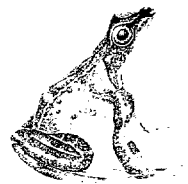
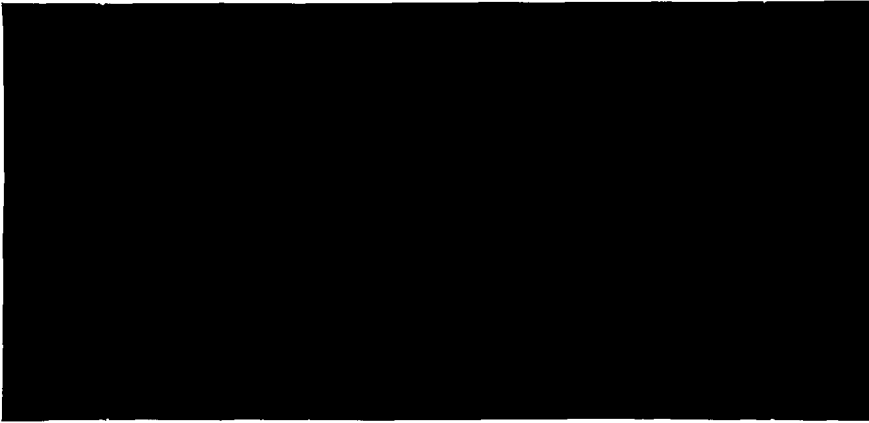


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**CONSULTANCY: REMOVAL OF PESTICIDES BY GAC AND  
GAC/OXIDANTS**

**DoE 2922**

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**CONSULTANCY: REMOVAL OF PESTICIDES BY GAC AND GAC/OXIDANTS**

**FINAL REPORT TO THE DRINKING WATER INSPECTORATE, DEPARTMENT OF THE ENVIRONMENT**

Report No: DoE 2922

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Contract No: TMU 9034

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## SUMMARY

Water companies are required to comply with the standards for pesticides set in the Water Supply (Water Quality) Regulations 1989. Companies have given undertakings to the Secretary of State, under Section 20 of the Water Act 1989, which require them to carry out improvement programmes to secure or facilitate compliance with these standards. The Drinking Water Inspectorate (DWI) is currently reviewing these undertakings and needs to be satisfied that the improvement programmes, and those in any new undertakings, represent the most practical and appropriate steps to take and the timescales are appropriate. Therefore, the DWI, on behalf of the Department of the Environment, has commissioned WRC to produce a report which sets out the current state of knowledge on the effectiveness and use of granular activated carbon (GAC) or of GAC/oxidants (particularly ozone) for the removal of triazine, uron and phenoxyalkanoic acid pesticides from drinking water.

Properly designed and operated granular activated carbon processes can be effective at removing triazines, urons and phenoxyalkanoic acids to below the maximum permissible concentration of 0.1µg/l in drinking water. However, the effectiveness of GAC filters, i.e. the magnitude of the regeneration interval, depends on the type of pesticide, the influent pesticide concentration, the type of GAC and empty bed contact time. Coal and wood based GACs appear to give longer bed lives than other types of GAC. The type of water treated would seem to have no effect on the order of effectiveness of the different types of GAC studied. However, treatment of groundwaters may lead to longer bed lives than for surface waters because groundwaters, in general, have a lower total organic carbon content.

GAC may be used to replace the sand in the rapid gravity filters. Rapid gravity beds are usually designed to operate with short contact times, which give high volumetric throughputs, and this may lead to a short GAC bed life. The bed life may be so short that the regeneration frequency becomes operationally impractical in which case purpose built GAC adsorbers can be installed as post-filter adsorbers. In general, each treatment plant needs to be looked at individually to determine the position of the GAC bed since it depends on several factors: the pesticides to be removed and their level of occurrence, the

type of treatment works and what is an operationally acceptable regeneration interval.

For the pesticides covered in this report, ozonation has been shown to reduce the concentrations of pesticides in water. The evidence so far indicates that higher percentage removals are obtained for urons and phenoxyalkanoic acids than for triazines. In general, the effectiveness of ozonation is dependent on the type of pesticide, the pesticide concentration and ozone dose.

Work is showing that atrazine is more readily removed by a combination of ozone and hydrogen peroxide, than by ozone on its own.

The position in the process stream where ozonation is installed may not be important for the removal of the pesticides discussed in this report. What appears to be more important than the position of ozonation in the process stream are the ozone dose and the type and concentration of pesticide present in the water. However, the position of the ozonation stage may be important for other uses of ozone.

For the pesticides covered in this report, combining GAC filtration with ozonation may extend the bed life of the GAC. If ozonation and GAC filtration are to be combined, ozonation should precede GAC filtration.

Breakthrough of bacteria populated carbon fines may be reduced by minimising changes in flow rate during normal operation. High influent turbidities to the GAC bed seem to increase the amount of bacteria on the carbon fines.

The formation of brominated trihalomethanes is strongly dependent on the ozone dose, bromide concentration, bicarbonate concentration, pH and type of organic substances present. Owing to this complex chemistry, it is difficult to predict the extent of the formation of brominated trihalomethanes at a particular site. It is also known that ozone will react with bromide in water to give bromate.

Ozone will react with organic matter in water to produce assimilable organic carbon (AOC) which could lead to biological aftergrowth in distribution. GAC (both as a sand replacement and a post-filter adsorber) or sand filters (both rapid gravity and slow sand filters) will reduce the AOC concentration but may not reduce the levels to those found before ozonation.

Desorption of adsorbed substances once a GAC bed is exhausted has not been observed to date for pesticides.

Limited work has been undertaken on assessing the extent and control of any potentially deleterious side effects from the use of GAC or GAC/ozone for the removal of pesticides and further work is needed to clarify the situation.

## CONTENTS

	PAGE
SUMMARY	(i)
SECTION 1 - INTRODUCTION	1
SECTION 2 - GRANULAR ACTIVATED CARBON	2
2.1    TRIAZINES	2
2.2    URONS AND PHENOXYALKANIC ACIDS	3
SECTION 3 - OZONATION	4
3.1    TRIAZINES	4
3.2    URONS AND PHENOXYALKANOIC ACIDS	5
SECTION 4 - GAC/OZONATION	6
SECTION 5 - PROCESS STEAM	7
5.1    GRANULAR ACTIVATED CARBON	7
5.2    OZONATION	7
5.3    GAC/OZONATION	8
SECTION 6 - POTENTIALLY DELETERIOUS SIDE EFFECTS	9
SECTION 7 - CONCLUSIONS	10

## SECTION 1 - INTRODUCTION

The Water Supply (Water Quality) Regulations 1989 set a maximum concentration in drinking water of 0.1µg/l for any individual pesticide. Hence there is a need to assess the effectiveness of any proposed treatment to reduce pesticide concentrations below the maximum permissible concentration.

WRc has been commissioned by the DoE to produce a report which sets out the current state of knowledge on the effectiveness and use of granular activated carbon (GAC) or of GAC/oxidants (particularly ozone) for the removal of pesticides from water supplies. Aspects of the treatment process to be included in the report are the type of source water, operating conditions, type of GAC, and how far it is possible to ensure that there will not be any potentially deleterious side effects from the use of GAC or GAC/oxidants. The pesticides to be covered are the triazines (atrazine and simazine), the urons (chlortoluron, isoproturon and diuron) and the phenoxyalkanoic acids (MCPA, MCPB, mecoprop and 2,4-D). These pesticides are the ones which presently cause the most problems in water supplies.

A similar study was undertaken by WRc for the DoE in 1989 and this report summarises the advances in the state of knowledge about the effectiveness of GAC and GAC/ozone on reducing pesticide concentrations in drinking water from 1989 to the present time.

Results from UK pilot plant trials (at lowland surface water and groundwater sites, each treating up to 3m<sup>3</sup>/hr) and laboratory experiments (for lowland surface water, upland surface water and groundwater), that were begun in 1989 and are still ongoing, on the removal of pesticides are summarised. The pesticide concentrations used in these studies (up to 1µg/l) are typical of those found in some water supplies in the UK, where pesticides are detected above 0.1 µg/l. No results are reported for lowland surface water treated by slow sand filtration. The pilot plant trials at the lowland surface water site are treating the water by chemical coagulation, clarification and rapid sand filtration.

In addition, results from studies in other countries are reported.



## SECTION 2 - GRANULAR ACTIVATED CARBON

### 2.1 TRIAZINES

Pilot plant studies are being undertaken to assess the effectiveness of different types of GACs at removing triazines (atrazine and simazine, in addition to other pesticides) from chemically coagulated, clarified and rapid sand filtered lowland surface water. The GAC columns are used under identical operating conditions (for example, the same empty bed contact times (EBCTs<sup>+</sup>)) with water from the same process stream and so the results can be compared directly.

With an average influent atrazine concentration of 0.2µg/l (range of 0.11 to 0.55µg/l) and an EBCT of 15 minutes, all columns removed atrazine to less than the maximum permissible concentration (0.1µg/l). The GAC bed lives\* ranged from 11 to greater than 42 weeks (in some instances a concentration of 0.1µg/l has not been exceeded after this period of time) and were dependent on the GAC type. Wood and coal based GACs had longer bed lives than peat and coconut GACs.

When atrazine and simazine occur in water supplies, atrazine is typically present in higher concentrations than simazine. With an average influent simazine concentration of 0.13µg/l (range of 0.06 to 0.63µg/l) and an EBCT of 15 minutes, the bed lives for simazine removal were longer than for atrazine removal because of the lower influent simazine concentration.

In addition to the columns operated with EBCTs of 15 minutes, a column containing a coal based GAC was operated with an EBCT of 5 minutes. The bed life of this column for atrazine removal was 30 weeks. Studies have shown that GAC bed lives are strongly dependent on the EBCT, and, as a rule of thumb, tripling the EBCT results in a tripling of the GAC bed life.

+ EBCT is defined as the bed volume divided by the volumetric flow rate through the bed.

\* Period when the GAC is capable of reducing the pesticide concentration to below 0.1 µg/l.

Laboratory studies with upland surface water, spiked with atrazine and simazine, and groundwater, taken from a borehole containing triazines above 0.1 µg/l, also indicated that longer bed lives will be obtained with coal and wood based GACs, than with peat and coconut GACs.

Groundwaters, in general, have lower levels of total organic carbon (TOC) than surface waters and laboratory tests have shown that GACs have a higher capacity for pesticides in groundwaters. Therefore, the bed lives of GACs used to treat groundwater are likely to be longer than those mentioned previously for lowland surface water as there is less competition for the adsorption sites from TOC. German studies, published in late 1989, have shown that for an average influent atrazine concentration of 0.2µg/l and EBCT of 11 minutes, the GAC bed life is over 100 weeks with groundwaters.

## **2.2 URONS AND PHENOXYALKANOIC ACIDS**

Laboratory tests with lowland surface water spiked with phenoxyalkanoic acid and uron pesticides indicate that urons are adsorbed as effectively as triazines, but the phenoxyalkanoic acid pesticides are not removed as effectively because the GACs tested so far (coal and peat based) have a lower capacity for these pesticides.

Similar experiments are underway with a groundwater spiked with phenoxyalkanoic acids and urons.

Pilot plant trials have shown that the concentration of phenoxyalkanoic acids can be reduced to below the maximum permissible concentration but a GAC bed life has not been determined because phenoxyalkanoic acids are only periodically present in the water supply that has been examined.

### SECTION 3 - OZONATION

Work up to 1989 showed that the most effective oxidant for reducing pesticide concentrations in drinking water was ozone. The advances, since 1989, on the effectiveness of ozonation for removing pesticides are discussed in this section.

#### 3.1 TRIAZINES

Pilot plant trials have been conducted with both raw and chemically coagulated, clarified lowland surface water to assess the effectiveness of ozonation without GAC adsorption for the removal of triazines. No difference was observed between the results obtained for the raw and chemically coagulated, clarified waters.

The tests showed that the degree of removal is strongly dependent on the influent pesticide concentration and the ozone dose. With ozone doses in the range of 1 to 3mg/l (i.e. typical of those traditionally used in water treatment) and typical contact times of 5 to 10 minutes, atrazine removals of the order of 15 to 30% and simazine removals of 20 to 35% were obtained. The tests show that higher degrees of removal (e.g. greater than 60%) are only obtained with much higher ozone doses (greater than 9mg/l).

The results show that ozonation alone, at typical doses of 1 to 3 mg/l, cannot be guaranteed to reduce triazine concentrations to below 0.1µg/l, unless the pesticides are present at concentrations below 0.12µg/l.

Tests with spiked upland surface water have been conducted on the laboratory scale and conclusions similar to those in the previous paragraphs have been drawn.

Laboratory tests with groundwater, taken from a borehole containing atrazine above 0.1 µg/l, have shown that higher atrazine removals of up to 60% are possible with ozone doses up to 3mg/l.

Work currently being undertaken in France is showing that atrazine is more readily removed by a combination of ozone and hydrogen peroxide, than by ozone on its own. Ozonation of tap water, at a dose of 5mg/l, and with a contact time of 10 minutes, produced an atrazine removal of 46% for an influent concentration of 0.37µg/l. When 2.8mg/l of hydrogen peroxide was added the removal increased to 89%.

### **3.2 URONS AND PHENOXYALKANOIC ACIDS**

Laboratory studies have indicated that ozonation is more effective at removing urons and phenoxyalkanoic acids than triazines from spiked lowland surface water. Ozone doses of 3 to 4mg/l have been shown to produce removals in the range of 40 to 90% for influent concentrations in the range of 0.3 to 0.5µg/l and with contact times in the range of 5 to 15 minutes.

Pilot plant studies with lowland surface water have shown that mecoprop concentrations can be reduced from 0.14µg/l to less than 0.1µg/l with ozone doses of 3 to 5mg/l, for a contact time of 10 minutes.

#### **SECTION 4 - GAC/OZONATION**

Laboratory tests with lowland surface water have shown that ozonation does not affect the capacity of coal and peat based GACs for removing triazines.

In theory, ozonation combined with GAC adsorption should give an additional benefit of extending the bed life of the GAC by reducing the amount of pesticide going on to the GAC. Pilot plant studies (at lowland surface water and groundwater sites) are underway to quantify the magnitude of this extension. This is likely to be strongly dependent on operating conditions and water quality, for example, the type of GAC, the ozone dose and influent pesticide concentration.

## **SECTION 5 - PROCESS STREAM**

### **5.1 GRANULAR ACTIVATED CARBON**

For conventional water treatment plants treating surface water by chemical coagulation and clarification there are generally two options for the use of GAC for pesticide removal within the process stream.

GAC may be used to replace the sand in the rapid gravity filters. Rapid gravity sand filters are usually operated with short contact times (EBCTs in the range of 4 to 6 minutes) which give high volumetric throughputs. High volumetric throughputs can lead to a short GAC bed life; there could be instances where the GAC bed life is so short that the treatment objective of 0.1µg/l may be achieved only at regeneration frequencies that are operationally impractical. In such circumstances, the second option is to install purpose built GAC adsorbers with longer EBCTs after the rapid gravity filters and before final chlorination of the treated water.

In general, the position of the GAC beds will depend on the type of treatment works, the pesticides to be removed, the pesticide concentrations and what is considered to be an operationally acceptable regeneration frequency.

### **5.2 OZONATION**

There are three possible positions in the process stream at a works treating surface water for installing ozonation units. Ozone can be installed at the inlet of the works, after clarification or after sand filtration. Pilot plant trials on the effectiveness of ozonation for the removal of triazines from raw and chemically coagulated, clarified lowland surface water (section 3.1) indicate that, for pesticide removal, the position of the ozonation stage in the treatment process may not be important. What is likely to be more important is the ozone dose that is used and the type and concentrations of pesticides that are present in the water being treated. However, the position of the ozonation stage

may be important for other uses of ozone, for example, removal of taste and odour problems.

### **5.3 GAC/OZONATION**

If a GAC filter and ozonation unit are to be used in combination, ozonation should precede GAC filtration.

## SECTION 6 - POTENTIALLY DELETERIOUS SIDE EFFECTS

An American study, published in 1987, with operating GAC filtration units has been conducted to determine the effect of operational variables on the breakthrough of bacteria populated carbon fines. The study showed that the breakthrough of carbon fines was related to increased flow rates and bed depth of the GAC filter but not to bed life. To combat this breakthrough, it was recommended that changes in flow rates during normal operation should be minimised. In addition, the amount of bacteria associated with the carbon fines was found to increase with increasing turbidity of the influent to the GAC filters.

The formation of brominated trihalomethanes (THMs) as a by-product from ozone oxidation of pesticides is known to be strongly dependent on ozone dose, bromide and bicarbonate concentrations, the type of organic substances present and pH. As a result, the prediction of the degree of formation of brominated THMs at a particular site is difficult. It is also known that ozone will react with bromide in water to give bromate.

Ozone will react with organic matter in water to produce assimilable organic carbon (AOC) which could lead to biological aftergrowth in distribution. It has been reported that GAC (both as a sand replacement and a post-filter adsorber) or sand filters (both rapid gravity and slow sand filters) will reduce the concentration of AOC. However, AOC levels after filtration may be still higher than those found before ozonation.

The phenomenon of desorption of adsorbed substances once a GAC bed is exhausted is well known for weakly adsorbed compounds, for example, chloroform and carbon tetrachloride. However, for pesticides, the existence of this phenomenon has not been observed to date.

The above paragraphs show that further work is required on assessing the presence and control of any potentially deleterious side effects to clarify the best methods of minimising their impact, if any.



## SECTION 7 - CONCLUSIONS

Properly designed and operated granular activated carbon processes can be effective at removing triazines, urons and phenoxyalkanoic acids to below the maximum permissible concentration of 0.1µg/l in drinking water. However, the effectiveness of GAC filters, i.e. the magnitude of the regeneration interval, depends on the type of pesticide, the influent pesticide concentration, the type of GAC and empty bed contact time. Coal and wood based GACs appear to give longer bed lives than other types of GAC. The type of water treated would seem to have no effect on the order of effectiveness of the different types of GAC studied. However, treatment of groundwaters may lead to longer bed lives than for surface waters because groundwaters, in general, have a lower TOC content.

GAC may be used to replace the sand in the rapid gravity filters. Rapid gravity beds are usually designed to operate with short contact times, which give high volumetric throughputs, and this may lead to a short GAC bed life. The bed life may be so short that the regeneration frequency becomes operationally impractical in which case purpose built GAC adsorbers can be installed as post-filter adsorbers. In general, each treatment plant needs to be looked at individually to determine the position of the GAC bed since it depends on several factors: the pesticides to be removed and their level of occurrence, the type of treatment works and what is an operationally acceptable regeneration interval.

For the pesticides covered in this report, ozonation has been shown to reduce the concentrations of pesticides in water. The evidence so far indicates that higher percentage removals are obtained for urons and phenoxyalkanoic acids than for triazines. In general, the effectiveness of ozonation is dependent on the type of pesticide, the pesticide concentration and ozone dose.

Work is showing that atrazine is more readily removed by a combination of ozone and hydrogen peroxide, than by ozone on its own.

The position in the process stream where ozonation is installed may not be important for the removal of the pesticides discussed in this report. What appears to be more important than the position of ozonation in the process

stream are the ozone dose and the type and concentration of pesticide present in the water. However, the position of the ozonation stage may be important for other uses of ozone.

For the pesticides covered in this report, combining GAC filtration with ozonation may extend the bed life of the GAC. If ozonation and GAC filtration are to be combined, ozonation should precede GAC filtration.

Breakthrough of bacteria populated carbon fines may be reduced by minimising changes in flow rate during normal operation. High influent turbidities to the GAC bed seem to increase the amount of bacteria on the carbon fines.

The formation of brominated trihalomethanes is strongly dependent on the ozone dose, bromide concentration, bicarbonate concentration, pH and type of organic substances present. Owing to this complex chemistry, it is difficult to predict the extent of the formation of brominated trihalomethanes at a particular site. It is also known that ozone will react with bromide in water to give bromate.

Ozone will react with organic matter in water to produce assimilable organic carbon which could lead to biological aftergrowth in distribution. GAC (both as a sand replacement and a post-filter adsorber) or sand filters (both rapid gravity and slow sand filters) will reduce the AOC concentration but may not reduce the levels to those found before ozonation.

Desorption of adsorbed substances once a GAC bed is exhausted has not been observed to date for pesticides.

Limited work has been undertaken on assessing the extent and control of any potentially deleterious side effects from the use of GAC or GAC/ozone for the removal of pesticides and further work is needed to clarify the situation.