Activated Carbon in Drinking Water Treatment: Herbicide Adsorption in the Presence of Natural Organic Material

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LICENTIATUPPSATS

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Appendix I Article published in Water Supply, 11, 139-148, 1993. Pesticide interaction with activated carbon in the presence of dissolved organic material

Abstract

Herbicides are a continuing threat to drinking water treatment, partly due to extreme seasonal variations in concentrations and loadings. Conventional drinking water treatment is not designed to remove herbicides, although activated carbon can provide effective removal under ideal conditions. It is known that dissolved organic material (DOM) can affect adsorption properties of organic micropollutants by activated carbon and in this study the competitive adsorption of DOM and herbicides at the activated carbon surface was investigated.

One of the potential mechanisms for DOM interference is competitive adsorption with herbicides at the activated carbon surface. Bench-scale adsorption isotherm experiments with the herbicides MCPA and atrazine, added to both ultrapure water and to lake water with DOM, were carried out. An indication of competitive adsorption was curvature in Freundlich adsorption isotherms, where the high concentration of DOM filled available sites and prevented herbicide adsorption, particularly where the active sites were limited experimentally. Curved isotherms are difficult to interpret, although carbon dosage plots showed that DOM greatly reduced adsorption capacity, especially for the phenoxy acid herbicide MCPA. An interesting distinction between the behaviour of MCPA and the triazine herbicide atrazine was that DOM interference disappeared for atrazine after pilot/full scale treatment of DOM with ozone/activated carbon, but not for MCPA. Adsorption at different pHs showed that the difference between atrazine and MCPA could not be explained on the basis of charge characteristics alone. Perhaps the most convincing evidence for competitive adsorption was found through dilution experiments, where lake water DOM was diluted to concentrations approaching those of the herbicides. At and below approximately equimolar concentrations, DOM interference for atrazine adsorption was removed, however MCPA adsorption continued to be sensitive to DOM interference. Further experiments will concentrate on establishing the mechanism of competitive adsorption by testing different DOM and experimental conditions.

Initial work also involved method development for the analysis of triazine and phenoxy acid herbicides. The general procedure was solid-phase extraction (SPE) followed by high-performance liquid chromatography (HPLC). Washing solutions were developed for removal of interfering DOM from the SPE column prior to elution of the herbicides with methanol. A washing solution of water and acetonitrile was used to remove DOM from SPE, although addition of 12% methanol was used to retain the triazines on the SPE. The eluted herbicides were separated by HPLC on an octadecyl bonded silica column, with an acidic methanol/phosphate buffer for the phenoxy acids and a neutral acetonitrile/water mobile phase for the triazines.

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Glossary of abbreviations

BAT	Best Available Tecnology
COD	Chemical Oxygen Demand
C	equilibrium concentration in the liquid phase, µg l^{-1}
C_0	initial concentration in the liquid phase, µg l^{-1}
C_{18}	octadecyl bonded silica
DOM	Dissolved Organic Material
EC	European Community
GAC	Granular Activated Carbon
HPLC	High-Performance Liquid Chromatgraphy
K	soil adsorption coefficient
K_f	Freundlich constant
K_{oc}	organic carbon normalised soil adsorption coefficient
m	carbon amount, mg
MAC	Maximum Admissible Concentration
MCL	Maximum Contaminant Level
n	Freundlich exponent
NOAEL	No Observed Adverse Effect Level
PAC	Pulverised Activated Carbon
q	equilibrium adsorbed amount on the activated carbon, µg mg^{-1}
RMCL	Recommended Maximum Contaminant Level
SPE	Solid-Phase Extraction
TDI	Tolerable Daily Intake
TOC	Total Organic Carbon
US EPA	United States Environmental Protection Agency
V	volume of water, l
WHO	World Health Organisation

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1. Background

Conventional drinking water treatment consists of a number of steps depending on the raw water quality. The design is based on relatively simple chemical group parameters such as turbidity, colour or COD (chemical oxygen demand) in the raw water. The treatment steps range from pH-adjustment and disinfection to more sophisticated treatment including flocculation, separation (sedimentation or flotation) and filtration through sand or activated carbon, in some cases even followed by slow-sand filtration or infiltration. Concern for the production of trihalomethanes by added disinfection chemicals (normally chlorine) has lead to the development of alternative disinfection methods. Taste and odour problems, often originating from algal blooms in surface water reservoirs, has lead to increasing interest in the use of activated carbon filters because they can remove the organic compounds responsible, such as geosmin and isoborneol.

At the typical levels of humic substances in surface and ground water (0.1-5 mg l^{-1}) treatment processes including flocculation and sand filtration lead to effective removal of these substances. Organic substances that occur at trace concentrations, usually at the $\mu g\ l^{-1}$ level, create a difficult problem for water treatment plants. These substances are often in concentrations that represent a challenge even for advanced analytical laboratories and may exhibit marked seasonal or unexpected concentration variations. The design of water treatment plants to cope with these variations therefore requires an in-depth understanding of the selected process.

The choice of pesticides as the micropollutant category to be investigated is due to increasing concern over their presence in the Swedish aquatic environment. It must be realised that pesticides are applied to the greater proportion of cultivated soils and are transported into agricultural streams and thereafter into surface and ground water. Relative water solubility and persistence will determine the extent of their threat to the quality of drinking water and, in the absence of source control, treatment plants need to be able to prevent pesticide detection in the produced drinking water.

In 1988 the Swedish National Food Administration carried out a survey of pesticides in 56 drinking water sources from 50 municipalities. Samples were taken from both raw water and drinking water. The result was a few positive pesticide samples in raw water, although the substances could not be detected in drinking water. On the other hand, other investigations in Sweden show findings of pesticides in private wells and in surface waters both in agricultural and non-agricultural areas. Reported investigations from other European countries show that seasonal variations in surface water are common, with high concentration during May to August when the pesticides are applied, frequently following surface runoff through a storm event. In the case of ground water, pesticide contamination represents a more long term threat, with gradual build-up in concentration and a lack of seasonal variations.

Several investigations show that conventional treatment methods do not have the capacity to remove pesticides. More effective methods for removal of pesticides have been developed but the mechanisms of removal are often poorly understood. Powdered activated carbon (PAC) may be applied when a peak concentration of pesticides has been detected in the raw water. Granular activated carbon (GAC) in fixed-bed adsorbers is used for the removal of dissolved organic material (DOM) and organic micropollutants. Oxidation techniques, for example ozonation, are also used for the removal of pesticides, although the formation of byproducts can be a problem. Therefore this study focused on an in-depth understanding of one treatment method, removal on GAC.

It is well known that humic substances decrease the adsorption capacity of activated carbon for organic micropollutants, including pesticides. This has been found both in laboratory studies and in full-scale treatment with GAC filters. To improve GAC filtration technology for the removal of pesticides and other organic micropollutants it is important to understand the mechanisms that are responsible for this decrease in removal capacity.

The experiments reported here investigate the interaction between pesticide and humic substances on the activated carbon surface using adsorption isotherms and other related methods. An adsorption isotherm describes the adsorption capacity of activated carbon for a specific substance and is carried out in the laboratory under controlled conditions. Mixtures of organic substances with different adsorption to activated carbon, for example pesticide and humic substances, give decreased adsorption capacities for all compounds. The extent of the decrease depends on the single-solute adsorption isotherm. Comparison between the adsorption isotherms for a single-solute and a mixture can reveal interactions at the activated carbon surface. Mathematical models which use adsorption isotherm data to describe adsorption behaviour during filtration have been developed, although are not included in this work.

The quality of the results from adsorption isotherms is highly dependent on the analysis of the organic substances tested. Therefore the development of analytical methods for measurement of pesticides in water was a necessary and important initial part of this work.

2. Aims and Objectives

The aims and objectives of this study were to

* develop analytical methods for the measurement of phenoxy acid and triazine pesticides in water with DOM present

* examine the adsorption of some selected pesticides to activated carbon in the presence of DOM by the use of adsorption isotherms

* understand pesticide interaction on the activated carbon surface in the presence of DOM.

3. Pesticides in the Environment

3.1 Introduction

Pesticides will be defined here in terms of chemicals used in agriculture for the eradication of unwanted organisms. Herbicides, insecticides and fungicides are the most important groups of pesticides in agriculture. In each of these groups there are different chemical substance groups that have an effect on target organisms. Phenoxy acids and triazines are important herbicides, organophosphorus containing compounds and chlorinated hydrocarbons are widely used as insecticides, and dithiocarbamates dominate among the fungicides.

The total amount of pesticides sold in Sweden has decreased during the last ten years (Table 3.1). The phenoxy acid MCPA is the most used herbicide in Sweden, with 311 tons sold in 1993 (Kemikalieinspektionen, 1994).

Table 3.1 Use of herbicides, insecticides and fungicides in Sweden (Berggren, 1989, Kemikalieinspektionen, 1991, 1994)

	Pesticides used (ton pure substance)		
	Herbicides	Insecticides	Fungicides
1972	3947[1]	206	436[2]
1982	4234	232	716
1988	2238	159	679
1990	1743	76	610
1993	1273	52	283

[1] Including plant growth regulators
[2] Including seed dressings

3.2 Persistence of pesticides

The persistence of pesticides is important for determining whether they are likely to reach raw water before degradation occurs. The time for the concentration of a pesticide to decrease by 50 percent is generally referred to as chemical persistence (Torstensson, 1988) and is calibrated through controlled laboratory experiments. More relevant in agricultural terms is the phytotoxic persistence of the pesticide which is defined as the time between application to the soil and crop sowing without risk of crop damage (Torstensson, 1988). Phytotoxic persistence is measured in the field and depends on the crop to be cultivated.

Table 3.2 Chemical and phytotoxic persistence of selected herbicides (from Torstensson, 1988).

	Persistence, days	
	Chemical	Phytotoxic
MCPA	7-28	7-28
TCA	130-365	130-365
Diquat	> 365	< 7
Glyphosate	130-500	7-14

For certain substances such as diquat and glyphosate, toxicity to crops decreases rapidly after application, allowing sowing. These substances are still chemically present but are probably adsorbed to the soil so that they are no longer bioavailable. The degradation of pesticides occurs through physical, chemical and biological processes (Coats, 1991). Even though the initial pesticide disappears, the degraded products may remain and in some cases, e.g. organophosphorus insecticide residues, retain toxicity (Torstensson 1988).

Chemical persistence is of more concern than phytotoxic persistence when investigating the possible contamination of ground and surface waters, as phytotoxic persistence is only relevant to agricultural technology.

3.3 Pesticide transport

After application pesticides can be transported, via particles, in surface runoff or into the atmosphere through wind and soil erosion. Chemical persistence in the environment may differ from controlled laboratory studies due to degradability conditions.

3.3.1 Atmospheric transport

Pesticides in the atmosphere can be washed out in rainfall, the extent of this process depending on soil handling, climate and topography. Trace concentrations of triazine herbicides has been found by Buser (1990) in rain and snow samples (Table 3.3). The data in Table 3.3 also reflects seasonal variations since the triazines could not be detected in snow samples. The detected concentrations are in the same range as other reported values. Richards et al (1987) found atrazine in a concentration range of 0.1 to 1.0 $\mu g\ l^{-1}$ and simazine at 0.1 to 0.5 $\mu g\ l^{-1}$ in rainwater in the northeastern United States.

Table 3.3 Concentrations of triazines in rain and snow at different locations in Switzerland.

Sampling location	Concentration, ng l^{-1}		
	Atrazine	Simazine	Terbutylazine
Wädensuil	nd-193	nd-47	nd-87
Zürich	2.8	1.2	21
Bachtel	2.5	1.3	0.5
Lägern	nd-600	nd-121	nd-198

nd = not detected

3.3.2 Mobility of pesticides in soil

Pesticides that come in contact with soil can either be adsorbed or follow the movement of water through the soil profile. The transport of pesticides through soil depends on factors connected to the soil; type, content of organic matter, pH, cation exchange capacity, water holding capacity, and to the pesticides; water solubility, dipolar structure and acid-base behaviour (Somasundaram et al, 1991).

Several attempts have been made to classify the potential of pesticides for soil transport. For example, Torstensson (1988) classified individual pesticides from 0 (totally soil adsorbed) to 3 (totally water soluble) with additional information on K (general soil adsorption coefficient) and K_{OC} (K/organic content of soil). Other methods for determining pesticide soil mobility include soil thin layer cromatography (Helling and Turner, 1968) and the use of mathematical models (Seiber, 1987). Mathematical models are usually based on hydrogeological data and parameters which indicate the probability that an individual pesticide will reach groundwater (Aller et al, 1986).

3.4 Pesticides in surface water and ground water

The low concentrations and difficulty of pesticide analysis in natural waters limits the possibility for the detection of pesticides in raw water sources. However, drainage channels for agricultural runoff provide concentrations high enough for the study of optimal applications to prevent leakage. Kreuger and Brink (1988) found eleven herbicides, five insecticides and two fungicides in agricultural runoff in southern Sweden. Pesticides were also detected outside the growing season with the triazine herbicide atrazine present through to October. The most frequently found compounds were two phenoxy acid herbicides, MCPA and dichlorprop.

A number of Swedish lakes which are used as drinking water sources have been investigated for the presence of pesticides (Sandberg and Erlandsson, 1990). The result was three positive samples at the 0.1 µg l^{-1} level in raw water of the herbicide bentazon and the phenoxy acid herbicides dichlorprop and MCPA. These substances could not be detected in drinking water. However, in 1990 pesticides were found in 8 of 11 sampled streams in the Göteborg area (City of Göteborg, Environment Protection Board, 1990). The concentration range was 0.1 to 0.3 µg l^{-1} and the detected compounds were the phenoxy acid herbicides MCPA, dichlorprop, 2,4-D, the triazine herbicides terbutylazine, atrazine, simazine, and the herbicide bentazone.

More comprehensive surveys have been conducted in Europe and the US which have shown the presence of agricultural pesticides in groundwater. A US survey found 17 different pesticides in the groundwater of 23 states, the most common substance being the carbamate insecticide aldicarb within a concentration range of 1-50 µg l^{-1} (Cohen et al, 1986). A study in Italy found atrazine in 63% and 15% of private and municipal water reservoirs, respectively (Dahlman, 1990).

Legrand et al (1991), made a survey in France of 13 sampling points, 11 wells and 2 rivers. They found 38 different pesticides although most were present in concentrations at or below the 0.1 µg l^{-1} level. The triazine herbicides atrazine and simazine were the only compounds detected at levels above 0.1 µg l^{-1} and were found in the rivers Seine and Marne. The phenoxy acid herbicide mecoprop was one of the compounds occasionally found at a concentration between 0.05 and 0.1 µg l^{-1}.

A survey of UK surface and ground water reported by Foster et al (1992) detected the triazine herbicides atrazine and simazine as most commonly occurring. Concentrations were frequently up to 0.6 µg l^{-1}, although maximum concentrations were 9.0 µg l^{-1} for atrazine and 2.8 µg l^{-1} for simazine. Another study also reported the phenoxy acid herbicide mecoprop, the phenylamide herbicide isoproturon and the organochlorine insecticide lindane as frequently found (Foster et al, 1992). A survey of the river Thames during July 1989 to December 1990 showed two triazine, two phenoxy acid and three phenylamide herbicides present during the entire sampling period. Peak concentrations appeared as a result of application of the pesticides combined with low river flow or precipitation after a period of dry weather. The study also showed that different pesticides have different seasonal variations depending on which time of the year the compounds were applied. The triazine herbicides atrazine, simazine and the phenylamide herbicide diuron had peak concentrations in the summer and autumn periods whereas the phenylamide herbicides isoproturon, chlortoluron, and the phenoxy acid herbicide mecoprop appeared in the winter and spring periods.

Waite et al (1992) studied five pesticides in a small agricultural watershed in Canada. Pesticide residues were found in 47% of 105 ground water samples and the concentration range was 0.6 to 4.88 µg l^{-1}. The most frequently found pesticide was the phenoxy acid herbicide diclofop, which also had the highest detected concentration. Frank et al (1982) studied the Great Lakes basin in Canada. They investigated the sources and transport routes for pesticides into stream or river water and suggested that if the concentration suddenly increases and then declines rather quickly, it is probably a spill event that caused the peak. This may be the direct result of careless procedures before spraying, or cleaning the equipment in the stream water or close to it. Peak concentrations can also appear as a result of heavy rainfall after pesticide application. Losses during spring runoff are often a significant proportion of total yearly loss. Their results showed that during the spraying season, May to June, 82% of the pesticide loss to water was wind-drift from spraying or spills. The remaining 18% was loss during storm runoff events. If the whole year is considered, the loss from spills was 22%, storm runoff 60% and baseflow 18%. Atrazine, simazine and the organochlorine insecticide endosulfan were detected year round. Sediment analyses in the streams showed no contamination of pesticides and the findings during winter time were probably a function of movement through the soil column by internal soil drainage. It was also shown that the pesticides werestable over a long period of time.

Spalding and Snow (1989) studied Shell Creek in Nebraska, USA. They observed low concentrations of pesticides in baseflow during May, when pesticide application was underway in the watershed. The anilide herbicide alachlor and the triazine herbicides atrazine and cyanazine were detected at concentrations of 1.5, 2.9 and 4.4 $\mu g\ l^{-1}$, respectively. The six other pesticides in the study (butylate, disulfoton, the carbamate herbicide EPTC, the acetamide herbicide metolachlor, the triazine herbicide metribuzine, propachlor and the aniline herbicide trifluralin) were not detected at this time. During a spring runoff event four days later, maximum concentration was reached for alachlor, atrazine and cyanazine. The other six pesticides were then detected within a concentration range of 0.1 to 3.0 $\mu g\ l^{-1}$.

Thurman et al (1992) found similar storm runoff distributions for atrazine as Spalding and Snow (1989) and Frank et al (1982). The major fraction of the pesticide transport occurred during spring runoff events whereas baseflow transported just a small part of the total. Their study also showed that the pesticide loadings transported in the river are a series of pulses from application in spring and during the summer to autumn. The pulses come after a storm event and decrease gradually both in frequency and intensity. Muir and Grift (1987) found the same pattern during May to October as in previous studies; low conentrations and then suddenly a peak together with a runoff event. In one case, they suspected a spillage into the river or spraying close to the river, a category that Frank et al (1982) identified as responsible for 82% of the loss of pesticides to rivers and streams during spring.

Atrazine has been studied with special interest because of its frequent appearance in surface and ground water. Pionke and Glotfelty (1992) found atrazine at high concentrations during the summer and at lower concentrations in the following spring before the next spraying season. Grandet et al (1989) have studied atrazine and the metabolite desethylatrazine in ground water and tried to correlate pesticide concentration with spraying and precipitation, however no direct correlation between atrazine and the degradation product desethylatrazine concentration and precipitation data could be established. They explained the result by suggesting that even if the amount of atrazine and desethylatrazine transported to ground water increases during rainfall there is a dilution with uncontaminated water and an increase in concentration cannot be seen.

From the literature it can be concluded that detectable amounts of pesticides can be found in rivers and streams during spring when spraying begins. Peak concentration correlates well with runoff events after application and throughout the summer and autumn. Peak concentrations not correlated to runoff events can be regarded as spillage and careless handling of the compounds or equipment. Some pesticides can be found during the non-spraying season, for example triazine compounds. However, the discharge into the aquatic environment is low compared to the amounts applied, in fact only about 0.1 % (Muir and Grift, 1987; Frank et al 1982).

It is difficult to compare different investigations because the results depend on when the sampling was done; either before/after application or during/between storm events. Other factors are for example the size of the drainage area, soil type and well depth. The pattern of contamination for surface water and ground water is also different.

4. Pesticides in Drinking Water and their Treatment

4.1 Acceptable pesticide levels in drinking water

The Economic Community (EC) have set acceptable limits, called Maximum Admissible Concentration (MAC), for pesticides in drinking water such that an individual pesticide should not exceed 0.1 $\mu g\ l^{-1}$ and total pesticides and low molecular weight organics should not exceed 0.5 $\mu g\ l^{-1}$ (Sandberg, 1991). The values do not account for different detection limits or toxicity of each pesticide, although they are useful as a general aim. The EC Commision has clearly stated that pesticides have no place in drinking water and the MAC value should therefore be set close to the detection limit (Mandl, 1992). In many areas of Europe it is doubtful whether more effective treatment processes alone can sufficiently reduce pesticide concentrations and it will be necessary to implement a management plan which controls the application of pesticides and includes treatment processes. There is no mention in the EC standards concerning analytical methods or water treatment technology, in contrast to the US regulations.

The United States Environmental Protection Agency (US EPA) has established Recommended Maximum Contaminant Level, RMCL, and Maximum Contaminant Level, MCL, for pesticides (Sandberg, 1991). When the US EPA set the contaminant levels, several aspects were taken into account, including health effects caused by exposure to the compound, analytical methods and monitoring techniques. The US EPA also recommends Best Available Technology (BAT) for the removal of contaminants at a reasonable cost (Sayre, 1988). A comparison of different standards is presented in Table 4.1. The US maximum contaminant level is enforceable whereas the other countries set non enforceable guidelines.

Table 4.1 Comparison of pesticide regulations in different countries (Sayre, 1988).

Pesticide	US Maximum Contamination Level mgl^{-1}	Canadian Maximum Acceptable Level mgl^{-1}	EC Maximum Admissible Level mgl^{-1}	WHO Guideline Value mgl^{-1}
2,4-D	0.1	0.1	NS	0.001
Endrin	0.0002	0.0002	NS	NS
Lindane	0.0004	0.004	NS	NS
Methoxychlor	0.1	0.1	NS	0.001
Pesticide	NS	0.1	0.005	NS
Toxaphene	0.005	0.005	NS	NS
2,4,5-TP	0.01	0.01	NS	NS

NS=no standard

Canada has quality guidelines for different organic compounds, including pesticides (Table 4.1). There is also a guideline for the total concentration of pesticides, set to 0.1 mg l^{-1} (Sayre, 1988). The WHO guidelines for pesticides are based on toxicity tests for each compound. A Tolerable Daily Intake, TDI, is calculated from a No Observed Adverse Effect Level, NOAEL, and the guideline value is 10% of the TDI for an adult (60 kg) assuming an intake of 2 litres of drinking water per day (Sandberg, 1991). Sweden has no set guideline. The drinking water ordinance of 1993 states that drinking water treatment plants have to report findings of pesticides to the National Food Administration (National Food Administration, 1993). Certainly, seasonal variations can easily be overlooked, even in sampling programs with quartile or monthly sampling.

4.2 Treatment of pesticides in water treatment plants

There is a significant literature concerning treatment methods to control pesticide residues in drinking water. It can be stated that the conventional treatment unit operations used by many waterworks today do not remove pesticides in general, even if they have some effect on certain compounds. Miltner et al (1989) have shown that chemical flocculation, rapid sand filtration, and chlorination do not have much of an effect on trace pesticide concentrations. Aeration is another conventional technique used for the removal of volatile organic contaminants in drinking water and Kruithof et al (1993) showed that aeration has no direct effect on the removal of pesticides. Normann et al (1987) reported full-scale treatment data with aeration, flocculation and sand filtration. The result was a poor removal, 0% to 33%, of the triazine herbicides atrazine, simazine, propazine, terbutylazine, and the herbicides metolachlor and metazachlor.

Certain pesticides, Miltner et al (1989) gave the triazine herbicide metribuzine as an example, are reduced in concentration after chlorination, but with a range of unidentified oxidation products in their place. Another example is that adjustment of pH to over 7 results in hydrolysis of the carbamate insecticide carbofuran. Foster et al (1992) have studied the removal of the triazine herbicide atrazine, the phenylamide herbicide isoproturon, the phenoxy acid herbicide mecoprop, and the organochlorine insecticide lindane in full-scale treatment. Pre-chlorination, chemical coagulation and clarification reduced isoproturon from 0.14 µg l^{-1} to 0.02 µgl^{-1} (an 86% reduction) but had no effect for the other pesticides. Rapid sand filtration gave no reduction for the compounds studied. Slow sand filtration reduced mecoprop from 0.08 µg l^{-1} to 0.03 µg l^{-1} (63%) and lindane from 0.15 µg l^{-1} to 0.05 µg l^{-1} (67%) whereas atrazine and isoproturon were unaffected.

When a drinking water source has been contaminated with pesticides more efficient treatment methods have to be adopted. The choice of treatment method depends on the pesticide but also on the preferred treatment result. Should the treatment method either a) remove the pesticide b) degrade the pesticide or c) degrade and remove the pesticide? Adsorption by activated carbon is a treatment method under a), oxidation can be used under b) and ozone, hydrogen peroxide and in some cases chlorination are common oxidation agents. However, the problem with formation of byproducts, known and unknown, has to be solved if oxidation processes are used. In general, oxidation processes only degrade the original contaminant to another and the problem with the health risks associated with drinking water consumption is not really solved. The combination of oxidation and adsorption processes is most often reported. Ozonation and activated carbon seem to be efficient alternatives in the full-scale treatment of pesticide contaminated water (Foster et al, 1992; Kruithof et al, 1993).

4.2.1 Oxidation of pesticides

A number of oxidants can be used in drinking water treatment, for example, chlorine compounds, ultraviolet (UV) light, hydrogen peroxide and ozone. These oxidants can also be used in combination, for example, UV and hydrogen peroxide, ozone and hydrogen peroxide, ozone and chlorine compounds.

Ozonation as an oxidation technique has been in use since the turn of the century. The treatment aims have been disinfection, taste and odour control, oxidation of iron and manganese, and more recently to enhance the flocculation of suspended solids in surface water (Glaze et al, 1987). Ozone is a strong oxidant and has two different pathways of reacting with organic compounds (Singer, 1990). One is a direct reaction with molecular ozone, O_3, which is highly selective. Many organic compounds react in this way, for example activated aromatic compounds, aliphatic alkenes and simple amines. The other pathway is indirect reaction with free radicals which form during the decomposition of ozone. The decomposition of ozone is promoted, for example, by alkaline pH and UV light. The indirect pathway is nonselective and can oxidise compounds that react slowly with molecular ozone, for example aldehydes, ketones, aliphatic acids and less activated aromatic compounds. Under conditions typically found in drinking water treatment, the free radical pathway tends to dominate (Singer, 1990).

Treatment with ozone can oxidise organic compounds in water and a number of known and unknown byproducts can occur depending on the parent compound. It is a question of whether any organic material really is removed or only degraded when an oxidation treatment method is used. In the literature, some authors use removal, others use degradation to describe the process. In the work of Kruithof et al (1993) degradation is used when they reported ozonation experiments with river water and a number of pesticides. Degradation levels between 90 to 100% at 2.2 mg l^{-1} ozone were reported for about half of the pesticides studied while other pesticides were degraded to between 25 and 90%. Atrazine was degraded by 60%.

4.2.2 Adsorption of pesticides by activated carbon

Activated carbon has been in use for some time for the removal of organic material causing taste and odour problems. Most applications here used the adsorptive capacity of activated carbon, but this makes the technique expensive compared to sand filters due to the need to regenerate the carbon. The development of biologically activated carbon filters provides a longer filter run time and a higher capacity for the removal of trace organics. This is due to degradation of adsorbed organic materials by surface-bound bacteria in addition to the carbon surface available for adsorption.

Laboratory studies of the adsorption isotherms for pesticides with activated carbon indicate, but do not necessarily predict, how effective a treatment step with activated carbon will be. This is due to the adsorption of high molecular weight substances, such as humic acids, which decrease the carbon adsorption capacity for pesticides and other low molecular weight compounds (Munz et al, 1990). There are also some difficulties in relating controlled laboratory studies, of the adsorption of high concentrations of pesticides, to real conditions where only trace concentrations of pesticides are present. However, certain mathematical models based on adsorption isotherms have been found to equate reasonably well with pilot scale studies after the introduction of empirical model parameters (Crittenden et al, 1987; Munz and Boller, 1989).

The type of activated carbon used in laboratory experiments also affects the characteristic adsorption isotherms, with the greatest differences between PAC and GAC. The usual practice is to pulverise GAC to PAC to reduce experimental equilibration time. Further, the application of adsorption isotherms will also be affected by differences in batches of the same activated carbon, different technical processes, different properties and concentrations of the pesticides to be removed (Huber et al 1989).

Pilot scale studies using packed columns usually lead to a rapid coverage of the surface by humic substances, however, low molecular weight compounds such as pesticides continue to be effectively adsorbed after the humic substances (Munz et al, 1990). Improved adsorption can be achieved through the use of "layered upflow carbon adsorption" where the carbon bed depth is successively increased over time by 0.3 m (Munz et al, 1990).

Full-scale applications of activated carbon are used by most treatment plants along the river Rhine to remove micropollutants (Huber et al, 1989). The presence of pesticides in both ground and surface water is a problem. Effective removal can be achieved through the use of a packed column of GAC. However, where a known one-off contamination is found the batch addition of PAC may be more satisfactory (Miltner et al, 1989). Wölfel (1989) made a comparison of the same activated carbon used in pilot scale columns and full scale filters. A more effective removal of the herbicide atrazine ($0.22\ \mu g\ l^{-1}$) and deethylatrazine, a degradation product of atrazine, in contaminated groundwater was found in the pilot scale column. This was explained by a longer retention time which may have allowed biological degradation of the compounds.

4.2.3 Biological degradation of pesticides on activated carbon

Biological growth on activated carbon is usually regarded as a problem which is avoided by short contact times and frequent backwashing. However, by allowing and even enhancing bacterial growth on activated carbon through longer contact times it may be possible to stimulate the natural degradation of pesticides. Biologically activated carbon has been shown to be effective for micropollutants such as chlorinated phenols (Speitel et al, 1989). Desorption due to varying incoming concentrations may not be a problem in the biological system as adsorbed substances may be degraded. In fact, the biological system should cope well with varying concentrations of pesticides as during low concentration exposure the adsorption surface can be regenerated by biological degradation to allow direct adsorption during high concentration exposure.

Laboratory and pilot tests usually employ either a one column system with bacteria in a part or in all of the column, or a two column system in series with one column free from bacteria to adsorb degradation products (Gmünder et al, 1989). In addition the latter prevents bacterial contamination of treated water (Bouwer and Crowe, 1988), although a further disinfection step is usually considered necessary. The organisms used in laboratory studies are usually those found in the incoming raw water and consequently a pre-disinfection step is of course avoided. The bacterial culture that grows on activated carbon is fast-growing and is adapted to colonising fresh surfaces (Bouwer and Crowe, 1988). One concern is an increased number of microorganisms in drinking water after treatment with biologically activated carbon filters. LeChevallier and McFeters (1990) reported in a comprehensive literature review that microorganisms are released from GAC filters through attachment to carbon particles that leave the filter and enter drinking water. However, the significance of the released microorganisms is unclear, especially the presence of coliforms and pathogens in the biofilm on the activated carbon particles.

Full scale tests on biologically activated carbon filters have been carried out at the Mülheim waterworks in Germany (Sontheimer 1978, Sontheimer et al 1978). Biological degradation of organic material decreased after pre-chlorination, but increased after pre-ozonation. The latter is due to partial degradation of organic substances by ozonation which increases the available substrate for the bacteria.

The effectiveness of biologically activated carbon in removing pesticides has not been widely tested. However, Selim and Wang (1993) have studied the breakdown of atrazine in a laboratory scale biologically activated carbon column. The result showed that 99% of the applied atrazine was degraded in the column. Complete mineralisation to CO_2 of atrazine and the atrazine degradation products, deethylatrazine, deisopropylatrazine and hydroxyatrazine, occurred.

It is also not known whether the pesticide concentrations found in contaminated raw water can have a toxic effect on the colonised bacteria. The sensitivity of the light-emitting bacteria *Photobacterium phosphoreum* (Microtox) and mixed algae/bacteria cultures to pesticides (McFeters et al, 1983) are shown in Table 4.2. Although the Microtox bacteria are not the same as those found in biological activated carbon filters, it does give an indication of the magnitude of pesticide concentration required to inhibit 50% of a population of bacteria. Cultures containing algae are effectively destroyed by low concentrations of chlorophyll acting herbicides. However, Microtox bacteria survive at concentrations (mg l^{-1} - g l^{-1}) well above those found even in contaminated raw waters (typically μg l^{-1} - lower mg l^{-1}). Although certain sensitive bacteria may be affected by pesticides, it would seem unlikely that pesticides will affect the bulk of the bacteria community and therefore the general performance of biological filters.

Table 4.2 Toxicity of herbicides (H) and insecticides (I) to algae/bacteria and *Photobacterium phosphoreum* (Microtox) populations.

	EC_{50}, mg l^{-1}	
	Algae/bacteria	Microtox
Diuron (H)	0.04	16
Simazine (H)	1.1	240
Malathion (I)	18	60
2,4-D (H)	250	62
Bromacil (H)	nt	7
Heptachlor-epoxide (I)	nt	25

nt = not tested

4.3 Conclusions

Pesticides have been identified in surface and ground waters at low concentrations, with seasonal variability in surface waters. Conventional drinking water treatment processes are unlikely to remove pesticides although pesticides are effectively adsorbed by activated carbon. However, the latter process is generally only regarded as cost-effective for special applications. Activated carbon with induced biological activity seems promising for pesticide removal as the colonising bacteria can withstand a relatively high pesticide dose.

5. Analytical Methods

5.1 Introduction

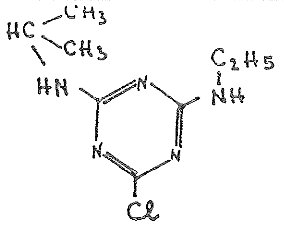
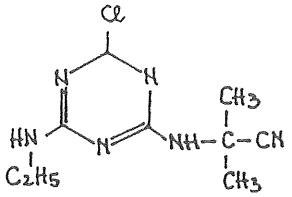
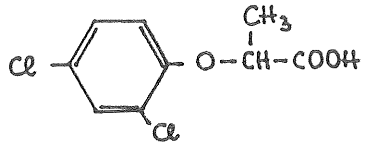
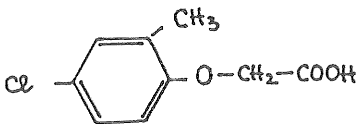
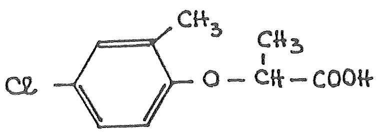
This chapter describes the development of methods for the enrichment and analysis of triazine and phenoxy acid herbicides. Solid-phase extraction (SPE) and high-performance liquid chromatography (HPLC) were used. The triazine compounds tested were atrazine and cyanazine, the phenoxy acid compounds were dichlorprop, MCPA and mecoprop. Table 5.1 shows the names, chemical structures, pK_a values and molecular weights for the studied herbicides.

5.2 Solid-phase extraction

Solid-phase extraction (SPE) is a technique for the extraction of organic and inorganic solutes from a liquid matrix. After elution from the solid phase, specific compounds can be analysed, for example by chromatographic techniques. It is also possible to separate analytes from a background matrix. One of the goals of this work was to develop a method to analyse pesticides in natural waters by HPLC with SPE as an efficient enrichment step, while at the same time decreasing the concentration of DOM. The advantage of SPE over the more traditional liquid-liquid extraction is the possibility of extracting large sample volumes both in the laboratory and in the field. This is particularly important for contaminants at low concentrations which require large volumes to achieve improved detection limits.

SPE is carried out using a small column, sometimes also called a cartridge, which is filled with the packing material of choice. A schematic diagram of a SPE column is shown in Figure 5.1. In this work octadecyl bonded (C_{18}) silica packing material was used as recommended by the supplier (Varian). A vacuum manifold or a syringe can be used to enable passage of the water sample and to extract solvents through the column. The column material retains the organic compounds contained in the sample. An organic solvent is used for elution of the organic compounds bound to the solid surface and the eluate can then be analysed. When spiked surface water was used, the DOM was adsorbed to the SPE material and coeluted together with the pesticides. The HPLC analysis suffered from a large background interference and it became clear that DOM should be eluted from the SPE column before the pesticides were eluted. It was decided to select a washing solution that could elute the DOM and leave the pesticides on the SPE material before final analyte elution.

Table 5.1 Name, chemical structure, pK_a value and molecular weight for the herbicides.

Herbicide	Chemical structure	pK_a	Molecular weight[b]
Triazine			
Atrazine (4-ethylamino-6-chloro-2-isopropylamino-1,3,5-triazine)		1.68[a]	215.7
Cyanazine (4-ethylamino-2-(1-cyano-1-methylethylamino)-6-chloro-1,3,5-triazine)			240.7
Phenoxy acid			
Dichlorprop (2-(2,4-dichlorophenoxy)-propanoic acid)		2.86[c]	235.1
MCPA (4-chloro-2-methyl-phenoxy acetic acid)		3.05[c] 3.62[c]	200.6
Mecoprop ((±)-2-(4-chloro-2-methylphenoxy)-propanoic acid)			214.6

[a] Base protonation constant. Pacakova et al (1988)

[b] Quentin et al (1987)

[c] Beilstein E IV 6

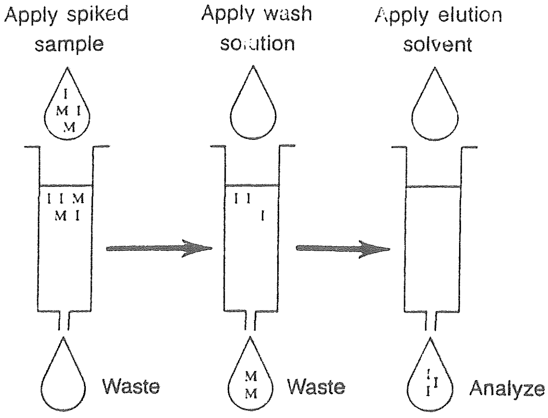


Figure 5.1 Schematic diagram of a SPE column from the Varian Instruction Manual.

5.2.1 Previous efforts to remove background interference

Hoke et al (1986) have analysed the phenoxy acid herbicides 2,4-D, 2,4,5-T and silvex in reagent water and surface water using SPE columns with C_{18} bonded silica. The phenoxy acids were eluted with two 1 ml portions of methanol and diluted with water to 5 ml before HPLC analysis. No attempt was made to wash the column to provide a lower content of DOM in the eluate. The recoveries after elution were much lower for natural waters than for reagent water. Hoke et al (1986) interpreted that result as indicating that the phenoxy acids were tightly bound to trace organic material. They made several attempts to improve the recovery, including the use of two SPE columns in series, filtering the water before spiking and addition of sodium chloride, with no positive results. Geerdink et al (1989) have used SPE columns with polymeric material, a macroporous polystyrene-divinylbenzene copolymer, for enrichment of the phenoxy acids MCPA, 2,4-D, MCPP, 2,4-DP and 2,4,5-T from samples of tap water and surface water. They used a washing step before the application of the samples with pesticides but this was designed to clean the SPE column and not to remove DOM. The washing solvent was acetonitrile:water (30%:70%) at pH 3. Wells and Michael (1987) have developed a method for separation of the two herbicides picloram and 2,4-D in distilled water and surface water using SPE columns with serial elution of the two substances. Coelution of the two compounds into one eluate would also include contaminants from surface water. Due to the different characteristics of picloram and 2,4-D, there is no need for a separate washing step to minimise dissolved organic material.

Clearly, the problem with DOM in HPLC analysis has not been solved. In this work, several washing solutions were tested to minimise the interference caused by DOM.

5.2.2 Screening to find a washing solution

The naturally occuring DOM in a lake water (Delsjön) was used to find a solvent that could preferentially elute the DOM but was weak enough to leave the pesticides on the SPE material. Lake water was passed through a SPE column and then the column was eluted with different elution solvents. The solvents were phosphate buffer at pH 3.0, dilutions of sodium hydroxide (NaOH), and mixed solutions of acetonitrile (CH_3CN), water (H_2O) and methanol (CH_3OH). Serial elution was employed, with methanol used as the last elution solvent to examine the effect of the previous elutions on the UV absorbance value of the methanol eluate. The eluates from five SPE columns were analysed in a UV-spectrophotometer at 254 nm, the wavelength that is typically used for the qualitative measurement of DOM content. DOM can have different UV-absorbance characeristics in different solvents but in this study it was assumed that a high measured value in absorbance units represents a high DOM content in the eluate. The results of the UV analysis are summarised in Table 5.2.

Table 5.2 UV measurement of different eluates.

	Eluate abs_{254}, cm^{-1}				
Elution solvent	SPE columns[a]				
	1	2	3	4	5
Phosphate buffer, pH 3.0	0.153	-	-	-	-
0.1 M HCl	0.025	-	-	-	-
0.1 M NaOH	1.574	1.317	-	-	-
0.01 M NaOH	-	-	0.548	-	-
H_2O:CH_3CN:CH_3OH, 50:38:12%	-	-	-	2.376	-
H_2O:CH_3CN, 55:45%	0.809	-	-	-	-
CH_3CN	-	-	-	-	1.966
MeOH	0.399	0.986	0.949	0.183	0.850

[a] Five Bond-Elute SPE columns

The eluates with high UV-adsorbance value were from elution with 0.1 M NaOH, H_2O:CH_3CN:CH_3OH, 50%:38%:12%, H_2O:CH_3CN, 55%:45%, and CH_3CN. They were then tested as washing solutions before elution of the herbicides. Lake water samples were spiked with the herbicides, extracted through SPE, the SPE columns were eluted with the washing solutions and final elution of the herbicides was with methanol. The results from the triazine samples are shown in Table 5.3.

Table 5.3 Test of washing solutions for triazine samples. The arithmetic mean of the recovery is in parentheses.

H_2O	CH_3CN	CH_3OH	% Recovery	
%	%	%	Cyanazine	Atrazine
50	38	12	95.3	102.9
			95.3 (95.3)	96.4 (99.7)
25	75		23.3	57.9
			24.5 (23.9)	57.9 (57.9)
75	25		93.1	99.6
			94.2 (93.6)	101.6 (100.6)

Washing with H_2O:CH_3CN, 25%:75% gave low recovery, especially for cyanazine, whereas the other two gave similar results. Washing with the solution containing methanol seemed to remove DOM better than the solution without methanol because the frontal peak in the chromatogram was smaller and with a improved baseline. The decision was to use the solution of H_2O:CH_3CN:CH_3OH, 50%:38%:12% as washing solution for the triazine enrichment procedure. For phenoxy acid samples 0.1 M NaOH, H_2O:CH_3CN:CH_3OH, 50%:38%:12% and H_2O:CH_3CN, 55%:45% were tested as washing solutions. The results are shown in Table 5.4. The recovery was highest for H_2O:CH_3CN, 55%:45% and was therefore chosen as washing solution for phenoxy acid samples.

Table 5.4 Test of washing solution for phenoxy acid samples. The arithmetic mean of the recovery is in parentheses.

	% Recovery		
Washing solution	MCPA	Dichlorprop	Mecoprop
0.1 M NaOH	58.7	80.7	85.1
	60.1 (59.4)	79.8 (80.3)	85.1 (85.1)
H_2O:CH_3CN:CH_3OH,	41.7	58.2	56.8
50%:38%:12%	53.0 (47.4)	56.8 (57.5)	65.1 (61.0)
H_2O:CH_3CN, 55%:45%	67.8	88.0	87.0
	83.4 (75.6)	89.1 (88.6)	87.1 (87.1)

The volume of the washing solution is also important for recovery. Table 5.5 summarises results from tests with different volumes of the washing solution, which is a nonoptimal solution composed of water and acetonitrile, 55%:45%. Ultrapure water and lake water were spiked with cyanazine and atrazine. Washing with 1.5 ml water:acetonitrile (55%:45%) eluted almost all cyanazine but atrazine was still adsorbed on the SPE column and gave a reasonable recovery. Tests with 0.5 ml washing solution increased the recovery for both substances when ultrapure water was used. However, tests with spiked lake water showed that 0.5 ml was not enough to remove the DOM from the SPE column. It was found that 0.7 ml of washing solution was the smallest volume that could elute the DOM without significant losses of cyanazine and atrazine. The same volume of washing solution was also used for samples containing phenoxy acid herbicides.

Table 5.5 The influence of washing solution volume on recovery of cyanazine and atrazine.

Volume ml	% Recovery	
	Cyanazine	Atrazine
1.5	trace[a]	83.0[a]
0.7	80.0[b]	87.0[b]
0.5	98.0[a]	101.5[a]

[a] spiked ultrapure water
[b] spiked lake water

5.2.3 The pH dependence of the SPE method

It is important to carry out the SPE enrichment at a suitable pH to get the highest recovery. Therefore the pH dependence of the SPE was tested in lake water spiked with phenoxy acids and triazines. For the phenoxy acids, a pH range of 2 to 5 was tested and the best recovery was obtained at pH 2 (Table 5.6). The triazines was tested over a pH range of 2 to 9 and the best recovery was obtained at pH 7.5 (Table 5.7).

Table 5.6 pH dependence for the recovery of phenoxy acids from a SPE. Standard deviations (SD) with number of samples (n) are also reported.

pH	MCPA % recovery	SD	n	Dichlorprop % recovery	SD	n	Mecoprop % recovery	SD	n
2.2	99.7	11.7	6	96.1	10.1	6	96.3	2.4	6
3.0	103.6	11.8	4	105.9	11.7	3	118.1	17.2	5
4.0	79.0	8.5	6	80.5	6.7	6	92.0	9.1	6
5.0	12.4	0	2	43.2	5.7	4	65.6	4.2	4

Table 5.7 pH dependence for the recovery of triazines from a SPE. Standard deviations (SD) and number of samples (n) are also reported.

pH	Cyazine % recovery	SD	n	Atrazine % recovery	SD	n
2.2	46.8	17.5	6	84.2	1.9	6
5.0	35.5	5.3	4	78.6	0.6	4
7.5	51.2	9.3	6	95.7	2.8	6
9.0	44.4	8.2	4	92.0	2.2	4

5.2.4 Final selected conditions

Conditioning of the SPE columns included elution with 2 ml of methanol and 2 ml of ultrapure water before sample extraction. Sample preparation to retain column condition involved addition of 1 ml of methanol to each 50-100 ml of sample for both phenoxy acid and triazine samples. The most suitable extraction pH for phenoxy acids was pH 2, whereas a neutral pH value was satisfactory for extraction of triazines. The washing solution for phenoxy acids was 0.7 ml of water and acetonitrile, 55%:45%, and 0.7 ml of water, acetonitrile and methanol, 50%:38%:12%, for triazine samples.

5.3 High-Performance Liquid Chromatography

5.3.1 Selection of HPLC conditions for phenoxy acids

The intent was to develop a reversed-phase HPLC method with an octadecyl bonded silica column and an acidic mobile phase. Hoke et al (1986) used an octyl (C_8) bonded silica column, a mobile phase of methanol and 1% acetic acid (68%:32%) and UV-detection at 280 nm. DiCorcia et al (1989) used an octadecyl (C_{18}) bonded silica column together with a mobile phase of methanol and 0.08% trifluoroacetic acid and UV-detection at 230 nm. The composition of the mobile phase affects the selection of the detection wavelength. Phenoxy acids have two UV absorption maxima, at 230 nm and 280 nm, as shown in the absorption curve in Figure 5.2. Detection at 280 nm gives a chromatographic peak that is low and broad, as previously reported in the literature (Hoke et al, 1986), while 230 nm gives a sharp peak. 235 nm was selected as the detection wavelength as it gives a sharp chromatographic peak. Hoke et al (1986) found a baseline with a high signal to noise ratio at 235 nm and a low sensitivity at 280 nm; similar results were found in this study as indicated by the chromatograms in Figure 5.3. An explanation for this result is given by DiCorcia et al (1989). They claim that acetic acid in the mobile phase gives problems with the baseline when 230 nm is used as the detection wavelength and in their method they replaced acetic acid with trifluoroacetic acid. However, in this work, tests showed that acetic acid could be replaced with 0.01 M phosphate buffer at pH 3. The baseline at 235 nm improved and a satisfactory separation was found between the phenoxy acids (Figure 5.4).

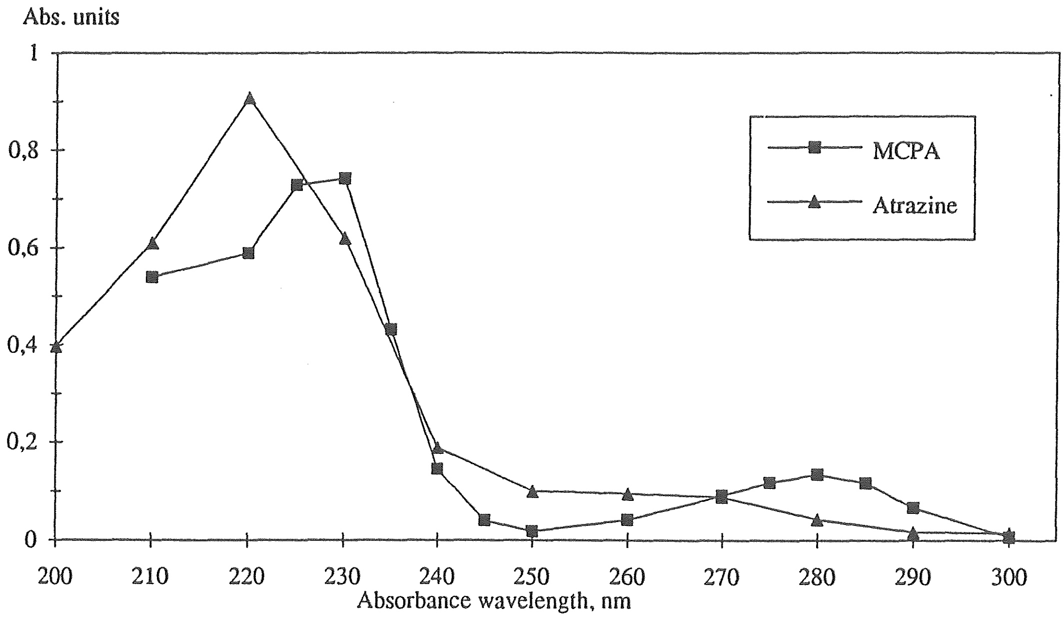


Figure 5.2 Measurement of UV absorbance of MCPA and atrazine.

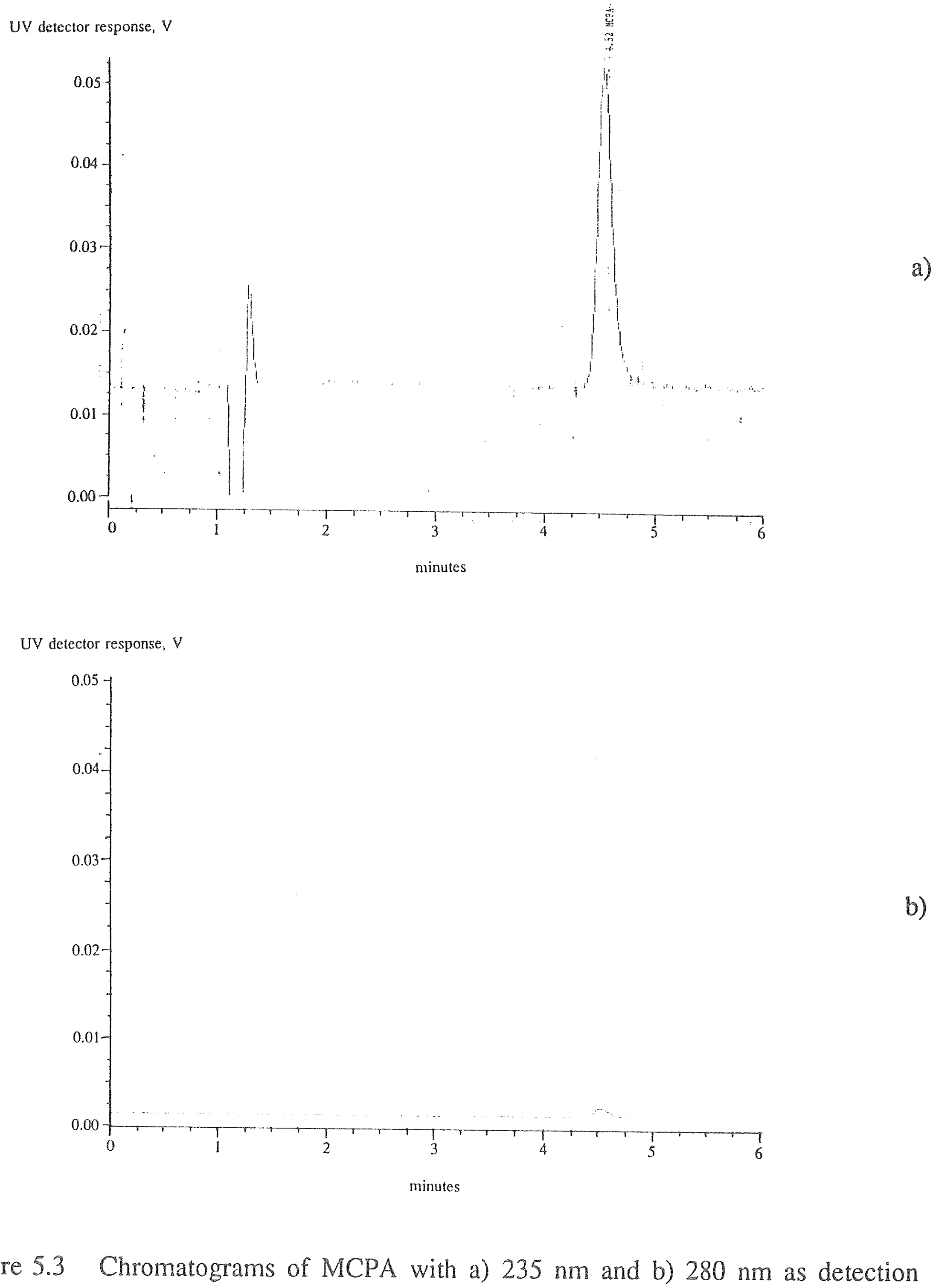


Figure 5.3 Chromatograms of MCPA with a) 235 nm and b) 280 nm as detection wavelength.

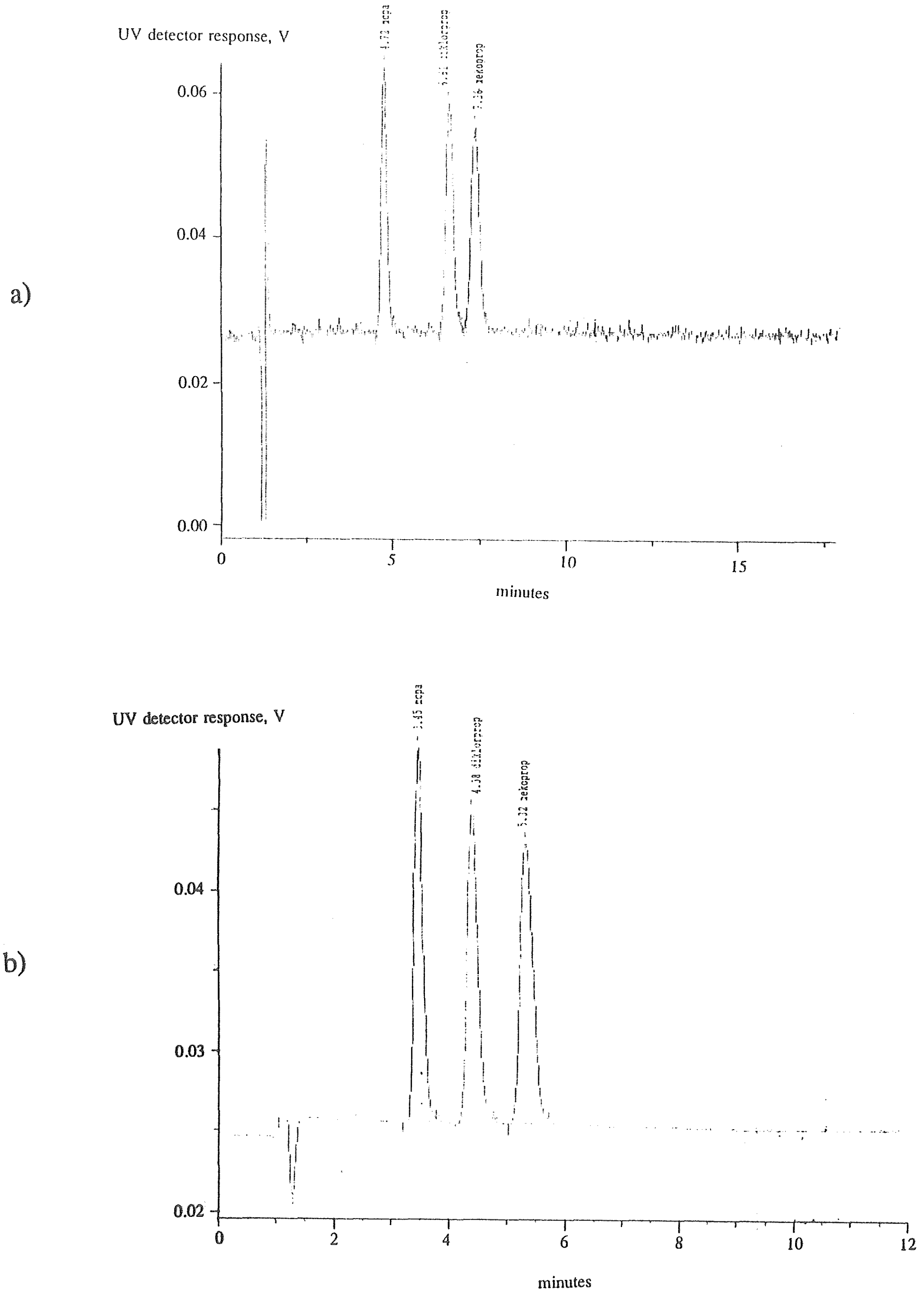


Figure 5.4 Comparison of mobile phase composition, 235 nm as detection wavelength.
a) methanol: 1% acetic acid 60%:40%
b) methanol: pH 3 phosphate buffer 60%:40%

The variation in retention time for MCPA for different mobile phase compositions and two types of C_{18} bonded silica columns is shown in Table 5.8. The system that had the shortest retention time for MCPA was chosen.

Table 5.8 Retention time for MCPA in different HPLC systems. C_{18} column, 1 ml min^{-1} flowrate, 60%:40% composition of mobile phase.

Mobile phase	Column	Retention time (min)
MeOH:CH_3COOH, 1%	NovaPak	4.5
MeOH:CH_3COOH, 1%	Resolve	5.0
MeOH:phosphate buffer, pH 3	Resolve	3.5

Tests were also carried out with a more concentrated phosphate buffer, 0.02 M at pH 3. This resulted in shorter retention times, as shown in Table 5.9. The mobile phase should have a salt content as low as possible because precipitation of buffer salt can damage the column and cause blockage in the connections, consequently a buffer strength of 0.01 M was chosen.

Table 5.9 Retention time for the phenoxy acids MCPA, dichlorprop and mecoprop at two buffer concentrations at pH 3.0.

	Retention time (min)	
	Phosphate Buffer concentration	
	0.01 M	0.02 M
MCPA	4.1	3.7
Dichlorprop	5.3	4.8
Mecoprop	6.5	5.9

The pK_a values of the phenoxy acids MCPA and dichlorprop are close to 3, as shown in Table 5.1. When the mobile phase has the same pH as the pK_a the mixture of protonated and unprotonated species can make the peak broader and decrease the separation between compounds compared to a mobile phase with lower or higher pH. The lower limit of pH of the mobile phase is set to 2 by the octadecyl silica material in the column. The only alternative in this system, to test if the pH affects the chromatographic performance, is to raise the pH. Therefore a mobile phase with methanol and 0.01 M phosphate buffer at pH 4.5, was tested. The result was that the retention times for the three compounds became shorter and the separation decreased. It was decided to continue to use a pH value of 3.

5.3.2 Selected final method for phenoxy acids

After the preliminary investigations and on the basis of reported literature, an octadecyl silica column, Resolve (Waters), together with a mobile phase consisting of methanol and phosphate buffer with a concentration of 0.01 M at pH 3, 60%:40% was chosen. The detection wavelength was set to 235 nm and the flow rate to 1 ml min^{-1}.

5.3.3 Selection of HPLC conditions for triazines

Triazine herbicides are weak bases which protonate and form cations at low pH values and are unprotonated at pH values of 6 to 7 (Loch, 1991; Pacakova et al, 1988). Battista et al (1989) suggested a reversed phase system with a mobile phase of acetonitrile and phosphate buffer (38%:62%, vol:vol) at pH 6.7 and 0.01 M together with an octadecyl bonded silica column and UV-detection wavelength of 220 nm. Results from tests of the method of Battista et al (1989) are shown in Table 5.10. Different proportions of acetonitrile and phosphate buffer at pH 6.7 and two different flow rates were tested.

Table 5.10 Retention time of atrazine.

Mobile phase CH_3CN:Buffer pH 6.7 %	Flow rate ml min^{-1}	Retention time min
30:70	1.0	8.4
38:62	1.0	4.8
38:62	2.0	2.5

The method worked well for a range of reversed phase columns (Table 5.11) although NovaPak was chosen on the basis of convenience. Further testing showed that 0.01 M phosphate buffer at pH 6.7 could be replaced by ultrapure water with a pH of 6 to 6.5, thereby simplifying the method. It was found that a NovaPak C_{18} column successfully separated atrazine from cyanazine. The samples were 1.0 mg l^{-1} standard solutions of atrazine, atrazine and cyanazine in ultrapure water.

Table 5.11 Test with different columns and mobile phase compositions. Flow rate 1 ml min^{-1}

Column	Mobile phase %	Retention time (min)	
		Atrazine	Cyanazine
NovaPak C_{18} 150*3.9 mm	CH_3CN:buffer pH 6.7 38:62	4.8	na
NovaPak C_{18} 150*3.9 mm	$CH_3CN:H_2O$ 45:55	3.7	2.6
NovaPak C_{18} 300*3.9 mm	$CH_3CN:H_2O$ 60:40	4.0	na
Supelcosil LC-PAH 250*4.9 mm	$MeOH:H_2O$ 60:40	6.0	na
µBondaPak C_{18} 150*3.9 mm	$CH_3CN:H_2O$ 60:40	2.9	na

na = not analysed

5.3.4 Selected final method for triazines

The octadecyl silica column, NovaPak (Waters), was chosen together with a mobile phase composition of acetonitrile and water, 45%:55% by volume. The detection wavelength was set to 220 nm and the flow rate to 1 ml min^{-1}.

6. Adsorption studies

6.1 Experimental

Based on the developed methods for the analysis of atrazine and MCPA it was possible to devise experiments to investigate herbicide interactions with activated carbon on a laboratory scale. These experiments drew on previous work reported in the literature and attempted to provide a mechanistic understanding of humic/herbicide interaction at the activated carbon surface.

6.1.1 Preparation and known properties of the activated carbon

The activated carbon selected for the adsorption experiments was Filtrasorb 300 (Chemviron Carbon), commonly used in drinking water treatment, with the typical properties as shown in Table 6.1. Filtrasorb 300 is GAC manufactured from bituminous coal.

Table 6.1 Characterisation of Filtrasorb 300 (from Chemviron Carbon specifications).

Property	Value
Physical	
Mesh size, U.S. Sieve Series	
>8 mesh (2.36 mm), % maximum	15
<30 mesh (600 μm), % maximum	4
Effective size, mm	0.8-1.0
Mean particle diameter, mm	1.6
Uniformity coefficient	1.8
Bed density (backwashed and drained), g l^{-1}	460
Particle density (wetted in water), g ml^{-1}	1.2
Physico-chemical	
Iodine number, minimum	950
Methylene blue number, minimum	230
Total surface area (N_2, BET-method), m^2 g^{-1}	1000
Phenol loading at 1 mg l^{-1}, expressed as %	4.3
Detergent (TPBS) loading, expressed as mg g^{-1}	150
Micropollutant loading:	
Atrazine at 1 μg l^{-1}, expressed as mg g^{-1}	15
Lindane at 1 μg l^{-1}, expressed as mg g^{-1}	35
Toluene at 1 mg l^{-1}, expressed as mg g^{-1}	85

In this study the GAC was crushed in a mortar and passed through a 63 µm nylon sieve. The pulverised carbon was dried in a oven at 110°C for 24 hours and stored in a dessicator until use. GAC has a long adsorption equilibrium time, up to 30 days, whereas pulverised carbon can reach equilibrium after 3-5 days (Peel and Benedek, 1980). Randtke and Snoeyink (1983) have shown that pulverisation of GAC has no influence on the carbon adsorption capacity but failure to reach equilibrium in adsorption studies can give an underestimation of the adsorption capacity.

6.1.2 Adsorption isotherms

Adsorption isotherms were determined by adding different carbon amounts (m) to a constant volume of water (V) with an initial concentration (C_o) of herbicides as described by Haist-Gulde (1991). After equilibration the pesticide concentration in the liquid phase (C) was measured. The adsorbed amount of herbicide (q) was calculated from equation 6.1:

$$q = (C_o - C)/(V/m) \qquad (6.1)$$

The adsorption isotherms were carried out in 1 l glass beakers stirred with a paddle and filled to 0.5 l (V) with test water. Each experimental series included 13 beakers with carbon and one control without carbon. The carbon was added as a slurry prepared from approximately 0.1 g carbon mixed with 1 l ultrapure water for 2-3 hours with a magnetic stirrer. The carbon amount (m) in the experiments was in the range 0.2 to 5.0 mg. The slurry was dispensed to the samples with a micropipette (2 ml to 5 ml) or volumetric pipette (6 ml to 50 ml). The exact amounts of the added carbon were calibrated by filtering a known volume of each carbon dose through dried and weighed cellulose acetate filters (0.45 µm) which were redried and reweighed. Samples of 50 ml were withdrawn every 24 hours through 0.45 µm cellulose acetate filters (Minisart, Sartorius). The herbicides used in this study were a phenoxy acid, MCPA, and a triazine, atrazine. Stock solutions of 100 mg l^{-1} were prepared for each compound; in methanol for MCPA and in acetonitrile for atrazine. The initial aqueous sample concentration (C_0) in the experiments was 100 µg l^{-1} of herbicide. The herbicide content (C) was analysed, as described in chapter 5, by SPE enrichment and HPLC for separation and detection. In the first series of experiments, samples were taken every 24 hours for seven days but it was found that equilibrium was reached after 24 hours. Therefore an equilibration time of 24 hours was used in the remainder of the experiments. In a study by Peel and Benedek (1980), an equilibration time of 3-5 days was recommended for adsorption isotherms with PAC and chlorophenol. However, 80% of the adsorptive capacity was achieved during the first few hours.

Throughout the study, all waters were filtered through a glass fibre filter (GF/F, Whatman) to remove heterogeneous suspended solids and adjusted to pH 7 with phosphate buffer prior to use in the adsorption experiments. Ultrapure water from a Barnstead apparatus was used as an organic-free reference water. The dissolved organic background was measured spectrophotometrically at 254 nm.

6.1.3 Description of full-scale and pilot-scale plant

Several waters with varying contents of DOM were used. Raw water from Lake Delsjön, a drinking water source for Göteborg, represented DOM before treatment. Lake Delsjön is used for storage of water from the Göta River, which is pumped to the lake. The water quality of Lake Delsjön is strongly affected by the Göta River water. Treated waters from the Lackarebäck drinking water plant were also tested including flocculated water and filtered water (GAC as filter media). In a pilot-scale plant, ozonation, flocculation, sedimentation and rapid sand filtration were carried out with the same raw water source as for the full-scale plant. Ozonated raw water and finished treated water from the pilot plant were utilised in the adsorption study.

The full-scale treatment plant at Lackarebäck consists of pre-chlorination (0.3 g m^{-3} Cl_2), flocculation (40 g m^{-3} $Al_2(SO_4)_3$), sedimentation, GAC filtration and post-chlorination (0.8 g m^{-3} Cl_2). The GAC filter had been running for two and a half years since regeneration when samples of the water were taken. The pilot-scale treatment plant was located at Lackarebäck and the treatment train was pre-ozonation (2 g m^{-3}), flocculation (44 g m^{-3} $Al_2(SO_4)_3$), sedimentation and sand filter.

6.1.4 pH-adsorption experiments

The effect of pH on adsorption was investigated in the pH range 3 to 9, at one carbon dosage (1.3 mg) and two water qualities (ultrapure water and lake water from Delsjön). Phosphate buffer salts were used to adjust the pH and the pH value was measured before and after the adsorption experiments. The initial concentration of the herbicides was 100 µg l^{-1} and herbicide analyses were conducted as described in chapter 5.

6.1.5 Lake water dilution experiments

Lake water was diluted with ultrapure water so that the DOM concentration could be decreased below the herbicide concentration. Previous Total Organic Carbon (TOC) measurements of Lake Delsjön were 5 mg l^{-1} and it was assumed that the raw water had nearly the same value during this study. The content of DOM is expressed as % lake water in ultrapure water; 1%, 10%, 25% and 100%. For all dilutions, the pH was adjusted to 7 with phosphate buffer and the initial concentration of the pesticides was 100 µg l^{-1}. The carbon amount was 1.3 mg and the sample water volume was 0.5 l.

6.2 Pure substance adsorption isotherms

There are basically two types of adsorption isotherms which have been used to describe experimental data on the adsorption of organic compounds to activated carbon (Sontheimer et al, 1988) Those based on physico-chemical or thermodynamical models, such as Langmuir, do not adequately describe binding to activated carbon under all conditions because the surface sites are heterogeneous. There has therefore been a move towards a more empirical approach and here the Freundlich adsorption isotherm has been most frequently used. The Freundlich isotherm equation (equation 6.2) has been found to satisfactorily describe the binding of organic micropollutants to activated carbon (Sontheimer et al, 1988).

$$q = K_f + n\log C \tag{6.2}$$

In equation 6.2, q is the equilibrium adsorbed amount of herbicide per mass of adsorbent (in $\mu g\ mg^{-1}$), q is calculated from C_0 and C (equation 6.1), C is the measured concentration (in $\mu g\ l^{-1}$) in the solution at equilibrium. Usually the Freundlich isotherm is used in the logarithmic form (equation 6.3).

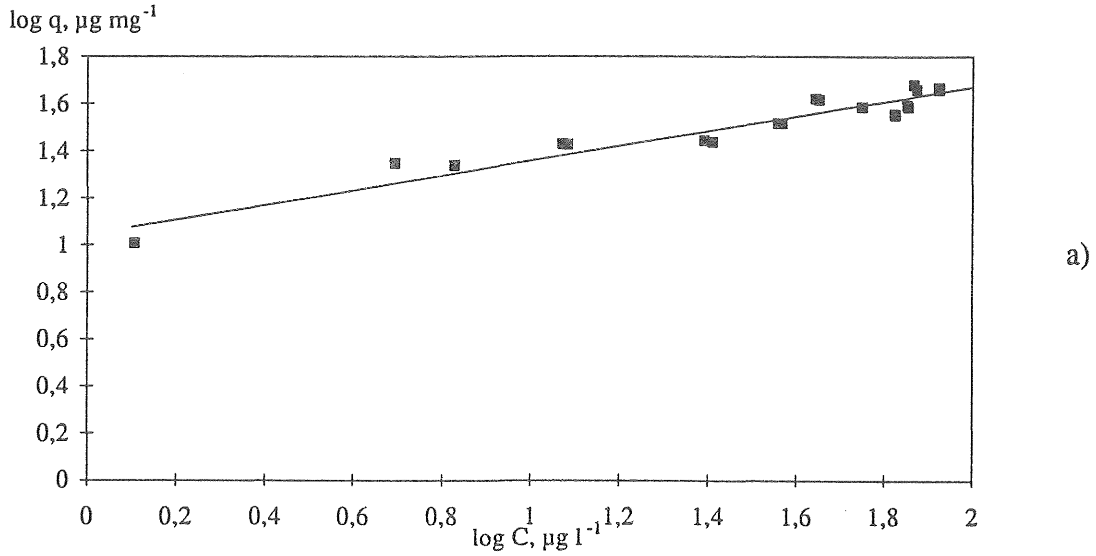
$$\log q = \log K_f + n\log C \tag{6.3}$$

The adsorption isotherm is a plot of logq versus logC and forms a straight line if the adsorption follows the Freundlich model. The slope is the exponent n, and K_f, the Freundlich constant, is equal to the adsorbed concentration, q, when C=1. K_f provides information about the adsorbability of the compound whereas n relates to the driving force of the adsorption and the distribution of energy of the adsorption sites (Carter et al , 1992). Previous studies have shown that both n and K_f are dependent on the initial concentration of the compound in the experiment and therefore it is important to have the same conditions when comparing different n and K_f values (Sontheimer et al, 1988).

Tests of the Freundlich adsorption isotherm for describing the adsorption of atrazine and MCPA to activated carbon in ultrapure water showed a linear relationship (Figure 6.1). The Freundlich constant, K_f, and the exponent, n, were calculated from the isotherm data and are presented in Table 6.2 together with the coefficient of determination, r^2, from a linear regression model. The MCPA data has a low r^2 value and the Freundlich adsorption model does not completely describe the adsorption data. However, the adsorption capacity can still be presented in the form of carbon dosage plots, which are shown in 6.3.3.

Table 6.2 The Freundlich constant, K_f, the exponent, n, and the coefficient of determination, r^2, for atrazine and MCPA in ultrapure water.

Pesticide	K_f	n	r^2
Atrazine	11	0.31	0.94
MCPA	14	0.23	0.57



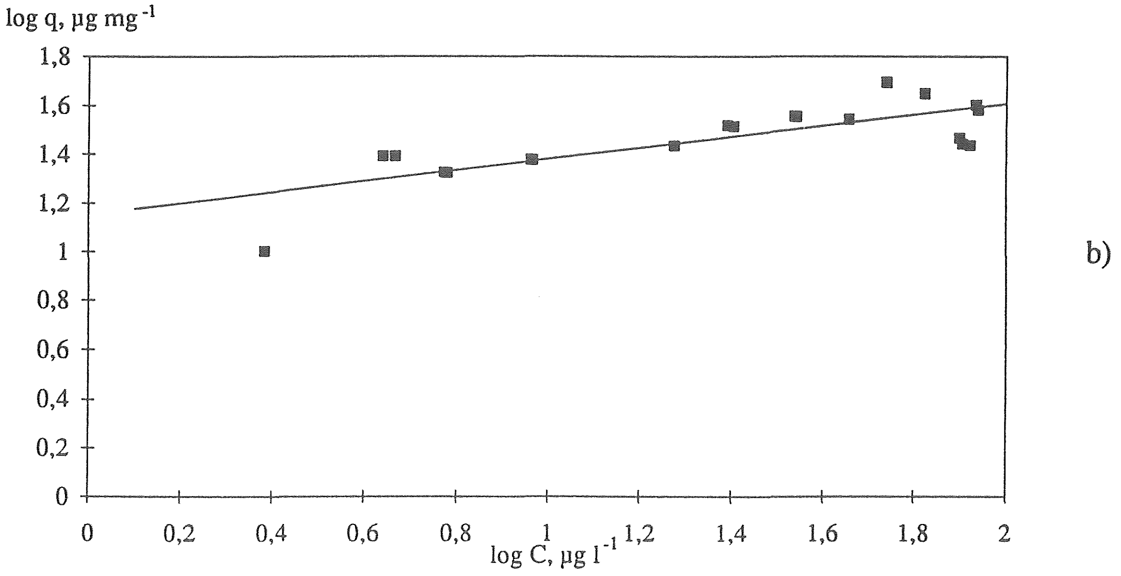


Figure 6.1 Adsorption isotherm of a) atrazine and b) MCPA in ultrapure water.

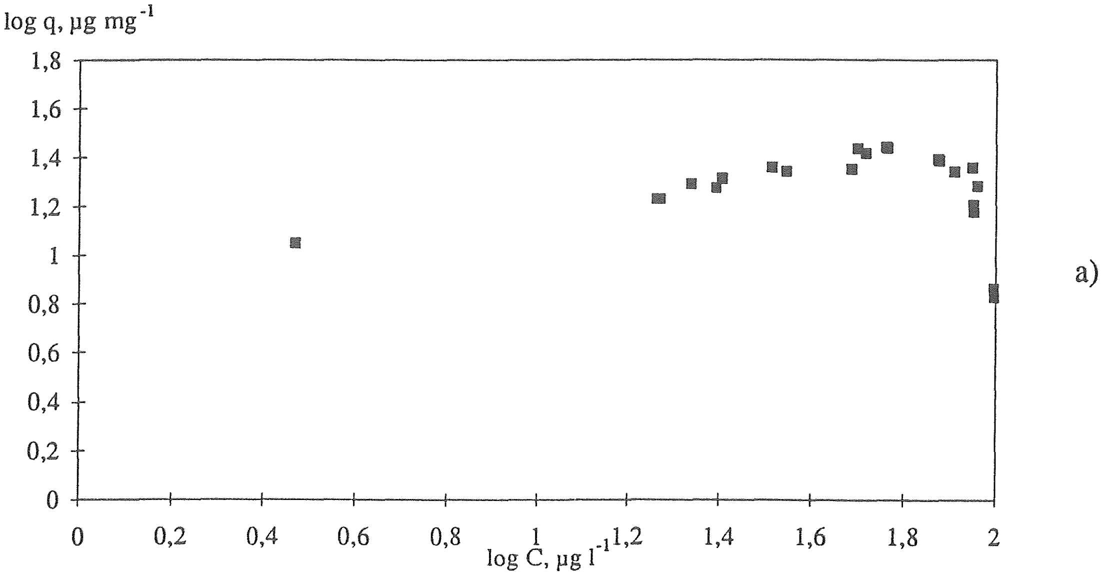
6.3 Effect of organic material

It is known that natural organic material can interfere with the adsorption of organic micropollutants to activated carbon (Najm et al, 1991). A number of theories have been put forward to explain this interference, including micropollutant adsorption to humic substances and competitive adsorption (Pribazari et al, 1992). In this study, a number of approaches were used to investigate the effect of organic material on herbicide adsorption, including adsorption isotherms, carbon dosage plots and background organic dilution.

6.3.1 Adsorption isotherms in the presence of DOM

Adsorption isotherms for atrazine and MCPA in lake water showed non-linearity probably due to the presence of DOM. The isotherms are shown in Figure 6.2. Lake water from Delsjön has a TOC concentration of 5 mg l^{-1}, the DOM is of unknown structure and is probably of humic and fulvic acid type. The range of molecular weight is large and there may be fractions that approach the same molecular weight as atrazine and MCPA, i.e. 200 g $mole^{-1}$, that could compete for adsorption sites at the activated carbon surface. It is now generally accepted that fulvic acid has a molecular weight of around 1000, however, clearly structure will also be important in both binding to sites on the activated carbon and blockage of micropores.

The usual explanation for non-linear isotherms is competition for adsorption sites on the activated carbon (Sontheimer et al, 1988). Different adsorbates in solution have different access to adsorption sites. A competition between the adsorbates for the adsorption sites occurs and the concentration of adsorbate in the liquid phase, C, increases compared to the result for a single-adsorbate isotherm. For a fixed initial concentration, an increase in liquid-phase concentration means a decrease in solid-phase concentration. Thus, the adsorption capacity is reduced for all components in the solution and the extent of this effect depends on the single-solute adsorption isotherms. If the compounds have similar adsorption isotherms then the reduction of adsorption capacity is similar. However, if they have different adsorption isotherms, as is the case with organic micropollutants and DOM, the stronger adsorbed compound will have a considerable influence on the less strongly adsorbed compound. The curved adsorption isotherms for atrazine and MPCA in lake water are probably a consequence of the existence of a preferentially adsorbed compound in the solution, i.e. DOM.



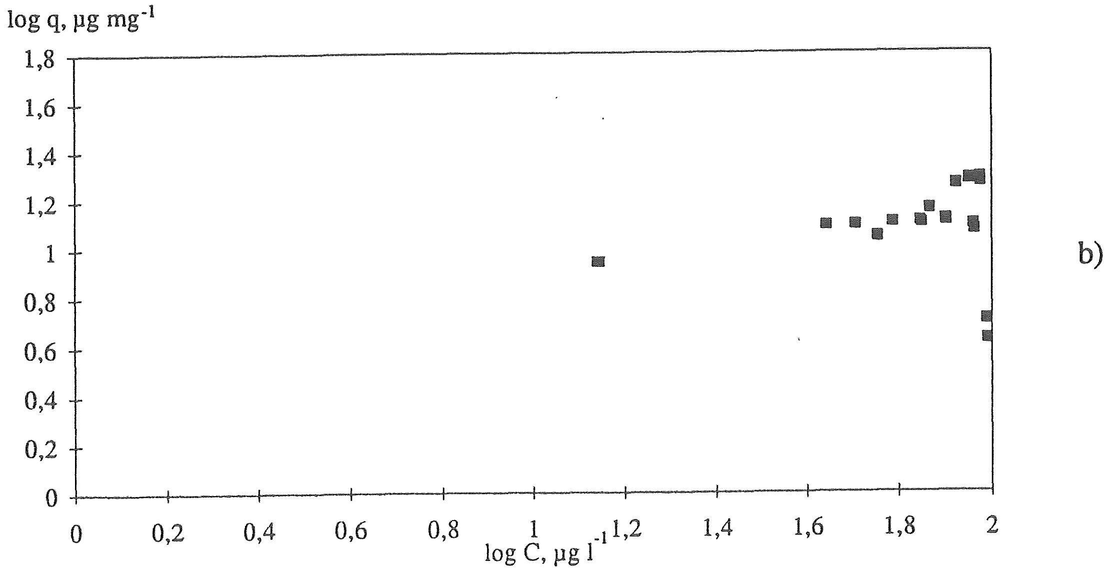


Figure 6.2 Adsorption isotherm of a) atrazine and b) MCPA in lake water.

6.3.2 Effect of treatment processes on adsorption interferences

The herbicide adsorption capacity of activated carbon was tested to look for improved adsorption of herbicides after treatment. In Table 6.3 the DOM contents measured as UV_{254} of the treated waters are shown.

Table 6.3 DOM content, measured as UV_{254} absorbance, of lake water and treated waters.

	UV_{254} (cm^{-1})
Lake water	0.115
Full scale treatment	
Flocculation and sedimenation	0.033
GAC filtration	0.033
Pilot scale treatment	
Ozone	0.102
Ozone, flocculation, sedimentation and sand filtration	0.031

The adsorption results for atrazine in GAC filtered water and in ozone treated water from the pilot plant gave linear isotherms as shown in Figure 6.3. The decrease in DOM after GAC filtration and ozonation apparently improves the adsorption of atrazine to the activated carbon. In Table 6.4 the calculated Freundlich constants, K_f and n, are presented. The coefficient of determination, r^2, from the linear regression is also shown in Table 6.4 and demonstrates a good correlation in the regression model for all tested waters besides flocculated water. In the case of flocculated water the n-value has little meaning as the adsorption isotherm is curved and does not fit a linear model.

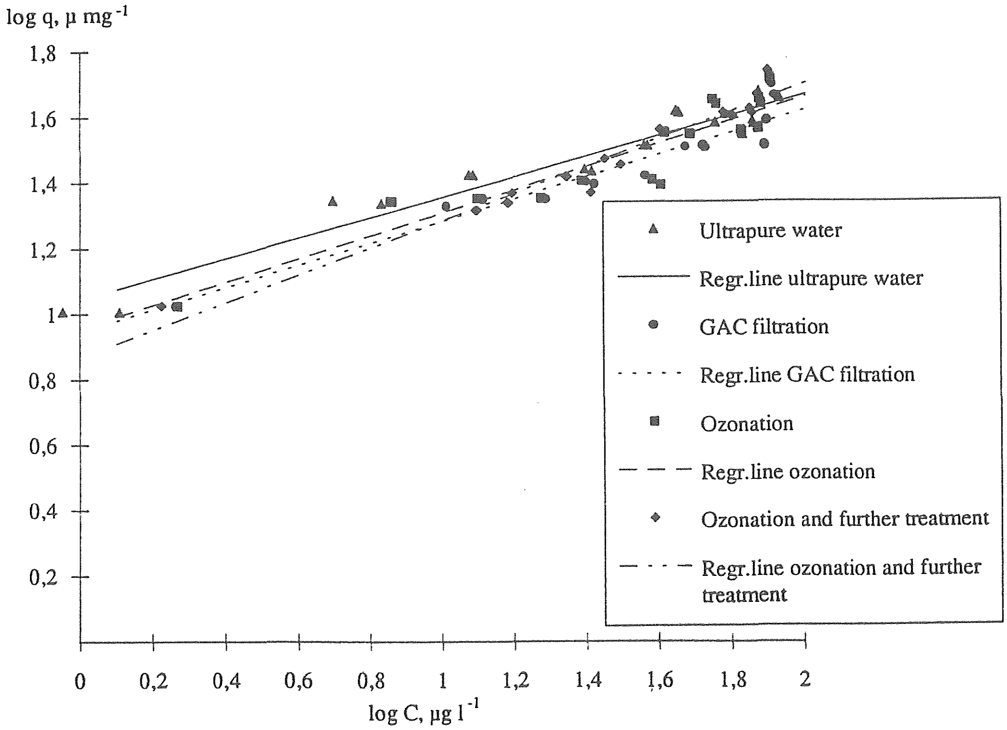


Figure 6.3 Adsorption isotherms of atrazine in ultrapure water and water after GAC filtration, ozonation, and ozonation, flocculation, sedimentation and sand filtration (ozonation and further treatment).

Table 6.4 The Freundlich constant, K_f, the exponent, n, and the coefficient of determination, r^2, for atrazine in ultrapure water and treated waters.

	K_f	n	r^2
Ultrapure water	11	0.31	0.94
Full scale treatment			
Flocculation and sedimentation	34	-0.17	0.24
GAC filtration	8.8	0.34	0.90
Pilot scale treatment			
Ozonation	9.1	0.35	0.85
Ozonation, flocculation, sedimentation and sand filtration	7.4	0.42	0.95

Statistical analysis with Student t-test showed a significant difference in the n values of ultrapure water and ozonated and treated water. An increase of n value compared to the single substance isotherm shows the presence of less adsorbable components in the water (Sontheimer et al, 1988). It could be possible that ozonation and the following treatment with flocculation and sand filtration have changed the composition of the remaining DOM and improved the adsorption of atrazine to activated carbon.

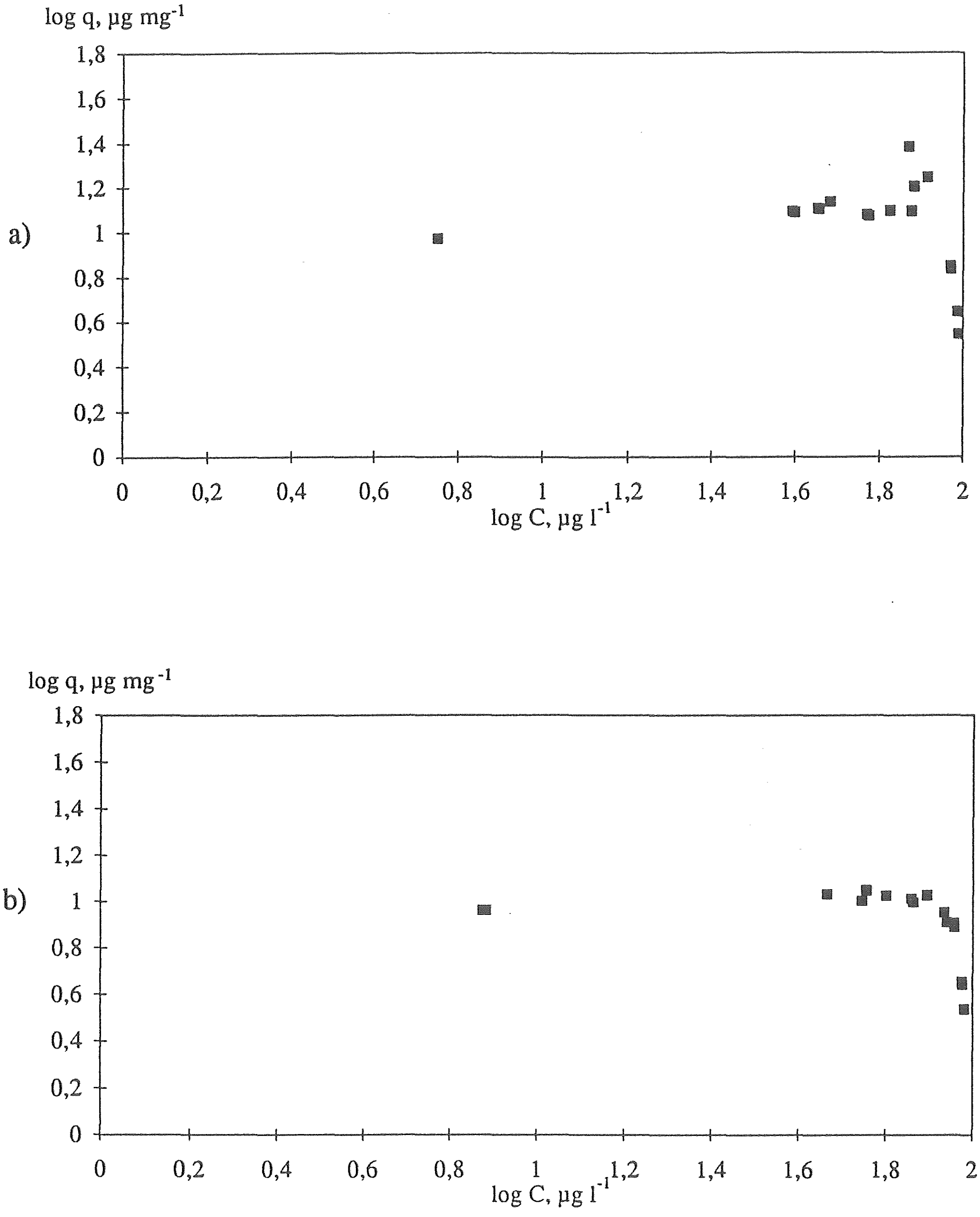


Figure 6.4 Adsorption isotherm of MCPA in water after a) flocculation and sedimentation, and b) GAC filtration.

For MCPA, the result with full-scale treated water is similar to the result of tests with lake water (Figure 6.4) with non-linear isotherms. In Table 6.5 the K_f, n and r^2 are calculated, although the Freundlich adsorption model does not appear to describe the adsorption data satisfactorily. The competitive effect of DOM clearly disturbs the adsorption of MCPA to activated carbon even after the steps in water treatment studied here.

Table 6.5 The Freundlich constant, K_f, the exponent, n, and the coefficient of determination, r^2, for MCPA in ultrapure water, lake water and two water qualitites from full scale treatment.

	K_f	n	r^2
Ultrapure water	14	0.23	0.57
Lake water	6.1	0.17	0.06
Flocculation and sedimentation	11	0.01	0.00
GAC filtration	14	-0.13	0.08

6.3.3 Comparison of carbon dosage plots for MCPA and atrazine

The adsorption isotherms in lake water and some treated waters showed non-linearity and therefore another method of presenting the data was used to analyse the adsorption capacity for atrazine and MCPA. Sontheimer et al (1988) showed that the adsorption capacity can be visualised when the equilibrium concentration of pesticide in the liquid phase is plotted against the carbon dosage. The results in Figure 6.5 demonstrate that the activated carbon has a similar adsorption capacity for MCPA and atrazine in ultrapure water. However, in the presence of DOM, the adsorption capacity for atrazine is higher than for MCPA as shown by the lower concentration of atrazine in the liquid phase than MCPA, at the same carbon dosage. The reason for this is probably due to the difference in chemical structure between atrazine and MCPA. The chemical structures of atrazine and MCPA are shown in Table 5.1. MCPA is an acid and therefore more sensitive to competitive adsorption from DOM which also has acidic properties. Further experiments therefore investigated variations of adsorption of atrazine and MCPA to activated carbon with pH.

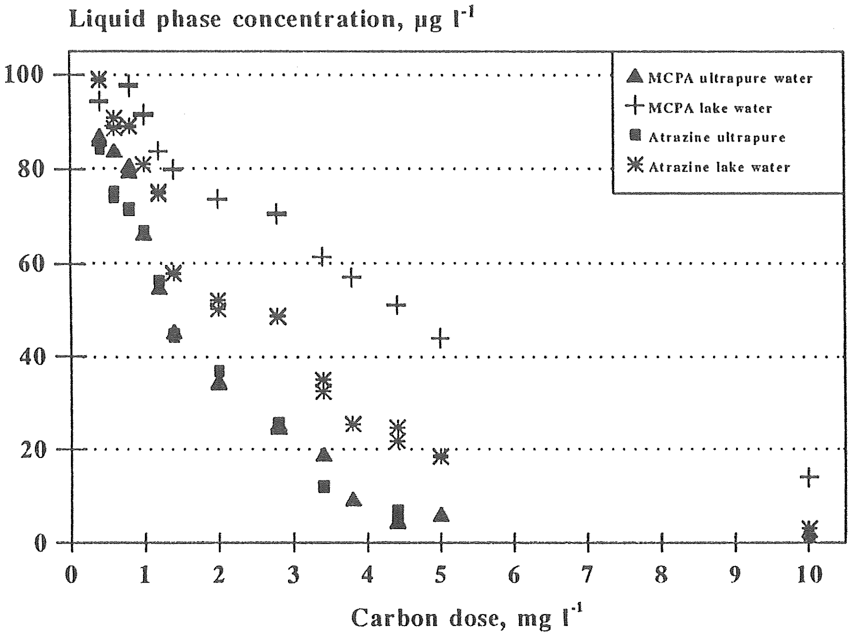
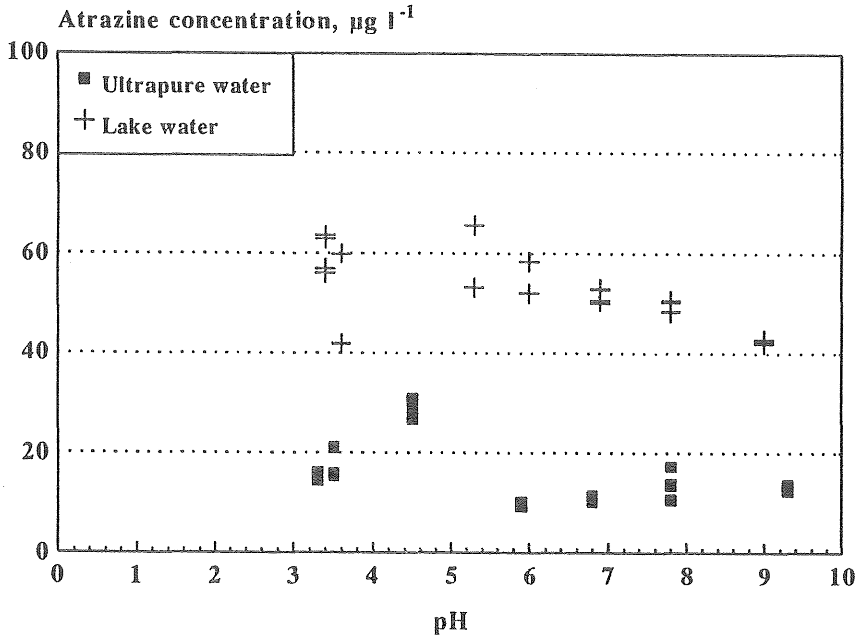


Figure 6.5 Carbon dosage plots for atrazine and MCPA.

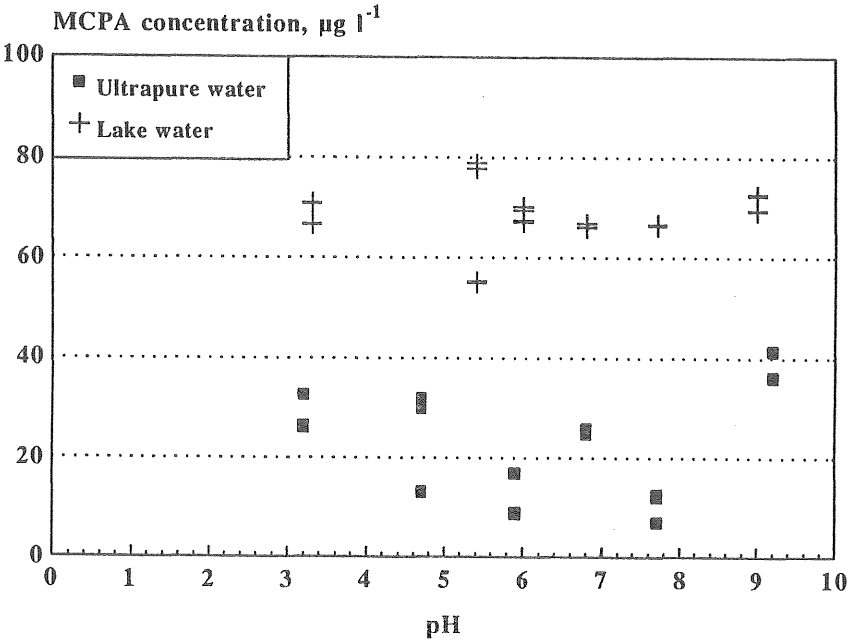
6.3.4 pH-adsorption experiments

pH-adsorption experiments were carried out to study the pH dependence of the adsorption of atrazine and MCPA to activated carbon. Previous studies have shown that activated carbon adsorption capacity generally increases with a decrease in pH (Randtke and Snoeyink, 1983). The adsorption of DOM in lake water to activated carbon could change due to pH-induced changes in DOM conformation and alter the competitive adsorption. Complexation of pesticides to DOM is also a possible mechanism for the decrease in adsorption capacity observed in the adsorption isotherm studies reported in the previous chapters. Pirbazari et al (1992) suggests three reasons for a decrease in activated carbon adsorption capacity for PCB and toxaphene to activated carbon in the presence of DOM; competitive adsorption, complexation to DOM, or a combination of both. If complexation of atrazine and MCPA with DOM occurs, then a change in pH should alter the adsorption properties. Kalouskova (1987) reports that atrazine forms a complex with humic acid. The formation of the atrazine-humic acid complex is pH dependent, with 3.4 times more atrazine complex bound at pH 2.6 compared to pH 6.1. This result is consistent with Wang et al (1990,1991,1992) who reported a decreased binding capacity of atrazine to fulvic acid, humic acid and soil with an increase in pH value.

The pH dependence of herbicide adsorption was tested in ultrapure water and in lake water. The results from the experiments are shown in Figure 6.6. The adsorption of MCPA showed no trend with pH in this pH interval. MCPA is an acid with a pK_a value of around 3 (see Table 5.1) and the protonated and the unprotonated form of the acid could have different adsorption capacities to activated carbon. However, it turned out to be practically impossible to test at a pH lower than 3 because of limitations in the phosphate buffer system used in the experiments. Atrazine showed a slight decrease in the liquid-phase concentration, which indicates an increase in the adsorbed concentration, at higher pH values in lake water. The conclusion from these experiments is that the adsorption of MCPA and atrazine to activated carbon is not pH dependent for the pH range studied. The observed decrease in adsorption capacity in the presence of DOM cannot be improved by a change in pH.



a)



b)

Figure 6.6 pH-adsorption experiments with a) atrazine and b) MCPA.

6.3.5 Dilution experiments

Dilution experiments were carried out to test the competitive adsorption theory (Sontheimer et al, 1988) on herbicides and DOM. The results of lake water dilution experiments showed that adsorption of atrazine and MCPA to activated carbon varies with DOM concentration. The molar DOM concentrations shown in Table 6.6 are estimated from 5 mg TOC l^{-1} and a molecular weight assumed to be 1000 g $mole^{-1}$. Because humics are a mixed substance and not fully characterised, it is not possible to calculate exact molarity and an approximation is therefore made here for comparative purposes only. The herbicide concentration in the experiments for atrazine was 0.46 µM and for MCPA was 0.52 µM. The lowest concentration of DOM is lower than the experimental herbicide concentration and the second lowest is approximately equivalent to the experimental herbicide concentration.

Table 6.6 DOM concentration in the experiments with diluted and buffered lake water.

Lake water %	Calculated DOM, µM
1	0.05
10	0.5
25	1.25
100	5.0

The results from the experiments are presented in Figure 6.7. When the DOM concentration is low the pesticide adsorbs to the carbon without competition from DOM. At DOM concentrations above a dilution of lake water to 25%, DOM dominates the adsorption sites. It can also be seen that atrazine is a stronger adsorbate than MCPA because atrazine has a lower concentration in the liquid phase, although the two compounds were not adsorbed from the same mixture. Because of the similarity in molecular weight it would be interesting to test the competition between atrazine and MCPA in ultrapure water and lake water.

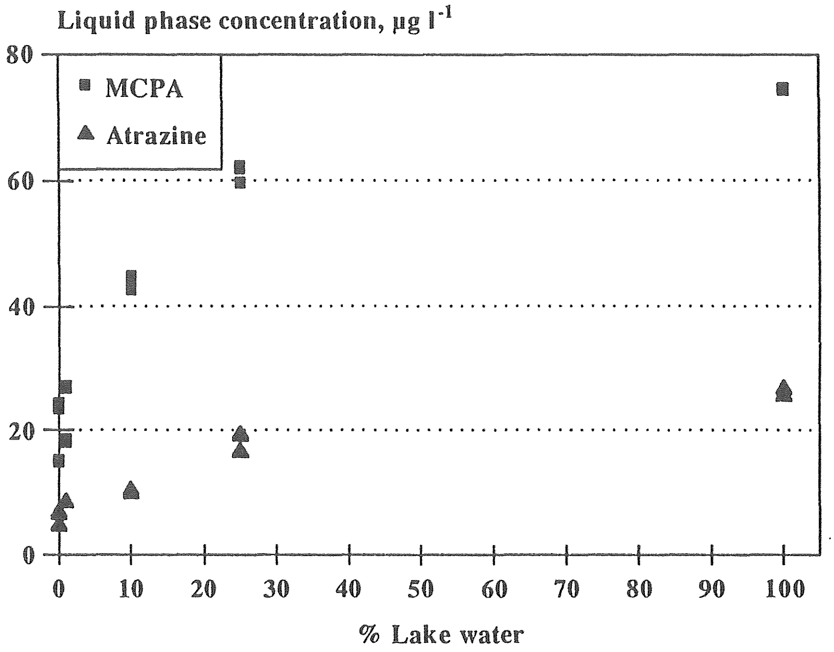


Figure 6.7 Dilution experiments of lake water with atrazine and MCPA.

7. Conclusions and Applications

Pesticides are found in surface and ground water in Sweden and other countries, although the concentrations are low. Conventional drinking water treatment methods are not suitable for the removal of pesticides and more effective treatment methods have to be adopted. GAC filtration and ozonation are two alternatives which have been put forward although ozone may lead to undesired byproducts.

In this work analytical methods, including SPE and HPLC, were developed for triazine and phenoxy acid herbicides with an emphasis on the avoidance of background organic interference. These methods were then used for studies of herbicide adsorption to activated carbon. The adsorption studies showed curved adsorption isotherms in the presence of DOM but could be interpreted through carbon dosage plots. The carbon dosage plots showed that atrazine and MCPA had the same adsorption capacity to activated carbon when ultrapure water was used and the presence of DOM decreased the adsorption capacity for both substances, although the decrease was more obvious for MCPA than for atrazine.

When the content of DOM had been reduced after certain water treatments, atrazine could be readily adsorbed to activated carbon. MCPA on the other hand was more sensitive to DOM interaction and no treatment process tested improved the adsorption to activated carbon. pH-adsorption experiments showed no pH effect on adsorption for either atrazine or MCPA.

Dilution experiments demonstrated a clear competitive mechanism of adsorption for both atrazine and MCPA in the presence of DOM. This will be important when choosing carbon type in water treatment.

8. Further Studies

Further studies will concentrate on the mechanism of the interaction of DOM and herbicides on the activated carbon surface. The study includes DOM adsorption isotherms, dilution experiments with lake water and different carbon types, pH-adsorption experiments with lake water around pH 3 to complement pH studies reported here, and adsorption of mixtures of herbicides to activated carbon. The work also aims to study previous work concerning the chemical structure of the activated carbon surface and of the DOM to support the mechanism of interaction.

The long term work includes studies of the interaction of DOM and herbicides on the activated carbon surface in pilot-scale GAC filters, the effect of filter contact time and biologically activated carbon, interaction after DOC breakthrough, and how the oxidation of DOM and herbicides before GAC filtration affects the interaction.

References

Aller, L., T. Bennett, J.H. Lehr and R. Petty (1986). DRASTIC: A system to evaluate the pollution potential of hydrogeological settings by pesticides. In, W.Y. Garner, R.C. Honeycutt, H.N. Nigg (Ed.), Evaluation of pesticides in ground water, ACS symposium series 315. American Chemical Society, Washington, DC. p. 141-158.

Battista, M., A. DiCorcia and M. Marchetti (1989). Extraction and isolation of triazine herbicides from water and vegetables by a double trap system. Anal. Chem., 61, 935-939.

Berggren, H. (1989). Skogsbruk och jordbruk - med ekologisk grundsyn. In, B. Hortlund, E. Leire, C. Malmgren, Å. Svenstam and C. Westenius (Ed.), En ren framtid. Fakta om miljövård. Liber Hermods, Malmö, p. 65-79. (In Swedish.)

Bouwer, E.J. and P.B. Crowe (1988). Biological processes in drinking water treatment. J. Amer. Water Works Ass., 80, 82-93.

Buser, H-R. (1990). Atrazine and other s-triazine herbicides in lakes and in rain in Switzerland. Environ. Sci. Technol., 24, 7, 1049-1058.

Carter, M.C., W.J. Weber Jr and K.P. Olmstead (1992). Effects of background dissolved organic matter on TCE adsorption by GAC. J. Amer. Water Works Ass., 84, 8, 81-91.

City of Göteborg, Environment Protection Board (1990). Sampling of watercourses during 1990, for pesticide identification. (In Swedish) Internal report.

Coats, J.R. (1991). Pesticide degradation mechanisms and environmental activation. In: Pesticide transformation products. Fate and significance in the environment. L. Somasundaram and J.R. Coats (Eds.) ACS symposium series 459. American Chemical Society, Washington, DC. p.10-30.

Cohen, S.Z, C. Eiden and M.N. Lorber (1986). Monitoring ground waters for pesticides. In, Evaluation of pesticides in ground waters, W.Y Garner, Honeycutt, R.C. and H.N. Nigg (Ed.) ACS symposium series 315. American Chemical Society, Washington, DC. p. 170-196.

Crittenden, J. C., D.W. Hand, H. Arora and B.W. Lykins Jr (1987). Design considerations for GAC treatment of organic chemicals. J. Am. Water Works Ass., 79, 1, 74-82.

Dahlman, M. (1990). Pesticide residues in private wells. (In Swedish). Vår Föda, 42, 244-252

DiCorcia, A., M. Machetti and R. Samperi (1989). Extraction and isolation of phenoxy acid herbicides in environmental waters using two adsorbents in one minicartridge. Anal.Chem, 61, 1363-1367.

Foster, D.M., A.J. Rachwal and S.L. White (1992). Advanced treatment for the removal of atrazine and other pesticides. Water Supply , 10, 133-146.

Frank, R., H.E. Braun, M. van Hove Holdrinet, G.J. Sirons and B.D. Ripley (1982). Agriculture and water quality in the canadian Great Lake basin: V. Pesticide use in 11 agricultural watersheds and presence in stream water, 1975-1977. J. Environ. Qual., 11, 3, 497-505.

Geerdink, R. B., C.A.A. van Balkom and H-J. Brouwer (1989). Determination of phenoxyacid herbicides in water. Polymeric pre-column preconcentration and tetrabutylammonium ion-pair separation on a PRP-1 column. J. Chrom., 481, 275-285.

Glaze, W. H. (1987). Drinking water treatment with ozone. Environ.Sci.Technol., 21, 3, 224-230.

Gmünder, A., J. Gnieser and E. Lopez (1989). Treatment of surface water for potable purposes for the community of Murten, Switzerland. Water Supply, 7, 155-162.

Grandet, M., K.E. Quentin and L. Weil (1989). Untersuchung zur Grundwasserbelastung mit Atrazin. Z. Wasser-Abwasser Forsch., 22, 231-235. (In German)

Haist-Gulde, B. (1991). Zur Adsorption von Spurenverunreinigungen aus Oberflächewässern. Diss.,University of Karlsruhe, Karlsruhe. (In German)

Helling, C. S. and B.C Turner (1968). Pesticide mobility: Determination by soil thin-layer chromatography. Science, 162, 562-563.

Hoke, S.H, E.E. Brueggemann, L.J. Baxter and T. Trybus (1986). Determination of phenoxy acid herbicides using solid-phase extraction and high-performance liquid chromatography. J. Chrom., 357 , 429-432.

Huber, L., G. Zimmer and H. Sontheimer (1989). Powdered or granular activated carbon for micropollutant removal, Aqua, 38, 118-130.

Kalousková, M. (1987). Interaction of humic acids with atrazine. J. Environ. Sci. Health, B22 (1), 113-123.

Kemikalieinspektionen (1991). Sold quantities of pesticides during 1990. (In Swedish) Kemikalieinsektionen, Solna.

Kemikalieinspektionen (1994). Sold quantities of pesticides during 1993. (In Swedish) Kemikalieinsektionen, Solna.

Kreuger, J. and N. Brink (1988). Losses of pesticides from arable land. Växtskydds-rapporter, Jordbruk, 49, 50-61.

Kruithof, J.C., R. Hopman, R.T. Meijers and J.A.M.H. Hofman (1993). Presence and removal of pesticides in Dutch drinking water practice. Presented at the 19th

International Water Supply congress and exhibition, Budapest, Hungary, 2 to 8 October 1993.

LeChevallier, M.W. and G.A. McFeters (1990). Microbiology of activated carbon. In: Drinking water microbiology: Progress and recent developments . G.A. McFeters (Ed.), Broch/Springer series in contemporary bioscience, Springer-Verlag, New York. p. 104-119.

Legrand, M.F., E. Constentin and A. Bruchet (1991). Occurence of 38 pesticides in various French surface and ground waters. Environ. Technol., 12, 985-996.

Loch, J.P.G. (1991). Effect of soil type on pesticide threat to the soil/groundwater environment. In: M.L. Richardson (ed.) Chemistry, agriculture and the environment. The Royal Society of Chemistry, Cambridge. p.291-307.

Mandl, V. (1992). Pesticides- the EG viewpoint. Water supply, 10, 7-11.

McFeters, G.A., P.J. Bond, S.B. Olson and Y.T. Tchan (1983). A comparison of microbioal bioassays for detection of aquatic toxicants. Water Res., 17, 1757-1762.

Miltner, R.J., D.B. Baker, T.F. Speth and C.A. Fronk (1989). Treatment of seasonal pesticides in surface water. J. Am. Water Works Ass., 81, 1, 43-52.

Muir, D.C.G. and N.P. Grift (1987). Herbicide levels in rivers draining two prairie agricultural watersheds (1984). J. Environ. Sci. Health B22(3), 259-284.

Munz, C and M. Boller (1989). Design considerations for the removal of chlorinated organics with layered upflow carbon adsorbers. Water Supply, 7, 191-202.

Munz, C., J.L. Walther, G. Baldauf, M. Boller and R. Bland (1990). Evaluating layered upflow carbon adsorption for the removal of trace organic compounds. J. Am. Water Works Ass., 82, 3, 63-76.

National Food Administration (1993). Drinking water ordinance. National Food Administration, Uppsala.(In Swedish)

Najm, I.N., V.L. Snoeyink and Y. Richards (1991). Effect of initial concentration of a SOC in natural water on its adsorption by activated carbon. J.Am. Water Works Ass., 83, 8, 57-63.

Normann, S., K. Haberer and U. Oehmichen (1987). Verhalten von stickstoffhaltigen Pflanzenschutzmitteln bei der Trinkwasseraufbereitung. Vom Wasser, 69, 233-249. (In German)

Pacakova, V., K. Stulik and M. Prihoda (1988). High-performance liquid chromatography of s-triazines and their degradation products using ultraviolet photometric and amperometric detection. J. Chromatogr., 442, 147-155.

Peel, R.G. and A. Benedek (1980). Attainment of equilibrium in activated carbon isotherm studies. Environ. Sci. Technol., 14, 66-71.

Pionke, H.B. and D.W. Glotfelthy (1990). Contamination of groundwater by atrazine and selected metabolites. Chemosphere, 21, 6, 813-822.

Pirbazari, M., B.N. Badriyha, S.H. Kim and R.J. Miltner (1992). Evaluating GAC adsorbers for the removal of PCBs and toxaphene. J. Am. Water Works Ass., 84, 2, 83-90.

Quentin, K.-E., M. Grandet and L. Weil (1987). Pestizide und Trinkwasserversorgung. DVGW-Schriftenreihe, Wasser, 53. (In German)

Randtke, S.J. and V.L. Snoeyink (1983). Evaluating GAC adsorptive capacity. J. Am. Water Works Ass., 75, 8, 406-413.

Richards, R.P., J.W. Kramer, D.B. Baker and K.A. Krieger (1987). Pesticides in rainwater in the northeastern United States. Nature, 327, 129-131.

Sandberg, E.C.H. (1992). Pesticides in drinking water. Residue limits and toxicological problems. In A. Helweg (Ed.), Pesticides in the aquatic environment. Appearance and effect. Ministry of Agriculture, Danish Institute of Plant and Soil Science, Slagelse. p.132-137.

Sandberg, E. and B. Erlandsson (1990). Pesticide residue in surface and ground waters. (In Swedish). Vår Föda , 42, 224-234.

Sayre, I.M. (1988). International standards for drinking water. J. Am. Water Works Ass., 80, 1, 53-60.

Selim, M.I. and J. Wang (1994). Fate of atrazine in biologically active granular carbon. Environ. Toxicol. Chem., 13, 3-8.

Seiber, J. N. (1987). Principles governing environmental mobility and fate. In, Ragsdale, N. N; Kuhr, R.J. (Ed.), Pesticide. Minimizing the risks. ACS symposium series 336, American Chemical Society, Washington, DC, p. 88-105.

Singer, Phillip C. (1990). Assessing ozonation research in water treatment. J. Am. Water Works Ass., 82, 10, 78-88.

Somasundaram, L., J.R. Coats and K.D. Racke (1991). Mobility of pesticides and their hydrolysis metabolites in soil. Environ. Toxicol. Chem., 10, 185-194.

Sontheimer, H. (1978). Biological treatment of surface waters in activated carbon. Ozonews, 5, 7.

Sontheimer, H., J.C. Crittenden and R.S. Summer (1988). Activated carbon in drinking water treatment. DVGW-Forschungsstelle, University of Karlsruhe, Karlsruhe.

Sontheimer, H.,E. Heilker, M.R. Jekel, H. Nolte and F.H. Vollmer (1978). The Mülheim process. J. Amer. Water Works Ass., 70, 7, 393-396.

Spalding, R.F. and D.D. Snow (1989). Stream levels of agrichemicals during a spring discharge event. Chemosphere, 19, 819, 1129-1140.

Speitel Jr, G., C. Lu, T. Mukesh and X. Zhu (1989). Biodegradation of trace concentrations of substituted phenols in granular activated carbon columns. Environ. Sci. Technol., 23, 68-74.

Thurman, M.E., D.A. Goolsby, M.T. Meyer, M.S. Mills, M.L. Pomes and D.W. Kolpin (1992). A reconnaissance study of herbicides and their metabolites in surface water of the midwestern United States using immunoassay and gas chromatography/mass spectrometry.Environ. Sci. Technol., 26, 2440-2447.

Torstensson, L. (1988). Pesticides in the environment - appearance, transport, effects. (in Swedish.), report no. 3536. Swedish Environmental Protection Agency, Solna.

Waite, D.T., R. Grover, N.D. Westcott, H. Sommerstad and L. Kerr (1992). Pesticides in ground water, surface water and spring runoff in a small Saskatchewan watershed. Environ. Toxicol. Chem., 11, 741-748.

Wang, Z., D.S. Gamble and C.H. Langford (1990). Interaction of atrazine with Laurentian fulvic acid: binding and hydrolysis. Anal. Chim. Acta, 232, 181-188.

Wang, Z., D.S. Gamble and C.H. Langford (1991). Interaction of atrazine with Laurentian humic acid. Anal. Chim. Acta, 244, 135-143.

Wang, Z., D.S. Gamble and C.H. Langford (1992). Interaction of atrazine with Laurentian soil. Environ. Sci. Technol., 26, 560-565.

Wells, M. J.M and J.L. Michael (1987). Recovery of picloram and 2,4-dichlorophenoxyacetic acid from aqueous samples by reversed-phase solid-phase extraction. Anal.-Chem., 59, 1739-1742.

Wölfel, P. (1989). Elimination von Pflanzenschutzmitteln aus dem Kartsquellwasser des Egauwasserwerks mittels Aktivkohlefiltration. GWF Wasser Abwasser, 130, 11, 565-569. (In German)

Appendix I

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Figures 1 and 2 shows adsorption isotherms of atrazine and MCPA with the natural logarithm, ln, on the axes. In the appended figures the axes have been corrected with logarithmic scales.

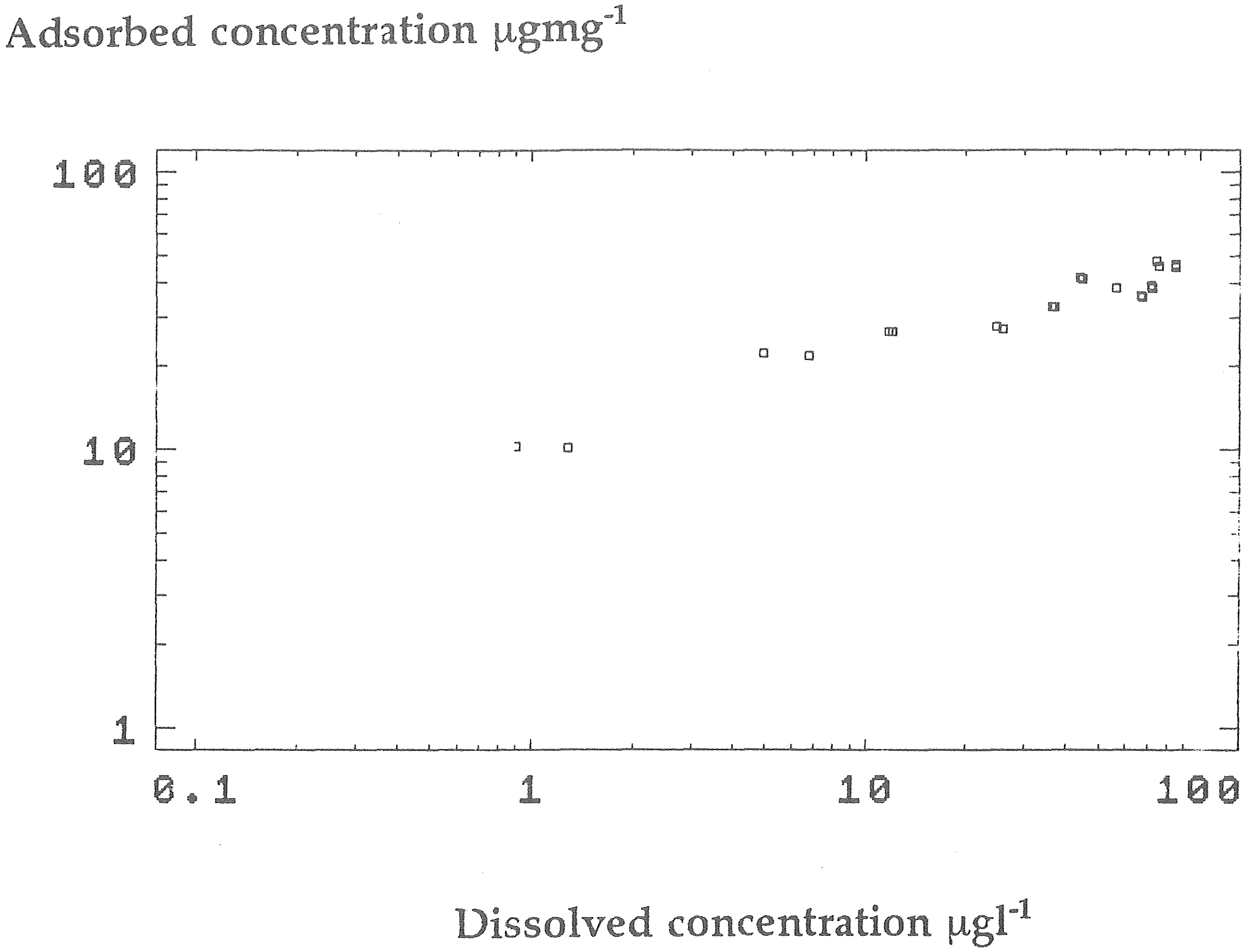

Fig. 1. Adsorption isotherm of atrazine in ultrapure water (C_o=100 μgl^{-1}, pH=7, equilibration time 24 hours).

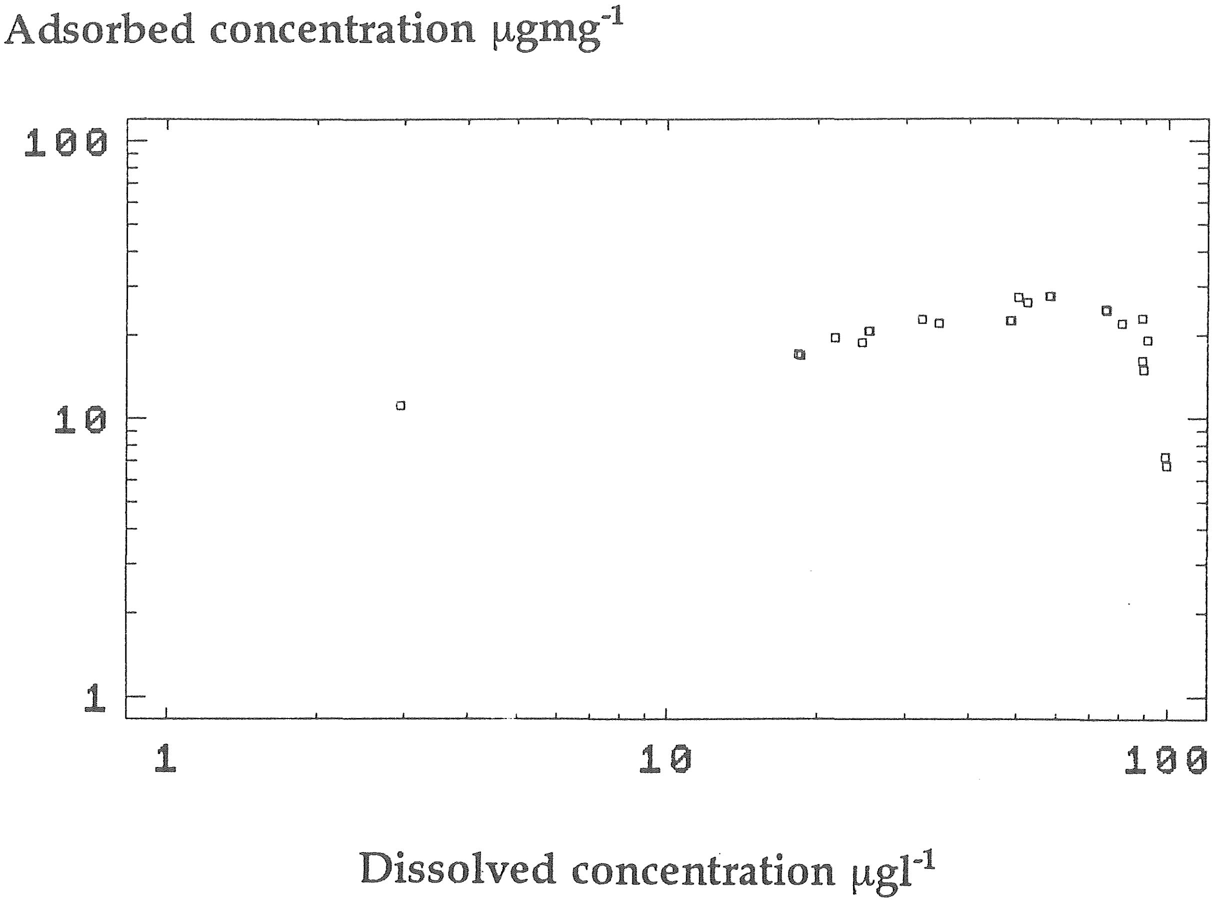

Fig.2a. Adsorption plot for atrazine in lake water (C_0=100 μgl^{-1}, pH=7, equilibration time 24 hours).

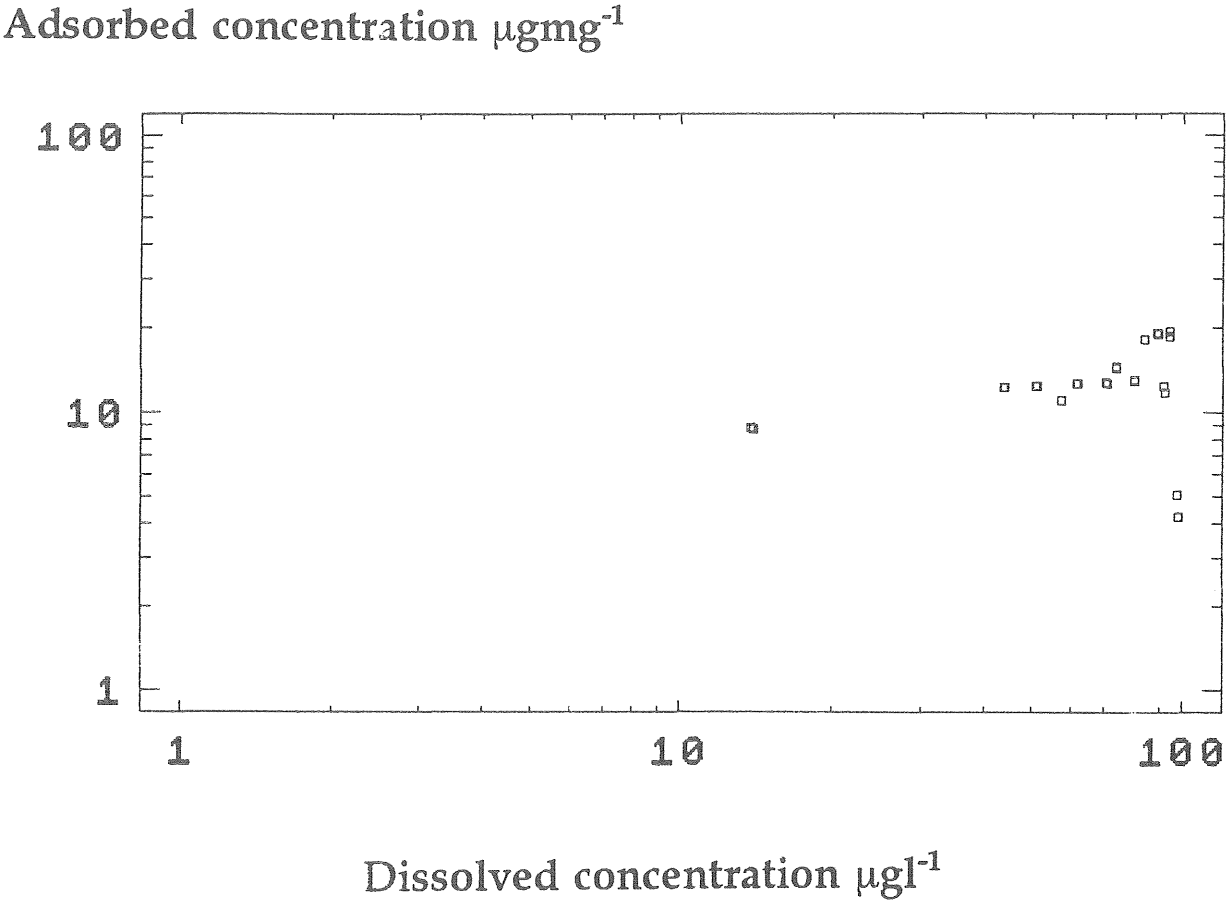

Fig. 2b. Adsorption plot for MCPA in lake water (C_0=100 µgl^{-1}, pH=7, equilibration time 24 hours).

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Pesticide interaction with activated carbon in the presence of dissolved organic material

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ABSTRACT

Une méthode a été développée pour l'analyse des pesticides atrazine, cyanazine, dichlorprop, MCPA, mecoprop et bentazone, par extraction de la phase solide (SPE) suivie d'une chromotographie du liquide. L'interférence de matériaux organiques dissous (DOM) lors de l'analyse finale a pu être évitée grâce à la sélection d'un éluent approprié dans la première partie du procédé (SPE). La méthode proposée a été utilisée pour l'analyse en laboratoire de l'adsorption de pesticides par du carbone activé (AC). L'adsorption de l'atrazine par le AC a été étudiée dans de l'eau purifiée ainsi que dans de l'eau provenant d'un lac, et comparée à de l'eau de lac après traitement à grande échelle par floculation de l'aluminium et AC, ainsi qu'après un essai-pilote de traitement à l'ozone. Il a été trouvé que DOM peut compétitionner avec l'atrazine pour les sites actifs du AC, même après floculation de l'aluminium et ozonation. DOM a le même effet sur l'adsorption de MCPA par AC dans de l'eau de lac non-traitée. Par conséquent, l'adsorption compétitive par DOM réduit la vie effective de la couche active et les prédictions du sueil de percée obtenues pour le AC à l'aide des données d'adsorption isotherme.

INTRODUCTION

There is an increasing concern over the possibility of pesticides entering the aquatic environment and contaminating drinking water at source. It is therefore appropriate to address the effectiveness of conventional drinking water treatment for pesticide removal.

Although agricultural application to crops is generally regarded as the major contribution of pesticides to source waters it is also recognised that in urban areas household and highway usage may also be significant. Certain groups of pesticides are more persistent in the aquatic environment including the s-triazines, phenoxyacids and bentazone. s-Triazines have been measured in French ground and surface waters (Legrand, 1991) and it has been estimated that 5-10 % of German water supplies have a pesticide problem (Opie, 1992). The low concentrations of pesticides can be determined by preliminary concentration/separation using solid-phase extraction (SPE) followed by high performance liquid chromatography (HPLC), (Barcelo, 1988; Junk, 1988).

Treatment for pesticides might include the use of activated carbon (AC). AC has been shown to successfully remove natural concentrations of s-triazines when incorporated in drinking water treatment (Marcomini, 1991). The bed-life and the breakthrough curves for individual pesticides are revealed if accurate adsorption isotherms can be obtained. Isotherm accuracy depends on a thorough consideration of parameters affecting adsorption including pH, ionic strength, dissolved organic material (DOM) and type of AC (Crittenden, 1987). Granular activated carbon (GAC) requires long equilibration times and therefore pulverised GAC is usually recommended for adsorption isotherms (Randtke, 1983), although equilibrium can still take up to three days.

The presence of DOM in water is known to affect the adsorption of pesticides to AC (Pirbazari,1992), although it is uncertain whether the reduction in capacity is due to complexation or competitive adsorption. Complexation involves the formation of DOM-pesticide complexes which may or may not be adsorbed by the AC surface. Competitive adsorption occurs between the pesticide and a physically or chemically similar fraction of the DOM for an active site on the AC.

Two groups of herbicides were regarded as interesting, phenoxy acids and s-triazines. One of the phenoxy acids, MCPA, is the most widely used herbicide in Sweden. Atrazine is forbidden in Sweden but residues are still found in the aquatic environment. Bentazone has been found in groundwater in the south of Sweden (Sandberg, 1990).

In this investigation a HPLC method for the analysis of selected pesticides in raw water and drinking water is improved. Laboratory bench-scale experiments are carried out to investigate the interaction of atrazine and MCPA with AC in the presence of DOM in lake water. Results are compared with the same lake water after full-scale treatment by aluminium flocculation and AC filtration and after pilot-scale treatment with ozone.

EXPERIMENTAL

Due to the different character of the compounds two different HPLC separation methods and enrichment procedures were developed. The phenoxy acids require a mobile phase at pH 3, whereas the s-triazines separate at neutral pH. The optimum absorbance wavelength is also different, phenoxy acids absorb at 235 nm and s-triazine at 220 nm.

Solid-Phase Extraction

The cartridge used for SPE was Bond Elute (Analytichem, Varian), octadecyl bonded silica, 500 mg with 3 ml cartridge volume and 75 ml reservoirs. The SPE column was placed in a small filter bottle attached to a filter pump and the samples were extracted at a flow rate of ~5 $mlmin^{-1}$. The SPE column was preconditioned with 3-6 ml of methanol and 3-6 ml ultrapure water. Spiked samples in ultrapure water or lake water were prepared in 100 ml or 1000 ml volumetric flasks from the 10 mgl^{-1} working standard, with the addition of 1 ml of methanol to retain the condition of the SPE columns. The sample was applied, followed by a few ml of ultrapure water to wash the volumetric flask and 0.7 ml of wash solution (see table 2). Finally the analytes were eluted with 1.5 ml methanol into a 2 ml volumetric flask. After dilution with ultrapure water or phosphate buffer to the mark, 100 µl was injected into the HPLC.

A control sample, representing 100% recovery was prepared in a 2 ml volumetric flask with 1 ml of methanol and a known pesticide standard and diluted with reagent water or phosphate buffer to the mark. 100 µl of this solution was injected into the HPLC.

HPLC Separation and Analysis

The HPLC-system was a Waters system, (Millipore,USA) including a gradient pump 600, multichannel UV-detector 490 and autoinjector satellite-WISP 700. The analytical columns used were Waters Nova Pak and Waters Resolve octadecyl bonded silica (C_{18}), 150*3.9 mm, 5 µm particle size. Precolumns were used. The s-triazines were separated on the Nova Pak C_{18} column with acetonitrile:water (45%:55%) as mobile phase. The detection wavelength was 220 nm. For the phenoxy acids, the Resolve C_{18} column was used with methanol:0.01 M phosphate buffer, pH 3.0 (60%:40%) as mobile phase. The detection wavelength was 235 nm.

In both methods the flow rate was 1.0 mlmin^{-1} and the sample volume was 100 µl. Calibration curves were obtained by means of three standards.

Reagents and Standards

Organic solvents, methanol and acetonitrile, were of HPLC-grade from Merck and ultrapure water was obtained from a Barnstead NanoPure system. The 0.01 M phosphate buffer pH 3.0, was made from NaH_2PO_4:H_2O, p.a grade and H_3PO_4 p.a grade from Merck. The buffer was filtered through a Durapore 0.45 µm filter (Millipore) before use.

The pesticides tested were atrazine, cyanazine, dichlorprop, MCPA, mecoprop and bentazone. Atrazine and MCPA were Certified Reference Material from the Laboratory of the Government Chemist, UK. The other pesticides were obtained from Dr Ehrenstorfer, Augsburg, Germany. The purity of the substances was in the range of 99.3% to 99.9%.

A stock solution of each compound containing 100 mgl^{-1} dissolved in methanol (phenoxy acids) or acetonitrile (s-triazines) was prepared. Dilutions were made with ultrapure water to produce 10 mgl^{-1} working standards of phenoxy acids and s-triazines.

Sampling

Lake water was sampled from Delsjön, which is an important source for the Göteborg drinking water treatment plant at Lackarebäck. Samples were taken after full scale treatment with alumninium flocculation, AC filtration and pilot scale ozone treatment, with and without aluminium flocculation and sand filtration. Water characteristics for the samples are presented in Table 1.

TABLE 1. Water characteristics

	pH	DOM, mgl^{-1}
Lake water	7.5	4.0
Full scale treatment		
Aluminium flocculation	6.4	1.1
AC filtration	6.7	1.1
Pilot scale treatment		
Ozone	7.2	3.6
Ozone,aluminium flocculation, sand filtration	6.6	1.0

Description of the Adsorption Studies

The adsorption studies were carried out in glass beakers (1 litre) stirred with a paddle. Each series of experiments contained 14 beakers. The samples were buffered with 0.01 M KH_2PO_4 and 0.01 M NaOH, pH 7. Lake water was initially filtered through glassfibre filters GF/C, but when bacterial growth was observed in the experiments, 0.45 µm cellulose acetate filters were used instead. The AC was Filtrasorb 300 (Chemviron) that was pulverised and sieved. The fraction that passed 63 µm was dried in 105°C for 24 hours and stored in a desiccator until used in the experiments. The AC was then weighed and suspended in ultrapure water (0.1 gl^{-1}). The carbon dosage range for the experiments was 0.2 to 5.0 mg and each experimental series contained 13 carbon dosages and a control without carbon. The initial concentrations of atrazine and MCPA were 100 μgl^{-1}. Samples (50 ml) for analysis were removed, through disposable 0.45 µm cellulose acetate filters, every 24 hours until equilibrium was achieved.

RESULTS AND DISCUSSION

Development of Procedures for Pesticide Analysis

DOM often causes analytical errors in the determination of organic micropollutants in natural waters. A comparisom has been made of the enrichment of pesticides with SPE and liquid-liquid extraction (LLE) from waters with a high content of DOM. The concentration of DOM was 10 mgl^{-1} as organic carbon (Johnson, 1991). They report that an interaction between pesticides and DOM occurs and leads to lower recoveries from SPE enrichment compared to LLE enrichment, although the difference was not statistically significant.

In this study DOM was found to be retained on the SPE column during the enrichment step and was observed as a brown to yellow layer on the top of the column. DOM also disturbs the HPLC-analysis because of high UV-absorption and the formation of a distinct frontal peak in the chromatogram. There is also the possibility of a decrease in separation capacity of the analytical column because of DOM irreversibly bound to the octadecyl silica. Therefore we considered it most satisfactory to attempt to reduce the amount of DOM in the final extract.

The naturally occurring DOM in lake water was used to allow a selection of the most suitable solvent for washing the SPE column before the elution of the isolates. Lake water was passed through a SPE column and then the column was extracted with different solutions.

TABLE 2. Pesticide recovery after washing of SPE column with different solutions

	Pesticide, % recovery				
Wash solution	MCPA	Dichlorprop	Mecoprop	Atrazine	Cyanazine
0.1M NaOH	59.4	80.3	85.1	-	-
$H_2O:CH_3CN:CH_3OH$ 4:3:1	47.3	57.3	61.0	102.7	89.5
$H_2O:CH_3CN$ 4:3	75.6	88.6	87.1	95.7	51.2

Experiments with lake water spiked with phenoxy acids showed that elution with water:acetonitrile (4:3) yielded the best recoveries. For the s-triazines it was found that water:acetonitrile:methanol (4:3:1) was suitable (Table 2).

One problem with using SPE columns is deciding whether they can be used once or several times. Two series of lake water spiked with phenoxy acids were tested. One series was tested with three enrichments in three different SPE columns and one series with only one SPE column to three enrichments. The results are shown in Table 3 where single use represents three different SPE columns and multiple use the same SPE column for three enrichments. Since the recoveries are similar for the two enrichment procedures, SPE columns can be used several times without carry-over or other errors.

TABLE 3. Pesticide recovery after single and multiple use of SPE columns

	Single use		Multiple use	
Pesticide	Recovery %	Confidence interval %	Recovery %	Confidence interval %
MCPA	99.7	12.3	89.2	9.3
Dichlorprop	96.1	10.6	89.7	1.3
Mecoprop	96.3	2.5	86.4	1.9
Atrazine	102.2	2.5	101.8	2.1
Cyanazine	89.5	1.9	88.0	1.9

The pH-dependence of the enrichment step was tested by adjusting the pH of lake water with concentrated HCl or 1 M NaOH. For the phenoxy acids, the pH range 2 to 5 was tested and for the s-triazines, pH 5 to 9. The best recoveries were obtained at pH 2 for phenoxy acids and at pH 7 for s-triazines. These results are important because they affect the sampling. A sample that has been acidified cannot be used for s-triazine analysis without pH-adjustment.

Adsorption Studies

The Freundlich isotherm equation has been found to satisfactorily describe the binding of organic micropollutants to AC (Sontheimer, 1988), and was therefore used in this study. The disadvantage is the concentration dependence for the constants, n and K. However, we always used the same initial concentration for each series of experiments and they are therefore comparable. In Fig. 1 the adsorption isotherm for atrazine in ultrapure water is shown. The isotherm lies within the 90% confidence interval, which is the second dashed line in the figure.

Adsorption isotherms for atrazine in lake water gave curved non-linear isotherms, Fig. 2, which made comparison difficult. From the literature this behaviour can be explained by competitive adsorption (Sontheimer,1988), or complexation to DOM, or a combination of both mechanisms (Pirbazari, 1992). At present it is difficult to resolve whether competitive adsorption or complexation is the more important process. Isolation of DOM in dialysis bags

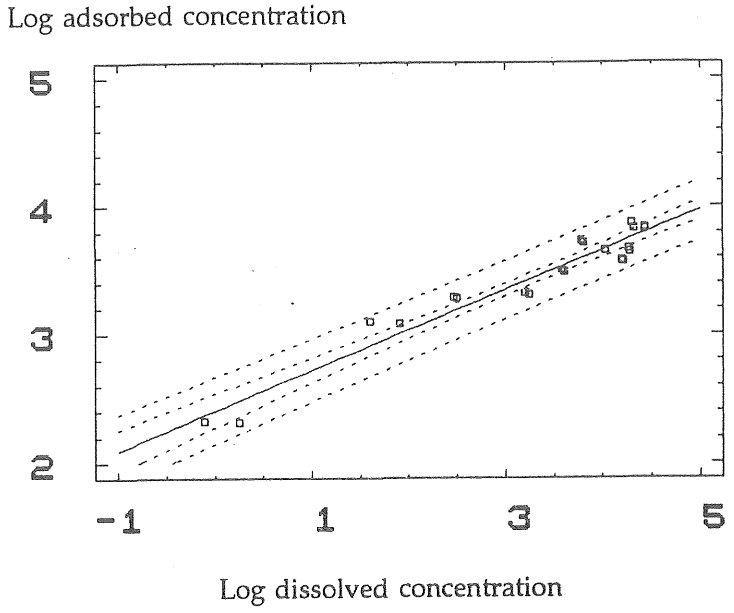

Fig. 1. Adsorption isotherm of atrazine in ultrapure water ($C_0=100\ \mu g l^{-1}$, pH=7, equilibration time=24 hours). The 90% and 95% confidence intervals are shown as dashed lines.

(Pirbazari, 1992) is an unsatisfactory method for studying complexation as fulvic acids may pass through the membrane. Ultrafiltration has, though, shown that some degree of complexation for atrazine by soil-extracted humic substances exists (Wang, 1992). To study the competitive effect of DOM on the adsorption isotherm of atrazine the carbon would have to be preloaded with DOM and this should more closely resemble the situation in an AC filter in a treatment plant.

Atrazine adsorption can be more readily interpreted from plots of concentration versus carbon dosage, Fig. 3. The dissolved concentrations are lowest in the ultrapure water (the solid lines) and increase when DOM is present. It interesting to note that even removal of organic material with aluminium flocculation and AC filtration still leaves a surplus of DOM which reduces the adsorption capacity. This provides further evidence that competitive adsorption prevents atrazine removal, as individual pesticide complexing material might be expected to be removed in an AC filter. The results suggest that competitive adsorbants are in such a high initial concentration that they successfully compete even after AC filtration. It follows that the remaining difference in adsorption is due to a competitive adsorption rather than a complexation mechanism for atrazine. Sontheimer (1988) has shown that the higher dissolved concentrations are due to competitive adsorption in multi-component mixtures. The substances that are most weakly adsorbed on AC have a greater concentration in the water phase. However, this could also be interpreted as complexation of the pesticides with DOM in the water phase. Figure 3 also shows an increase in the dissolved concentration of atrazine in ozone treated water. Clearly, even a reduction in the molecular size of DOM does not reduce the interaction of DOM with atrazine.

A similar adsorption behaviour was found for MCPA added to lake water, Fig. 4. MCPA seems to have a weaker adsorption to AC compared to atrazine, because MCPA has a higher concentration in the water phase. In general, charged compounds are more weakly adsorbed to AC than neutral compounds. The adsorption of MCPA to AC is expected to depend on pH, the pK_a of MCPA being 3. The uncharged acid would adsorb better to AC than the charged, although DOM also changes charge and even configuration with pH and ionic

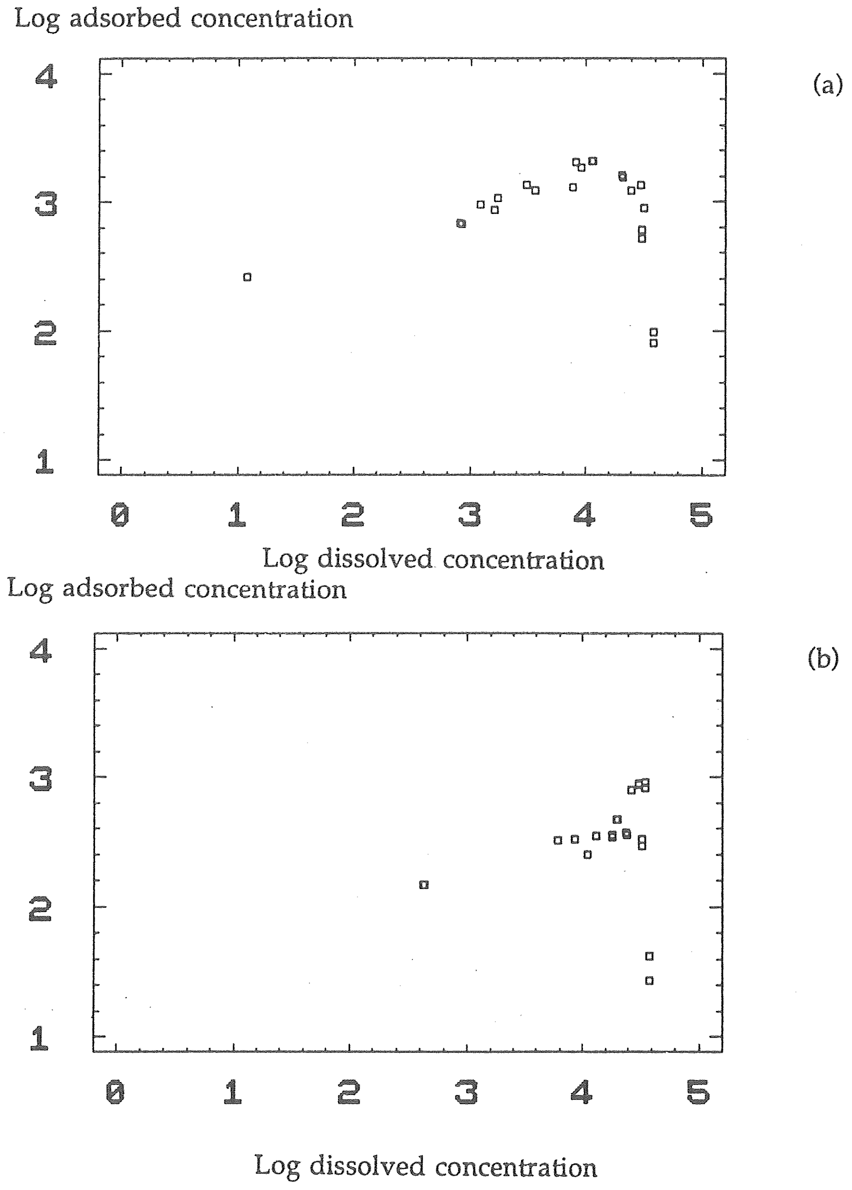

Fig. 2. Adsorption plots for (a) atrazine and (b) MCPA in lake water (C_0=100 μgl^{-1}, pH=7).

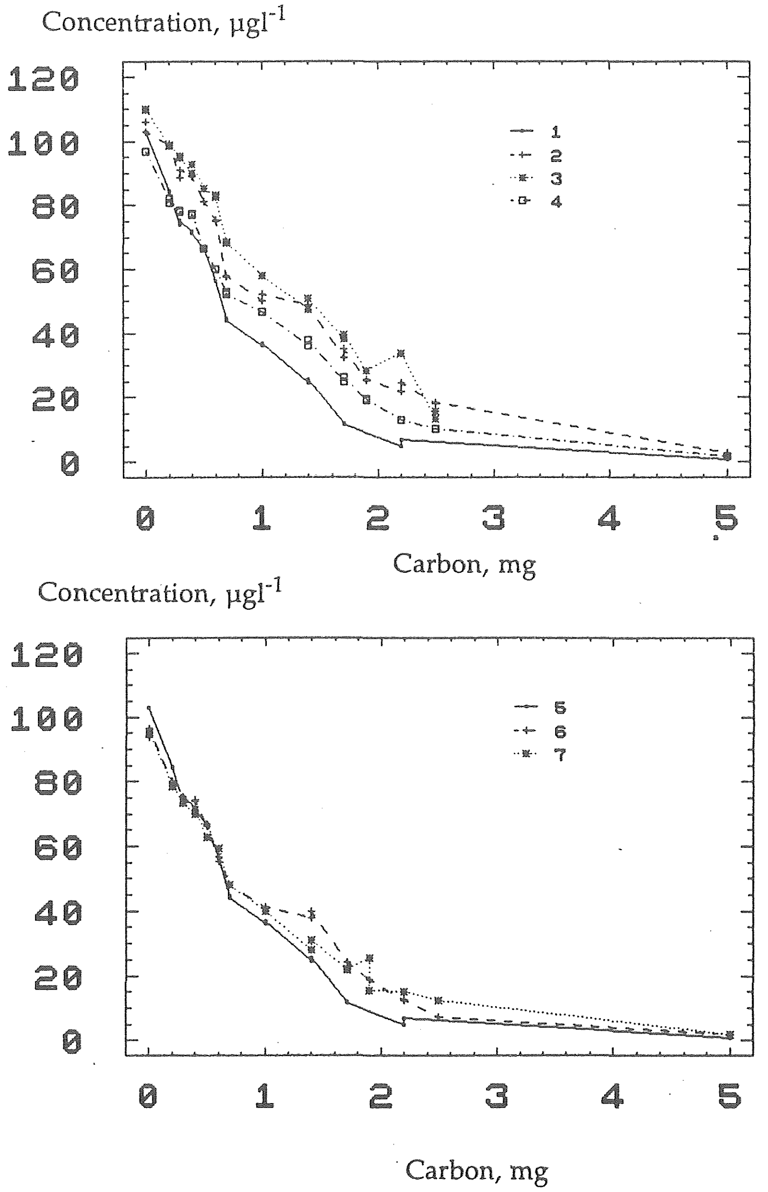

Fig. 3. Comparison of atrazine concentration versus carbon dosage plots (C_0=100 µgl^{-1}, pH=7, equilibration time=24 hours) for

1,5	Ultrapure water
2	Lake water
3	Lake water after aluminium flocculation
4	Lake water after aluminium flocculation and AC filtration
6	Lake water after ozone treatment
7	Lake water after ozone treatment, aluminium flocculation and sand filtration

strength. Elaboration of a discussion concerning the pH dependence of the adsorption of MCPA to AC in the presence of DOM therefore requires further experimentation. As phenoxy acids are the most widely used herbicides in Swedish agriculture, these results have important implications for the treatment of contaminated waters with AC. Further research would include removal conditions for phenoxy acids.

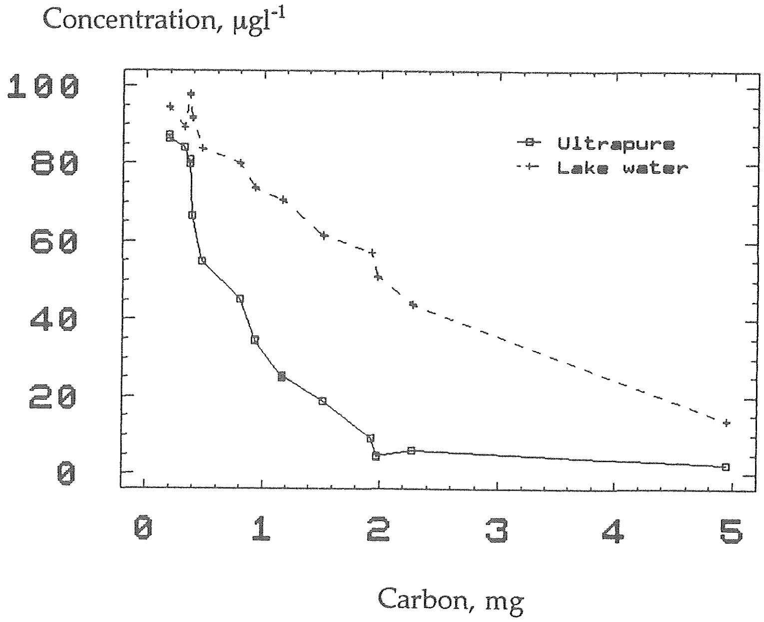

Fig. 4. Comparison of MCPA concentration versus carbon dosage plots. (C_0=100 $\mu g l^{-1}$, pH =7, equilibration time=24 hours.)

CONCLUSIONS

By selection of a suitable wash solution pesticides can be separated from DOM by SPE. This allows the analysis of phenoxy acids and s-triazines by HPLC.

DOM interferes with adsorption isotherms of atrazine and MCPA, in lake water and even after aluminium flocculation, AC filtration and ozone treatment. Possible mechanisms are competitive adsorption on AC, or complexation of the pesticides with DOM, or a combination of both. The adsorption of MCPA on AC is likely weaker than for atrazine, probably due to the charged chemical character of MCPA. The reduction of adsorption capacity of MCPA on AC in the presence of DOM is also greater than atrazine.

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REFERENCES

Barcelo, D. (1988). A review of liquid chromatography in environmental pesticide analysis. Chromatographia, 25, 10, 928-936.

Crittenden, J.C., D.W. Hand, H. Arora and B.W. Lykins Jr (1987). Design considerations for GAC treatment of organic chemicals. J. Am. Water Works Ass., 79, 74-81.

Johnson, W. E., N.J. Fendinger and J.R Plimmer (1991). Solid-phase extraction of pesticides from water: possible interferences from dissolved organic material. Anal. Chem., 63, 1510-1513.

Junk, G.A. and J.J Richard (1988). Organics in water: solid-phase extraction on a small scale. Anal. Chem., 60, 451-454.

Marcomini, A., G. Perin, S.Stelluto, M. da Ponte and P.Traverso (1991). Selected herbicides in treated and untreated surface water. Environ. Technol., 12, 1127-1135.

Opie, R. (1992). Detecting a trace. World Water and Environ. Eng., 3, 21.

Pirbazari, M., B.N. Badriyha, S-H. Kim and R. Miltner (1992). Evaluating GAC adsorbers for the removal of PCB:s and toxaphene. J. Am. Water Works Ass., 84, 83-90.

Randtke, S.J. and V.L. Snoeyink (1983). Evaluating GAC adsorptive capacity. J. Am. Water Works Ass., 75, 406-413.

Sandberg, E. and B. Erlandsson (1990). Pesticide residues in raw water and drinking water. Vår Föda, 42, 224-234. (In Swedish, summary in English.)

Sontheimer, H., J.C. Crittenden and R.S. Summers (1988). Activated carbon for water treatment. Second edition. DVGW-Forschungsstelle, Engler-Bunte institut, Karlsruhe. Chap. 3, p. 106-237.

Wang, Z., D.S. Gamble and C.H.Langford (1992). Interaction of atrazine with Laurentian soil. Environ. Sci. Technol., 26, 560-565.

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