1 is the best, i.e. largest floc size, clearest supernatant and fastest settling rate.

Table 10. Comparison of Removal Efficiency of Dieldrin under Different Conditions.in %

pH	Mg ²⁺ Dosage (mg/l)	Individually in PPE at 250 µg/l	Individually in PPE at 50 µg/l	Individually in PPE at 250 µg/l (elevated alkalinity)	Mixed in PPE at 250 µg/l	Mixed in raw sewage at 250 µg/l
10	0	31.9	3.1	15.5	23.1	38.9
	8	25.8	13.8	21.1	18.9	24.6
	17	36.8	7.7	16.9	34.6	18.9
	33	35.7	6.2	15.5	31.7	3.3
	50	29.1	4.6	14.1	27.5	38.9
10.7	0	47.4	17.6	25.0	27.5	17.5
	8	52.6	25.0	25.0	28.9	24.6
	17	51.3	29.4	27.8	26.1	23.2
	33	52.6	32.4	26.4	33.2	18.9
	50	55.3	47.1	29.2	67.0	26.1
11.4	0	77.9	68.4	72.0	24.6	75.0
	8	78.6	72.9	81.7	30.3	74.4
	17	82.1	71.7	73.1	40.8	80.9
	33	83.1	83.7	76.6	81.2	86.8
	50	87.9	81.6	88.1	83.5	86.5

Table 11. Comparison of Removal Efficiency of Aroclor 1254
Under Different Conditions, in %.

pH	Mg ²⁺ Dosage (mg/l)	Individually in PPE at 250 µg/l	Individually in PPE at 50 µg/l	Mixed in PPE at 250 µg/l	Mixed in raw sewage at 250 µg/l
10	0	20.0	31.8	41.9	47.8
	8	33.3	5.5	27.3	47.0
	17	25.6	13.6	36.9	46.7
	33	9.5	15.9	41.9	39.3
	50	19.0	0.0	48.5	55.6
10.7	0	35.0	5.1	49.5	53.5
	8	49.0	12.8	47.5	62.1
	17	37.0	23.1	45.5	54.5
	33	45.0	28.2	29.3	59.1
	50	51.0	5.1	75.5	57.6
11.4	0	86.6	89.5	49.5	83.6
	8	over 95.0	91.1	54.5	85.6
	17	67.7	94.7	63.1	91.2
	33	73.1	94.7	over 95.0	over 95.0
	50	71.1	94.7	over 95.0	over 95.0

Table 12. Comparison of Removal Efficiency of the Organic Parameters under Different conditions, in %.

pH	Mg ²⁺ Dosage	Dieldrin			Aroclor 1254			Dichlorvos			Pentachlorophenol			BOD
		1	2	3	1	2	3	1	2	3	1	2	3	
10	0	31.9	23.2	38.9	20.0	41.9	47.8	0.0	18.9	7.1	35.7	0.0	4.7	6.4
	8	25.8	18.9	24.6	33.3	27.3	47.0	7.6	20.3	7.1	46.4	10.7	12.5	0.0
	17	36.8	34.6	18.9	25.6	36.9	46.7	4.5	13.5	14.3	28.6	1.8	4.7	2.2
	33	35.7	31.7	3.3	9.5	41.9	39.9	3.0	13.0	8.6	32.1	7.1	9.4	3.1
	50	29.1	27.5	38.9	19.0	48.5	55.6	3.0	9.5	14.3	16.1	0.0	0.0	4.2
10.7	0	47.4	27.5	17.5	35.0	49.5	53.5	43.2	50.7	39.0	11.8	12.9	0.0	10.8
	8	52.6	28.9	24.6	49.0	47.5	62.1	20.5	59.5	61.6	73.5	25.8	15.8	15.5
	17	51.3	26.1	23.2	37.0	45.5	54.5	53.2	66.7	62.2	48.2	3.2	1.8	18.0
	33	52.6	33.2	18.9	45.0	29.3	59.1	34.5	58.7	37.8	41.8	25.8	8.8	15.0
	50	55.3	67.0	16.1	51.0	75.5	57.6	20.5	65.3	42.7	20.6	0.0	0.0	11.0
11.4	0	77.9	24.6	75.0	86.6	49.5	83.6	over 80	80	over 80	0.0	0.0	0.0	16.8
	8	78.6	30.3	74.4	over 95	54.5	85.6	over 80	80	over 80	41.2	23.2	15.5	18.2
	17	82.1	40.8	80.9	67.7	63.1	91.2	over 80	76.3	over 80	19.6	3.6	22.4	22.0
	33	83.1	81.2	86.8	73.1	over 95	over 95	over 80	over 80	over 80	56.5	72.5	25.9	32.2
	50	87.9	83.5	86.5	71.1	over 95	over 95	over 80	78.7	77.9	0.0	28.6	0.0	30.1

Note: (1) Individually in PPE at 250 µg/l
 (2) Mixed in PPE at 250 µg/l
 (3) Mixed in Raw Sewage at 250 µg/l

CHAPTER 4

CONCLUSIONS AND RECOMMENDATIONS

4.1. Conclusions

(a) General

- (1) Trace organics like Dieldrin, Aorclor 1254, Dichlorvos and Pentachlorophenol can be effectively removed by Lime-Magnesium Coagulation. The highest removal efficiencies at an initial concentration of 250 $\mu\text{g/l}$ were 88.1%, over 95%, over 80% and 73.5% respectively. However, these removals were not obtained under the same experimental conditions.
- (2) Two "optimum" conditions were found to exist: pH 10.7 with 8 mg/l of Mg^{2+} ; and pH 11.4 with 33 mg/l of Mg^{2+} . The second one generally provided a higher removal efficiency, but would give rise to a higher chemical costs, more sludge production and more extensive final pH adjustment.
- (3) Enhanced removal due to presence of magnesium ion is not obvious.
- (4) Removal ranges obtained in individual and mixed runs were comparable.

(b) Dieldrin

- (1) Significant removals were achieved at pH 11.4, with an average of over 73% being obtained.
- (2) Enhanced removal was found by increasing pH.

- (3) Enhanced removal was found at 50 mg/l of Mg^{2+} at both pH 10.7 and 10.0.
- (4) Lower percent removals were found at initial concentration of 50 μ g/l than at 250 μ g/l.
- (5) Elevated alkalinity did not give better removal.
- (6) Removed Dieldrin was trapped in the sludge, thus indicating that the supernatant would not be carrying partially decomposed forms of this compound which might still be toxic.

(c) Aroclor 1254

- (1) Significant removal at pH 11.4 was achieved, with an average of over 80% being obtained.
- (2) Enhanced removal was found by increasing pH.
- (3) Lower percent removals were found at initial concentration of 50 μ g/l than 250 μ g/l.

(d) Dichlorvos

- (1) Highest removals (80%) were obtained at pH 11.4, due to alkaline hydrolysis.
- (2) Lower removals were achieved for Dichlorvos than for Dieldrin and Aroclor 1254. This is perhaps due to the higher solubility of Dichlorvos in water.
- (3) Enhanced removal was achieved by increasing the pH.

(e) Pentachlorophenol

- (1) Unpredictable removals obtained appeared to be due

to formation of calcium phenate, which is highly soluble in water.

- (2) Optimum removals (30%) were found at 8 mg/l and 33 mg/l Mg^{2+} at all pH levels tested.
- (3) No enhanced removal was found by increasing pH.

4.2. Recommendations

At the present time, data on removal efficiency of BOD, suspended solids, colour, phosphorus, heavy metals and trace organics in wastewaters by Lime-Magnesium Coagulation are available. Whether or not this would be a cost effective process for Vancouver municipal wastewaters still needs further investigation. The following examples are cited:

- (1) Comparison of removal efficiencies and costs with other coagulants, e.g. alum, ferric salts seems necessary.
- (2) Testing of some other parameters such as ammonia nitrogen, surfactants, coliform and bioassay tests on the treated effluent may be required for more complete evaluation.
- (3) Handling of sludge and recycle processes for magnesium and lime should be given more consideration.
- (4) Economic analysis at the pilot scale is necessary before installation of a full-scale process into existing sewage treatment plants is undertaken.

- (5) Problems, operational difficulties and an implementation program should be evaluated for full scale development.

Appendix D gives more details concerning the recommendations.

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APPENDIX

Appendix A Preliminary Study on Detection Techniques

(1) Detection of Dieldrin, Aroclor 1254, Dichlorvos

The optimum conditions on the Gas Liquid Chromatograph were chosen from a combination of the conditions given in the literature search (21, 24-27, 34). The method was then carried out on the DC-11 column and OV-101 column and the results were satisfactory, (i.e. peaks were clearly separated, areas were conveniently counted, no irregularities in baseline and peak tailings occurred, normal peak shapes were obtained, etc). The final conditions were as shown in Section 2.5. Dieldrin was used for all these trials as a representative organic compound for this study.

Standing currents were checked from time to time to make sure that the detector was clean. The linear range were found by injecting different standards, calculating the areas and plotting the areas against total mass injected on log-log graph paper. For Dieldrin, total mass of 1, 1.5, 2 ng were tried and they were outside the linear plot of lower concentrations (Figure A-1). It was fortunate that the detection of these organics could be adjusted into the linear ranges either by controlling the volume of injection or concentration technique.

Usually injection volume would be within 10 μ l. so 10 μ l and 2 μ l injection volumes were chosen since five

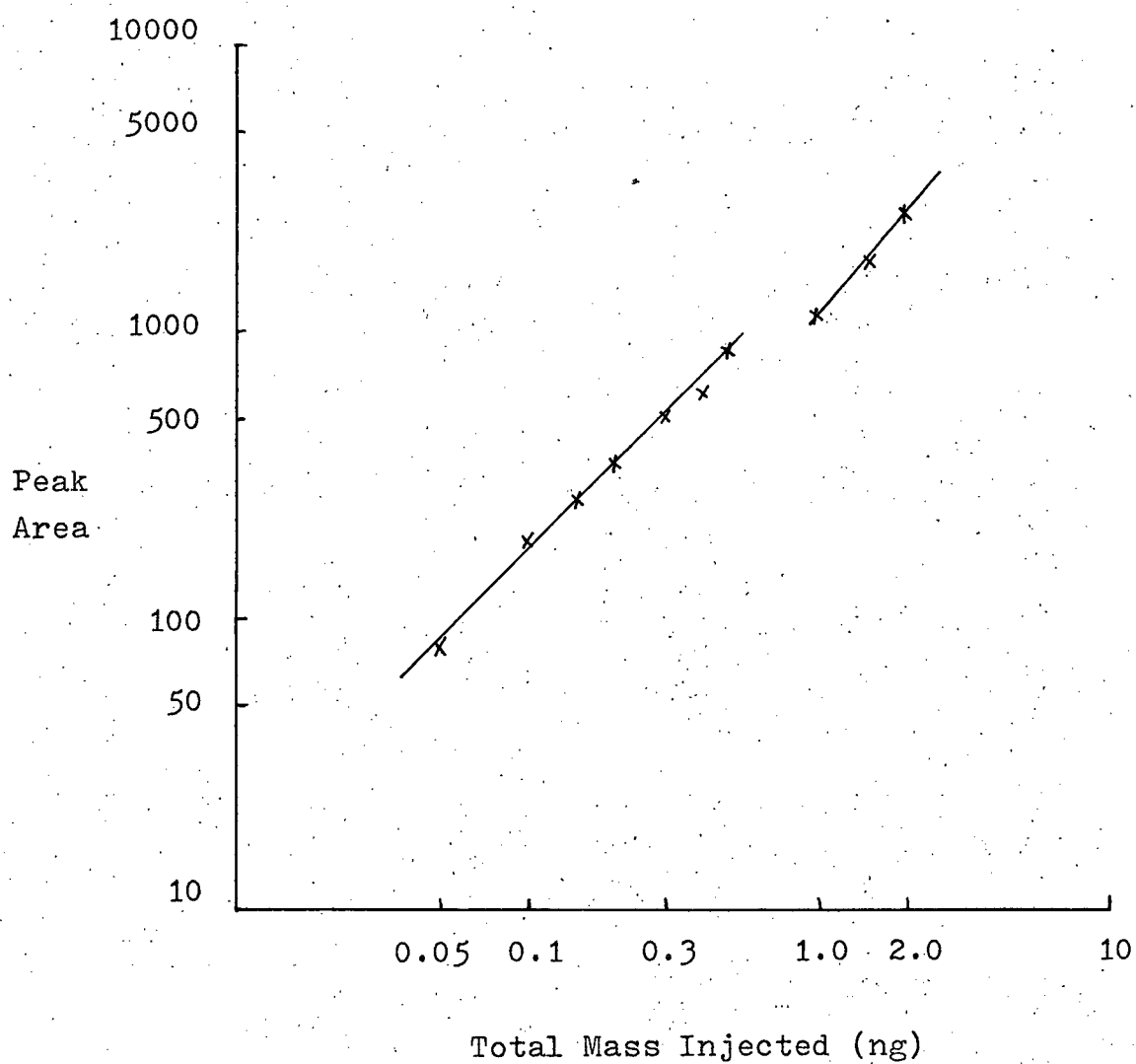


Figure A-1 Non-linear Standardization Curve of Dieldrin at Higher Concentrations

times dilution on the florisil column could be offset by an increase in injection volume by the same amount. Standards were checked with new standards periodically. Storage of standards and spike solutions even up to several weeks seemed to have no effect on the concentration, which might be altered by degradation of the organics, adsorption to the containers, decomposition, volatilization, etc.

Purity of solvents and chemicals was high. Existing impurities were too low to affect quantitative analysis. Apparatus and syringe contamination could be serious, but they can be avoided by solvent flushing and special cleaning.

Extraction volumes and portions were studied to contain good recovery and to use a minimum volume of solvent. Extraction efficiencies of 86-97% were obtained by 3 portions of 25 ml of hexane in sewage. Extraction efficiencies of 101-105% were obtained by the same amount of solvent in distilled water. With the amount extracted in 3 portions of 25 ml of hexane as 100%, 2 portions of 25 ml could extract 92-96%, and 1 portion of 25 ml could extract 86.6-87.2%. So the 2 portions of 25 ml extract was chosen with consideration given to solvent volume and time spent in extraction, since over 90% recovery was adequate for this research.

With a wider column, more florisil and anhydrous Na_2SO_4 could be used. For reuse, the column could be placed in a furnace at 105°C and cooled in a desicator before use to prevent deactivation. The most important property of the

column is the ability to store the desired parameter which can be eluted out later. The other factors to be considered are controlled elution rate, prevention of channelization, contamination and deactivation of the column during the column runs. The use of a new column for each sample could eliminate most of these problems. Of course, careful packing is required to prevent any of the above problems. 50 ml - 15% ethyl ether were used to elute Dieldrin from the column and over 99% was eluted. A lower percentage of ethyl ether could not elute Dieldrin completely. Over 30% ethyl ether would give a tailed baseline, so a lower percentage should be used as long as elution efficiency was adequate.

Injection precision was also calculated. The results were shown to be as follows:

Table A-1. Injection Precision

Injection	Peak Area	$X - \bar{X}$	$(X - \bar{X})^2$
1	321	-8.5	72.25
2	333	+3.5	12.25
3	339	+9.5	90.25
4	337	+7.5	56.25
5	327	-2.5	6.25
6	317	-12.5	156.25
7	320	-9.5	90.25
8	329	-0.5	0.25
9	331	+1.5	2.25
10	341	+11.5	132.25

$$\bar{X} = 329.5$$

$$s^2 = \frac{618.5}{10-1}$$

$$= 68.7$$

$$s = 8.29$$

$$\bar{X} = 329.5 \pm 8.29$$

$$\text{Probable error} = (0.6745)(8.29)$$

$$= 5.59$$

$$(\text{in } \%) = \frac{5.59}{329.5} \times 100$$

$$= 1.7\%$$

(2) Detection of Pentachlorophenol

The only thing that had to be carefully controlled in Pentachlorophenol detection was the derivatization process. The factors requiring attention were:

- Amount of Diazald used
- Bubbling rate and generation time, since both controlled the amount of diazomethane that was passed through the sample

By keeping the amount of Diazald (200 mg would be sufficient in this case) and bubbling rate (1-3 bubbles/sec as recommended in literature) constant, several generation times were tried to yield the highest chromatogram peak or complete derivatization. The results were shown as in the following table:

Table A-2. Generation Time vs. Peak Area

Generation Time (min)	Peak Area
3	87.5
5	535
7	1200
10	780
15	580

The reason for decrease in peak area was unknown and not a great deal of information could be found in the literature except that the above conditions were found to be critical and should be carefully controlled to give reproducible results. The 7 minute generation time was used throughout and it gave constant peaks during the research.

Appendix B. Formation of Organochlorines after Chlorination of Wastewaters.

For several years, people have been investigating the formation of organochlorines during the chlorination of wastewaters. Phenols, amines, aldehydes, etc were found to be easily chlorinated. However, other impurities present might retard the oxidation of these organics by chlorine, (e.g. ammonia and other reducing agents), or enhance the reaction by their catalytic nature, (e.g. iron). Of course, PCB formation under similar conditions as wastewater disinfection would be unlikely for it requires high temperature, pressure and catalysts in its commercial manufacture. Experimental research on primary and secondary effluents showed that there was an increase in chlorine-containing peaks. In view of the massive use of chlorine each day, even the 1% which was incorporated in organochlorine formation would lead to potential hazard in the future. Dechlorination only removes free chlorine whereas chlorine residuals are mainly chloramines. Moreover, dechlorination does not remove chlorinated hydrocarbons formed during prechlorination and post-chlorination. Removal of trace organics in PPE from wastewaters may be helpful as they act as precursors for the formation of organochlorines. The other approach may be removal of trace organics after post-chlorination which would also remove organochlorines formed during the chlorination process. In conclusion, the application of a removal mechanism for trace organics,

especially organochlorines, to wastewaters should take the above considerations into account.

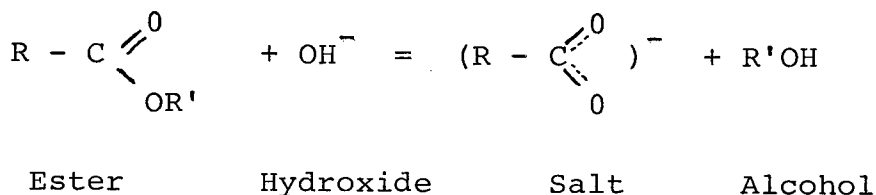
Appendix C. The Choice of 2,4-D (herbicide) as an Organic Parameter.

2,4-D is a very widely used pesticide. It is the most common herbicide still being used at present. Its manufacture began in 1945 and its production in 1958 was over 25 million pounds in the U.S. As it is an acid, it is corrosive. Similar to many other pesticides, it is very persistent in natural systems (it can exist for 120 days in surface waters of pH 5-8 at 3 mg/l), is phytotoxic and its LD₅₀ for rats is 375 mg/Kg.

2,4-D was among those organic pesticides found in polluted waters. As it is usually directly applied to surface water at 1-2 mg/l to control aquatic plants, water contamination by 2,4-D is not surprising. Taste and odour problems in well waters are common occurrences. Crop damage is also frequently encountered.

It is manufactured in three forms: acid, amine salt and isopropyl ester. Only the ester form can be chromatographed directly under similar conditions to those used for the other organic parameters chosen in this research. So the ester form was chosen as one of the organic pollutants among the pesticides. However, alkaline hydrolysis of the ester during coagulation occurred according to the following

equation: (37)



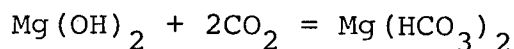
This reaction was not easily reversible, which made detection of residual 2,4-D very difficult, so it was not used. Later, it was found that 2,4-D acid and ester could be derivatized in a similar way to Pentachlorophenol preceded by a saponification process (44). However, it was too late for 2,4-D to be incorporated into this research.

Appendix D. Sludge Handling, Magnesium and Lime Recovery, Economic Evaluation, Full-Scale Development.

In wastewater treatment practice, where suspended and dissolved constituents are separated from wastewater, a variety of residues remain after the clarified supernatant is discharged. These residues are usually referred to as sludge. Sludge handling may involve disposal and/or recycling. For disposal, there are many alternatives available. Often, thickening, dewatering or drying processes are employed before final disposal such as landfill, incineration, use as a fertilizer, etc. Sometimes, polyelectrolytes are added to improve settling and dewatering properties. In view of the energy crisis today, reclamation of useful by-products, e.g.

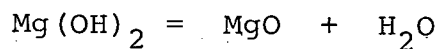
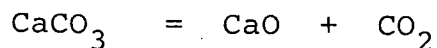
coagulants and chemicals, can be beneficial. Moreover, recycling reduces the volume of sludge to be handled, extends the life of disposal sites, alleviates leachate problems and certainly has some bearing on the aesthetic and legal aspects of sludge disposal. However, some sludge is contaminated to a certain degree with impurities, e.g. heavy metals, so that the recycle process becomes very expensive.

Magnesium, when in its hydroxide form, is highly hydrated and gelatinous. Such characteristics make dewatering very difficult and costly. Recarbonation solubilizes the magnesium in the sludge as magnesium bicarbonate:



Then it can be recovered by vacuum filtration and the filtrate can be recycled and reused. Demonstrations in water treatment plants showed that recycled magnesium was as effective as fresh material (49).

Lime can also be recycled from the sludge by recalcination using fluidized bed furnaces at temperatures from 870°-1100°C. The following reactions take place.



The buildup of magnesium in reclaimed lime may be troublesome,

but recycle of magnesium preceding the lime recycle eliminates such problem. Besides, carbon dioxide can also be recovered from this process for recarbonation.

Economic evaluation of the pilot scale study is necessary. Although bench and pilot scale demonstrations showed enhanced removal of BOD and S.S., reduction of colour and turbidity, over lime treatment alone, many other factors have to be considered during a complete evaluation. For example, nature of the wastewater, its buffering capacity, alkalinity and magnesium background concentrations; filtration which may be required; dewatering and settling of sludge; recycle efficiency of magnesium and lime; final pH adjustment; use in conjunction with advance treatment processes such as carbon adsorption; etc are all important. Data on BOD, COD, S.S., colour, turbidity, phosphorus, heavy metals and trace organics removal are available. Further investigations may include ammonia-nitrogen removal, surfactants removal, coliform counts, sludge disposal, etc. In summary, in view of the many advantages and high removal of many impurities, an economic evaluation on an optimized pilot scale is worthy of consideration.

Design parameters have to be obtained before full-scale development is viable. Often, a lowering of removal efficiency leading to poorer effluent quality occurs at a full-scale plant. Hydraulic conditions, variations in flow, mixing and settling conditions, etc all have to be scaled up.

from parameters obtained from bench or pilot scale. Of course, continuous pilot scale study tends to produce data more applicable to the full-scale situation. The pilot plant should be designed to produce exact simulation of the full scale development and factors of safety or scaling factors should be used in places where exact simulation is difficult to achieve.

Appendix E. Chromatograms

The chromatograms of the standards of the chosen organic parameters are given together with their retention times, peak areas or peak heights.

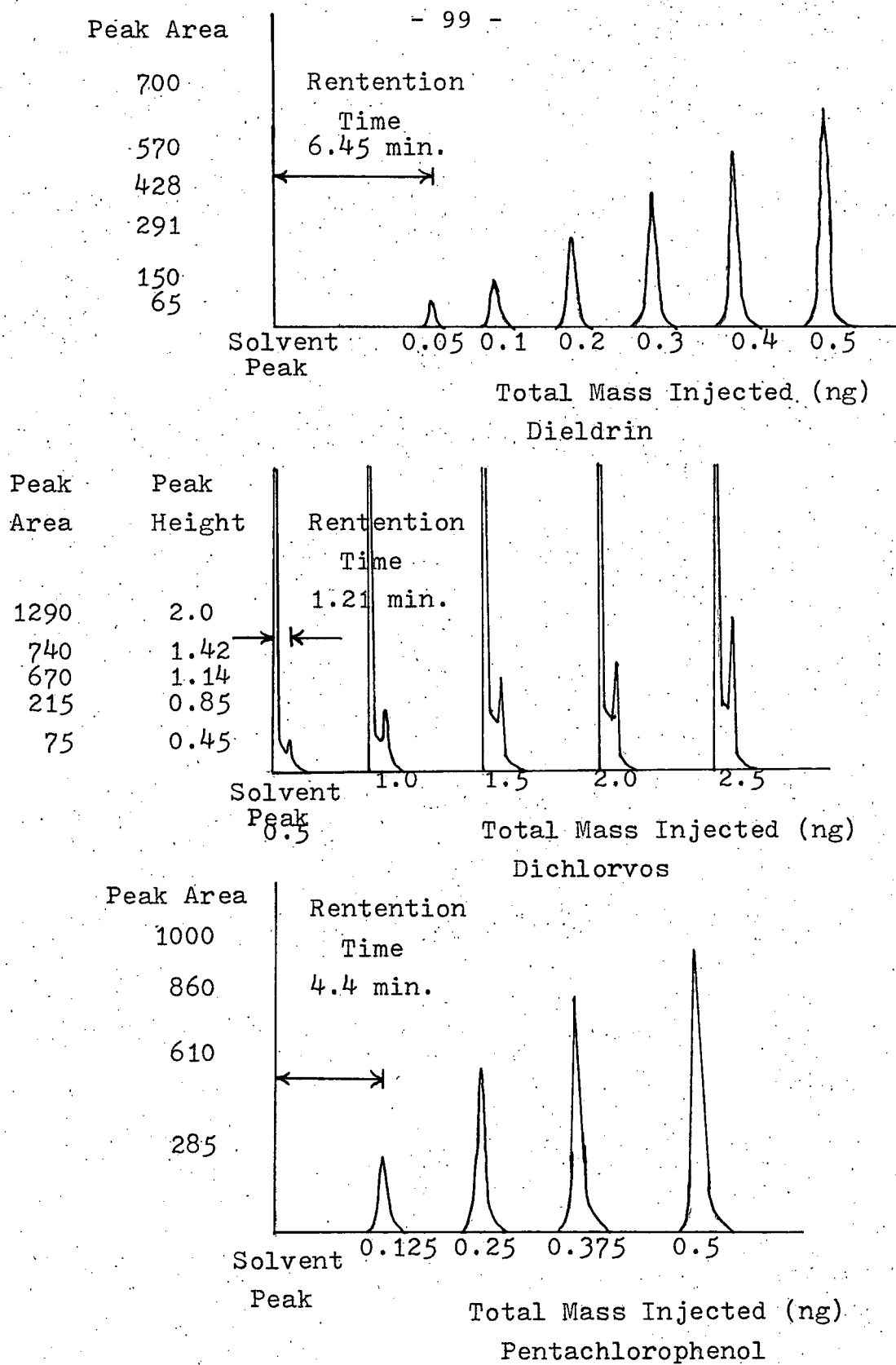


Figure E-1 Chromatograms of Standards

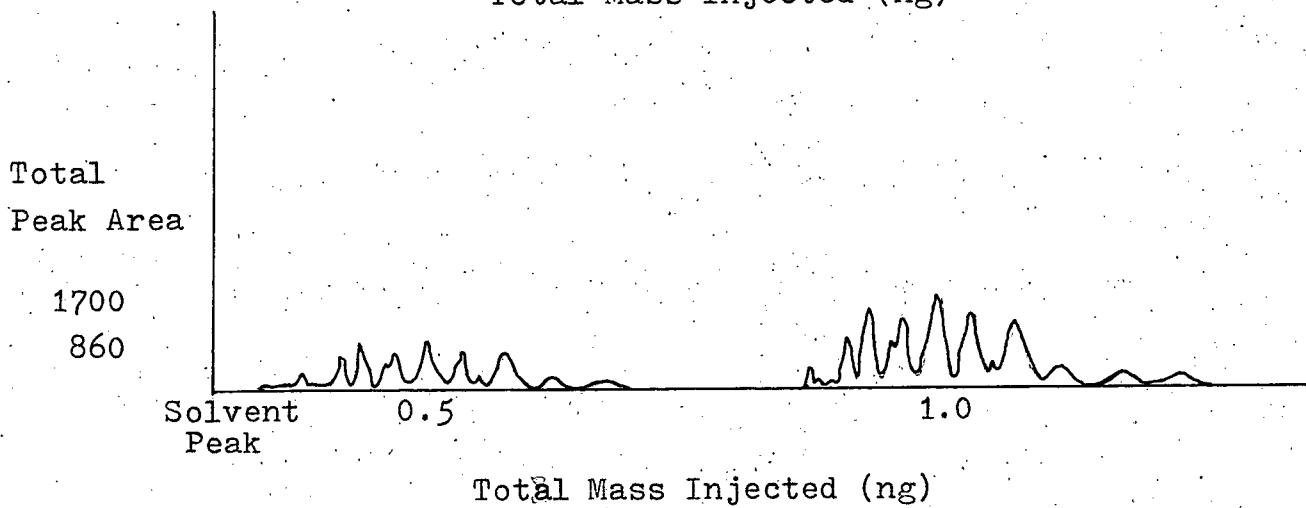
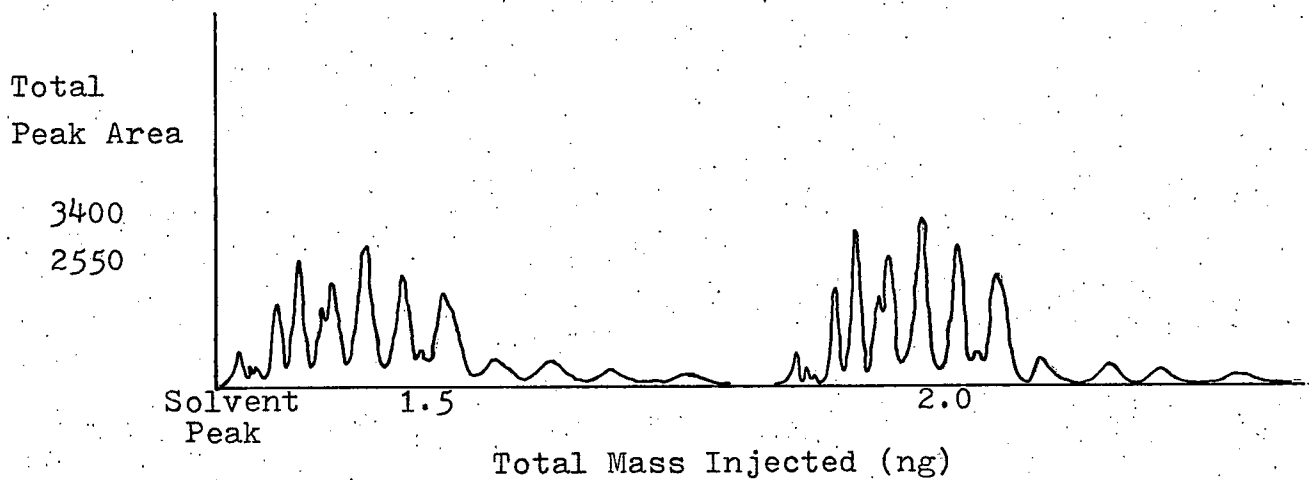
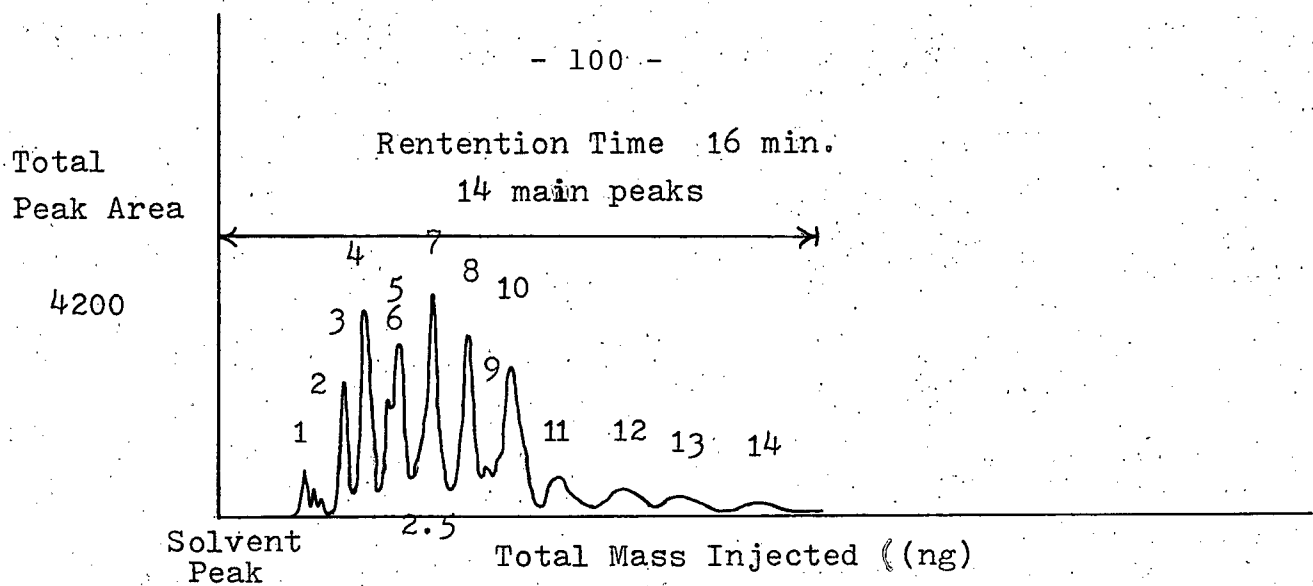


Figure E-2. Chromatograms of Standards of Aroclor 1254

Appendix F. BOD Result Calculations

Dissolved oxygen in dilution water = 8.17 mg/l

Dissolved oxygen in raw sewage (seeding) = 1.1 mg/l

Dissolved oxygen in PPE = 2.1 mg/l

Volume of seeding used = 2 ml

BOD₅ for raw sewage (seeding) = 33.66 mg/l

Volume of BOD bottle = 300 ml

Take the sample at pH 10.7 and 17 mg/l Mg²⁺ as an example:

Volume of sample (ml)		Dissolved oxygen at the end of incubation period (mg/l)
a)	20	4.4
b)	20	4.6
c)	25	3.6
d)	25	3.4

A complete mass balance on:

Total oxygen in the BOD bottle at the beginning of incubation	=	Total oxygen in the BOD bottle at the end of incubation
		+
		Dissolved oxygen consumed by seeding
		+
		BOD ₅ for sample

$$\begin{aligned}\text{For a)} \quad & (20)(2.1) + (2)(1.1) + (278)(8.17) \\ & = (300)(4.4) + (2)(33.6) + (20)(\text{BOD}_5)\end{aligned}$$

$$\text{Therefore } \text{BOD}_5 = 46.41 \text{ mg/l}$$

Similarly,

$$\text{for b)} \quad \text{BOD}_5 = 43.41 \text{ mg/l}$$

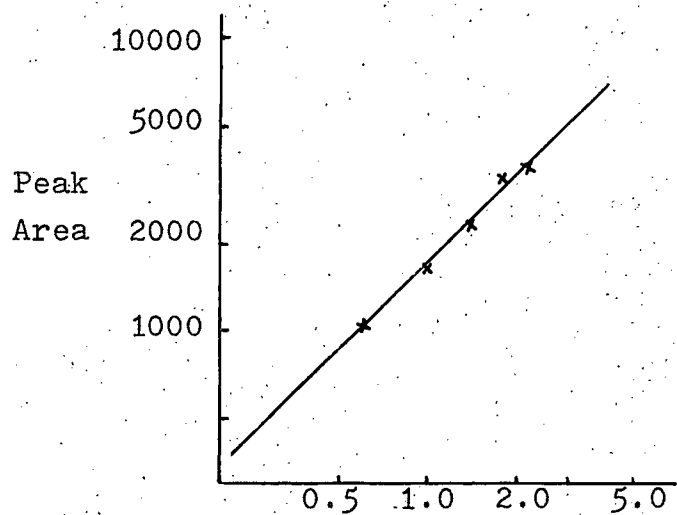
$$\text{for c)} \quad \text{BOD}_5 = 46.17 \text{ mg/l}$$

$$\text{for d)} \quad \text{BOD}_5 = 48.57 \text{ mg/l}$$

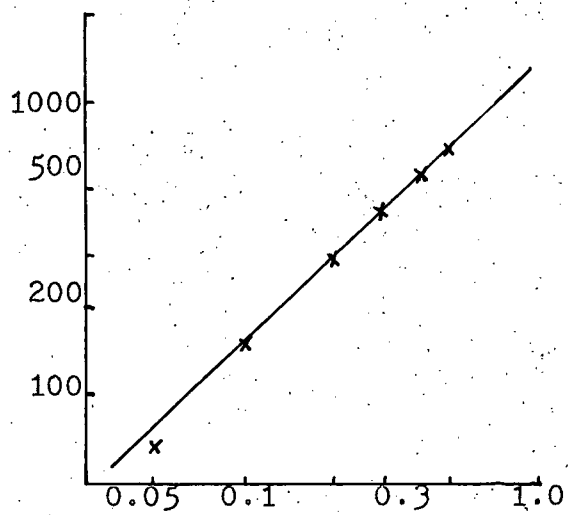
$$\text{Therefore average } \text{BOD}_5 = 46.14 \text{ mg/l}$$

Note: There was no change in dissolved oxygen in dilution water at the beginning and end of incubation.

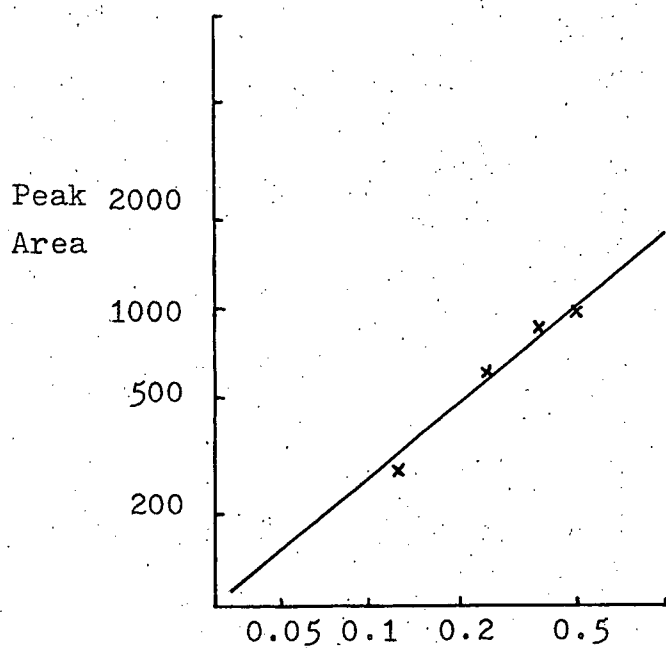
Appendix G. Tables of Experimental Results



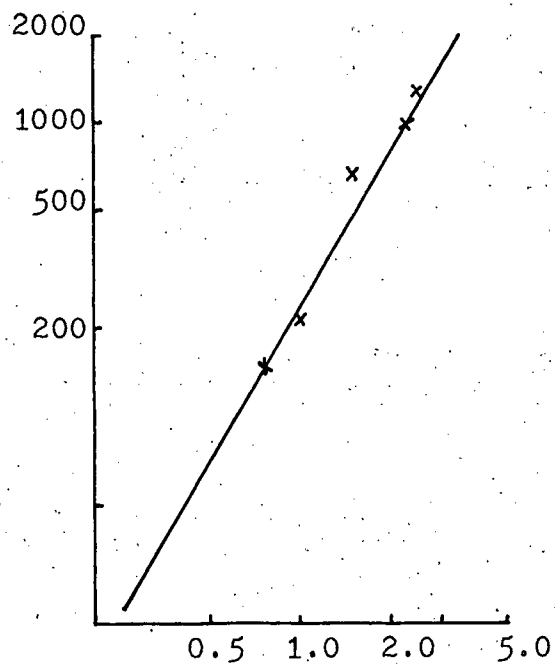
Aroclor 1254



Dieldrin



Pentachlorophenol



Dichlorvos

Figure G-1 Standardization Curves

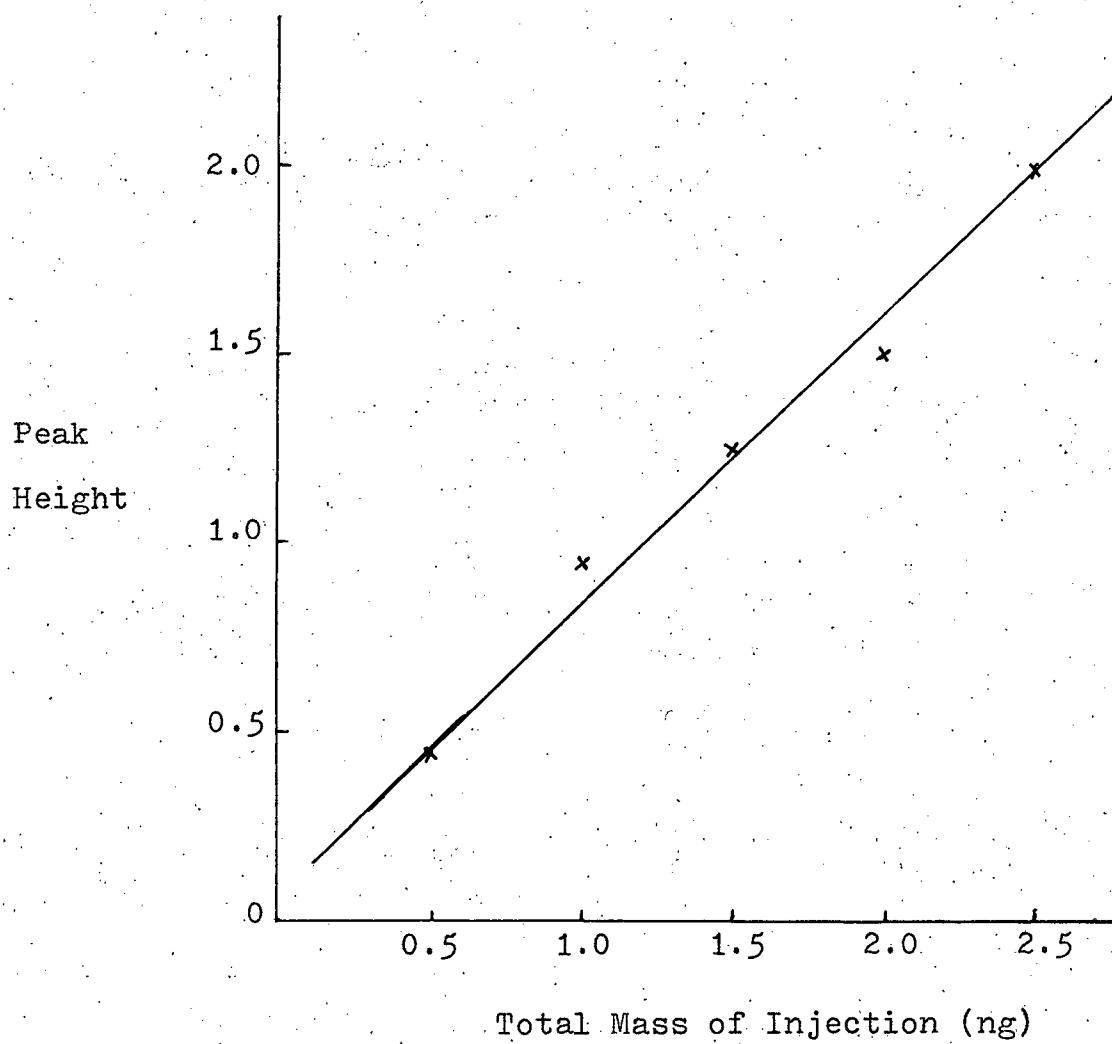


Figure G-2 Standardization Curve : Dichlorvos

Table G-1. Data Sheet: Percent Removal for Dieldrin at an initial concentration = 250 µg/l

pH	Mg ²⁺ Dosage (mg/l)	Average Peak Area	Total Mass (ng)	Removal % *
10.0	I.C. [‡]	532	0.364	-
	0	374	0.248	31.9
	8	396	0.270	25.8
	17	350	0.230	36.8
	33	354	0.234	35.7
	50	380	0.258	29.1
10.7	I.C.	540	0.380	-
	0	295	0.200	47.4
	8	263	0.180	52.6
	17	273	0.185	51.3
	33	263	0.180	52.6
	50	249	0.170	55.3
11.4	I.C.	420	0.290	-
	0	99	0.064	77.9
	8	96.5	0.062	78.6
	17	81.5	0.052	82.1
	33	77.5	0.049	83.1
	50	56	0.035	87.9

[‡]I.C. = For each run (either individually or mixed together) an initial concentration sample (at 250 µg/l or 50 µg/l) was spiked in exactly the same manner as other samples. It was then put aside for detection without any lime and/or magnesium addition.

* Removal % calculation was based on the equation in Section 2.4 with respect to each individual I.C.

Table G-2. Data Sheet: Percent Removal for Dieldrin at
an initial concentration = 50 µg/l

pH	Mg ²⁺ Dosage (mg/l)	Average Peak Area	Total Mass (ng)	Removal %
10.0	I.C. [‡]	465	0.325	-
	0	453	0.315	3.1
	8	407	0.280	13.8
	17	430	0.300	7.7
	33	439	0.305	6.2
	50	445	0.310	4.6
10.7	I.C.	488	0.340	-
	0	405	0.280	17.6
	8	370	0.255	25.0
	17	350	0.240	29.4
	33	340	0.230	32.4
	50	268	0.180	47.1
11.4	I.C.	481	0.332	-
	0	160	0.105	68.4
	8	138	0.090	72.9
	17	142	0.094	71.7
	33	84	0.054	83.7
	50	95	0.061	81.6

[‡]I.C. = see footnote to Table G-1

Table G-3. Data Sheet: Percent Removal for Aroclor 1254
at an initial concentration = 250 µg/l

pH	Mg ²⁺ Dosage (mg/l)	Average * Peak Area	Total Mass (ng)	Removal %
10.0	I.C. [‡]	3256	1.95	-
	0	2645	1.56	20.0
	8	2210	1.30	33.3
	17	2465	1.45	25.6
	33	2988	1.80	9.5
	50	2683	1.58	19.0
10.7	I.C.	3330	2.00	-
	0	2210	1.30	35.0
	8	1740	1.02	49.0
	17	2170	1.26	37.0
	33	1895	1.10	45.0
	50	1685	0.98	51.0
11.4	I.C.	3350	2.01	-
	0	500	0.27	86.6
	8	80	under 0.10	over 95.0
	17	1140	0.65	67.7
	33	950	0.54	73.1
	50	1010	0.58	71.1

[‡]I.C. = see footnote to Table G-1.

*Total area of the 14 main peaks as no peak could be
chosen as a representative one

Table G-4. Data Sheet: Percent Removal for Aroclor 1254
at an initial concentration = 50 µg/l

pH	Mg ²⁺ Dosage (mg/l)	Average Peak Area	Total Mass (ng)	Removal %
10.0	I.C. [‡]	3700	2.20	-
	0	2545	1.50	31.8
	8	3370	2.08	5.5
	17	3160	1.90	13.6
	33	3105	1.85	15.9
	50	3815	2.20	0
10.7	I.C.	3270	1.95	-
	0	3100	1.85	5.1
	8	2900	1.70	12.8
	17	2520	1.50	23.1
	33	2370	1.40	28.2
	50	3100	1.85	5.1
11.4	I.C.	3150	1.90	-
	0	370	0.20	89.5
	8	320	0.17	91.1
	17	185	0.10	94.7
	33	160	0.10	94.7
	50	180	0.10	94.7

[‡]I.C. = see footnote to Table G-1.

Table G-5. Data Sheet: Percent Removal for Dichlorvos
at an initial concentration = 250 µg/l

pH	Mg ²⁺ Dosage (mg/l)	Average Peak Area	Total Mass (ng)	Removal %
10.0	I.C. [‡]	0.70	0.825*	-
	0	0.70	0.825	0.0
	8	0.65	0.763	7.6
	17	0.67	0.788	4.5
	33	0.68	0.800	3.0
	50	0.68	0.800	3.0
10.7	I.C.	0.75	0.880	-
	0	0.45	0.500	43.2
	8	0.60	0.700	20.5
	17	0.38	0.412	53.2
	33	0.50	0.576	34.5
	50	0.60	0.700	20.5
11.4	I.C.	0.75	0.800	-
	0	under 0.20	under 0.175	over 80.0
	8	under 0.20	under 0.175	over 80.0
	17	under 0.20	under 0.175	over 80.0
	33	under 0.20	under 0.175	over 80.0
	50	under 0.20	under 0.175	over 80.0

[‡]I.C. = see footnote to Table G-1.

* As Dichlorvos is fairly soluble in water, only about 40% can be extracted by hexane.

Table G-6. Data Sheet: Percent Removal for Pentachloro-phenol at an initial concentration = 250 µg/l

pH	Mg ²⁺ Dosage (mg/l)	Average Peak Area	Total Mass (ng)	Removal %
10.0	I.C. [‡]	1018	0.56	-
	0	785	0.36	35.7
	8	663	0.30	46.4
	17	850	0.40	28.6
	33	828	0.38	32.1
	50	998	0.47	16.1
10.7	I.C.	750	0.34	-
	0	660	0.30	11.8
	8	222	0.09	73.5
	17	410	0.176	48.2
	33	457	0.198	41.8
	50	595	0.27	20.6
11.4	I.C.	1073	0.51	-
	0	1150	0.55	0.0
	8	665	0.30	41.2
	17	890	0.41	19.6
	33	505	0.222	56.5
	50	1195	0.58	0.0

[‡]I.C. = see footnote to Table G-1.

Table G-7. Data Sheet: Percent Removal for Dieldrin
(mixed in PPE) at an initial concentration
= 250 µg/l

pH	Mg ²⁺ Dosage (mg/l)	Average Peak Area	Total Mass (ng)	Removal %
10.0	I.C. [‡]	500	0.35*	-
	0	393	0.27	23.2
	8	415	0.29	18.9
	17	338	0.23	34.6
	33	249	0.24	31.7
	50	372	0.26	27.5
10.7	I.C.	500	0.35*	-
	0	371	0.26	27.5
	8	366	0.26	27.5
	17	376	0.26	26.1
	33	345	0.24	33.2
	50	177	0.12	67.0
11.4	I.C.	500	0.35*	-
	0	384	0.27	24.6
	8	355	0.25	30.3
	17	305	0.21	40.8
	33	101	0.066	81.2
	50	89	0.058	83.5

[‡] I.C. = see footnote to Table G-1

* An average I.C. of 0.35 ng was used (see Discussion for explanation)

Table G-8. Data Sheet: Percent Removal for Aroclor 1254
(mixed in PPE) at an initial concentration
= 250 µg/l

pH	Mg ²⁺ Dosage (mg/l)	Average Peak Area	Total Mass (ng)	Removal %
10.0	I.C. [‡]	3400	1.98*	-
	0	1974	1.15	41.9
	8	2423	1.44	27.3
	17	2144	1.25	36.9
	33	1953	1.15	41.9
	50	1771	1.02	48.5
10.7	I.C.	3400	1.98*	-
	0	1711	1.00	49.5
	8	1788	1.04	47.5
	17	1864	1.08	45.5
	33	2378	1.40	29.3
	50	806	0.486	75.5
11.4	I.C.	3400	1.98*	-
	0	1709	1.00	49.5
	8	1564	0.90	54.5
	17	1277	0.73	63.1
	33	166	under 0.1	over 95
	50	147	under 0.1	over 95

[‡] I.C. = see footnote to Table G-1

* An average I.C. of 1.98 ng was used (see Discussion for explanation)

Table G-9. Data Sheet: Percent Removal for Dichlorvos
(mixed in PPE) at an initial concentration
= 250 µg/l

pH	Mg ²⁺ Dosage (mg/l)	Average Peak Area	Total Mass (ng)	Removal %
10.0	I.C. [‡]	150	0.74	-
	0	103	0.60	18.9
	8	99	0.43	20.3
	17	115	0.64	13.5
	33	118	0.644	13.0
	50	124	0.67	9.5
10.7	I.C.	152	0.75	-
	0	45	0.37	50.7
	8	37	0.304	59.5
	17	23	0.25	66.7
	33	33	0.31	58.7
	50	23	0.26	65.3
11.4	I.C.	152	0.75	-
	0	9.5	0.15	80.0
	8	9.9	0.15	80.0
	17	12.6	0.178	76.3
	33	4.3	under 0.15	over 80.0
	50	11.2	0.16	78.7

[‡]I.C. = see footnote to Table G-1.

Table G-10. Data Sheet: Percent Removal for Pentachloro-phenol (mixed in PPE) at an initial concentration = 250 µg/l

pH	Mg ²⁺ Dosage (mg/l)	Average Peak Area	Total Mass (ng)	Removal %
10.0	I.C. [‡]	1178	0.56	-
	0	1184	0.58	0.0
	8	1105	0.50	10.7
	17	1145	0.55	1.8
	33	1095	0.52	7.1
	50	1300	0.64	0.0
10.7	I.C.	1287	0.62	-
	0	1155	0.54	12.9
	8	983	0.46	25.8
	17	1250	0.60	3.2
	33	975	0.46	25.8
	50	1340	0.66	0.0
11.4	I.C.	1165	0.56	-
	0	1165	0.56	0.0
	8	920	0.43	23.2
	17	1133	0.54	3.6
	33	365	0.154	72.5
	50	860	0.40	28.6

[‡]I.C. = see footnote to Table G-1.

Table G-11. Data Sheet: Percent Removal for Dieldrin
(mixed in raw sewage) at an initial concentration = 250 µg/l

pH	Mg ²⁺ Dosage (mg/l)	Average Peak Area	Total Mass (ng)	Removal %
10.0	I.C. [‡]	500	0.35*	-
	0	317	0.215	38.9
	8	387	0.265	24.6
	17	415	0.285	18.9
	33	488	0.34	3.3
	50	314	0.215	38.9
10.7	I.C.	500	0.35*	-
	0	422	0.29	17.5
	8	385	0.265	24.6
	17	392	0.27	23.2
	33	414	0.285	18.9
	50	376	0.26	26.1
11.4	I.C.	500	0.35*	-
	0	135	0.088	75.0
	8	138	0.09	74.4
	17	103	0.067	80.9
	33	73	0.047	86.8
	50	75	0.048	86.5

[‡]I.C. = see footnote to Table G-1.

* An average I.C. of 0.35 ng was used (see Discussion for explanation).

Table G-12. Data Sheet: Percent Removal for Aroclor 1254
(mixed in raw sewage) at an initial concentration = 250 µg/l

pH	Mg ²⁺ Dosage (mg/l)	Average Peak Area	Total Mass (ng)	Removal %
	I.C. [‡]	3400	1.98*	-
10.0	0	1766	1.034	47.8
	8	1783	1.05	47.0
	17	1801	1.06	46.7
	33	2012	1.19	39.9
	50	1538	0.88	55.6
	I.C.	3400	1.98*	-
10.7	0	1602	0.92	53.5
	8	1304	0.75	62.1
	17	1572	0.90	54.5
	33	1393	0.81	59.1
	50	1471	0.84	57.6
	I.C.	3400	1.98*	-
11.4	0	1589	0.325	83.6
	8	518	0.285	85.6
	17	325	0.175	91.2
	33	116	under 0.1	over 95.0
	50	72	under 0.1	over 95.0

[‡]I.C. = see footnote to Table G-1

An average I.C. of 1.98 was used (see Discussion for explanation)

Table G-13. Data Sheet: Percent Removal for Dichlorvos
(mixed in raw sewage) at an initial concentration = 250 µg/l

pH	Mg ²⁺ Dosage (mg/l)	Average Peak Area	Total Mass (ng)	Removal %
10.0	I.C. [‡]	134	0.70	-
	0	119	0.65	7.1
	8	118	0.65	7.1
	17	103	0.60	14.3
	33	117	0.64	8.6
	50	103	0.60	14.3
10.7	I.C.	173	0.82	-
	0	75	0.50	39.0
	8	34	0.315	61.6
	17	33	0.31	62.2
	33	78	0.51	37.8
	50	68	0.47	42.7
11.4	I.C.	153	0.76	-
	0	4.9	under 0.15	over 80
	8	7.2	under 0.15	over 80
	17	4.6	under 0.15	over 80
	33	4.7	under 0.15	over 80
	50	11.6	0.168	77.9

[‡]I.C. = see footnote to Table G-1.

Table G-14. Data Sheet: Percent Removal for Pentachloro-phenol (mixed in raw sewage) at an initial concentration = 250 $\mu\text{g/l}$.

pH	Mg ²⁺ Dosage (mg/l)	Average Peak Area	Total Mass (ng)	Removal %
10.0	I.C. [‡]	1315	0.64	-
	0	1263	0.61	4.7
	8	1173	0.56	12.5
	17	1275	0.61	4.7
	33	1200	0.58	9.4
	50	1380	0.67	0.0
10.7	I.C.	1190	0.57	-
	0	1223	0.59	0.0
	8	1015	0.48	15.8
	17	1150	0.56	1.8
	33	1098	0.52	8.8
	50	1283	0.62	0.0
11.4	I.C.	1208	0.58	-
	0	1203	0.58	0.0
	8	1030	0.49	15.5
	17	957	0.45	22.4
	33	920	0.43	25.9
	50	1230	0.594	0.0

[‡]I.C. = see footnote to Table G-1.

Table G-15. Data Sheet: Percent Removal for Dieldrin
(elevated alkalinity) at an initial concentration = 250 µg/l

pH	Mg ²⁺ Dosage (mg/l)	Average Peak Area	Total Mass (ng)	Removal %
10.0	I.C. [‡]	503	0.355	-
	0	435	0.30	15.5
	8	405	0.28	21.1
	17	430	0.295	16.9
	33	433	0.30	15.5
	50	440	0.305	14.1
10.7	I.C.	518	0.36	-
	0	392	0.27	25.0
	8	395	0.27	25.0
	17	380	0.26	27.8
	33	388	0.265	26.4
	50	371	0.255	29.2
11.4	I.C.	498	0.35	-
	0	148	0.098	72.0
	8	98	0.064	81.7
	17	144	0.094	73.1
	33	124	0.082	76.6
	50	65	0.042	88.1

[‡]I.C. = see footnote to Table G-1.

Table G-16. Data Sheet: Percent BOD Removal in PPE
 BOD_5 for PPE = 56.29 mg/l

pH	Mg ²⁺ Dosage (mg/l)	Average (a) BOD (mg/l)	Removal %*
10	0	52.70	6.4
	8	57.80	0.0
	17	55.07	2.2
	33	54.54	3.1
	50	53.90	4.2
10.7	0	50.19	10.8
	8	47.57	15.5
	17	46.14	18.0
	33	47.83	15.0
	50	50.12	11.0
11.4	0	46.82	16.8
	8	46.03	18.2
	17	43.89	22.0
	33	38.15	32.2
	50	39.35	30.1

$$* \text{ Removal } \% = \frac{\text{BOD}_5 \text{ of PPE} - (a)}{\text{BOD}_5 \text{ of PPE}}$$