Preliminary N-Methyl Carbamate Pesticides Cumulative Risk Assessment

# II.D Appendices: Drinking Water Exposure

## 3. Drinking Water Treatment Effects on N-methyl Carbamate Pesticides

Based on available data, this section provides an analysis of the effects of water treatment methods on N-methyl carbamates, including aldicarb, aldicarb sulfone, aldicarb sulfoxide, carbaryl, carbofuran, formetanate HCL, methiocarb, methomyl, oxamyl, pirimicarb, propoxur, and thiodicarb. This current review of data is an update to the previous literature review, which was used to support OPP's Water Treatment Science Policy (USEPA, 2000; USEPA 2001)

An evaluation of laboratory and field monitoring data indicate that N-methyl carbamates may be effectively removed from drinking water by lime softening and activated carbon. With the exception of aldicarb, lime softening processes degrade N-methyl carbamates through alkaline-catalyzed hydrolysis. Abiotic hydrolysis studies conducted in pH 9 buffer solutions indicate that carbamates are susceptible to degradation during lime softening. In addition to lime softening, sorption on activated carbon using granular activated carbon (GAC) or powdered activated carbon (PAC) appears to be effective in removing N-methyl carbamates from drinking water. Other treatment methods, such as chlorination, chloramination, chlorine dioxide, and potassium permanganate, appear tp be only effective in oxidation of N-methyl carbamate compounds containing a methylthio group (CH3-S-), e.g., methiocarb and aldicarb. These compounds are expected to oxidize to sulfoxide and sulfone.

Available USGS water treatment plant monitoring data indicate that N-methyl carbamates and their degradation products have a low detection frequency in raw and finished water samples. The low detection frequency, coupled with sample handling issues, prevent an estimate of pesticide removal through typical water treatment plants. However, an analysis of occurrence for carbamate degradation products in the monitoring study and the laboratory studies suggest they were formed through both environmental and water treatment processes.

### A. Environmental Fate Data Pertinent to Treatment Effects

With the exception of aldicarb, the N-methyl carbamates are rapidly degraded through alkaline catalyzed hydrolysis. As a group, they are generally non-persistent and mobile in aerobic soil and form oxidative degradation products. Table II.D.3.1 provides a summary of the environmental properties of the n-methyl carbamate pesticides. Based on environmental fate data, N-methyl carbamates are expected to degrade via base-catalyzed hydrolysis during lime softening as well as by oxidation when water is treated with oxidative disinfectants.

**Table II.D.3.1: Environmental Fate Data for Selected N-methylcarbamates1**

| Pesticide | Abiotic Hydrolysis (pH=9) at 25°C | Aerobic Soil Metabolism | Soil Partitioning |
|---|---|---|---|

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| | Half-life (days) | Degradation Products | Half-life (days) | Degradation Products | Coefficient Kf |
|---|---|---|---|---|---|
| Aldicarb | 197 | | 2.3 | aldicarb sulfoxide<br>aldicarb sulfone | < 1 |
| Aldicarb sulfoxide | 2.3 | | Stable | | <1 |
| Aldicarb sulfone | | | Stable | | <1 |
| Carbaryl | 0.13 | 1-naphthol | 4 | 1-naphthol | 2-3 |
| Carbofuran | 0.63 | carbofuran phenol | 150-321 | 3-ketocarbofuran<br>carbofuran phenol | 0.72 (median) |
| Forme-tanate Hydro-chloride | 1 | N'-(3-hydroxy phenol) -N,N-dimethyl formamide hydrochloride | 6.4 | 3-formaminophenyl methylcarbamate,<br>3-dimethylamino-methylene-iminophenol hydrochloride,<br>3-aminophenylcarbamate,<br>3-aminophenol | < 3.43 |
| | | 3-formamido-phenyl methyl-carbamate | | | |
| Methiocarb | < 1 | Mesurel phenol<br>Mesurel sulfoxide phenol | No Data | No Data | |
| Methomyl | 30 | S-methyl-N-hydroxythioacetimidate | 30-45 | No Data | < 1.5 |
| Oxamyl | 0.125 | Oxime | 11-27 | Oxime<br>Dimethyl oxamic acid | < 1 |
| Pirimicarb | Stable | | 7-294 | 5,6-dimethyl-2-methylamino-4'-hydroxypyrimidine;<br>5,6-dimethyl-2-methylamino-4'-hydroxypyrimidin-carbamate | |
| Propoxur | 1.6 | | 112-180 | | <1 |
| Thiodicarb | 0.5 | Methomyl | 1.5 | methomyl | 2-14 |

1- Data were obtained from most recent Re-registration Eligability Document assessments or EFED One-Liner Database

## B. Review of Available EPA Studies

### B.1 Preliminary Water Treatment Effects for Selected N-methyl Carbamates (Miltner, R.J. June, 2005. Status Report: Summary of ORD/WSWRD Studies to Control N-methyl Carbamates in Drinking

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**Water. USEPA/ORD/ WSWRD. Cincinnati, OH)etermination of Timing of Carbamate Applications**

## Background / Purpose

EPA's Office of Research and Development / Water Supply and Water Research Division (ORD/WSWRD) conducted bench-scale screening-level water treatment studies to assess the effect of common water treatment processes on removal of selected N-methyl carbamates. Screening-level treatment processes included coagulation/clarification, lime softening, adsorption to PAC, and oxidation with chlorine, chloramines, chlorine dioxide, and potassium permanganate. The data are considered preliminary because they have not been subject to a formal peer review process. A qualitative summary of the preliminary data is presented in a summary report, which will be followed by a more comprehensive final report.

## Materials and Methods

Bench-scale water treatment studies were conducted at room temperature.

Non-radiolabeled carbamates were spiked into these waters at concentrations ranging from 44 to 88 µg/L. Concentrations of carbamates were determined using GC/MS. Degradation (transformation) products were not identified. In all studies, control samples were held for the duration of the process reaction times to ensure that there was no background loss of the carbamates that could be attributed to the treatment.

## Coagulation, Clarification and PAC Adsorption

Coagulation/clarification studies were conducted in jar tests using raw surface water from the Winton Woods Lake with alum coagulant doses adjusted to control turbidity under typical full-scale drinking water treatment conditions. These studies also were conducted with and without PAC to assess the impact of activated carbon on pesticide adsorption. Alum (aluminum sulfate) is the most commonly used coagulant. Winton Woods Lake is not a source of drinking water, but is typical of surface waters with regard to levels and fluctuations in turbidity and total organic carbon (TOC). Prior to spiking carbamates into these waters, preliminary studies were conducted to determine proper alum doses for control of turbidity. Hydrodarco B, a commonly employed PAC, was used. PAC doses spanned from 10 mg/L, which is typical of doses used for taste and odor (T&O) control, to 60 mg/L, which is relatively atypical and high. 30 mg/L is representative of high-end doses of PAC.

## Softening

Lime softening studies were conducted in jar tests using Great Miami Aquifer water. Lime doses raised pH according to typical full-scale conditions. In

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addition to pH, alkalinity, turbidity, calcium hardness, magnesium hardness and total hardness were monitored. The Great Miami Aquifer is the source of drinking water for the Cincinnati Water Works' Bolton Water Treatment Plant. Prior to spiking carbamates into these waters, preliminary studies were conducted to determine the conditions that would control calcium hardness, magnesium hardness and total hardness. Although lime softening was used in these studies, it was found that lime/soda softening would be required to control calcium hardness and turbidity at the higher pHs required for control of magnesium hardness. Settling took place for one hour. To prevent loss of the carbamates at the high pHs of softening, samples were acidified upon collection.

**Oxidation**

Oxidation studies using chlorine, chloramine, chlorine dioxide, and potassium permanganate were conducted in laboratory waters. For chlorine, chloramine and chlorine dioxide, studies were conducted over 24 hours and at doses that would be high for drinking water treatment. Doses were Recommended Maximum Disinfection Residuals (RMDLs) as defined in the Disinfectant/Disinfection Byproduct (D/DBP) Rule. For permanganate, studies were conducted over 6 hours and the dose was 1 mg/L. Six hours is representative of time through a water treatment plant in the presence of permanganate, and doses beyond 1 mg/L may impart undesired color in finished drinking water. These oxidation studies were designed to assess the extent of these reactions at relatively high doses and in lab waters (very low TOC, very low ionic strength) offering no significant demand on the oxidant. These studies were controlled by sampling non-oxidant treated samples held to assess background stability during the reaction time. Where these reactions are significant, follow up studies will examine reaction rates.

**QA / QC Studies**

These studies were conducted at ORD's laboratories in Cincinnati under contract 68-C-00-159 with the University of Cincinnati (UC). Battelle Laboratories in Columbus OH, a subcontractor to UC, performed the GC/MS analyses after developing methods for the combination of carbamates (aldicarb, carbaryl, methiocarb, oxamyl and propoxur). Significant QA/QC was a part of this effort. A stability study was conducted to define sample holding times and required preservatives. All samples were acidified upon collection. A study was conducted to find the reducing agent (sulfite) that would not cause analytic interference. Dilution series in the various waters were submitted as blinds. The QA/QC program required recovery checks, replication and analyses of blanks with each sample set. Replication included both bench-scale treatment samples and laboratory splits of submitted treatment samples.

## B.2 Softening and Chlorination Screening Studies for Select Pesticides (Speth and Pisigan. 2001. Softening and Chlorination Screening

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**Studies for Selected Pesticides. USEPA/ORD/ WSWRD. Cincinnati, OH)**

**Background / Purpose**

The Office of Pesticide Programs (OPP) requested that the ORD/WSWRD generate drinking water treatment data for a select group of pesticides. Specifically, OPP requested data on lime softening and chlorination processes and chose ten pesticides to study for each process. Methomyl was the only N-methyl carbamate studied with softening. Aldicarb was the only N-methyl carbamate studied with chlorination.

These studies were conducted at ORD's laboratories in Cincinnati under contract 68-C-99-211 with the IT Corporation. IT Corp subcontracted the analytical measurements to Environmental Health Laboratories (EHL) and Environmental Micro Analysis, Inc. (EMA). EHL analyzed aldicarb and EMA analyzed methomyl.

**Materials and Methods**

Based on analytical methods, pesticides were broken into four groups for the softening study, and three groups for the chlorination study. Aldicarb and methomyl were measured by EPA Method 531.1. Pesticides were spiked into the ground water at concentrations near 100 ug/L. In all studies, control samples were held for the duration of the process reaction times to ensure that there was no background loss of the carbamates that could be attributed to the treatment. Degradation (transformation) products were not searched for.

These studies were conducted with Great Miami Aquifer water collected from the Cincinnati Water Works' Bolton Water Treatment plant.

**QA/QC Studies**

Prior to conducting the softening and chlorination studies, QA/QC studies were completed. The pesticides were spiked into the water at concentrations near 100 µg/L in several analytic groupings and analyzed to confirm that the groundwater matrix did not interfere with the analyses, the spiking procedure was adequate, the grouping of pesticides did not cause analytical interferences, and the analytical precision was acceptable. Preservation, shipping and stability were also defined. Thiosulfate was determined to be the dechlorinating agent that would not cause analytic interference. All samples for carbamates were acidified upon collection.

**Lime softening**

The softening screening-level studies consisted of jar tests with Great Miami Aquifer water. The lime pellets used in the study were also obtained from the

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Bolton plant. In preliminary studies, varying amounts of lime were added to a series of jars to determine the lime dose that matched the effluent pH of the Bolton plant's lime contactor basin (calcium softening) and to achieve a pH of 11 (magnesium softening). Soda ash was not considered for this limited study because elevated calcium levels were not important in the final magnesium-softened water. Floc would be present for any possible pesticide/floc complexation, and the pH would be elevated for base catalyzed reactions.

From preliminary studies, the calcium-softening dose was determined to be 150 mg/L. This was the same dose as that used in the Bolton Waterworks and resulted in the same final pH as that seen in the Bolton plant. The magnesium-softening dose was determined to be 300 mg/L.

All jars were allowed to settle for two hours before the softened samples were collected. Softening samples were acidfied upon collection to prevent base catalyzed loss of the carbamates. Two hours of settling was chosen because it resulted in adequate settling, and it gave a reasonable amount of time at a high pH to observe base-catalyzed degradation.

**Chlorination**

In the chlorination studies, chlorine was dosed under added at uniform formation conditions (UFC) (Summers et al., 1996) to pesticide-spiked Bolton water. UFC represents mean national distribution system conditions for chlorination and were developed for studies examining the formation and control of disinfection byproducts in drinking water. They are: a chlorine residual of 1 mg/L at 20 degrees C, 24 hours and pH 8. A chlorine demand study was conducted to determine the appropriate chlorine dose to give this residual under these conditions.

**Data Analyses**

For both the softening and chlorination studies, a one-way analysis of variance (anova) model was used to determine whether the pesticide was lost through treatment. Treatments were compared at the 5% significance level using a t-test. Control samples were also evaluated to determine whether the pesticide naturally degraded, or was lost, over the process reaction time.

## B.3 EPA/ORD Monitoring Data (Miltner et al., 1989, Treatment of Seasonal Pesticides in Surface Waters, Journal AWWA)

In full-scale water plant treatment studies, Miltner et al. (1989) monitored a number of pesticides through three full-scale water treatment plants following pesticide application and Spring-time runoff. Conventional treatment (coagulation, clarification and filtration, lime or lime/soda softening, adsorption

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onto PAC, adsorption onto GAC, and oxidation by chlorine were monitored at the full-scale. Samples were collected before and after treatment processes with the downstream sample always collected after the upstream sample based on the utility's expertise with time of travel through the plants, and their experience with responding to Spring-time runoff events. PAC doses ranged up to the maximum fed for T&O control in order to assess adsorption capacities. The N-methyl carbamate carbofuran was one of the monitored pesticides.

Miltner et al. supplemented the full-scale monitoring with bench-scale studies wherein pesticides, including carbofuran, were spiked into field waters in EPA's laboratories in Cincinnati. Field waters included those from the monitored full-scale plants and Ohio River water. Coagulation/clarification, adsorption onto PAC, and oxidation by chlorine and chlorine dioxide were studied at the bench-scale. Coagulant doses, chlorine doses and chlorine dioxide doses were representative of full-scale treatment. Coagulation was by alum. PAC doses ranged from those typical of T&O control to those relatively atypical and high in order to assess adsorption capacities. Hydrodarco B and WPH PACs were studied; both are commonly used in drinking water treatment. Bench-scale studies were conducted at room temperatures.

Additionally, adsorption isotherms were conducted at the bench scale; the isotherms for carbofuran are also reported in Speth and Miltner (1990).

### B.4 EPA/ORD Adsorption Isotherm Studies (Speth and Miltner, 1998, Technical Note: Adsorption Capacity of GAC for Synthetic Organics, Journal AWWA; Speth and Miltner, 1990, Technical Note: GAC Adsorption Capacity for SOCs, Journal AWWA)

Adsorption isotherms measure the maximum capacity of activated carbon to remove contaminants from water. In these studies, Filtrasorb 400, a GAC commonly used in drinking water treatment, was employed. The studies were conducted at room temperature. Two waters were studied: laboratory water to assess maximum capacities without competition from organics in field waters, and Ohio River water to assess lowered capacities in the presence of competing organics. These studies included the N-methyl carbamates aldicarb, carbofuran, methomyl and oxamyl. Control samples were reacted without carbon for the duration of the process reaction times to ensure that there was no background loss of the carbamates that could be attributed to the adsorption. All carbamate samples were acidified upon collection.

### B.5 Results and Discussion

A qualitative summary of water treatment data is shown in Table II.D.3.2. A "No" designation indicates no control was observed for the particular treatment process.

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A "YES" designation indicates that pesticide control was observed. For the process-specific discussions that follow, the appropriate references are as given in Table II.D.3.2.

**Table II.D.3.2: Qualitative Assessment of Water Treatment Data for N-methyl Carbamates**

| Pesticide | Coagu-lation | Soften-ing | Activated Carbon | | Oxidation | | | |
|---|---|---|---|---|---|---|---|---|
| | | | GAC | PAC | Chlorine | Chloramine | KMnO4 | ClO2 |
| Aldicarb | No (a) | No (a) | Yes (b) | Yes (a) | Yes (a,c) | Yes (a) | Yes (a) | Yes (a) |
| Carbaryl | No (a) | Yes (a) | X | Yes (a) | No (a) | X | No (a) | No (a) |
| Carbofuran | No (d) | Yes (d) | Yes (b,d) | Yes (d) | No (d) | X | X | No (d) |
| Methiocarb | No (a) | Yes (a) | X | Yes (a) | Yes (a) | Yes (a) | Yes (a) | Yes (a) |
| Methomyl | X | Yes (c) | Yes (e) | X | X | X | X | X |
| Oxamyl | No (a) | Yes (a) | Yes (b) | Yes (a) | No (a) | X | No (a) | No (a) |
| Propoxur | No (a) | Yes (a) | X | Yes (a) | No (a) | No (a) | No (a) | No (a) |

X - Indicates no data were available to assess treatment process.
(a) Miltner, 2005; (b) Speth and Miltner, 1990; (c) Speth and Pisigan, 2001; (d) Miltner et al., 1989; (e) Speth and Miltner, 1998

### Coagulation and Clarification

Coagulation and clarification was not found to be effective for the control of N-methyl carbamates. They are water soluble and not-well sorbed to the particulates that are targeted for removal by coagulation and clarification. Given analytic precision, coagulated and clarified N-methyl carbamate concentrations could not be differentiated from raw water N-methyl carbamate concentrations. Coagulation and clarification provided expected results with a drop in the pH in clarified waters and control of turbidity to levels below 2 ntu in clarified waters.

### Adsorption onto PAC

Table II.D.3.3 summarizes the control provided by PAC giving the approximate percent removal at 10 mg/L, a common PAC dose for T&O control, and at 30 mg/L, an upper-end dose for T&O control. These results indicate good removal at typical T&O control doses and better removal when doses approach the upper end of what treatment plants may be able to feed. Carbofuran, carbaryl, methiocarb and propoxur have higher molecular weights and rings structures that may account for their better control than oxamyl and aldicarb with lower molecular weights and branched structures.

**Table II.D.3.3. Adsorption of N-methyl Carbamates onto PAC**

| Pesticide | Percent Removal | |
|---|---|---|
| | 10 mg/L PAC | 30 mg/L PAC |

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| | | |
|---|---|---|
| Carbaryl | 62 | 75 |
| Methiocarb | 61 | 74 |
| Carbofuran | 57 | 83 |
| Propoxur | 44 | 57 |
| Oxamyl | 25 | 39 |
| Aldicarb | 20 | 38 |

**Adsorption onto GAC**

Aldicarb, oxamyl, carbofuran and methomyl were found to be strongly adsorbed onto GAC. The data were regressed using the Freundlich adsorption model. The Feundlich K value gives the adsorption capacity when the equilibrium concentration (concentration in water) is 1 ug/L. The resulting order of adsorbability was carbofuran (16830 ug adsorbed per gram of carbon) > aldicarb (8270) > methomyl (4780) > oxamyl (1740). Although adsorbability depends on several factors, carbofuran's higher molecular weight and included ring structure may account for its higher adsorption capacity. Aldicarb and carbofuran were also studied in coagulated and clarified Ohio River water where adsorption capacities would be expected to be lower as other organics would compete with the carbamates for adsorption sites. The resulting order of adsorbability was carbofuran (13065) > aldicarb (4160).

A K value of 300 ug/gram is generally considered a cost effective measure of adsorbability indicating several years of GAC bed life at typical full-scale operating conditions. These K values suggest control of carbamates to non-detect levels for several years before GAC replacement when GAC contactors would be utilized downstream of coagulated and clarified Ohio River water. GAC is a designated Best Available Technology for many pesticides regulated in drinking water, including the N-methyl carbamates carbofuran and oxamyl.

**Softening**

With the exception of aldicarb, all the N-methyl carbamates degraded during lime softening (Table II.D.3.4). One exception was aldicarb, which only degraded 22 percent at pH 11.25. Because aldicarb does not undergo rapid alkaline catalyzed hydrolysis (t1/2=197 days at pH 9, Table1), this observation was expected.

For studies with Great Miami Aquifer water, the calcium concentration decreased to the greatest extent under calcium-softening conditions. The percent removal of magnesium was less than 10 percent under calcium-softening conditions. Under magnesium-softening conditions, the magnesium was reduced to greater than 90 percent. The increased calcium in the magnesium-softening samples as compared to the calcium-softening samples was not surprising because of the water's initial alkalinity, indicating that this water requires lime soda ash softening to control calcium at magnesium-softening conditions. This was confirmed in other ORD/WSWRD studies.

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During calcium softening, removal of N-methyl carbamates ranged from 87 to 99 percent, with the exception of aldicarb. During magnesium softening, their removal ranged 99 to 100 percent, with the exception of aldicarb. In studies by Speth and Pisigan (2001) thiodicarb demonstrated 90 percent removal during magnesium softening 1, although no removal during calcium softening. The similarity in structure between methomyl and thiodicarb may have resulted in their similar behavior under higher-pH magnesium-softening conditions. Thiodicarb is not an N-methyl carbamate, but is a dimer of methomyl and degrades to methomyl (Table II.D.3.1). Its larger structure may have prevented it from being degraded under calcium-softening conditions.

Although the studies for most of these N-methyl carbamates were done at the bench-scale in jar tests, carbofuran was monitored in full-scale treatment plants practicing magnesium softening (Miltner et al., 1989). Results were similar to those of the other N-methyl carbamates.

Although the mechanism of pesticide removal was not incorporated into these studies, base-catalyzed degradation likely explains the results. Possible transformation products are given in Table II.D.3.1.

**Table II.D.3.4. Control of N-methyl Carbamates by Lime Softening**

| Carbamate | Ref. | Calcium Softening | | | Magnesium Softening | | |
|---|---|---|---|---|---|---|---|
| | | pH | Lime Dose, mg/L | % R | pH | Lime Dose, mg/L | % R |
| aldicarb | (a) | 10.26 | 130 | 6 | 11.25 | 220 | 22 |
| carbaryl | (a) | 10.26 | 130 | 99 | 11.25 | 220 | 99 |
| carbofuran | (d) | | | | 10.9, | | 100 |
| methiocarb | (a) | 10.26 | 130 | 99 | 11.1 | 220 | 99 |
| methomyl | (c) | 10.15 | 150 | 87 | 11.25 | 300 | 99 |
| oxamyl | (a) | 10.26 | 130 | 99 | 11.2 | 220 | 99 |
| propoxur | (a) | 10.26 | 130 | 99 | 11.25 | 220 | 99 |
| | | | | | 11.25 | | |

% R = percent removal
(a) Miltner, 2005, Great Miami Aquifer
(c) Speth and Pisigan, 2001, Great Miami Aquifer
(d) Miltner et al., 1989, Maumee River, Sandusky River

**Oxidation**

Oxidation studies with chlorine, chloramine, chlorine dioxide, and potassium permanganate showed that aldicarb and methiocarb degraded through chemical oxidation with each oxidant. Generally, control of aldicarb and methiocarb by chlorine, chloramine and chlorine dioxide exceeded 95 percent removal, where as control by permanganate was only 31 and 23 percent respectively. This would be expected as permanganate is a weaker oxidant than the others and generally used for T&O control and manganese control rather than for disinfection. In contrast, carbofuran, carbaryl, oxamyl, and propoxur were not oxidized when treated with

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the various oxidants. Given analytic precision, oxidized N-methyl carbamate concentrations could not be differentiated from control N-methyl carbamate concentrations. One possible explanation is that methiocarb and aldicarb contain a methylthio group (CH3-S-) which is prone to oxidize during oxidative disinfection processes. Although not identified in these studies, sulfoxide and sulfone are the expected transformation products of aldicarb and methiocarb.

Aldicarb's reaction with chlorine was examined under different conditions in two studies. Both studies utilized pH 8, room temperature and 24-hour reaction times. Results were similar in laboratory water with a higher 4 mg/L chlorine dose (Miltner, 2005) and in Great Miami Aquifer water under UFC conditions with a lower chlorine dose of 1.6 mg/L (Speth and Pisigan, 2001).

In studies by Speth and Pisigan (2001) under UFC conditions, molinate, a related carbamate, also showed 99 percent removal when oxidized by chlorine. Because molinate has an ethylthio group, the oxidation process is expected to yield sulfoxide and sulfone transformation products.

### B.6 Other Treatment Processes

Although these studies did not include membranes, these are expected to be effective in removing N-methyl carbamates. Reverse osmosis membranes, and likely ultrafiltration membranes, would physically remove these carbamates from drinking water.

## C, Open Literature: Oxidation Studies

### C.1. Chlorine

Miles et al. (1988) studied the fate of carbaryl and propoxur, at 1.0 mg/L, in phosphate-buffered water treated with 10 mg/L of hypochlorite at pH 7 in the dark. The chlorine degradation of carbaryl was slightly faster than that for propoxur. The first-order kinetic half-lives of carbaryl were 3.5 days at pH 7.0 and 0.05 days at pH 8.0. For propoxur, the half-lives were 9.2 days at pH 7.0 and 0.29 days at pH 8.0. Structural elucidation of the chlorination products was not performed.

In another separate laboratory experiment, Miles and Oshiro (1990) monitored the degradation of 0.1 uM of methomyl by 1 uM chlorine. Methomyl, which contains a methylthio group, was transformed to methomyl sulfoxide and N-chloromethomyl, which were eventually converted to acetic acid, methanesulfonic acid, and dichloromethyl amine.

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Miles (1991) found that 0.01mM of aldicarb in 0.1 mM phosphate buffered solution reacted with 0.1 - 10 mM hypochlorite at pH 6 - 9. Aldicarb initially underwent oxidation to form aldicarb sulfoxide and upon further chlorine oxidation, aldicarb sulfoxide was converted to aldicarb sulfone. An additional chlorine addition reaction led to the formation of N-chloroaldicarb sulfone, which can decompose to an acid and dichlorodimethylamine. Mason et al (1990) also found that chlorination of aldicarb led to formation of ten degradation products. Four of the degradation products were identified as aldicarb sulfoxide, aldicarb sulfoxide oxime, aldicarb sulfone, and aldicarb oxime. Both aldicarb sulfoxide and aldicarb sulfone were also found by Miles (1991). A summary of the chlorination degradation products of methomyl and aldicarb are shown in Table II.D.3.5.

**Table II.D.3.5. Chlorination Products of Methomyl and Aldicarb**

| Carbamate | Chlorine Transformation Products | Reference |
|---|---|---|
| Methomyl | methomyl sulfoxide, N-chloromethomyl, acetic acid, methanesulfonic acid, dichloromethylamine | Miles and Oshiro, 1990 |
| Aldicarb | aldicarb sulfoxide, aldicarb sulfone, N-chloroaldicarb sulfone, aicd form, dichloromethylamine | Miles, 1991 |
| | aldicarb sulfoxide, aldicarb sulfoxide oxime, aldicarb sulfone, aldicarb oxime | Mason et al, 1990 |

## C.2. Ozone and Advanced Oxidation Processes

Advanced oxidation processes (AOPs) are those which utilize hydroxyl radicals for chemical oxidation. Ozone has a higher oxidation potential (2.07 V) than does an oxidant like chlorine. The hydroxyl radical produced by AOPs has an oxidation potential of 2.8 V. Therefore, contaminants in drinking water like carbamates can be oxidized by the ozone molecule or by the hydroxyl radical. The hydroxyl radical can be created by AOPs combining processes (ozone/UV, ozone/H2O2, ozone/H2O2/UV). Ozonation at higher pH (greater than pH 8) also creates hydroxyl radicals. With the inclusion of UV, photolysis can also contribute to the reaction mechanism. Because these are very reactive processes, the concentrations of pesticides like carbamates can be significantly lowered in drinking water, but a significant number of transformation products can be created. Ozonation and AOPs, however, are used by less than 2 percent of drinking water treatment plants.

Ikehata and Gamal El-Din (2005) reviewed the literature for ozonation and advanced oxidation processes for their control of pesticides, including the N-methyl carbamates aldicarb, carbaryl, carbofuran, fenobucarb, isoprocarb, methomyl, metolcarb, oxamyl and propoxur. Where conditions were similar to those of drinking water treatment, the following may be summarized as follows:

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- Ozonation at 1 mg/L of applied ozone at pH 8.3 resulted in complete conversion of aldicarb at 9.5 ug/L , with aldicarb sulfoxide identified as a byproduct. In the ozonation of river water at pH 7.2, the order of reactivity of N-methyl carbamates was: carbaryl > propoxur > fenobucarb > isoprocarb > metolcarb. It was proposed that the isopropoxy group on propoxur was more susceptible to ozone attack than the sec-butyl or isopropyl groups on fenobucarb and isoprocarb, respectively.

- In ozone/UV reactions with propoxur, the hydroxyl radical accounted for over half the reaction, whereas the ozone molecule accounted for less than one-fifth, and photolysis for less than one-third.

- Ozonation byproducts of carbaryl were found to be: 1-naphthol, naphthoquinone, phthalic anhydride and N-formylcarbamate of 1-naphthol.

- Ozonation of carbofuran was improved when combined with UV (ozone/UV).

- Fast reaction kinetics were reported for the ozonation of oxamyl and methomyl.

- Mineralization of n-methyl carbamates by ozone or AOPs under drinking water treatment conditions has not been demonstrated.

## D. Field Monitoring Data

### D.1 Pesticide Occurrence Data from the USGS/EPA Pilot Reservoir Monitoring Program (Bloomquist et al., 2001)

EPA's Office of Pesticide Programs (OPP) analyzed USGS/EPA pilot reservoir monitoring data to assess concentrations of carbamates and their degradation products in raw and finished waters and to examine trends, when possible, in whole plant water treatment effects on pesticide removal and transformation (Blomquist et al, 2001). Reservoir ("outfall") samples, although collected, were not considered. Analysis and summary statistics for carbamates are discussed below:

**Factors Affecting Interpretation of Reservoir Monitoring Data**

- The USGS/EPA pilot reservoir monitoring study was designed to provide pesticide occurrence data in raw and finished water (Blomquist et al., 2001). Data analysis objectives included the following: provide pesticide data for human and ecological exposure assessment; assessment of

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sampling frequency for capturing peak pesticide concentrations in community water system (CWS); assessment of general relationships of pesticide concentrations in finished drinking water in relation to source water and overall understanding of whole system water treatment effects; establishment of relationships of pesticide concentrations in reservoirs to watershed and reservoirs characteristics; and validation and testing of watershed and reservoir models.

- Raw and finished water were not temporally paired to account for travel time of the pesticide and its transformation products through the water treatment plant. (The lack of temporal pairing limits a direct linkage of pesticide removal by treatment and degradation and formation of degradation products during water treatment.) Although the water samples were not temporally-paired, the results were expected to show a general relationship in concentration differences between raw and finished water samples. Temporal variability in pesticide concentrations was expected to be lower when compared to flowing water bodies because the source water was derived from reservoirs. Additionally, water samples were taken on the same time scale (hours) as the water treatment cycles for the water utilities.

  An analysis of sample pairing time, expressed as a percentage of the reservoir flow-through time, indicated that timing and sequencing of pairing were not consistent among the reservoirs (Figure II.D.2.1). The quality assurance plan (QAP) for the pilot reservoir monitoring program did not specify a pairing sampling strategy of raw and finished water samples. The water sampling time and sequence were at the discretion of the person(s) sampling the water treatment plants.

  In some cases, finished water samples were taken before the "paired" raw water samples. This situation indicates that the slug of sampled finished water was ahead of the "paired" raw water sample, which leads to negative percentage in sample pair times relative to average water plant flow time. Negative sample pair times were found in all the treatment plants except TX.

  Raw water samples were also taken prior to the finished water samples. Under these conditions, the percentage in sample pairing time relative to average water plant flow time would be positive. The mean percentage of sampling pairing time typically accounted for less than 20% of the water flow through time in the plant. An exception to this observation is was the NY reservoir where the mean percentage of sample pairing time accounted for 57% of water treatment flow through time. Exact raw and finished water sample pairing (100%) was found for three water samples at the LA water treatment plant.

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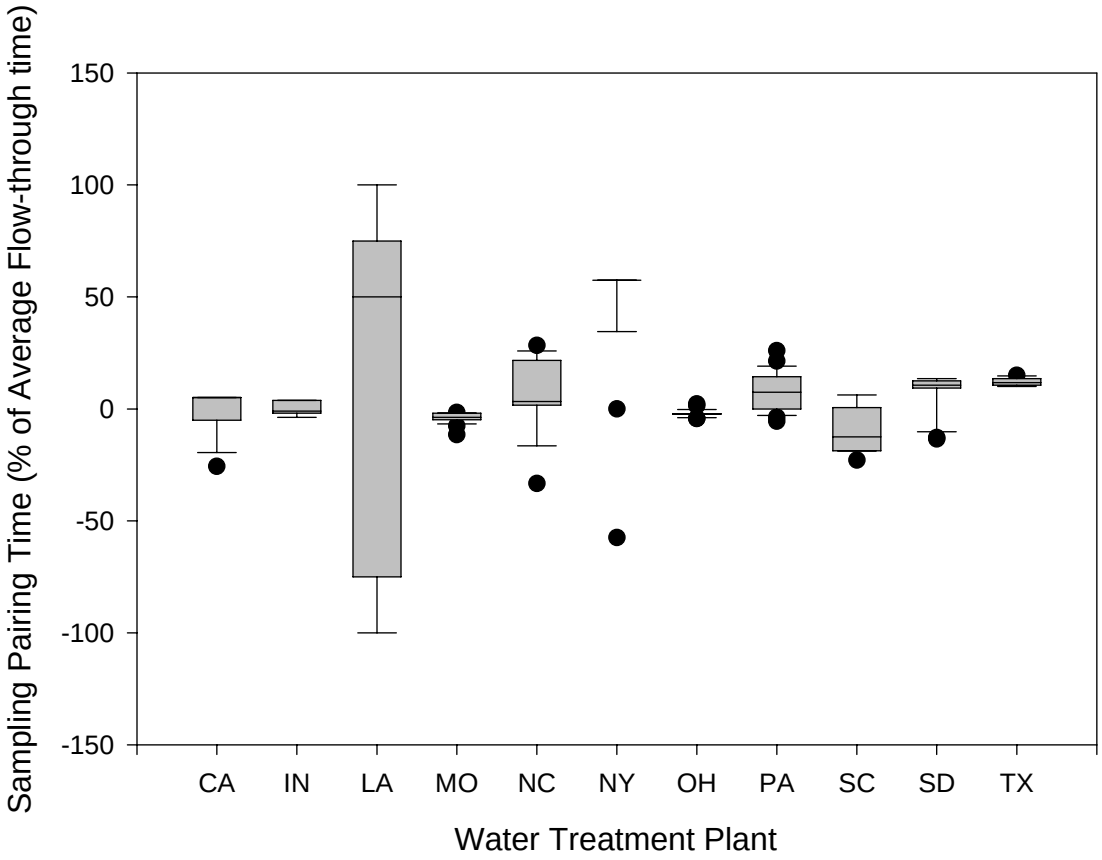
**Figure II.D.2. 1 - Range of Sample Pairing Time (expressed as a percent of average water treatment plant flow-through time) Among the Water Treatment Plants. Box represents 90th and 10th percentiles; whiskers represent 95th and 5th percentiles; bar in box is median; points are outliers.**




There were high deviations in the sample pairing time among the water treatment plants. The most variable sampling pairing times were associated with the LA water treatment plant. In most cases, the standard deviation was equal to or higher than the mean percentage of sample pairing time.

- Pesticide concentrations in finished water samples were determined in "unquenched" water samples. The lack of quenching of free chlorine in finished water samples does not eliminate the possibility of continued chemical oxidation during storage and analysis. Water treatment plant processes in the reservoir monitoring study employ pre- and post-disinfection treatment processes, using chlorine as the disinfectant. Hence, the absence of quenching may limit the detection and definitive quantification of pesticides and transformation products prone to oxidation during storage. Recoveries in matrix-spiked finished water samples and sample storage times are presented to assess the impact of non-quenching pesticide stability (Table II.D.3.8).

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- Ancillary data on weather, pesticide use, and watershed vulnerability need to be considered when interpreting occurrence data. Sampling was extended through 2000 because of extreme drought conditions in the northeastern United States and California during the 1999 sampling season. Lower than average rainfall may have impacted pesticide runoff and resulted in fewer detections of pesticides.

- Three analytical methods (2001, 9002, and 9060) were used in the reservoir monitoring study. Method 2001 was conducted using C-18 solid phase extraction and gas chromatography/mass spectrometry (GC/MS) (Zaugg et al., 1995). This method has been validated and is approved for use in the National Water Quality Assessment (NAWQA) program. Methods 9002 and 9060 were provisional (under development and validation) during the course of the study, but are now currently approved by USGS. Method 9002 (now referred to as method 2002) is was conducted using C-18 solid phase extraction and GC/MS (Sandstrom et al., 2001). Method 9060 (now referred 2060) is was conducted using solid phase extraction and high performance liquid chromatography/mass spectrometry (HPLC/MS) (Furlong et al., 2001). These methods were used to expand information on occurrence of pesticides and degradation products.

- For Method 9060, the data from March 1, 1999 to December 31,1999 have been flagged with supplemental USGS data quality (Written Communications from Joel Blomquist, USGS 9/23/02). The flagging was performed because, in 1999, the analytical demand for Method 9060 exceeded the instrumental analysis capacity. This delay led to long-storage times (180 days) in refrigerators of unextracted samples. Interpretation of the 1999 data requires careful consideration of median half-life of the pesticides during storage of unquenched samples with respect to sample holding times.

- The qualified "estimate" designation, according to USGS protocol, has been extended for data from USGS Method 9060 to account for background concentrations of pesticides in blank water samples (Verbal Communication J. Blomquist, 10/7/02). Because background concentrations in blank water samples approached minimum reporting limits (<0.003 ug/L) for several compounds, the qualified estimate designation (E) is limited to concentrations greater than or equal to 0.003 ug/L. Concentrations below 0.003 ug/L are not considered as estimated concentrations. This designation was adopted to ensure reliable estimates of detections above background concentrations.

**Methods of Data Analysis**

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Data from USGS/EPA Reservoir Monitoring Data (Blomquist et al., 2001) were reformatted in an a spreadsheet to accommodate formatting requirements for Statistical Analysis Systems (SAS is a Trademark of SAS Institude. Inc., Cary NC). Sampling dates in the original data set were modified to facilitate translation of date variables. After the modification step, EXCEL data sets for USGS schedules 2001, 9060, and 9002 were merged into a common data set using a SAS program.

**Summary Statistics**

Summary statistics, including the mean, median, standard deviation, minimum, and maximum pesticide concentrations in raw and finished water samples, were determined using Statistical Analysis Systems (SAS) procedures.

**Pesticide Concentration Difference for Raw and Finished Water Samples**

Raw water removal percentages were not calculated because of their known instability in finished water, low detection frequencies, and low concentrations in raw and finished water samples.

**Assessment Criteria for Assessing Pesticide Transformation**

A set of criteria were used to identify possible pesticide transformation during water treatment.

- ❑ Pesticide degradation products detected in only finished water samples.
- ❑ Parent pesticides in only raw water samples.
- ❑ Co-occurrence of parent pesticides in only raw water samples and detection of degradation product in only finished water samples for the same paired water sample.
- ❑ Low recoveries of matrix spikes from finished water in combination with high recoveries in matrix spikes from raw water.

The premise is that at least one of these conditions may indicate possible pesticide transformation during water treatment.

**Water Treatment Trains and Basic Water Quality Data**

Although the water quality parameters, including pH, hardness, and total organic carbon, varied among the 12 reservoirs (Table II.D.3.6), the physical construct of the treatment train processes was similar.

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Source Water → Prechlorination (Preoxidation) → Coagulation and Clarification → Filtration → Post Oxidation → Clear well

**Table II.D.3.6: Average Water Quality Parameters for Raw Water at Candidate Reservoirs**

| Water Systems | Avg Flow Through Time (hr) | Water Quality Properties | | | |
|---|---|---|---|---|---|
| | | pH | Alkalinity mg/L as CaCO3) | Hardness (mg/L as CaCO3) | TOC* (mg/L) |
| MO | 26 | 7.9 - 9.2 | 63-120 | 90 - 145 | 4.7 |
| TX | 10 | 7.7 | 100 | 108 | 4-8 |
| OH | 23 | 7.7 | 95 | 126 | 5.2 |
| OK | NA | 7.9-8.8 | 137 | 150 | 5.8 |
| CA | 3.25 | 7.5 | 91 | 250 | 6-8 |
| IN | 8.75 | 8.2 | 128 | 200 | 4 |
| SD | 12-13 | 9.2 | 32 | NA | NA |
| SC | 4 | 6.9 | 17 | 15 | 3.8 |
| NC | NA | 7 | 12 | NA | NA |
| LA | NA | NA | NA | NA | NA |
| NY | 0.29 | 7.8-9.0 | 40-100 | 140 | 4.4 |
| PA | 7-9 | 7.2 | 7.2 | 172 | 2-3 |

NA-Not available
* TOC= Total Organic Carbon

The average water flow-through time at each treatment plant was less than 24 hours. The most common treatment practices included prechlorination and post disinfection, coagulation, and pH adjustment processes. Chlorine and chlorine dioxide were the most common disinfectants used in the prechlorination process, while chlorine and chloramines were the most common disinfectants used in the post disinfection process. The most common coagulants used in the treatment trains were aluminum salts and polymers. The data also shows that pH was adjusted by adding lime and sodium hydroxide. Several of the treatment plants used activated carbon in the treatment train. Powdered activated carbon was used in the PA, NY, SC and , IN water utilities, while GAC was used at the MO, OK and OH water utilities.

### Monitoring Results for Carbamate Pesticides

Twenty-eight carbamates pesticides and their degradation products were analyzed in the reservoir monitoring study (Table II.D.3.7).

**Table II.D.3.7. Selected carbamate pesticides and their degradation products included in the reservoir study, USGS Analytical Schedules.**

| Pesticide | IUPAC Name | Degradates |
|---|---|---|
| Alidcarb | 2-methyl-2-(methylthio)propionaldehyde O-methylcarbamoyloxim | Aldicarb sulfone, Aldicarb sulfoxide |
| Carbaryl | 1-naphthyl methylcarbamate | 1-naphthol, 1,4-naphthoquinone |
| Molinate | S-ethyl azepane-1-carbothioate | |

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**Table II.D.3.7. Selected carbamate pesticides and their degradation products included in the reservoir study, USGS Analytical Schedules.**

| Pesticide | IUPAC Name | Degradates |
|---|---|---|
| Methomyl | S-methyl-(EZ)-N – (methyl-carbamoyloxy)thioacetimidate | Methomyl oxime |
| Triallate | S-2,3,3-trichloroallyl di-isopropylthiocarbamate | |
| Butylate | S-ethyl di-isobutylthiocarbamate | |
| Oxamyl | N,N-dimethyl-2-methylcarbamoyloxyimino-2-(methylthio)acetamide | Oxamyl oxime |
| Pebulate | S-propyl butyl(ethyl)thiocarbamate | |
| Methiocarb | 4-methylthio-3,5-xylyl methylcarbamate | |
| Propoxur | 2-isopropoxyphenyl methylcarbamate | |
| Bendiocarb | 2,3-isopropylidenedioxyphenyl methylcarbamate | |
| Thiobencarb | S-4-chlorobenzyl diethyl(thiocarbamate) | |
| Cycloate | S-ethyl cyclohexyl(ethyl)thiocarbamate | |
| Benomyl | methyl-1-[(butylamino)carbonyl]-H-benzimidazol-2-ylcarbamate | |
| Propham | isopropyl phenylcarbamate | |
| Carbufuran | 2,3-dihydro-2,2-dimethylbenzofuran-7-yl methylcarbamate | 3-hydroxycarbofuran |

**Quality Assurance and Quality Control Assessment**

The carbamate pesticides and their degradation products were analytes on the 2001, 9002, and 9060 USGS analytical schedules. Methods 9002 and 9060 were undergoing QA/QC testing during the monitoring program.

In 1999, water samples for Method 9060 were stored for extremely long periods of time (median holding time of 90 days) prior to extraction (Written Communications from Joel Blomquist, USGS 9/23/02). The USGS conducted a comparison of storage times with median half-lives in organic blank water, ground water, and surface water. The data indicated that the carbamate pesticides and their degradation products measured by Method 9060 have median half-lives ranging from 4.5 days for methomyl oxime to 28.9 days for propham, which are much shorter than the median sample holding time of 90 days in 1999. This long median storage time relative to the median half-lives is expected to create a systematic bias toward lower concentrations. Any detections in raw and finished water samples, however, should be considered as strong evidence of pesticide occurrence. Reliable quantification of carbamate concentrations in finished water may be compromised if carbamate pesticides undergo oxidation and hydrolysis in finished drinking water.

For the carbamate pesticides, the mean recovery in raw water, ranged from 2% - 140%, the maximum recovery ranged from 17% - 194%, and the minimum

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recovery ranged from 0% - 96% (Table II.D.3.8). For finished water, the mean recovery ranged from 1% - 134%, the maximum recovery ranged from 9% - 195%, and the minimum recovery ranged from 0% - 72%. The mean recovery values for the carbamate pesticides in finished water samples were significantly lower (P□0.05; t-test) than the mean recovery values for the raw water samples.

**Table II.D.3.8: Summary statistics of fortified laboratory set and matrix samples for carbamate pesticides from USGS methods 2001 and 9060 (decimal percentage)**

| Compound | No. of Samples | Mean % recovery | Standard Deviation | Maximum Recovery | Median Recovery | Minimum Recovery | Schedule Number |
|---|---|---|---|---|---|---|---|
| **Raw Water Samples** | | | | | | | |
| Propoxur | 31 | 78% | 19% | 103% | 82% | 29% | 9060 |
| 3-Hydroxy-carbofuran | 32 | 78% | 23% | 116% | 83% | 28% | 9060 |
| Aldicarb | 32 | 11% | 15% | 49% | 2% | 0% | 9060 |
| Aldicarb sulfone | 32 | 23% | 31% | 179% | 17% | 0% | 9060 |
| Aldicarb sulfoxide | 32 | 36% | 23% | 83% | 40% | 0% | 9060 |
| Bendiocarb | 32 | 69% | 30% | 123% | 80% | 0% | 9060 |
| Benomyl | 32 | 73% | 37% | 148% | 77% | 0% | 9060 |
| Butylate | 34 | 124% | 30% | 192% | 115% | 86% | 2001 |
| Carbaryl | 23 | 139% | 30% | 185% | 142% | 88% | 2001 |
| Carbofuran | 23 | 140% | 28% | 194% | 142% | 96% | 2001 |
| Carbofuran | 32 | 84% | 21% | 124% | 91% | 29% | 9060 |
| Imidacloprid | 31 | 124% | 37% | 193% | 131% | 29% | 9060 |
| Methomyl | 32 | 77% | 30% | 144% | 78% | 0% | 9060 |
| Molinate | 34 | 106% | 22% | 190% | 100% | 86% | 2001 |
| Oxamyl | 32 | 62% | 31% | 116% | 68% | 0% | 9060 |
| Oxamyl oxime | 31 | 2% | 4% | 17% | 0% | 0% | 9060 |
| Triallate | 33 | 105% | 17% | 174% | 104% | 82% | 2001 |
| **Finished Water Samples** | | | | | | | |
| Propoxur | 28 | 74% | 22% | 101% | 80% | 0% | 9060 |
| 3-Hydroxy-carbofuran | 30 | 71% | 28% | 117% | 79% | 0% | 9060 |
| Aldicarb | 30 | 4% | 11% | 56% | 0% | 0% | 9060 |
| Aldicarb sulfone | 30 | 12% | 12% | 39% | 6% | 0% | 9060 |
| Aldicarb sulfoxide | 30 | 29% | 40% | 142% | 10% | 0% | 9060 |
| Bendiocarb | 30 | 63% | 31% | 109% | 77% | 0% | 9060 |
| Benomyl | 30 | 35% | 45% | 122% | 3% | 0% | 9060 |
| Butylate | 31 | 31% | 50% | 153% | 0% | 0% | 2001 |
| Carbaryl | 21 | 122% | 41% | 163% | 135% | 26% | 2001 |
| Carbofuran | 26 | 134% | 32% | 189% | 132% | 63% | 2001 |
| Carbofuran | 30 | 75% | 24% | 104% | 81% | 0% | 9060 |
| Imidacloprid | 30 | 113% | 36% | 148% | 123% | 0% | 9060 |
| Methomyl | 30 | 27% | 34% | 100% | 7% | 0% | 9060 |
| Molinate | 31 | 26% | 42% | 111% | 0% | 0% | 2001 |
| Oxamyl | 30 | 48% | 32% | 99% | 54% | 0% | 9060 |
| Oxamyl oxime | 28 | 1% | 3% | 9% | 0% | 0% | 9060 |
| Triallate | 31 | 41% | 43% | 117% | 18% | 0% | 2001 |

**Summary Statistics**

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The carbamate pesticides and their degradation products exhibited extremely low detection frequencies in raw and finished water samples (Table II.D.3.9). Out of the 28 compounds analyzed by USGS Methods 2001, 9002, 9060, 18 carbamate pesticides or degradation products were detected. The summary statistics were identified by analytical schedules because several carbamate pesticides are analytes on the Method 9060 analytical schedule. As previously mentioned, the data for Method 9060 in 1999 should be considered as minimum concentrations. Additionally, the lack of a detection is not conclusive evidence that the compound was not present because carbamates are unstable in finished water samples.

Other considerations are associated with analytical recoveries of the carbamates. There was a difference in analytical recovery of carbamate pesticides between raw and finished water, with lower recoveries lower in the finished water. For USGS Method 2001, carbaryl and carbofuran were considered permanently qualified estimates because of variable recoveries (Zaugg, et al. 1995). Aldicarb, aldicarb sulfone, aldicarb sulfoxide, and oxamyl oxime were classified as qualified estimates for Method 9060 because recoveries were biased outside the acceptable range of median recoveries (< 60% and >120%) (Furlong et al., 2001) The USGS defines estimated concentrations when low analytical recoveries are observed or when qualitative detections of concentrations are less than the statistically determined limit of detection (LOD).

**Table II.D.3.9: Summary Table for Detections of Carbamates and their Degradation Products**

| Pesticide | schedule | Raw Water | | | | | Finished Water | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | N | No. detects | Pct detects | Max Conc. (ug/L) | Mean Conc. (ug/L) | N | No. detects | Pct detects | Max Conc. (ug/L) | Mean Conc. (ug/L) |
| 1,4-Naptho-quinone | 9002 | 316 | 3 | 0.95% | 0.0054 | 0.0036 | 220 | 1 | 0.45% | 0.0025 | 0.0025 |
| 1-Napthol | 9002 | 316 | 3 | 0.95% | 0.2280 | 0.0806 | 220 | 0 | | | |
| 3-Hydroxy-carbofuran | 9060 | 311 | 0 | | | | 224 | 1 | 0.45% | 0.0094 | 0.0094 |
| 3-keto-carbofuran | 9060 | 311 | 0 | | | | 224 | 0 | | | |
| 4-Chlorobenzyl-methyl sulfo | 9002 | 316 | 0 | | | | 220 | 0 | | | |
| Aldicarb | 9060 | 311 | 0 | | | | 224 | 0 | | | |
| Aldicarb sulfone | 9060 | 311 | 1 | 0.32% | 0.0074 | 0.0074 | 224 | 0 | | | |
| Aldicarb sulfoxide | 9060 | 311 | 0 | | | | 224 | 0 | | | |
| Bendiocarb | 9060 | 311 | 0 | | | | 224 | 1 | 0.45% | 0.0042 | 0.0042 |
| Benomyl | 9060 | 309 | 20 | 6.47% | 0.0382 | 0.0247 | 223 | 2 | 0.90% | 0.2150 | 0.1102 |
| Butylate | 2001 | 323 | 1 | 0.31% | 0.0022 | 0.0022 | 227 | 0 | | | |
| Carbaryl | 2001 | 323 | 7 | 2.17% | 0.0465 | 0.0137 | 227 | 2 | 0.88% | 0.0041 | 0.0035 |
| | 9060 | 311 | 2 | 0.64% | 0.0063 | 0.0059 | 224 | 0 | | | |
| Carbofuran | 2001 | 323 | 2 | 0.62% | 0.0188 | 0.0155 | 227 | 3 | 1.32% | 0.0095 | 0.0082 |
| | 9060 | 311 | 2 | 0.64% | 0.0100 | 0.0074 | 224 | 1 | 0.45% | 0.0041 | 0.0041 |
| Cycloate | 9002 | 316 | 0 | | | | 220 | 0 | | | |
| | 9060 | 311 | 0 | | | | 224 | 0 | | | |
| EPTC | 2001 | 323 | 25 | 7.74% | 0.0373 | 0.0154 | 227 | 11 | 4.85% | 0.0286 | 0.0135 |
| Methiocarb | 9060 | 311 | 0 | | | | 224 | 0 | | | |

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**Table II.D.3.9: Summary Table for Detections of Carbamates and their Degradation Products**

| Pesticide | schedule | Raw Water | | | | | Finished Water | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | N | No. detects | Pct detects | Max Conc. (ug/L) | Mean Conc. (ug/L) | N | No. detects | Pct detects | Max Conc. (ug/L) | Mean Conc. (ug/L) |
| Methomyl | 9060 | 311 | 0 | | | | 224 | 0 | | | |
| Methomyl oxime | 9060 | 311 | 0 | | | | 224 | 0 | | | |
| Molinate | 2001 | 323 | 1 | 0.31% | 0.0023 | 0.0023 | 227 | 0 | | | |
| Oxamyl | 9060 | 311 | 0 | | | | 224 | 0 | | | |
| Oxamyl oxime | 9060 | 307 | 0 | | | | 220 | 2 | 0.91% | 0.0139 | 0.0135 |
| Pebulate | 2001 | 323 | 0 | | | | 227 | 0 | | | |
| Propham | 9060 | 311 | 0 | | | | 224 | 0 | | | |
| Propoxur | 9060 | 307 | 1 | 0.33% | 0.0048 | 0.0048 | 220 | 1 | 0.45% | 0.8230 | 0.8230 |
| Thiobencarb | 2001 | 323 | 0 | | | | 227 | 0 | | | |
| Triallate | 2001 | 323 | 1 | 0.31% | 0.0022 | 0.0022 | 227 | 0 | | | |

Parent carbamate compounds found in raw water samples included benomyl, butylate, carbaryl, carbofuran, EPTC, molinate, propoxur, and triallate. EPTC had the highest detection frequency, 7.74% (25 detections in 323 samples) in raw water and 4.85% (11 detections in 227 samples) in finished water. With the exception of benomyl and EPTC, the reported concentrations for parent carbamates and their degradation products were considered qualified estimates.

Parent carbamate detections were found in the raw water of the OK, PA, SC, MO, NC, LA, NY, and SD water treatment plants (Table II.D.3.10). In finished water, parent carbamate detections were found in OK for bendiocarb, MO and NY for benomyl, MO and PA for carbaryl, PA for carbofuran (Method 2001 and 9060), and PA and SD for EPTC. No carbamate detections were found in the TX water treatment plant.

**Table II.D.3.10: Summary statistics for water type, year, and water utility for carbamate pesticides and their degradation products (ug/L)**

| Chemical | schedule | State | Year | Water Type | Nondetects | | Conc. Estimated | | Conc. Measured | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | No. | LOD Range | No. | Range | No. | Range |
| 1,4-Napthoquinone | 9002 | OK | 2000 | Raw | 19 | 0.008 | 1 | 0.0054 | . | . |
| | 9002 | PA | 2000 | Finish | 10 | 0.008 | 1 | 0.0025 | . | . |
| | 9002 | PA | 2000 | Raw | 10 | 0.008 | 1 | 0.0037 | . | . |
| | 9002 | SC | 2000 | Raw | 23 | 0.008 | 1 | 0.0017 | . | . |
| 1-Napthol | 9002 | MO | 1999 | Raw | 19 | 0.005 | 1 | 0.228 | . | . |
| | 9002 | PA | 2000 | Raw | 10 | 0.005 | 1 | 0.006 | . | . |
| | 9002 | SC | 1999 | Raw | 19 | 0.005 | 1 | 0.0077 | . | . |
| 3-Hydroxy-carbofuran | 9060 | NC | 1999 | Finish | 9 | 0.0623 | 1 | 0.0094 | . | . |
| Aldicarb sulfone | 9060 | NY | 1999 | Raw | 9 | 0.16 | 1 | 0.0074 | . | . |
| Bendiocarb | 9060 | OK | 1999 | Finish | 9 | 0.0612 | 1 | 0.0042 | . | . |
| Benomyl | 9060 | MO | 2000 | Finish | 15 | 0.0219 | 1 | 0.215 | . | . |
| | 9060 | NY | 2000 | Finish | 9 | 0.0219 | 1 | 0.0053 | . | . |
| | 9060 | OK | 1999 | Raw | 13 | 0.0219 | 7 | 0.0187- | . | . |

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**Table II.D.3.10: Summary statistics for water type, year, and water utility for carbamate pesticides and their degradation products (ug/L)**

| Chemical | schedule | State | Year | Water Type | Nondetects | | Conc. Estimated | | Conc. Measured | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | No. | LOD Range | No. | Range | No. | Range |
| | | | | | | | | 0.0382 | | |
| | 9060 | OK | 2000 | Raw | 12 | 0.0219 | 6 | 0.0243-0.0363 | 1 | 0.0242 |
| | 9060 | PA | 1999 | Raw | 11 | 0.0219 | 2 | 0.0259-0.0301 | . | . |
| | 9060 | PA | 2000 | Raw | 8 | 0.0219 | 3 | 0.0089-0.0163 | . | . |
| | 9060 | SC | 2000 | Raw | 23 | 0.0219 | 1 | 0.006 | . | . |
| Butylate | 2001 | NY | 2000 | Raw | 10 | 0.002 | 1 | 0.0022 | . | . |
| Carbaryl | 2001 | MO | 1999 | Finish | 10 | 0.003 | 1 | 0.0041 | . | . |
| | 2001 | MO | 2000 | Raw | 18 | 0.003-0.041 | 1 | 0.008 | . | . |
| | 2001 | NC | 1999 | Raw | 9 | 0.003 | 1 | 0.0039 | . | . |
| | 2001 | OH | 2000 | Raw | 9 | 0.003 | 1 | 0.012 | . | . |
| | 2001 | PA | 2000 | Finish | 10 | 0.003-0.041 | 1 | 0.0028 | . | . |
| | 2001 | PA | 2000 | Raw | 7 | 0.003-0.041 | 4 | 0.0054-0.0465 | . | . |
| | 9060 | PA | 2000 | Raw | 10 | 0.0628 | 1 | 0.0054 | . | . |
| | 9060 | SC | 1999 | Raw | 19 | 0.0628 | 1 | 0.0063 | . | . |
| Carbofuran | 2001 | PA | 2000 | Finish | 8 | 0.003-0.03 | 3 | 0.0075-0.0095 | . | . |
| | 2001 | PA | 2000 | Raw | 9 | 0.003-0.05 | 2 | 0.0121-0.0188 | . | . |
| | 9060 | PA | 2000 | Finish | 9 | 0.0566 | 1 | 0.0041 | . | . |
| | 9060 | PA | 2000 | Raw | 9 | 0.0566 | 2 | 0.0048- 0.01 | . | . |
| EPTC | 2001 | LA | 2000 | Raw | 10 | 0.002-0.03 | 1 | 0.011 | . | . |
| | 2001 | NY | 1999 | Raw | 6 | 0.002-0.01 | . | . | 5 | 0.0101-0.0373 |
| | 2001 | NY | 2000 | Raw | 3 | 0.002-0.007 | 3 | 0.0021-0.0033 | 5 | 0.0057-0.0132 |
| | 2001 | PA | 2000 | Finish | 10 | 0.002 | 1 | 0.0015 | . | . |
| | 2001 | PA | 2000 | Raw | 10 | 0.002 | 1 | 0.0017 | . | . |
| | 2001 | SD | 1999 | Finish | 6 | 0.002 | . | . | 4 | 0.0128-0.0286 |
| | 2001 | SD | 1999 | Raw | 6 | 0.002 | . | . | 4 | 0.0134-0.0362 |
| | 2001 | SD | 2000 | Finish | 5 | 0.002 | . | . | 6 | 0.0048-0.0186 |
| | 2001 | SD | 2000 | Raw | 5 | 0.002-0.01 | . | . | 6 | 0.0093-0.0302 |
| Molinate | 2001 | SC | 1999 | Raw | 20 | 0.004 | 1 | 0.0023 | . | . |
| Oxamyl oxime | 9060 | OK | 1999 | Finish | 8 | 0.0644 | 2 | 0.0131-0.0139 | . | . |
| Propoxur | 9060 | IN | 1999 | Finish | 10 | 0.0594 | . | . | 1 | 0.823 |
| | 9060 | MO | 1999 | Raw | 18 | 0.0594 | 1 | 0.0048 | . | . |
| Triallate | 2001 | CA | 1999 | Raw | 7 | 0.001 | 1 | 0.0022 | . | . |

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With the exception of 1,4-napthoquinone, the degradation products of carbamates were detected in finished or raw water samples. There was no evidence of co-occurrence of parent carbamate pesticides and degradation products in raw and finished water samples. Although 3-hydroxycarbofuran and oxamyl oxime were detected in finished water samples, there are no concurrent detections of carbofuran or oxamyl in "paired" raw water samples to conclude transformation during treatment. Although 1,4-napthoquinone was detected in a finished and raw water at the PA site. There was no co-occurrence of carbaryl in the paired finished or raw water sample to associate 1,4-napthoquione formation to carbaryl degradation. Because aldicarb sulfone (an oxidative degradation product of aldicarb) and 1-napthol (hydrolysis degradate of carbaryl) were only detected in raw water, they are most likely environmental degradation products.

**Results and Discussion**

The USGS monitoring data for selected drinking water treatment plants on reservoirs indicates a low detection frequency (<1% of samples) of carbamate pesticides in raw and finished drinking water. The carbamates with the highest detection frequencies (6.5 to 7% of samples) in raw water samples were benomyl and EPTC. In finished water samples, carbofuran and EPTC had the highest detection frequencies (1 to 4% of samples). Because the monitoring program was not targeted to carbamate use areas and sample handling issues, the reported detection frequencies and concentrations may underestimate the occurrence for carbamates in raw and finished drinking water.

Because carbamate degradation products were detected in both raw and finished water samples, carbamate degradation products were formed through environmental processes. However, laboratory studies indicate that degradation products can be formed through water treatment processes.

The uncertainties associated with monitoring data limit a clear definitive analysis of water treatment effects.

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