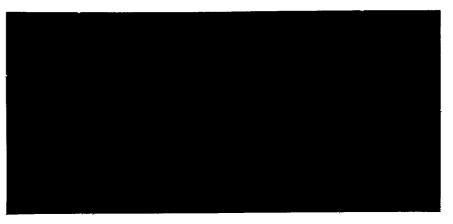114/1/8

SURVEY OF THE EFFECTIVENESS OF OZONE AND
ULTRA-VIOLET LIGHT IN REDUCING THE
CONCENTRATION OF PESTICIDES IN DRINKING
WATER(WTT 9891SLG)

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SURVEY OF THE EFFECTIVENESS OF OZONE AND ULTRAVIOLET LIGHT IN REDUCING THE CONCENTRATION OF PESTICIDES IN DRINKING WATER (WTT 9891 SLG)

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SUMMARY

I   **OBJECT**

The objective of this work was to perform a review of available literature with the aim of determining the suitability of ozone and ultra-violet light for treating water containing pesticides.

II   **REASONS**

Water Authorities and companies have been proposing the use of ozone and/or ultra-violet light in water treatment for the removal of one or more pesticides from drinking water. The Department of the Environment (DoE) have been concerned that programmes for capital expenditure in this area are based on inadequate process design data for some of the pesticides present in water. Therefore, they commissioned WRc to perform a literature review to assess the potential of ozone, as well as ultra-violet light, to reduce concentrations of any of the 19 pesticides that have been detected in drinking water supplies at concentrations above the EC Directive standard from water.

III   **CONCLUSIONS**

The overall conclusion from the study is that there is very little experience with the use of ozone and/or ultra-violet light to remove any of the pesticides on the DoE list of 19 from water. Of the list of 19 there is only information on 8 that relates to the two processes. These are atrazine, simazine, propazine, linuron, 2,4-D, MCPA, MCPB and malathion.

Most of the information available is from laboratory scale work, with high pesticide concentrations at the mg/l level. Ozone is effective at removing pesticides at these concentrations, but the results indicate that the reactivity is low.

Contact times of greater than 15 minutes are required for pesticide removal. However, from the published data it is not possible to demonstrate a relationship between contact time and degree of removal.

No assessment of the required dose was possible for individual pesticides. Therefore, no cost estimates were possible for the removal of pesticides by ozone.

IV   RECOMMENDATIONS

The lack of information about the removal of pesticides from water by ozone and/or ultra-violet light indicates that there is a need for more work to be performed in this area, particularly for the listed pesticides encountered in drinking water at concentrations above the EC Directive standard.

V   RESUMÉ OF CONTENTS

A review of literature related to the use of ozone and/or ultra-violet light for the control or removal of the listed pesticides from water is presented.

CONTENTS

SECTION 1 - INTRODUCTION

The DoE have commissioned WRc to conduct a survey of the effectiveness of ozone and ultra-violet light at reducing the concentration of pesticides in drinking water.

The objective of the work was to survey published literature to assess the efficiency and cost effectiveness of ozone and/or ultra-violet light at removing pesticides from water. This was to take into account process operating conditions, type and concentration of pesticide, physiochemical properties of the water treated and the degree of confidence in the data presented.

Nineteen pesticides specified by the DoE were to be studied. These were placed by the DoE in two groups of high and medium priority, and were:

High priority:

Atrazine

Simazine

Isoproturon

Mecoprop

Chlortoluron

Propazine

2,4-D

Linuron

MCPB

Dicamba

EPTC.

Medium priority:

Chlorpyralid

Bromoxynil

Malathion

Dichlorprop

MCPA

Prometryne

Dimethoate

Carbetamide.

Where possible, the results from the literature have been presented in terms of
the initial pesticide concentration, percentage removed, ozone consumption
(ozone applied minus ozone residual) and the applied dose (ozone added) in
mg O_3 per mg of pesticide removed and the applied ultra-violet power
consumption.

SECTION 2 - LITERATURE SURVEY

A survey of the published literature has only found reference to 8 of the 19 listed pesticides that related to their removal by ozone and/or ultra-violet light. These 8 were:

Atrazine

Simazine

Propazine

Linuron

2,4-D

MCPB

MCPA

Malathion.

For these compounds the published data range from laboratory to full scale work. A distinction has been made where possible.

The pesticides of interest have been grouped into five groups that classify them by their chemical structure. These are:

(a)   Triazines; atrazine, simazine, propazine, prometryne;

(b)   Chlorphenoxy: mecoprop, 2,4-D, MCPB, MCPA, dichlorprop;

(c)   Phenylamides: isoproturon, chlortoluron, linuron;

(d)   Organophosphorus: malathion, dimethoate; and

(e)   Others: bromoxynil, carbetamide, chlorpyralid, dicamba, EPTC.

Since the processes of ozonation and ultra-violet irradiation involve oxidation reactions, similar reactions may occur with pesticides in the same group. Therefore, an indication of the possible effect of ozone and ultra-violet light may possibly be inferred from the results from the work on other pesticides in the same group, where no information is available on the particular pesticide of interest.

2.1   TRIAZINES

Laboratory scale experiments, on drinking water spiked with triazines (atrazine, simazine and propazine), showed that complete removal was not possible by ozonation, at ozone doses typically used to treat water. Initial concentrations of the pesticides were from 0.25 to 0.74µg/l, which are those typically found in the River Rhine[1]. Table 1 shows the removals obtained for different ozone doses.

Table 1 - The effectiveness of ozone at removing triazines from water

PESTICIDE	INITIAL CONCENTRATION (µg/l)	REMOVAL (%) AT DIFFERENT OZONE DOSES		
		1mg/l	2mg/l	3mg/l
Atrazine	0.74	17	22	42
Simazine	0.25	23	27	53
Propazine	0.64	19	23	39

Contact times of between 20 and 80 minutes were used for the ozonation, however, the effect of contact time was not specified and is not shown in Table 1. The results presented in Table 1 show that even for low pesticide concentrations, and typical ozone doses, the EC Directive standard of 0.1µg/l cannot be met. The lowest concentration achieved was for simazine, which was reduced from 0.25 to 0.11µg/l, at the highest ozone dose.

From Table 1, for the high ozone doses, the applied ozone doses can be determined; these are 9600, 2300 and 1200mg O_3 per mg of pesticide removed for atrazine, simazine and propazine respectively. It can be seen from these results that it is easier to oxidise atrazine than the other two pesticides.

A laboratory scale bubble column reactor was used to oxidise atrazine with ozone[2]. The reactor had a volume of 3 litres and was operated by

recirculation of the atrazine solution. Ozone was generated from air, the gas flowrate being 11 litres/hour, with an ozone content of 14.9mg O_3/l. It took 100 minutes to achieve what was considered to be 100% removal of atrazine (detection limits were not given), for an initial concentration of 20.3mg/l, and at pH 5.5. At this point the ozone applied was 4.5mg O_3 per mg of atrazine, whereas the ozone consumption was 0.71mg/mg.

Two decomposition products of atrazine were identified through mass spectrometer analysis. One was 2-chloro-4-amino-6-isopropyl-amine-1,3,5-triazine. The final structure of the other decomposition product was not determined.

Simazine solutions, concentration 2.8mg/l, were ozonated with ozone doses of 2 to 24mg/l, but no reaction occurred. No other information was given[3].

Atrazine and simazine were present in German drinking water extracted from the Lower Rhine. Ozonation, at two waterworks, was used in treating this water after it had filtered through the soil of the river bank, but process conditions were not given[4]. At one waterworks a removal of 42% for an initial concentration of 0.19μg/l of atrazine was reported. At the other, an atrazine removal of 29% for an initial concentration of 0.17μg/l. Simazine removals were 53 and 40% at the two waterworks for initial concentrations of 0.15 and 0.09μg/l respectively. After ozonation, the atrazine concentration was still above 0.1μg/l at the two waterworks.

Pilot scale ozonation, dose of 2mg O_3/l, of clarified and filtered Mississippi River water, contaminated with atrazine, resulted in an average removal of 83% for a concentration range of 0.02 to 0.26μg/l[5].

The removal of atrazine by ultra-violet light, at Bergamo in Italy, was ineffective[6]. High intensity ultra-violet lamps were used, but no details other than this were given. The effect of water flowrate was studied. Increasing flowrates were found to reduce the effectiveness of ultra-violet irradiation. For an initial atrazine concentration of

0.86µg/l the following final concentrations were obtained: 0.69, 0.72 and 0.78µg/l, for flowrates of 5, 10 and 15 litres/minute respectively.

2.2   CHLORPHENOXY

Ozone can provide thorough destruction of 2,4-D[7]. Thorough destruction was assumed because of the formation of chloride ions. A 35 minute contact time was required to reduce a 2,4-D concentration of 22mg/l down to 1mg/l in laboratory scale tests. Ozonation was found to produce a drop in pH, therefore, the experiments were conducted in phosphate buffered solutions at pH 6.9. An ozone consumption of 1.4mg O_3 per mg of 2,4-D was reported, whereas the applied dose was 5.7mg/mg.

Other laboratory work has also looked at the ozonation of 2,4-D and MCPA[8]. A bubble column reactor (volume 3.5 litres), with ozone produced at 200 to 220mg/hour in an ozone-air mixture circulated at a flowrate of between 3.3 and 3.5 litres/hour, was used. The initial concentrations of 2,4-D and MCPA were 22.1 and 30mg/l respectively. In each case a 100% removal was reported after a contact time of 30 minutes. The ozone consumption for 2,4-D and MCPA were reported as 0.87 and 0.48mg O_3 per mg of pesticide respectively, but the applied doses were approximately 1.4 and 1.0mg/mg.

The effectiveness of ozone at removing chlorphenoxy pesticides, in buffered solutions at pH 8 has been reported[9]. The results are shown in Table 2.

Table 2 - The effectiveness of ozone at removing chlorphenoxy pesticides

PESTICIDE	PESTICIDE CONCENTRATION (µg/l)		OZONE CONCENTRATION (mg/l)		CONTACT TIME (minutes)	REMOVAL (%)
	INITIAL	FINAL	INITIAL	FINAL		
2,4-D	79.6	43.6	4.25	2.28	30	45.3
MCPA	18.3	0.2	4.35	2.81	32	99.0
MCPB	18.6	0.2	4.35	2.81	30	99.0

Table 2 shows that ozone is more effective at removing MCPA and MCPB than 2,4-D but that higher ozone doses were applied. For MCPA and MCPB the applied ozone doses were 240 and 236mg O_3 per mg of pesticide removed, whereas for 2,4-D the dose was 118mg/mg. The corresponding ozone consumptions were 85.1, 83.7 and 54.7mg O_3/mg.

2.3 PHENYLAMIDES

Laboratory scale ozonation was used to treat an aqueous solution containing 24.9mg/l of linuron. Ozonation was carried out in a 2.2 litre reactor with an air flowrate of 0.5 litres/minute, at an ozone concentration of 14.5mg O_3/litre. Decomposition of linuron occurred under alkaline conditions, although pH had little influence on the removal for the pH range studied, i.e. 7 to 12. To achieve complete removal (the detection limit was not given so the final concentration cannot be assessed) a contact time of approximately 50 minutes was required. The ozone consumption was found to be 3.3 to 3.6mg O_3 per mg of linuron removed, but the applied ozone dose over the 50 minutes was 14.7mg/mg[10].

No information is available on the destruction of linuron, chlortoluron or isoproturon by ultra-violet light. However, the destruction of neburon (another phenylamide) by ultra-violet irradiation and ultra-violet catalysed chlorination has been studied[11]. Two 15W ultra-violet lamps,

producing radiation at a wavelength of 254nm, were used for the experiments. Buffered solutions at pH 7 were used. When only ultra-violet irradiation was used, the neburon removal was 30%. This was increased to 45% when ultra-violet catalysed chlorination was used, with a chlorine dose of 10mg/l.

2.4 ORGANOPHOSPHORUS

Ozonation of malathion produces malaoxon, but this was a first step intermediate and was oxidised to H_3PO_4 and other, unidentified, oxidation products[12].

Ozonation of a 10mg/l aqueous solution of malathion, using an ozone dose of 3.5mg/l, resulted in the malathion concentration being reduced to 2mg/l. When the ozone dose was increased to 9.8mg/l the malathion concentration was reduced to 1mg/l. To cause total destruction of malathion, an ozone dose of 26mg/l was required, this corresponds to an ozone consumption of 2.5mg O_3 per mg of malathion[13].

Results of experiments which treated malathion with ozone and ultra-violet irradiation have been reported[14]. These results are presented in Table 3.

Table 3 - Malathion removal by ozone and/or ultra-violet light

MALATHION CONCENTRATION (mg/l)		CONTACT TIME (minutes)	APPLIED OZONE DOSE (mg O_3/mg malathion)	ULTRA-VIOLET DOSE (W/l)
INITIAL	FINAL			
90	<1.0	15	1.2	0.0
6	<1.0	30	37.0	0.0
62	6.0	120	0.0	4.5
58	<1.0	120	0.0	4.5
94	<1.0	15	1.2	1.5
82	<1.0	15	1.1	1.5
80	<0.5	30	1.8	14.3
55	<0.1	30	3.7	4.5

Table 3 shows that ultra-violet can be used to remove malathion but longer contact times are required than for ozone. Combining ozone and ultra-violet irradiation resulted in a slightly faster degradation. After a contact time of 30 minutes, the malathion concentration was less than 0.1mg/l for an initial concentration of 55mg/l.

2.5 CONCLUSIONS

Ozonation has been reported for the removal of 8 of the list of 19 pesticides from water. Laboratory scale ozonation has shown that ozone is effective at reducing high concentrations of pesticide, but low concentrations have rarely been considered. Therefore, it is difficult to assess the viability of ozone for removing low concentrations of pesticides to below EC Directive standard.

The work that has considered low concentrations at laboratory scale, has found that ozone, at doses of 1 to 3mg/l, is ineffective at reducing triazine concentrations to below 0.1µg/l. Also, that the applied ozone doses are much higher for lower pesticide concentrations. However, the results from full scale works for low concentrations of simazine (below 0.15µg/l) showed that ozone could be used to reduce the concentration to less than 0.1µg/l.

The results of the ozone work show that ozone reacts with pesticides. However, a wide range of experimental conditions are used in terms of applied dose, contact time, pesticide concentration and raw water quality. Most of the work reported has been for laboratory scale experiments. It is , therefore, difficult to assess the effectiveness of ozone at removing pesticides on a full scale plant. This is especially so, since no direct comparision between laboratory work and full scale plant data has been made.

In some cases, the ozone dose and residual are not quoted. Therefore, it is not possible to specify an ozone dose for the removal of a given pesticide.

Contact times of between 15 and 120 minutes have been used but the effect of contact time has not been fully documented. For the chlorphenoxy pesticides a lower contact time of typically 15 minutes is required, whereas for the other types of pesticide, 60 minutes or more is necessary.

The application of ultra-violet light is relatively ineffective at removing pesticides when compared to ozone. However, when both processes are combined, pesticides are removed more effectively with lower contact times being required. Most of the work that has considered ultra-violet irradiation, however, has only been for high pesticide concentrations.

SECTION 3 - COSTS

To assess the effectiveness of a process an assessment of technical feasibility needs to be made. It is also useful to be able to make cost estimates for the installation of the process. For the removal of pesticides from water using ozone and/or UV light no costs estimates have been made because of the lack of available information on applying such technology for this purpose.

Most of the work related to ozonation has been for laboratory scale experiments, and information concerning pilot or full scale work is scarce. This means that it is difficult to assess the ozone doses required to reduce pesticide concentrations to $0.1\mu g/l$. Laboratory work, in general, only gives the ozone consumption for the pesticide in solution without the presence of other organics. Therefore, for a full scale plant, where the raw water contains other organics, it is not possible to specify ozone requirements from laboratory studies. For this reason the cost estimates can not be determined for the removal of individual pesticides, or a mixture of pesticides.

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