

The Evaluation of Metham Sodium and Dichlobenil Impacts on
Activated Sludge Nitrification

by

Timothy Nelson Ake

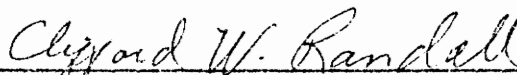
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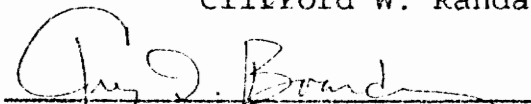
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ENVIRONMENTAL ENGINEERING

APPROVED


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Abstract

**THE EVALUATION OF METHAM SODIUM AND DICHLOBENIL IMPACTS ON
ACTIVATED SLUDGE NITRIFICATION**

by
Timothy Nelson Ake

Clifford W. Randall, Chairman
Environmental Engineering

Sanafoam Vaporooter II is a trademark name for a process which uses metham sodium and dichlobenil to remove tree roots from municipal sewer and storm drain lines. One or more of the chemicals in this process, or their degradation products, have been suspected of disrupting the nitrification process in waste treatment plants downstream of the points of application. This work was undertaken to identify the chemical responsible for the disruption, and to recommend means for assuaging the problem.

The impacts of the herbicides used in the Vaporooter II process were separately tested in bench scale reactors. Metham sodium was found to be the herbicide responsible for disrupting nitrification. It did so at concentrations of 4 mg/L or higher in systems which have a mixed liquor volatile suspended solids concentrations of 1800 mg/L. This corresponds to a herbicide to biomass ratio of 0.017 moles/gram.

The stability of metham sodium was also tested in bench scale experiments. The compound was found to be fairly stable at the pH values, temperatures and oxygen concentrations typically found in sewage collection systems, and so undergoes little degradation after application.

Powdered activated carbon (PAC) is effective in absorbing metham sodium from raw sewage. In bench scale reactors, application rates of 10 mg PAC per 1 mg metham sodium reduced metham sodium concentrations to levels which did not disrupt the nitrification process.

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John Ericson of Zeneca's Western Research Center in Richmond, California offered consultation regarding metham sodium's chemical properties and methods for determining its concentrations in solution.

Westvaco graciously supplied a sample of their Nuchar-SA powdered activated carbon for use in these experiments.

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I. INTRODUCTION

Sanafoam Vaporooter II (SVII) is the trademark name for a process which uses herbicides to remove tree roots from municipal sewage collection pipes and storm drain lines. In this process two herbicides, metham sodium and dichlobenil, are applied by foam directly into the drain line. The foam fills the pipe, bringing the herbicides into contact with tree roots throughout the system. In larger pipes, (generally 36 inch diameter and larger), the foam does not fill the pipe, but is sprayed to cover the inside surfaces of the pipes. Metham sodium kills tree roots on contact while dichlobenil has a residual property which controls their regrowth. The dead roots subsequently decompose by natural means.

The foam is applied during periods of low flow. During periods of rain, sewer and storm lines are often filled to near capacity levels with storm water. As such, tree roots would be below the water level during these times, and so be out of contact with the foam. Also, as flow velocities are fairly high after storms, the foam would be washed away before full effectiveness is achieved. The application of SVII during low flows allows sufficient space in the pipe for proper application as well as sufficient contact time. This also means that the herbicides would be more concentrated in the raw sewage than would be seen during

high flow times.

About an hour after application the foam collapses and is washed downstream by normal gravity flow. It is treated as a normal part of sewage at the waste treatment plant into which the lines empty.

On numerous occasions, disruption of nitrification processes have occurred in sewage treatment plants downstream of where this process has been applied. Plant operators have perceived this disruption to be caused by the chemicals used in the SVII process. In a personal communication, Duke gave a partial list of customers reporting these problems. These customers included the Western Carolina Regional Sewer Authority in Greenville, South Carolina, the Hatborough Joint Sewer Authority in Willow Grove Pennsylvania, and the City of Asheboro in North Carolina.

When problems occurred, typically nitrification was completely lost within hours following application, and several days were required for complete recovery. This loss has caused ammonia discharge limits to be above required effluent limits.

The Sanafoam Vaporooter II process has been previously analyzed for microorganism toxicity by Anlab², whose conclusions were:

"there is little or no impact on the biological

process of either activated sludge or pond water treatment systems when the dosing concentration of SV-II is 40 ppm or lower.

However, when SV-II dosing rates reach 50 ppm and higher the biological activity of these plants can be dramatically affected."

The same report also stated that treatment plants with nitrification were affected at similar doses.

It needs be noted that the concentrations used in the Anlab report are for the applied herbicide solution, which is 24.25% metham sodium and 1.95% dichlobenil (see Appendix A). The appropriate material fractions should be applied to the above doses to convert to absolute herbicide concentrations.

Duke's Root Control Services (Duke) has been using the Sanafoam Vaporooter II process at numerous sites throughout the country. According to information Duke received from Anlab, the concentrations of metham sodium they have been using are too low to cause an observable effect in sewage treatment plants. Also, as dichlobenil coats the pipe system and largely does not wash downstream, but metabolizes in place, it should not have affected treatment plants at all. However, after numerous customer complaints, Duke concluded that work needed to be performed to determine if indeed either metham sodium or dichlobenil, the two acting

together, or their degradation products, were causing disruption of the nitrification process.

Duke has responded to these complaints by placing activated carbon downstream of the application point to adsorb remaining herbicides. This procedure apparently lessened the impact at the sewage plants, but was very costly. Duke wished to please their customers, but did not want to incur costs for problems they were not causing. As such, Duke sponsored this study to determine the following:

- 1) Is metham sodium or dichlobenil, or their degradation products, the cause of the loss of nitrification in these sewage treatment plants?
- 2) If so, which chemical has been responsible and at what doses?
- 3) What steps can be taken to minimize or prevent the loss of nitrification?

Duke was questioned as to whether they had ever performed an optimization study to determine the optimum dose of chemicals to use in this process. This was asked as lowering the dose may be one way to eliminate the problem. They responded they have not, and did not wish to pursue the matter. The reason was that they did not want to risk underdosing during the process and so not completely kill the tree roots. To do so would give them a reputation of being ineffective in their treatments, and they would lose

business.

Also, Duke currently anticipates the EPA may phase out the use of metham sodium in the near future. They related a story where in the late 1980's a railroad tank car of metham sodium overturned and spilled its contents into a California river. While the environmental impact of this spill was short lived, it focused more attention on the chemical and lead to more scrutiny as to its safety. Some subsequent tests showed metham sodium may be a teratogen (see Appendix B). If it is, the herbicide will be banned. In anticipation of this possibility, Duke is currently examining other herbicides to replace metham sodium. As this search and subsequent testing and licensing may take several years, Duke wanted testing on the current SVII process to continue in order to please their customers.

II. LITERATURE REVIEW

Metham sodium and dichlobenil are widely used in agriculture as soil fumigants. Most information available about both compounds come from papers which examined their uses in soil to control weeds, fungi and insects.

A. Metham Sodium

Metham sodium, also simply called metham, is the common name of sodium N-methyldithiocarbamate (Chemical Abstract Service Number 137-42-8). Another common name is metam-sodium¹¹. Trade names include VPM⁶ (trademark of DuPont) and Vapam⁶ (trademark of Stauffer Chemical Company). Metham sodium is part of a group of compounds called carbamates. Carbamates are esters of carbamic acid (NH_2COOH) and are frequently used as fungicides and insecticides¹². They are well known as cell growth inhibitors, blocking and disrupting mitotic activity¹².

Metham sodium in its commercial form of Vapam is primarily used in agriculture as a soil fumigant prior to planting. It is effective in killing germinating seeds, rhizomes, tubers, roots and stems of weeds, as well as insects¹¹. Vapam has a wide application as a pre-treatment in soils used for lawns, seed beds, flower beds, grape vines, fruit trees and row crops¹¹. It is effective at low concentrations. It has been found to be lethal to most soil organisms at concentrations less than 10 ppm. In commercial

use, proper application is made by starting with moist cultivated soil and applying at a rate of 1 to 2 pints of Vapam (32.7% solution) per 100 square feet¹¹. Vapam is normally applied either by spraying of dilute mixtures or by mixing in irrigation water. Planting may take place 2 to 3 weeks after application.

While metham sodium is an effective herbicide itself, much of its fumigating activity in soils is due to the fact that it decomposes into methyl isothiocyanate (known by its acronym MITC and having a Chemical Abstract System number of 556-61-6)⁶. This degradation product has very strong herbicidal abilities. It is very volatile and moves quickly through the soil as a vapor. MITC⁵ has a $K_{w/g}$ partition coefficient of about 100, indicating it is very volatile. Often the ground is covered with a plastic tarpaulin following application of metham sodium to delay the escape of the gaseous MITC to the atmosphere.

Metham sodium has the molecular formula $C_2H_4S_2NNa$, and a molecular weight of 128.17. It is an aliphatic compound with the structural formula:



In its pure physical state, metham sodium is a white crystalline solid. As a solid, though, it is unstable. To allow for long term storage, the commercial formulation

Vapam is sold as a concentrated 32.7% solution in alkaline water¹¹ (pH about 9). In this state Vapam will remain stable, with only slight decomposition, for several years when stored in glass containers¹¹. Metham sodium decomposes under acidic conditions¹¹. Gray⁶ states that in dilute water solutions (near neutral pH) metham decomposes slowly over a period of several weeks.

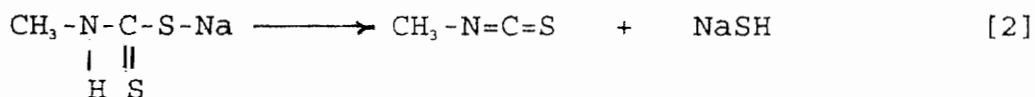
Metham sodium is readily soluble in water¹¹ with a solubility of 722 g/l at 20°C. It is sparingly soluble in acetone, xylene and kerosene, and moderately soluble in ethanol¹¹. The commercial product has a boiling point¹¹ of 110°C.

Metham sodium is a very reactive substance. It is very corrosive to aluminum metal¹¹ with a corrosion rate of 0.7 mg/day/m² in mild steel¹¹. It is toxic to humans, is a skin and eye irritant, and an inhalant hazard¹¹. Recent works suggest it may be a teratogen (see Appendix B). In animal experiments¹¹ it had an acute oral LD₅₀ in male rats of 820 mg/kg and in male mice of 285 mg/kg.

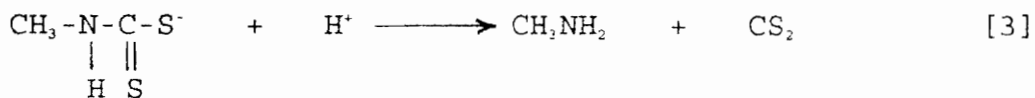
As a herbicide, metham sodium works very rapidly. Its mechanism for killing tree roots is that following absorption, some material is translocated to the vascular tissue. There it kills cells on contact¹¹. In studies of its mode of action as a fungicide¹, it was seen to perform non-specific interference with sulfhydryl enzymes in fungal

cells.

Metham sodium has a short lifetime once it is applied to soils. It breaks down in soil, usually in 1 to 8 hours, to MITC. This rate is strongly dependent upon the soil moisture content and temperature, as well as its concentration in the pore water⁵. The rate of decomposition increases at low moisture and high temperature conditions. Its decomposition is a chemical reaction rather than one mediated by soil micro-organisms¹¹. The reaction occurs in soil as follows⁶:



Under acidic conditions (pH < 5) metham sodium can be hydrolyzed to methyl amine and carbon disulfide⁴:



B. Dichlobenil

Dichlobenil is the common name for 2,6-dichlorobenzonitrile (Chemical Abstract Services Number 1194-65-6). Its trade name is Casoron¹⁰, and is available both as a powder and as granules. It is classed as a benzoic acid herbicide⁷.

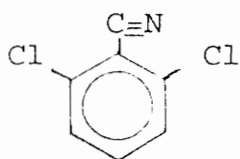
Dichlobenil is more selective than metham sodium, being

used only to control weeds, not other soil organisms. It is primarily effective against germinating seeds and young plants. Its typical use is for controlling perennial weeds, including high grasses and broadleaf species, and also for controlling aquatic weeds⁷.

Dichlobenil owes its effectiveness to absorption by roots. As such, it is applied to soils and not foliage. Application is by wettable powder or granules. Under high temperature or very dry conditions, dichlobenil can readily evaporate, so preferably it is applied under moist conditions. Soils with high humus content seem to retain dichlobenil strongly.

The herbicide is used to control weeds around bearing and non-bearing fruit trees, cranberries, ornamental plants and trees, and as a sprout inhibitor in potatoes, transplanted rice and winter wheat¹⁰. Application rates are 9 to 27 pounds per acre for total weed control in soils, and 5 to 15 pounds per acre for aquatic weed control¹⁰.

Dichlobenil is a white, crystalline solid with an aromatic odor¹⁰. Its molecular formula is $C_7H_3Cl_2N$, with a molecular weight of 172.0. It is a chlorinated benzene compound with a structural formula of:



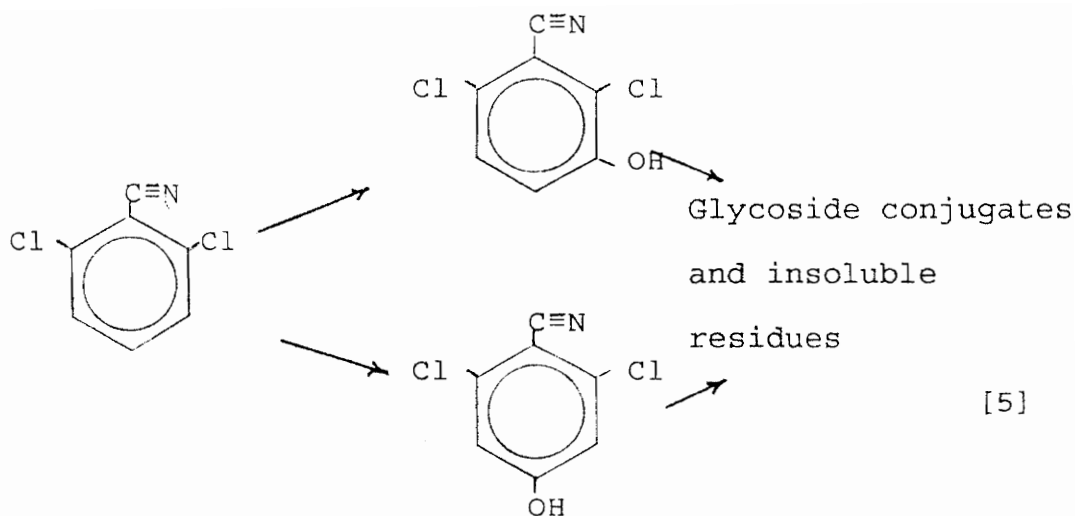
[4]

Its melting point is 145°C and boiling point 270°C at atmospheric pressure. Dichlobenil is much less soluble in water than metham sodium, its solubility being 18 ppm at 25°C. It is slightly soluble in most organic solvents¹⁰.

Dichlobenil is chemically very stable. As a suspension in water it does not deteriorate, exposure to sunlight has no effect, and it is extremely stable thermally¹⁰. It hydrolyzes only under strong acid or base conditions. Both the wettable powder and granules are essentially noncorrosive¹⁰. Its shelf life is at least two years when stored in a cool, dry place¹⁰.

When applied as a herbicide, dichlobenil is mainly absorbed by roots, where it primarily acts on growing points and root tips¹⁰. It is rapidly absorbed by roots followed by slow movement upwards in sapstream. In the cells there is a prompt cessation of growth, followed by gross disruption of the tissues. The end result is swelling and collapse of the stem, root and petiole. Cessation of photosynthesis or respiration in leaves is not evident. The addition of Ca⁺⁺ suppressed observed physiological and biochemical responses of dichlobenil in some plants⁷.

Dichlobenil can degrade after absorption into plants. Metabolism rates in roots are very low, but high in the leaves. The principal pathway for metabolism is ring hydroxylation followed by phenol conjugation⁷:



Dichlobenil is very persistent in soils. Its half life ranges from several weeks to many months, depending on local factors. High moisture content, low temperature and high amounts of humus aid in persistence. Its low water solubility favors absorption by organic matter and limits its downward mobility through soil⁷.

Dichlobenil has been seen to stop nitrification in soil⁷. Evidence of how well soil microflora adapt to dichlobenil is inconclusive, but some studies indicate that microbial activity aids in its degradation⁷.

C. Nitrification

Nitrification is the first step in biological treatment systems for the removal of ammonia. In this process, ammonium ions (NH_4^+) are first metabolized to nitrite ions (NO_2^-) then subsequently to nitrate ions (NO_3^-). Two bacteria genera are responsible for these two steps⁸. *Nitrosomonas* is responsible for the conversion of ammonium to nitrite, and *Nitrobacter* is responsible for the conversion of nitrite to nitrate.

These two genera are sensitive organisms extremely susceptible to inhibition from a variety of causes⁸. The pH of the system is significant, with an optimal range for growth being 7.5 to 8.6. Cool temperatures, low dissolved oxygen content, and lack of an inorganic carbon source can also inhibit growth.

Studies have shown that toxic compounds have a stronger inhibitory effect on nitrifying bacteria than on heterotrophic bacteria in the same systems⁹. Partially, this is due to their slower growth rate, which makes them more susceptible to washout when toxic conditions occur. Also, there is less specie diversity in nitrifying bacteria than in heterotrophic bacteria, making acclimation to changing conditions more difficult.

The nitrification process is frequently performed in

the same reactor that removes carbonaceous organic material at waste treatment plants. Levels of toxic materials which may not disrupt the removal of organic carbon may disrupt the nitrification process. This is the situation of concern in these studies. Waste treatment plants with single-stage nitrification have been having nitrification disrupted by the chemicals used in the Vaporooter II process, but without disruption of the removal of organic carbon.

III. METHODS AND MATERIALS

Determining the impact of metham sodium and dichlobenil on nitrification at waste treatment plants required research to be performed in three areas. This section will describe the facilities, equipment, materials, methods and procedures used in determining:

- °the chemical behavior of these herbicides in a sewer/waste treatment system
- °the methods for determining the concentrations of these herbicides at which nitrification is impacted
- °methods for determining the effectiveness of interception methods.

As most of what has been published on these herbicides has to do with their behavior in agricultural systems, work was performed to understand the chemical behavior of these herbicides in a sewer and waste treatment system. The causes of the degradation of metham sodium to MITC were studied to determine whether the parent compound or the degradation compound was the compound of concern. Dichlobenil is much more stable than metham sodium, and as such was assumed to be stable in a sewer system environment for the time frames of concern.

A. Facilities: Constant Temperature Room

All experiments were performed in Norris Hall at VPI&SU

in a room whose temperature was kept constant at 20°C. Materials used in these experiments were also stored in this room.

B. Equipment

pH Meter

All pH values were measured with a Fischer Accumet pH Meter, model 610A, manufactured by Fischer Scientific Corporation. The meter was calibrated before each use against known standards of pH 4, 7 and 10.

Dissolved Oxygen Meter

Dissolved oxygen was determined using a YSI Model 54 Oxygen meter, manufactured by Yellow Springs Instrumentation Corporation, Yellow Springs, Ohio 45387. Before each use, it was calibrated according to the instructions written on the back of the device. Settings were based on conditions in the constant temperature room: 20°C and 2200 feet above sea level.

Spectrophotometer

A Spectronic 20 spectrophotometer manufactured by the Milton Roy Company was used in these experiments.

Filters

The following filters were used:

Gelman 0.2 micron membrane filters, 25 mm. Catalogue number 60300

Gelman 0.45 micron membrane filters, 25 mm. Catalogue number 63068

Whatman 934-AH glass microfiber filters, 55 mm.

Catalogue number 1827 055

Balance

All weights were made on a Mettler H10 scale, Mettler Instrument Corporation, Hightstown, NJ.

Biochemical Oxygen Demand (BOD) Apparatus

A Manometric BOD Apparatus was used to observe oxygen demand in activated sludge. Model 2173A manufactured by the Hach Chemical Company was used in this procedure. The apparatus consists of five amber glass bottles, each capable of holding about 500 ml of liquid. Each bottle sets on a magnetic stirring device, and has a magnetic stirring bar inside to allow gentle mixing during the experiment. The cap of each bottle seals it from the atmosphere, and, through a tube connected to the cap, allows the air space inside to be connected to a closed end mercury manometers. As the oxygen is consumed by the bacterial processes in each bottle, carbon dioxide is produced. This carbon dioxide is

absorbed by a lithium hydroxide solution contained in the air space above the liquid. The overall effect is for pressure to be reduced in the bottle, and the mercury manometer correspondingly responds. Calibration of the manometer allows a relationship to be established between the pressure change in the bottle and the amount of BOD exerted.

C. Materials

Activated Sludge and Sewage

A number of these experiments required activated sludge, raw sewage or settled sewage. All three of these were obtained from the Stroubles Creek Waste Treatment Plant.

Activated sludge was obtained from the main aeration basin. Samples were collected in 20 liter (L) plastic carboys and promptly taken to the constant temperature room. To maintain biological activity, air was constantly bubbled through the sludge via an air diffuser. If the sludge was kept more than overnight, 10 liters was placed in a tank with air supplied through a diffuser. Once a day, approximately 2 grams of bacto-peptone was added to supply nutrients. The pH was monitored daily, and if it fell below 7, a small amount of sodium bicarbonate was added to adjust the pH to a range of 7.5 to 8.0. Activated sludge was kept

up to a week by this method.

Raw sewage was obtained from the outlet of the grit chamber, and settled sewage from the overflow weir of the primary clarifier. Samples were placed in gallon plastic bottles or 20 L carboys, depending on quantity required, and stored in the constant temperature room. Samples were kept no more than two days before use in experiments.

Metham Sodium

Duke Root Control Services provided a plastic gallon bottle of commercial Vapam (metham sodium), manufactured by Zeneca Agricultural Products, 1200 South 47th Street, Richmond, California 94804-0023. According to information printed on the bottle, the solution was 32% metham sodium. This bottle was stored in the constant temperature room in a dark cabinet.

Dichlobenil

Duke Root Control Services provided several pounds of commercial grade dichlobenil in a plastic bag. It was in the form of a powder, 50% dichlobenil - 50% inert ingredients by weight. This bag was kept in the constant temperature room in a sealed plastic box, inside a dark cabinet.

Methyl Isothiocyanate

A bottle containing 25 gram (gm) of laboratory grade MITC was obtained from Sigma Chemical Company (catalogue number M-8632). The product was a solid, consisting of small beads which tended to stick to each other. MITC is volatile, and so manufacturer's instructions were followed and the bottle stored in a refrigerator (not frozen).

Powdered Activated Carbon (PAC)

Powdered Activated Carbon (PAC) was used in experiments to adsorb metham-sodium from various solutions. To determine the proper PAC for this application, a representative of a manufacturer of PAC was contacted. A discussion was held with a customer representative of Westvaco on January 25, 1995. She suggested using their Nuchar-SA PAC. The literature describing this form of PAC is given in Appendix C. A summary of its properties as described in that literature are as follows:

It was developed to be particularly applicable for the adsorption of high molecular weight organic materials, and has a large preponderance of pores in the transitional and macro pore range. The specifications of Nuchar-SA are:

Iodine Number	900 min
Molasses Decolorizing Index	14.0 min
Filtering Time	50 - 100 sec
Moisture, As Packed	10% max
pH	4-6

Typical Properties are:

Apparent Density	21 - 23 lb/cu ft
Ash	3-6%
Surface Area (Nitrogen BET Method)	1400 - 1800 m ² /g
Total Pore Volume	2.2 - 2.5 cm ³ /g
Water Solubles	1-3%
Sieve Analysis:	
Thru 100 mesh	95 - 100%
Thru 200 mesh	85 - 95%
Thru 325 mesh	65 - 85%

Powdered Metals

Aluminum and iron powders were obtained from Fischer Scientific company. The catalogue numbers for the aluminum and iron powders were A-547 and I-62, respectively.

D. Methods and Procedures

Colorimetric Method for Determining Metham Sodium Concentrations in Solutions

A simple colorimetric method was used to determine the concentration of metham sodium in water solutions, raw and settled sewage, and activated sludge. This method has been described by Gray⁶. It is based on the yellow color produced when dilute cupric chloride is added to a solution containing metham sodium. The reagent used to make this yellow color was composed of 0.5 gm of cupric chloride (CuCl₂) dissolved in a mixture of 75 milli-liter (mL) distilled water and 25 mL glacial acetic acid.

The method suggested by Gray uses a blue filter with a

400 to 465 nanometer (nm) range in a Klett-Summerson photoelectric colorimeter. The spectrophotometer used here could be set to an exact wavelength. A frequency of 420 nm was chosen as a frequency representative of that used by Gray.

To calibrate the spectrophotometer to metham sodium concentration, standard concentrations of metham sodium from 0 to 80 ppm were developed. Into separate half-inch glass tubes, 5 mL of each standard solution was placed along with 0.5 mL of reagent. The tube was gently agitated, then its transmittance read within one minute. Transmittance must be read promptly as the solution will form a precipitate after about one minute, which introduces an error into the reading. Transmittance was mathematically converted to absorbance by the relationship:

$$A = -\log(T/100) \quad [6]$$

where A = absorbance

T = transmissivity in percent.

A plot of absorbance versus metham sodium concentration was made, and is shown in Figure 1, with the data points shown in Table 1.

Concentrations above 100 ppm could not be directly measure with this method. At these concentrations, the solution promptly formed a precipitate, which turned the solution cloudy. To avoid this problem, during experiments

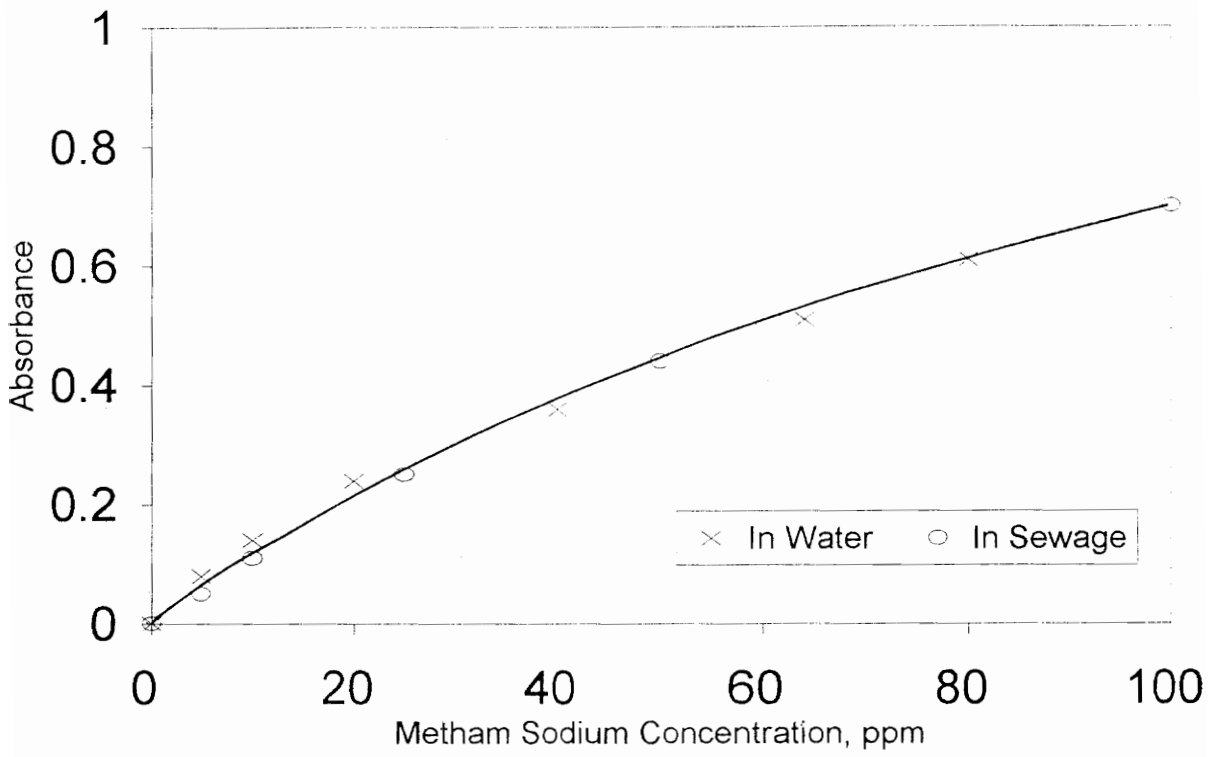


Figure 1. Light Absorbance vs. Metham Sodium Concentration in Water and Raw Sewage

Table 1
Calibration of Spectrophotometer

Metham Sodium Concentration in Water

<u>ppm</u>	<u>Absorbance</u>
0	0
5	0.08
10	0.14
20	0.24
40	0.36
64	0.51
80	0.61

Metham Sodium Concentration in Settled Sewage

<u>ppm</u>	<u>Absorbance</u>
0	0
5	0.05
10	0.11
25	0.25
50	0.44
100	0.70

where metham concentrations were anticipated to be greater than 80 ppm, the samples were diluted before testing. The resulting measured concentration was then multiplied by the dilution factor.

Similar standard solutions were made using settled sewage as the diluent. Metham sodium was added to settled sewage at known concentrations. The solution was filtered through a 0.45 micron filter and the transmittance read. The resulting absorbance was plotted versus metham sodium concentration and was found to be the same as for distilled water. These points are also shown in Figure 1 and given in Table 1.

Experimental data was obtained by adding 0.5 mL reagent to 5 mL of test sample and promptly reading the transmissivity. The metham sodium concentration was determined using Figure 1 for the corresponding absorbance. For experiments containing suspended solids, such as settled sewage, raw sewage and activated sludge, a Gelman 0.45 micron filter was used to filter the solution before the reagent was added. This was found to be acceptable. However, in experiments where PAC was also included in the solution, enough carbon fines passed through this filter to cause interference. Not only did the residual carbon cause additional light absorbance, but also prompted a precipitate to quickly form and turn the solution too cloudy to read.

To address this situation, a Gelman 0.2 micron filter was used instead of the 0.45 micron filter. This resolved some of the differences. Above 30 ppm concentrations, though, a precipitate still quickly formed. This was overcome by diluting the sample and multiplying the determined metham sodium concentration by the dilution factor.

MLSS and MLVSS Determination

Mixed Liquor Suspended Solids (MLSS) and Mixed Liquor Volatile Suspended Solids (MLVSS) were determined routinely for the activated sludge according the procedure 2540 B of *Standard Methods*¹. Suspended solids were measured each day activated sludge was used. The procedure involved cleaning Whatman 934-AH filters with distilled water then drying them in a 550°C furnace. Measured amounts of activated sludge were drawn by a vacuum pump through the filter, then the filter with solids was dried at 110°C to determine the total suspended solids (TSS). After weighing, the organic solids were burned off the filter at 550°C. The filter with solids was weighed following each step. The MLSS were determined by:

$$\text{MLSS (mg/L)} = (B - A)/V \times 10^6 \quad [7]$$

where A = weight of clean dry filter (g)

B = weight of dry filter after 110°C drying (g)

V = volume of activated sludge in sample (mL)

The MLVSS were determined by:

$$\text{MLVSS (mg/L)} = (C - B)/V \times 10^6 \quad [8]$$

where C = weight of filter after 550°C drying (g)

B and V are as for MLSS

Settleable Solids

The settleable solids concentration in raw sewage was measured with an Imhoff cone. The procedure given in Section 2540 F of *Standard Methods*¹ was used. One liter of raw sewage was placed in an Imhoff cone and allowed to settle for 45 minutes. At that time, the sides were scraped with a spatula, being careful not to disturb the already settled material. The contents were then allowed to settle an additional 15 minutes. The cone is calibrated to indicate the number of mL of solids settled in the bottom. Results are reported as mL of settleable solids per liter of sewage.

Dilution of Metham Sodium

Quantities of metham sodium were obtained from the bottle of Vapam supplied by Duke and diluted to desired concentrations. The dilute concentration, C, was determined by:

$$C \text{ (ppm)} = (v * 320)/V$$

where v = mL of metham sodium

V = L of dilute solution produced

320 = number of mg/mL of metham sodium in a
32% solution

To produce concentrations below 1600 ppm, a high concentration solution of metham sodium was first produced, then this solution was further diluted. For example, 5 mL of Vapam diluted in 1 liter produced a 1600 ppm solution. One hundred mL of this solution plus 100 mL of distilled water created an 800 ppm solution. One hundred mL of this solution plus 100 mL of distilled water created a 400 ppm solution, and so forth. Typically a Class A transfer pipette and a Class A volumetric flask were used to make the initial dilution. Volumes in further dilutions were measured using graduated cylinders, or with graduated pipettes when less than 10 mL of sample was being handled. For safety, dilutions were performed under a ventilation hood.

Measurement of Dichlobenil

As this was a dry powder, samples were simply removed from the bag and weighed as needed. They were not premixed with any liquid, but added directly into the activated sludge used for the various experiments.

Dilution of MITC

The MITC beads did not easily dissolve directly in water. When needed in solution, small amounts were carefully weighed and then dissolved in a beaker containing a small amount of methanol. This was gently agitated until the MITC had dissolved. Water was then added to this solution to obtain the desired concentration.

Oxygen Demand in Activated Sludge

For these experiments, activated sludge was placed into each bottle of the Hach BOD Manometric apparatus. Typically 160 mL of activated sludge was used, along with measured amounts of ammonium chloride (NH_4Cl) as an ammonia source, and desired concentrations of metham sodium. The apparatus was kept in the constant temperature room and allowed to run for up to several days.

Theoretically, the bottles with the increased amount of ammonia would draw a higher BOD. A relationship between ammonia concentration and BOD could be measured. By placing varied amounts of metham sodium in the bottles, the concentration of metham sodium at which nitrification is lost would be evident by the observation that oxygen consumption would be the same as when no added ammonia was present.

Timed Studies of Metham Sodium Degradation

Experiments were run to determine the degradation rates of metham sodium in the presence of acid, base, metals and a metal oxide. Each of these were run in a similar manner.

To determine the degradation rate in the presence of acids and bases, a 50 ppm solution of metham sodium in tap water was prepared. Two hundred mL of solution was placed into 250 mL flasks, which were then covered with aluminum foil to minimize evaporation. Using sulfuric acid (H_2SO_4) or potassium hydroxide (KOH), the pH was adjusted to values ranging from 4 to 11.

The solutions were allowed to sit for 48 hours. Periodically, 5 mL samples were taken from each flask and the amount of metham sodium still present measured using a colorimeter. Using this data, a plot of metham sodium concentration versus time was developed. Also, the pH of each flask was measured at the end of the experiment and compared to the starting value.

A similar experiment was run to determine the degradation rates of metham sodium in the presence of metals and a metal oxide. Solutions of 50 ppm metham sodium in tap water were prepared. Into three flasks, a small quantity (about enough to cover half the bottom) of iron powder, aluminum powder or ferric oxide (Fe_2O_3) was added. The 50 ppm solution was then added to the flasks. Over a

period of 48 hours the concentration of metham sodium was periodically measured with a colorimeter. Samples from the ferric oxide containing flask were filtered through a Gelman 0.45 micron filter before testing with the colorimeter to remove ferric oxide particles suspended in water. The samples with iron and aluminum powder did not need filtering. The data was used to produce a plot of metham sodium concentration as a function of time.

Degradation of Metham Sodium in Presence and Absence of Air

Gray⁶ stated that metham sodium in dilute solutions degrades over a period of several weeks. Experiments were run to determine if the presence or absence of oxygen had any impact on the degradation rate.

One liter glass bottles were used for this experiment. They were kept in the constant temperature room, and covered with aluminum foil to prevent any possible photolysis from occurring. To prepare an oxygen free solution, 950 mL of tap water was placed into one of the bottles. Nitrogen gas was then bubbled through this water until an oxygen probe indicated less than 0.8 mg/L of oxygen remained in the water. Promptly, a 50 mL aliquot of 1000 ppm metham sodium solution was added (giving a 50 ppm solution). The bottle was then capped with a rubber stopper. Through the stopper ran a glass tube connected to a bottle of nitrogen gas.

(The inside end of the glass tube was *not* immersed in the solution to prevent bubbling nitrogen gas from stripping metham sodium from solution.) Nitrogen gas was then allowed to slowly flow into the bottle to provide a nitrogen blanket. The gas exited through a second tube, the far end of which was immersed in a beaker of water. Bubbles from the exit tube were monitored to ensure a constant gas flow was maintained.

A second one liter bottle was prepared, also with 950 mL of tap water and a 50 mL aliquot of 1000 ppm metham sodium, giving a 50 ppm solution. Oxygen was not removed from this water, and the bottle was left open to the atmosphere.

Periodically over the course of a week, samples were removed from both bottles with a pipette and the amount of metham sodium present measured with a colorimeter. This data was used to create a plot of metham sodium concentration as a function of time.

Degradation of Metham Sodium by Microbial Action

Experiments were developed to determine if microbial action causes degradation of metham sodium in a sewage/waste treatment environment. Seven amber, narrow necked bottles, each with 200 mL of activated sludge and 10 ppm of metham sodium, were used to determine if metham sodium is

metabolized. The bottles simulated anoxic, anaerobic and aerobic conditions, containing either activated sludge only or a 50/50 mixture of activated sludge and settled sewage. A seventh bottle provided a tap water blank.

Seven bottles were set up as follows, each having 10 ppm metham sodium added to the solution:

- 1) Anoxic Activated Sludge: 200 mL activated sludge + 20 ppm NO_3^- (from KNO_3). N_2 gas was first bubbled through the sludge to remove dissolved oxygen, then the solution was kept under a nitrogen blanket.
- 2) Anoxic Activated Sludge + Settled Sewage: same as in bottle 1 except using 100 mL activated sludge + 100 mL settled sewage.
- 3) Anaerobic Activated Sludge: 200 mL activated sludge from which dissolved oxygen was removed by bubbling nitrogen gas through it. The bottle was sealed under a nitrogen blanket.
- 4) Anaerobic Activated Sludge + Settled Sewage: same as in bottle 3 except using 100 mL activated sludge + 100 mL settled sewage
- 5) Aerobic Activated Sludge: 200 mL activated sludge kept aerated by bubbling air through the solution
- 6) Aerobic Activated Sludge + Settled Sewage: same as in bottle 5 except using 100 mL activated sludge + 100 mL settled sewage

7) Tap water: 200 mL tap water in an open container as a control

The seven bottles sat in the temperature controlled room for just over 24 hours. The concentration of metham sodium was measured periodically in each bottle using the colorimetric method. The resulting data was used to show metham sodium concentration as a function of time.

Determination of Ammonia Nitrogen Concentrations

The titrimetric method described in Section 4500-NH₃ E of *Standard Methods*¹ was used to determine ammonia nitrogen concentrations. The solutions mentioned here were prepared according to the instructions given in this method.

Distillation flasks are first cleaned, filled with about 150 mL tap water to which several drops of 1N NaOH were added. The flasks were then placed on distillation heaters and allowed to boil for about 20 minutes. The flasks were then rinsed with tap water.

The activated sludge to be tested was prepared by passing it through a clean Whatman 934-AH filter, pulled by a vacuum pump. The filtrate was collected, and 70 mL placed in a prepared distillation flask. To each flask was also added 10 mL prepared borate buffer and 70 mL ammonia free water. One distillation flask was prepared with just 140 mL ammonia free water and 10 mL Borate Buffer to act as a

control blank.

After each flask was filled, its pH was measured. The pH was then adjusted to a value equal to or greater than 9.5 by adding drops of 1N NaOH, then the flask promptly placed on a distillation heater. The distillate was collected in 100 mL beakers containing 20 mL of Boric Acid Indicating Solution.

After distillation, the collected distillate was titrated against 0.02N sulfuric acid (H_2SO_4). The amount of ammonia in solution was determined by the relationship:

$$\text{ppm } NH_4\text{-N} = (A-B) \times 280/V \quad [9]$$

where A = mL 0.02N H_2SO_4 titrated for the sample

B = mL 0.02N H_2SO_4 titrated for the blank

V = mL of sample

Determination of Total Kjeldahl Nitrogen (TKN)

The procedure given in section 4500- N_{org} B., Macro Kjeldahl Method, of *Standard Methods*¹ was used to determine TKN concentrations. The solutions used here were prepared according to the instructions given in this section.

For each determination of TKN, 50 ml of sample was placed in a Kjeldahl digestion flask along with several glass and teflon beads. To the sample was added 10 ml of digestion reagent and the sample swirled to mix. The flask was then placed on a burner under a ventilation hood.

Medium heat was applied until the water had boiled off and white fumes had formed. At this time the heat was increased to a high setting and the sample heated for 30 minutes. Heat was then removed and the flask allowed to cool.

Ammonia free water was added to each flask and the contents swirled. The mixture was then poured into ammonia distillation flasks. This was repeated until all sample material was dissolved and removed. The total amount of ammonia free water used for each sample was 100 ml.

To each ammonia distillation flask was added 10 ml of the prescribed sodium hydroxide/ sodium thiosulfate solution. The mixture was swirled and the flask promptly placed on a distillation apparatus. The mixture was heated and the distillate collected in 100 mL beakers containing 20 mL of Boric Acid Indicating Solution.

After distillation, the collected distillate was titrated against 0.02N sulfuric acid (H_2SO_4). The amount of TKN in solution was determined by the relation:

$$\text{ppm TKN} = (A-B) \times 280/V \quad [10]$$

where A = mL .02N H_2SO_4 titrated for the sample

B = mL .02N H_2SO_4 titrated for the blank

V = mL of sample

Nitrite and Nitrate Concentration Determination

The concentration of nitrite (NO_2^-) and nitrate (NO_3^-)

were determined with a Dionex Advanced Chromatography Module. Standard samples of 20 ppm nitrite-nitrogen and nitrate-nitrogen were used to calibrate the machine.

Samples were filtered through a 0.2 micron filter before injection. The software with the chromatograph integrates the resulting peaks. The ratio of the area under the peak for each ion to the area under the corresponding peak in the standard sample was determined. This ratio was then multiplied by 20 ppm to determine the concentration of nitrite-nitrogen or nitrate-nitrogen, as applicable, in the sample.

Batch Reactors

Batch reactors were used to determine the concentration of metham sodium at which nitrification was impacted. Each reactor was comprised of a beaker into which 300 mL of activated sludge was placed. Air was bubbled through each beaker through an air diffuser to provide both oxygen content and thorough mixing to the solution. Stock solutions of ammonium chloride (NH_4Cl) and sodium bicarbonate (NaHCO_3) were prepared so that 1 mL of each, when placed in the reactor, gave a concentration of 20 ppm ammonia nitrogen and 100 ppm bicarbonate. Dilute metham sodium or measured dichlobenil powder was added to give the desired herbicide concentration.

Each reactor sat in the constant temperature room overnight (12-16 hours). At that time, the contents of each beaker was filtered through a Whatman 934-AH filter, pulled by a vacuum pump, and the filtrate collected. The ammonia content of the filtrate was then determined by the ammonia distillation process. The dissolved ammonia would have been consumed by nitrifying bacteria if the metham sodium had no impact on the process. Dissolved ammonia would still be present if nitrification was inhibited. The use of a vacuum pump should not influence the amount of ammonia-nitrogen in solution, as any volatile ammonia would have already been stripped from solution by the air diffusing in the batch reactor. The ammonium ion would remain in solution, and is the dominant form of ammonia at the pH ranges studied here.

The pH of the solution was measured at the start and end of the experiment. The ideal pH for nitrification is 8 to 8.5. If the pH was significantly greater than this, the batch was discarded and a new batch made with less bicarbonate. This was to prevent the ammonium ion (NH_4^+) from converting to free ammonia (NH_3), which occurs to a great extent at pH greater than 9. At equilibrium conditions, in a solution at pH 8.5, 8% of the ammonium ion converts to free ammonia, and 5% converts at a pH of 8.0. Free ammonia can be toxic to the nitrifiers in solution, and also could be removed from solution by the forced air

diffusing through the batch. In both situations, final measured ammonia values would be misleading.

PAC Adsorption Isotherms

Freundlich Isotherms were determined for the adsorption of metham sodium by Powdered Activated Carbon (PAC). This was performed for solutions separately using water and raw sewage as diluent.

Solutions were made of metham sodium to desired concentrations. Into 250 mL flasks, 100 mL of solution and carefully weighed amounts of PAC were placed. The flasks were capped with aluminum foil to minimize spillage, then placed on a shaker table. The shaking speed was set at approximately 100 displacements per minute.

First, a set of timed experiments was performed. Shaking typically occurred over a period of 18 to 24 hours. Samples were periodically taken from each flask, filtered through a 0.2 micron filter, and the amount of metham sodium still in solution measured with a colorimeter. The time required to reach equilibrium was determined by this method.

After the time required to reach equilibrium was determined, additional experiments were repeated using different metham sodium concentrations and PAC concentrations. All experiments were run until equilibrium was reached. The resulting data was subsequently to derive

the coefficients for the Freundlich isotherm equation:

$$X/M = K_f C_e^{1/n} \quad [11]$$

where:

$$X = \text{amount of metham sodium adsorbed} = X_i - X_f \quad [12]$$

where: X_i = initial amount in solution, in mg/L

X_f = final amount in solution, in mg/L

M = concentration of PAC in mg/L

C_e = the amount of metham sodium left in solution.

$K_f, 1/n$ = empirical constants

Bench Scale Models of the Interception of Metham Sodium by PAC in Raw Sewage

A bench scale apparatus was set up to simulate PAC being applied to raw sewage to intercept metham sodium in solution, followed by sedimentation and activated sludge treatment. The occurrence of nitrification was determined and related to the ratio of the concentration of metham sodium originally present to the amount of PAC applied.

To perform this experiment, 100 mL samples of raw sewage were placed in 250 mL flasks and dosed with metham sodium and PAC, the same procedure used to determine Freundlich Isotherms. These solutions were placed on a shaker table and agitated for four hours. This was to simulate the mixing of PAC in the raw sewage during transfer through the collection system.

Duplicates of each mixture were made and simultaneously shaken. At the end of the four hours of shaking, the duplicate samples were mixed together, creating a single 200 ml sample. (Two separate flasks for each sample was used because the required quantity of each mixture was greater than could be placed in a single mixing flask.)

At the end of the four hours of shaking, 5 mL samples were withdrawn, filtered through a 0.2 micron filter, and the residual amount of metham sodium determined colorimetrically.

The remaining solution was poured into Nessler tubes, which are glass tubes about one-half inch in diameter, filled to a depth of 12 inches. These were allowed to sit in the tubes for one hour, during which time most of the PAC and much of the settleable solids settled to the bottom. This procedure was performed to simulate the settling which occurs in a primary clarifier. As each Nessler tube held 100 ml, two Nessler tubes were used for each sample. To enhance settling, the pH in each tube was adjusted to a value between 7 and 8 by adding a few drops of 1N sulfuric acid (H_2SO_4). The pH tended to be around 9 without adjustment because of the buffers in the Vapam. Poor settling characteristics were observed when the pH was this high.

After settling, 75 mL of liquid was extracted from the

top of one Nessler tube per sample using a 25 mL pipette, being careful not to disturb the settled material in the bottom of the tube. This extracted liquid was placed in a beaker containing activated sludge, so that the final mixture was 25% settled sewage, and 75% activated sludge. (Note: the activated sludge had been allowed to settle and some clear liquid tapped off to concentrate the solids to achieve a final settled sewage/activated sludge mixture having an MLSS concentration of about 2000 mg/L.)

From the second set of Nessler tubes, 50 ml samples were taken and used to determine the TKN of each settled sewage/PAC mixture.

Air was bubbled through the sewage/sludge mixture using an air diffuser, and the mixture allowed to react overnight (about 12 hours). The next morning the concentration of ammonia, nitrite and nitrate nitrogen, and soluble TKN in each batch reactor was determined.

One control batch was run simultaneously with these using settled raw sewage with neither PAC nor metham sodium added. This was to determine the amount of nitrification that should be expected if metham sodium and PAC did not influence nitrification.

Also, the amount of metham sodium dissolved in each batch reactor was colorimetrically measured at the end of each overnight test.

IV. RESULTS

Experimental results provided information regarding:

- ° the means by which and rates at which metham sodium chemically degrades
- ° the means by which and rates at which metham sodium biologically degrades by heterotrophic activity
- ° the toxicity of metham sodium, MITC and dichlobenil to nitrifying bacteria
- ° the ability of powdered activated carbon (PAC) to adsorb metham sodium from solution
- ° the ability of PAC to intercept metham sodium in a waste stream and reduce its impact on nitrification

A. Chemical Degradation of Metham Sodium

The first set of experiments involved examining the degradation of metham sodium in water solutions. Results distinguished several factors which did or did not influence degradation.

Effects of pH on Metham Sodium Concentrations in Water

Dilute solutions of metham sodium were created under acid, neutral and alkaline conditions. Eight solutions were created with pH values ranging from 4 to 11. Over a period of 46 hours, the concentration and pH in each solution were measured. Figure 2 shows the change in metham sodium

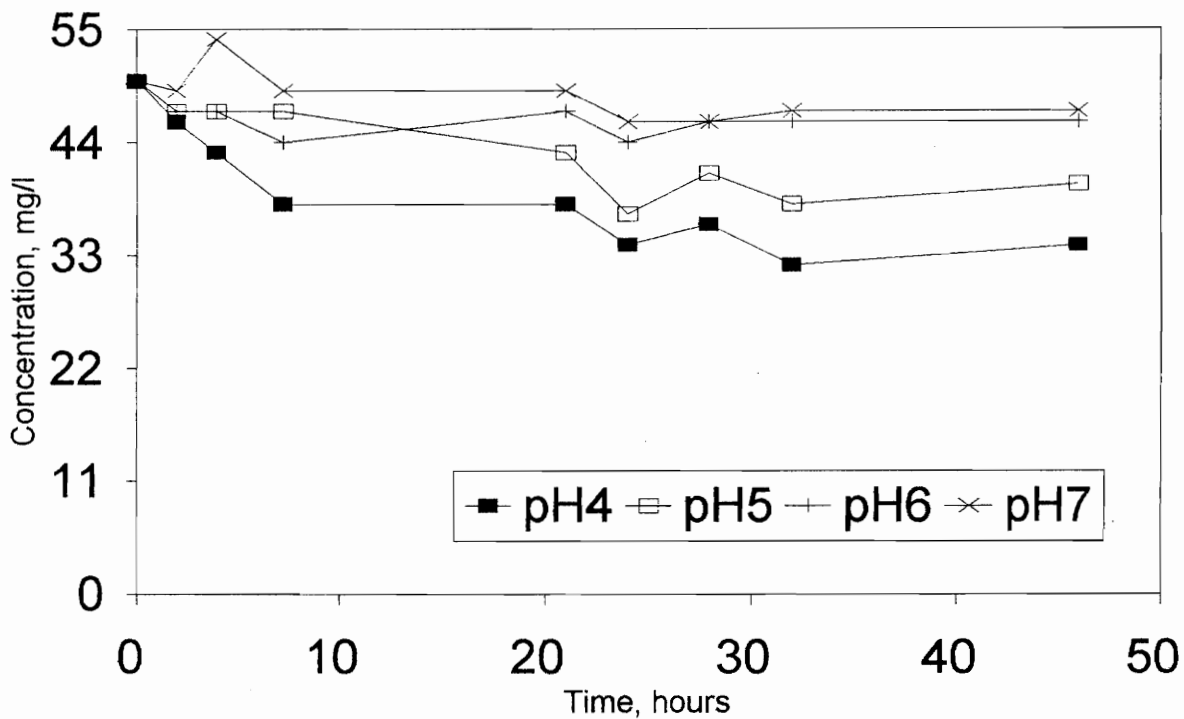


Figure 2. Chemical Degradation of Metham Sodium at Acidic and Neutral Conditions

concentration with time in the acid to neutral ($\text{pH} \leq 7$) solutions. Figure 3 shows similar data for the alkaline ($\text{pH} > 7$) solutions. Table 2 gives pH values at the beginning, at 5 hours and at the final time of the experiment. The data in these two figures show that at a pH range of about 6 to 10, little change in concentration occurred. Concentrations changed less than 4 mg/L over 46 hours. The corresponding pH values over time also changed little, and these generally toward neutral conditions. The only exception was that the solution which started at pH 7 ended at pH 7.8.

In solutions where the initial pH was less than 6, changes in concentration were more evident, along with significant changes in pH. The solution with initial pH of 4 had a concentration change from 50 mg/L to 38 mg/L in 7 hours, then changed only another 4 mg/L over the next 39 hours. This solution had a final pH of 6.31, the largest pH change of all solutions.

The solution at initial pH of 11 degraded continually over the time of the experiment. The concentration changed from 50 mg/L to 29 mg/L in 46 hours. The rate was steady, with leveling off of concentration evident only after about 35 hours. The pH changed, but only from 11.01 to 10.16.

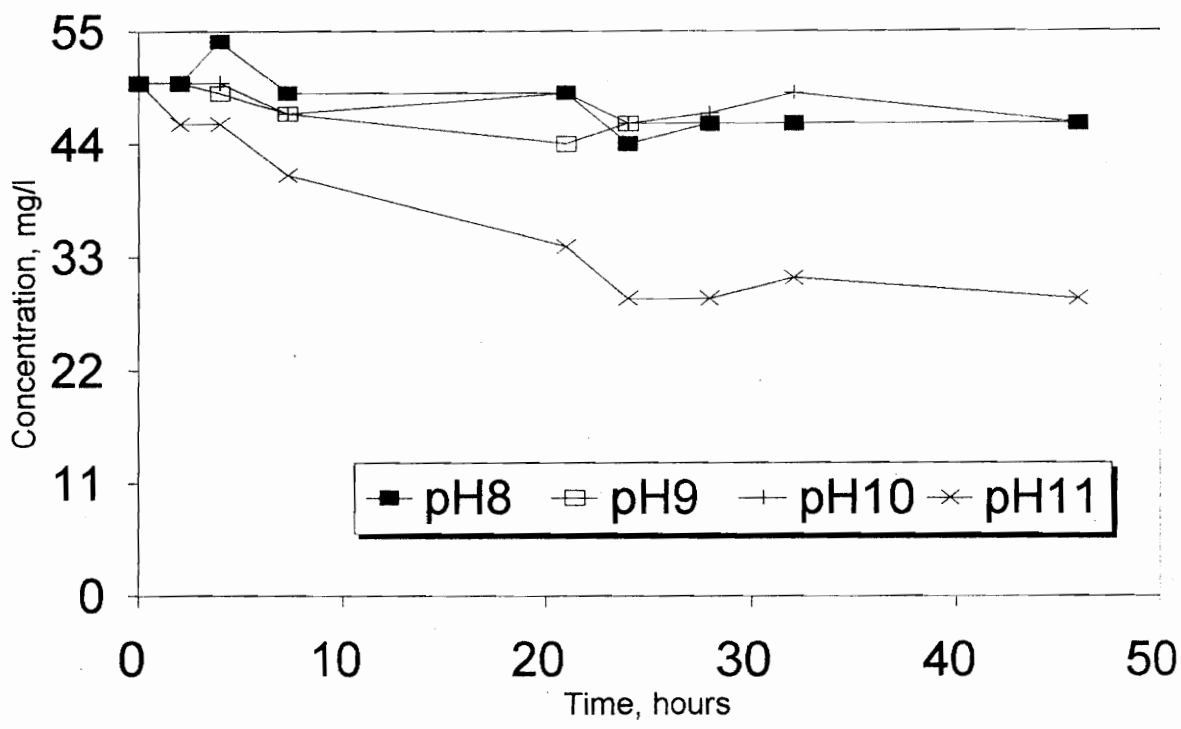


Figure 3. Chemical Degradation of Metham Sodium at Alkaline Conditions

Table 2

Measured pH of Metham Sodium Solutions
under Acidic and Alkaline Conditions

<u>Nominal</u> <u>Initial pH</u>	<u>Measured</u> <u>Initial pH</u>	<u>pH at</u> <u>5 hours</u>	<u>pH at</u> <u>46 hours</u>
4	3.98	4.58	6.31
5	5.03	5.29	6.68
6	6.03	6.15	7.19
7	7.01	6.99	7.79
8	8.00	7.87	8.11
9	9.04	8.88	8.24
10	10.02	9.95	9.12
11	11.01	10.91	10.16

Effects of the Presence and Absence of Dissolved Oxygen

Figure 4 shows the results of an experiment to determine if the presence or absence of dissolved oxygen has an effect on the degradation of metham sodium. The figure shows two lines, one for the concentrations of metham sodium in an oxygen free solution and kept under a nitrogen blanket, the second shows the concentration in a similar solution but exposed to the atmosphere. The experiment was run at near neutral (pH = 7) conditions by adding small amounts of sulfuric acid to counter the alkaline buffers present in Vapam. The pH was monitored over the course of the experiment and small amounts of sulfuric acid periodically added to keep pH near 7. About the same amount of acid was added to both bottles. This addition may have been ill advised. The concentration decreased after each acid addition, and so the change observed in both bottles was most likely due to the reaction of metham sodium with the acid.

The changes in concentration with time were similar for the two conditions. For the first forty eight hours, the concentrations were nearly identical. As the experiment was allowed to run for several more days, the concentration became slightly lower in the beaker open to the atmosphere compared to the one in the closed container. Evaporation was not strictly controlled in the solution with oxygen

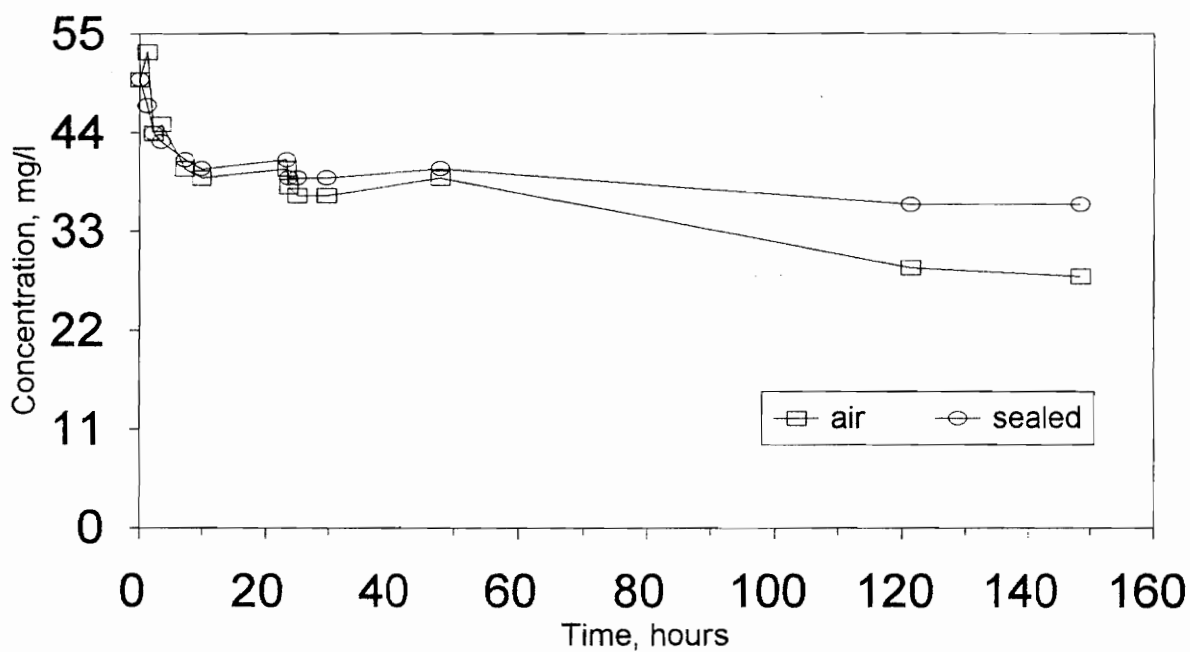


Figure 4. The Effect of Dissolved Oxygen on the Chemical Degradation of Metham Sodium

present, which is the likely cause for the difference in concentration at the latter times.

Dissolved oxygen was measured at the start and end of the experiment in the low oxygen bottle. At the start, 0.8 mg/L of oxygen was present. After 148 hours (about 6 days) the oxygen concentration was 1.4 mg/L. The oxygen in the bottle open to the atmosphere was measured at 7.7 mg/L at the end of the experiment, about what was present at the beginning.

Effects of the Presence of Iron, Aluminum and Ferric Oxide

Powdered iron, powdered aluminum and powdered ferric oxide were added to solutions containing about 50 mg/L of metham sodium. The concentration in each solution was measured over one to two day periods.

The solutions with powdered iron and aluminum changed concentration by only about 4 mg/L over a period of thirty hours (see Appendix E). This was the amount seen in the experiments investigating degradation at near-neutral pH ranges. Thus, it can be concluded that the presence of these materials did little to degrade metham sodium.

The concentration in the presence of ferric oxide changed substantially, though. The results of this experiment are shown in Figure 5. It can be seen in this figure that metham sodium degraded as a first order reaction

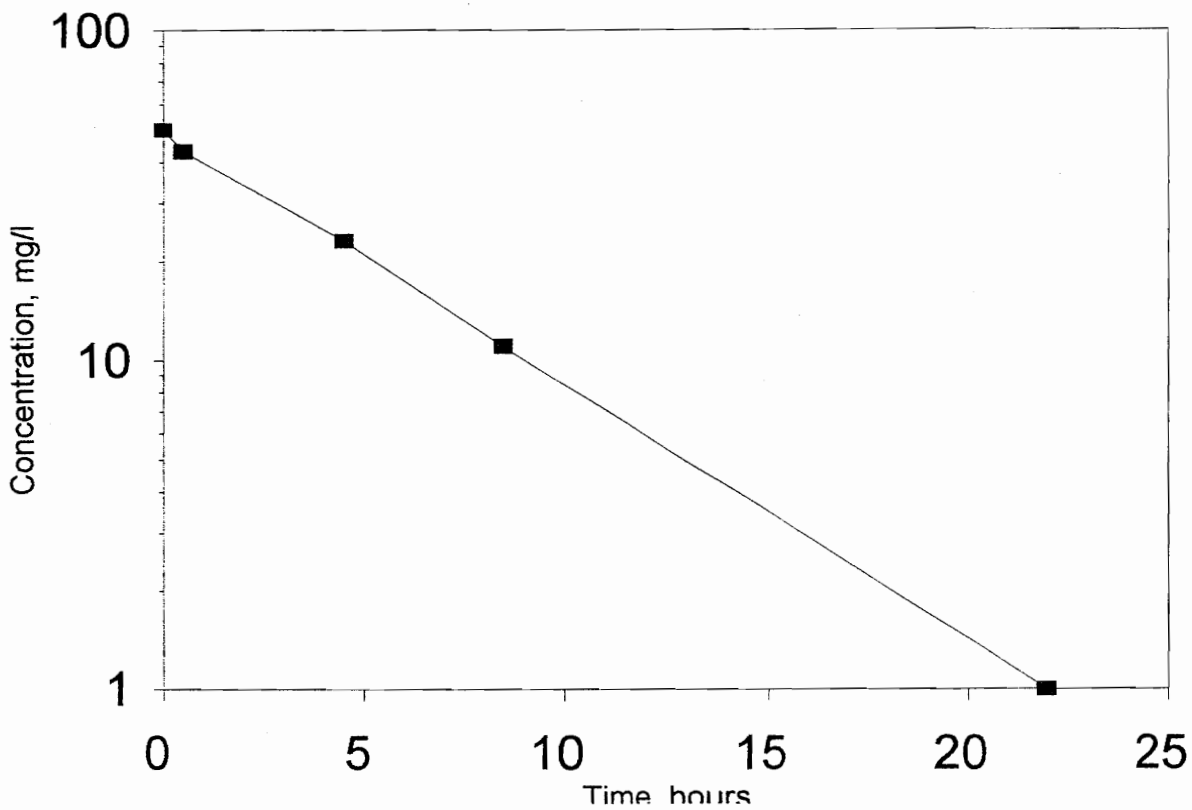


Figure 5. Metham Sodium Removal by Ferric Oxide

with a half life of 4 hours. No measurable amount of metham was discernable after 22 hours.

B. Biological Degradation of Metham Sodium

Experiments were performed to determine if heterotrophic activity in activated sludge would biologically degrade metham sodium. Reactors were set up to simulate anaerobic, anoxic and aerobic conditions. Some contained only activated sludge, while some contained 50/50 mixtures of activated sludge and settled sewage.

The initial metham sodium concentration in each reactor was initially set at 10 mg/L. This was chosen as a concentration that, according to Anlab², does not impact heterotrophic activity. Each reactor was allowed to operate for 28 hours.

Table 3 shows the measured metham sodium concentrations with time. No change in concentration was seen under anoxic or anaerobic conditions. Some loss was seen in the tap water blank, most likely due to evaporation. However, under aerobic conditions, metham sodium was degraded from 10 to 2 mg/L in just over a day. Whether metham sodium was consumed or chemically changed was not evident in these tests as no tests were made to check for by-products. However, the effect appeared to be due to microbial activity, as the change was significantly different than what was observed in

Table 3 - Degradation of Metham Sodium by
Heterotrophic Bacteria

<u>Reactor Conditions</u>	<u>Concentration of Metham Sodium, mg/L</u>		
	<u>17 hours</u>	<u>21 hours</u>	<u>28 hours</u>
Anoxic sludge	10	10	9
Anoxic sludge+ settled sewage	10	10	10
Anaerobic sludge	10	10	10
Anaerobic sludge+ settled sewage	10	10	10
Aerobic sludge	6	2	2
Aerobic sludge+ settled sewage	6	4	2
Tap water blank	10	8	7

Initial concentration in each reactor was 10 mg/L

the tap water blank.

C. Toxicity to Nitrifying Bacteria

The concentrations at which metham sodium, MITC and dichlobenil impacted nitrification were determined in batch tests. Small reactors were set up with activated sludge which contained active nitrifying bacteria. Into each reactor was placed a quantity of chemical ammonia (in the form of ammonia chloride), bicarbonate for a carbon source, and various amounts of herbicides. If nitrification was not impacted by the presence of the herbicide, all ammonia would be consumed by the bacteria during an overnight test, based on control experiments. If nitrification was impacted, the original amount of ammonia would still be present. Partial amounts of residual ammonia would indicate that nitrification was impacted, but the reactor had some ability to recover.

Impact of Metham Sodium

Batch reactors of activated sludge tested the impact of metham sodium at concentrations between 0 and 48 mg/L. Metham sodium caused a complete loss of nitrification at concentrations 8 mg/L and above. Between 4 and 8 mg/L, nitrification was incomplete, whereas below 4 mg/L nitrification was not impacted. This is illustrated in

Figure 6.

Table 4 gives pertinent data for one set of experiments examining metham sodium concentrations from 0 to 8.5 mg/L. The activated sludge had a solids concentration of 2174 mg/L, typical for samples obtained from Stroubles Creek Waste Treatment Plant. The activated sludge as obtained had a pH of 7.6. The addition of bicarbonate to the sludge buffered the solution to an initial pH of 8.3.

In the reactor with a metham sodium concentration of 8.5 mg/L the pH was essentially unchanged after sitting overnight, and the initial amount of ammonia added was nearly all still present. This is consistent with what had been seen in other batch tests where concentrations of 8 mg/L and above prevented nitrification from occurring. Below 4 mg/L, no ammonia was present after sitting overnight, and the pH had changed from 8.3 to 7.7. This indicates the nitrifying process was not impacted. The decreased value of pH indicates that bicarbonate had been consumed and the sludge returned to its original pH.

At 4.3 mg/L, some ammonia nitrogen was still measured. A significant fraction had been consumed, but the process had not accomplished full consumption of the ammonia. This data suggests that between 4 and 8 mg/L the nitrification process was inhibited, but not fully stopped.

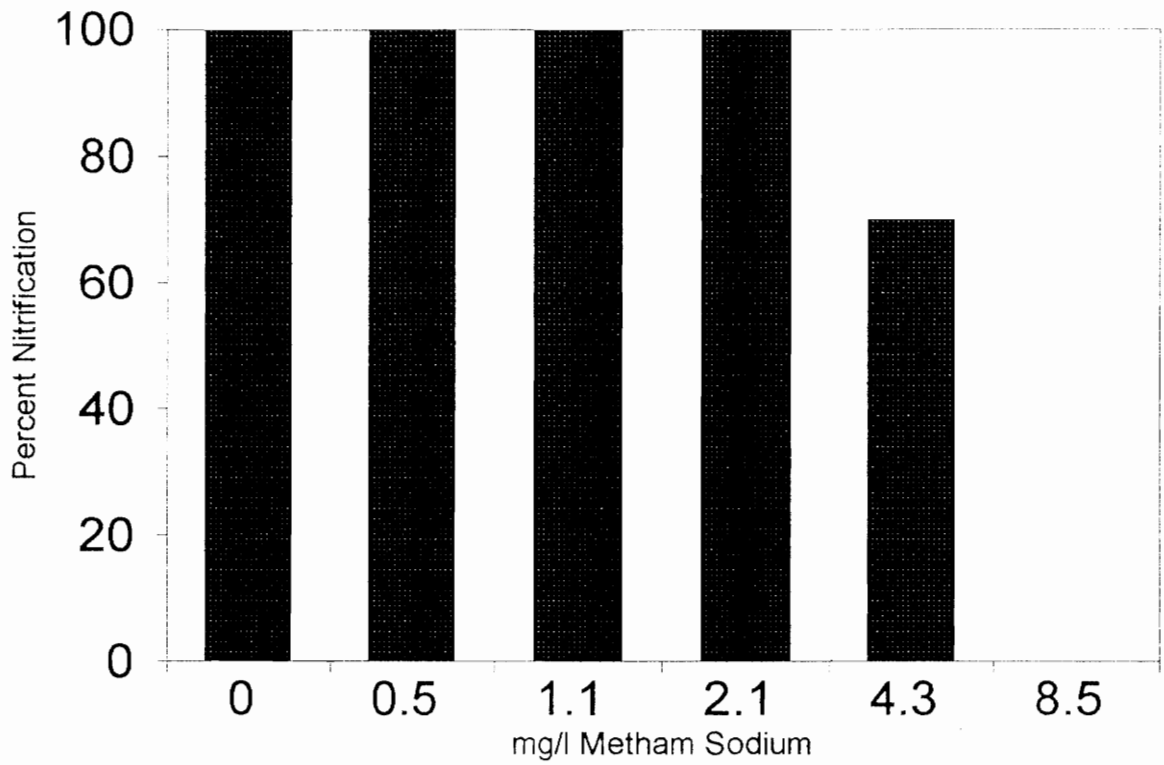


Figure 6. Impact of Metham Sodium on Nitrification

Table 4 -Test Conditions for Experiment Studying the
Effect of Metham Sodium on Nitrification

Activated sludge: MLSS = 2170 mg/L
 pH = 7.6
 date of test: Sept 15-16, 1994
 time of reaction: 17 hours

To each Reactor: 20 mg/L NH₄-N added chemically
 100 mg/L bicarbonate added chemically

<u>Metham mg/L</u>	<u>Initial pH</u>	<u>Final pH</u>	<u>Final NH₃-N (mg/L)</u>	<u>% Nitrification</u>
8.5	8.28	8.36	18.5	0
4.3	8.26	8.29	5.6	70
2.1	8.39	7.70	0	100
1.1	8.28	7.68	0	100
0.5	8.34	7.70	0	100
0	8.27	7.58	0	100

Impact of MITC

As MITC is a degradation product of metham sodium, its toxicity to nitrifying bacteria was likewise determined. Activated sludge batch reactors were used to measure the impact of MITC at concentrations between 0 and 20 mg/L. The chemical caused a complete loss of nitrification at concentrations 10 mg/L and above. Between 2 and 10 mg/L nitrification was incomplete, and below 2 mg/L nitrification was not impacted. This is illustrated in Figure 7.

Table 5 gives pertinent data for one set of experiments examining MITC concentrations from 0 to 20 mg/L. The activated sludge had a solids concentration of 2200 mg/L and a pH of 7.36. This was very similar to the conditions for the comparable test of metham sodium. The addition of bicarbonate to the sludge buffered the solution to an initial pH of about 8.3.

After sitting overnight in the reactors with an MITC concentration of 10 and 20 mg/L, the pH was essentially unchanged and the initial amount of ammonia added was still present. Below 4 mg/L, some ammonia was present after sitting overnight and the pH had decreased significantly. This indicates that nitrification process was still occurring as the bicarbonate was being consumed, but the reactor was still not achieving full nitrification. The presence of a trace amount of ammonia in the reactor with no

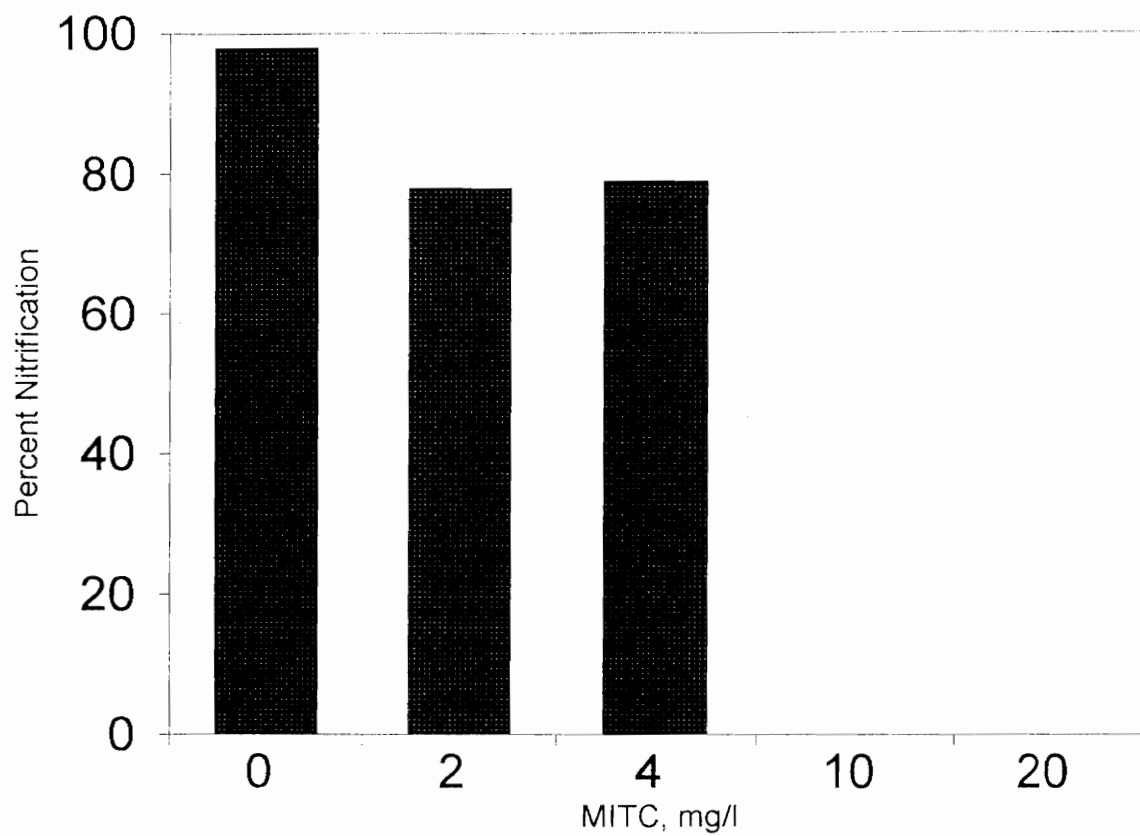


Figure 7. Impact of MITC on Nitrification

Table 5 -Test Conditions during the Experiment Studying
The Effect of Methyl Isothiocyanate on Nitrification

Activated sludge: MLSS = 2200 mg/L
 MLVSS = 1740 mg/L
 pH = 7.36
 date of test: Jan 18-19, 1995
 time of reaction: 16 hours

To each Reactor: 20 mg/L NH₄-N added chemically
 100 mg/L bicarbonate added chemically

<u>MITC</u> <u>mg/L</u>	<u>Initial</u> <u>pH</u>	<u>Final</u> <u>pH</u>	<u>Final NH₃-N</u> <u>(mg/L)</u>	<u>%</u> <u>Nitrification</u>
20	8.36	8.10	20.0	0
10	8.41	8.11	20.4	0
4	8.36	7.51	4.3	79
2	8.33	6.76	4.4	78
0	8.43	7.20	0.4	98

MITC present was probably due to contamination of samples during the titration process used to determine the ammonia concentrations. (The ammonia free water had several tenths of a mg/L of ammonia in it, apparently due to the depletion of the resin bed in the laboratory's water de-ionizing column.)

This data suggests that between 2 and 10 mg/L, the nitrification process was being impacted by MITC. The NOEL effect was less than 2 mg/L. This indicates that MITC is more toxic than metham sodium to nitrification.

Impact of Dichlobenil

Dichlobenil did not affect nitrification at the concentrations studied in these experiments. Batch reactors of activated sludge tested the impact of dichlobenil at concentrations between 0 and 36 mg/L. In the Vaporooter II process, dichlobenil is applied at only one-tenth the amount of metham sodium. As such, if dichlobenil was at a concentration of 36 mg/L in activated sludge, the metham sodium concentration would be 360 mg/L. Such a concentration would stop all biological activity in a waste treatment plant. As such, it is felt that the concentrations studied here encompassed concentrations of concern.

Table 6 gives pertinent data for one set of experiments

Table 6 -Test Conditions of Experiment Studying
The Effect of Dichlobenil on Nitrification

Activated sludge: MLSS = 1990 mg/L
 MLVSS = 1700 mg/L
 pH = 7.3
 date of test: Sept 28-29, 1994
 time of reaction: 17 hours

To each Reactor: 20 mg/L NH₄-N added chemically
 100 mg/L bicarbonate added chemically

<u>Dichlobenil</u> <u>mg/L</u>	<u>Initial</u> <u>pH</u>	<u>Final</u> <u>pH</u>	<u>Final NH₃-N</u> <u>(mg/L)</u>	<u>%</u> <u>Nitrification</u>
36	8.22	6.64	0	100
23	8.20	6.24	0	100
0	8.26	6.45	0	100

examining dichlobenil at concentrations from 0 to 36 mg/L. The activated sludge had a solids concentration of 1988 mg/L and a pH of 7.32. The addition of bicarbonate to the sludge buffered the solution to an initial pH of about 8.3.

After sitting overnight, all reactors showed complete consumption of the added ammonia, and the pH decreased significantly. This indicates that the nitrification process was still occurring as both the ammonia and the bicarbonate were consumed.

D. Adsorption of Metham Sodium by Powdered Activated Carbon

The generation of Freundlich isotherms of the adsorption of metham sodium by Powdered Activated Carbon (PAC) first required that the time for adsorption to go to equilibrium be established. Samples were shaken until X/M, the ratio of the mass of metham sodium adsorbed to mass of PAC, did not change. The time required for this was strongly dependent on the X/M. Figure 8 shows a plot of X/M versus time for metham sodium in water. For X/M less than 1, equilibrium was reached in 4 hours. As X/M increased, the time required increased. For an X/M of 3.2, eighteen hours were required.

The time to reach equilibrium in the raw sewage solutions was longer than it was in water. Figure 9 shows the results from a similar test for the adsorption by PAC of

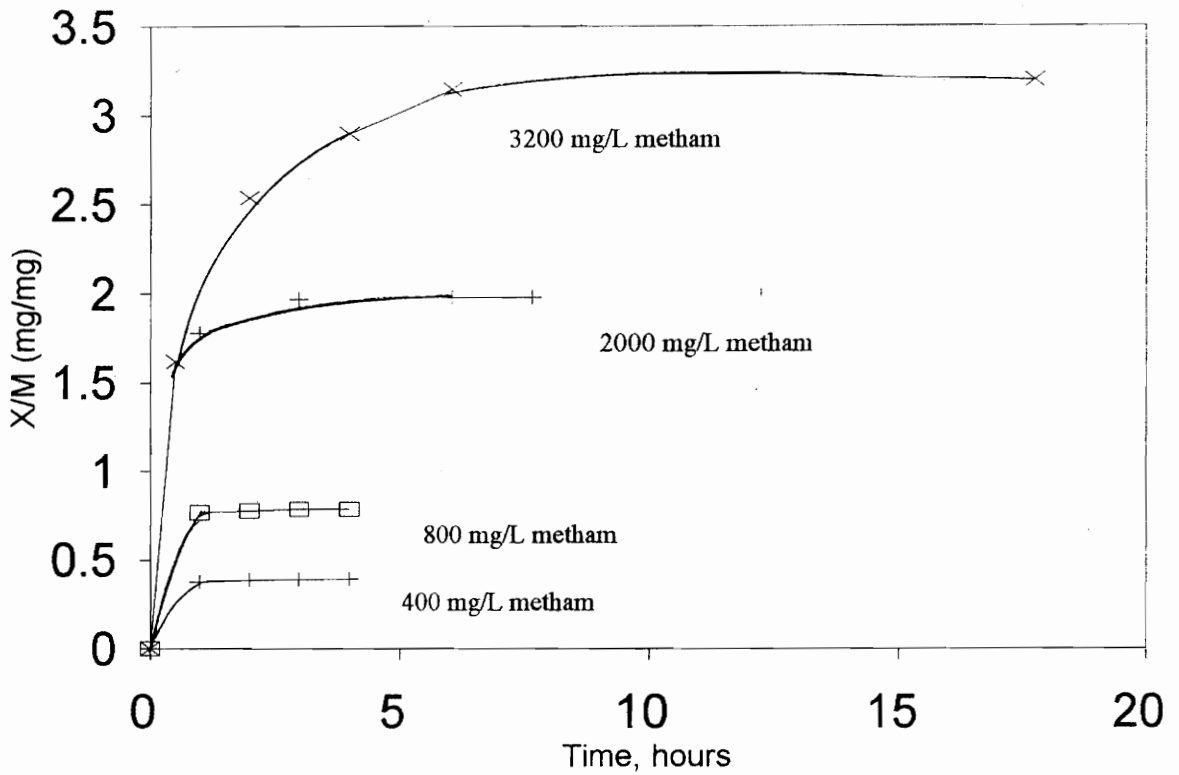


Figure 8. PAC Adsorption of Metham in Water as a Function of Time (1000 mg/L PAC)

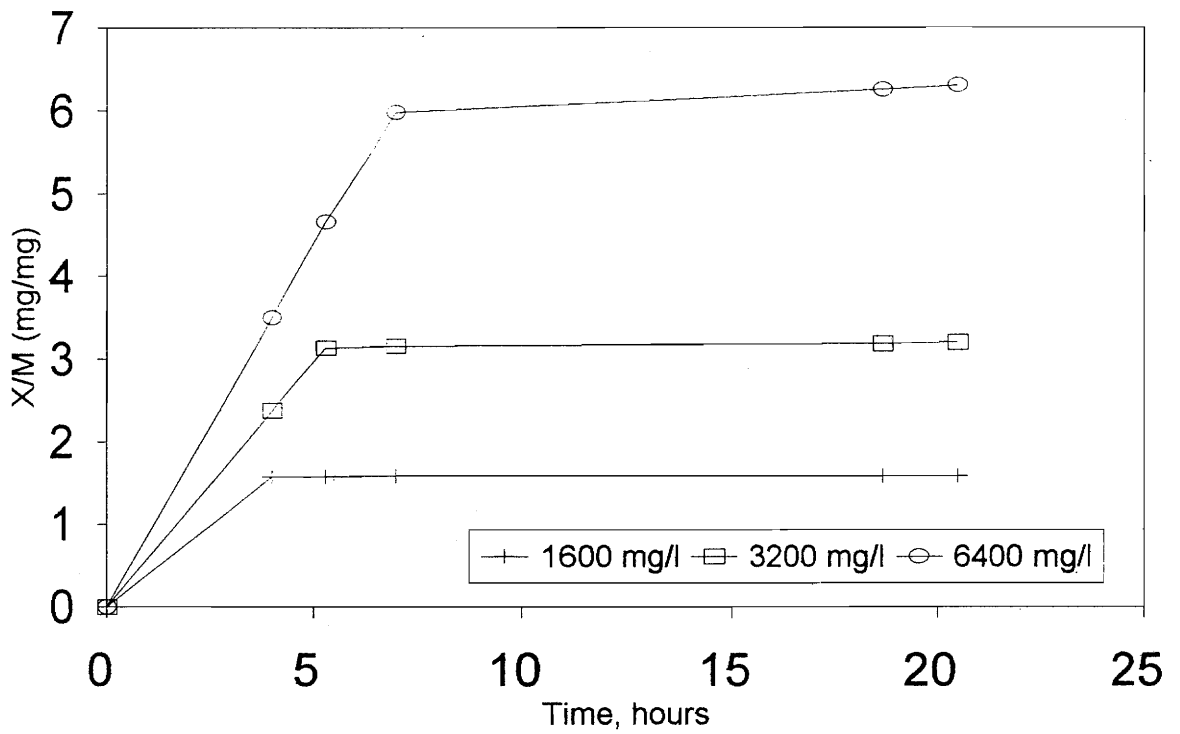


Figure 9. PAC Adsorption of Metham in Raw Sewage as a Function of Time (1000 mg/L PAC)

metham sodium dissolved in raw sewage. Eighteen hours was required to reach equilibrium for most concentrations.

Figures 10 and 11 shows plots of X/M as functions of the residual concentration, C_e , for metham sodium dissolved in water and raw sewage, respectively. To ensure that these data points represent equilibrium conditions, shaking was performed for a minimum of eighteen hours for both water and raw sewage solutions.

Empirical coefficients appropriate to the Freundlich equation were generated for the lines fitted through the data. For Figure 10, with metham sodium dissolved in water, the Freundlich equation is:

$$X/M = 0.042C_e^{1.24} \quad [13]$$

For Figure 11, the Freundlich equation for metham sodium in raw sewage is:

$$X/M = 0.23C_e^{1.0} \quad [14]$$

E. Bench Scale Models of the Interception of Metham Sodium by PAC

Table 7 gives a summary of the test conditions and results of a bench scale model of the interception of metham sodium by PAC in raw sewage, and its effect on nitrification. PAC was added in concentrations of 500 mg/L, and metham sodium was varied from 0 to 200 mg/L. The other amounts of metham sodium were chosen to give final X/M

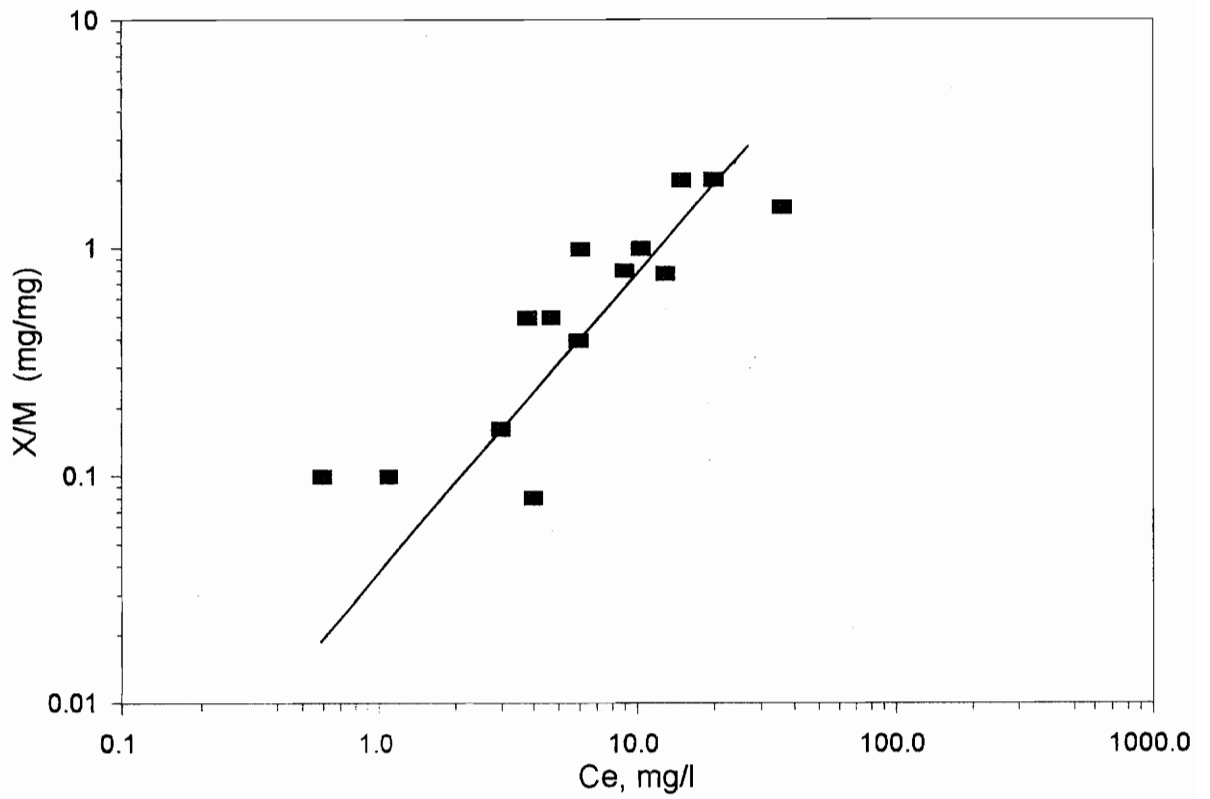


Figure 10. PAC Adsorption of Metham in Water

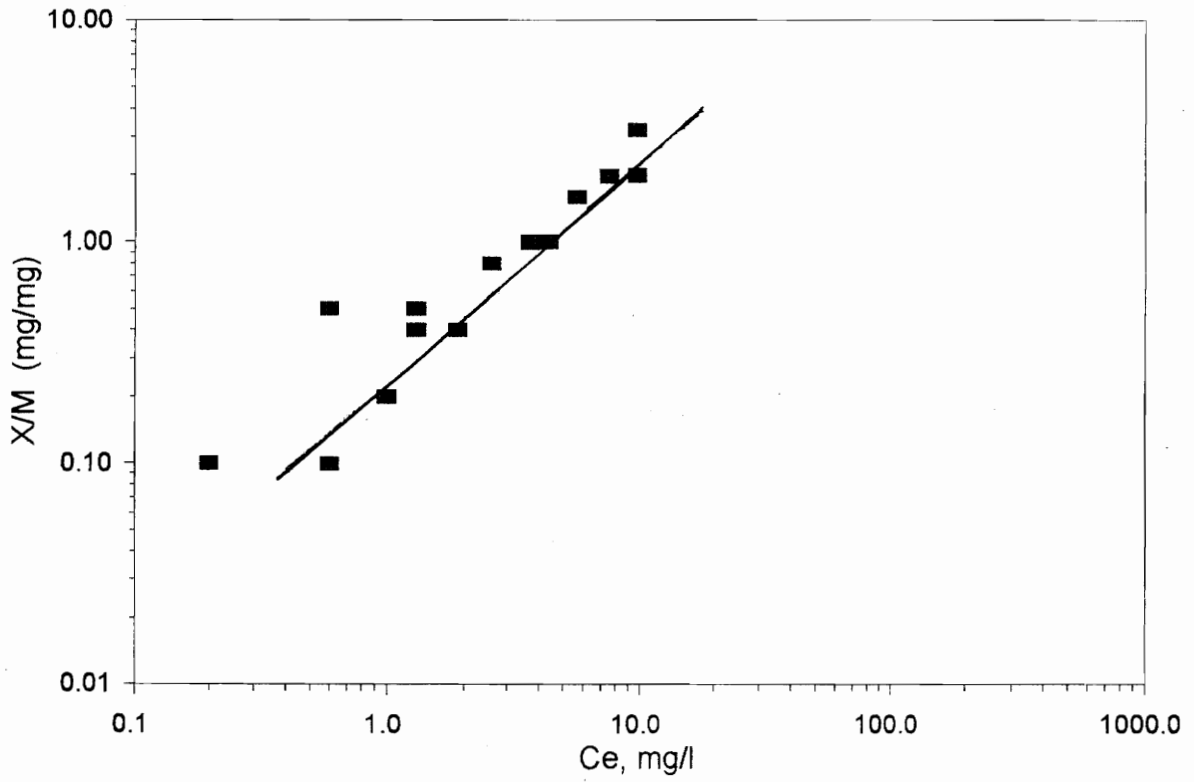


Figure 11. PAC Adsorption of Metham in Raw Sewage

**Table 7 - Bench Scale Reactors Characteristics and Results
For Experiment Performed March 7-8, 1995**

Raw Sewage Characteristics

Date and Time Obtained	March 6, 1995 1:00 pm
TSS, mg/L	420
TVSS, mg/L	380
Percent Volatile Material	92%
Imhoff Test, ml/L	21
pH	6.8
Initial TKN, mg/L	24

Activated Sludge Characteristics

Date Obtained	March 6, 1995 1:00 pm
MLSS*, mg/L	1940
MLVSS*, mg/L	1600
Percent Volatile Material*	82%
Nitrate*, mg/L	73
Initial pH	7.6

**Results of 4 Hour Shaking of Raw Sewage, Metham Sodium and
PAC Mixture**

	Reactor				
	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>
Initial metham, mg/L	0	50	100	150	200
PAC, mg/L	0	500	500	500	500
Final metham, mg/L	0	< 1	< 1	1	< 1
X/M, mg/mg	-	0.10	0.20	0.30	0.40
Final TKN(mg/L)	23.5	26.9	31.5	35.3	35.8
Nitrate (mg/L)	0	0	0	0	0
Final pH	6.84	7.56	8.11	8.63	8.84
Adjusted pH**	6.84	7.56	7.23	6.67	6.98

Table 7 (continued) - Bench Scale Reactors Characteristics and Results For Experiment Performed March 7-8, 1995

Results of Batch Reactors - Overnight Test

	Reactor				
	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>
Initial pH	7.78	8.20	7.92	8.10	7.97
Final pH	8.07	8.21	8.31	8.54	8.55
Final NH ₃ -N,mg/L	0	0	9.2	12.0	17.6
Initial TKN ^{***} ,mg/L	5.9	6.7	7.9	8.8	9.0
Final TKN,mg/L	0	0	7.8	NA	17.4
Final Nitrate,mg/L	77.1	81.9	62.3	63.6	59.5
Final metham,mg/L	0	< 1	< 1	< 1	< 1

* As occurred in batch reactors (mix of 75ml settled sewage + 225 ml activated sludge)

** sulfuric acid added to lower pH to achieve better settling

*** Based on 25% of TKN of raw sewage

values ranging from 0 to 0.4 mg/mg. Also, one control reactor was run without metham sodium and PAC.

After reacting overnight, the reactor with no metham sodium present and the reactor with an X/M of 0.1 had no ammonia still present. The TKN of the raw sewage added plus the nitrates originally in the activated sludge equaled within 5% of the amount of nitrates in the batch reactor. No nitrite was found in either the raw sewage, original activated sludge or the batch reactor after sitting overnight. This indicated that full nitrification had occurred, and that all organic and ammonia nitrogen had been converted to nitrate.

The batch reactors with X/M values of 0.2 to 0.4 showed no signs of nitrification. After sitting overnight, no increase was seen in the amount of nitrates in solution. The TKN actually increased slightly, indicating some amount of de-aminization had occurred.

The amount of metham sodium was measured in each batch reactor at the end of the overnight experiment. The results were inconclusive. Even after filtering through a 0.2 micron filter, enough color was left in the sample to cause a slight amount of light absorption. This was seen when the batch reactor which had no metham sodium applied showed a slight positive reading on the colorimeter. Even after adjusting for this reading, it was difficult to accurately

gauge the results of the other batch reactors. The readings, though, show that the amount of metham sodium was low, probably less than or equal to 2 mg/L.

Table 8 shows the results of an earlier set of experiments performed with 500 mg/L of PAC and 200 to 800 mg/L metham sodium. One reactor was again run as a control with no PAC or metham sodium. After reacting overnight, the ammonia levels were measured, but no measurements for TKN or nitrates were made. The control had achieved complete nitrification. All other reactors showed residual ammonia in concentrations of 10 to 16 mg/L. This was consistent with the tests reported in Table 3 in that at X/M values greater than 0.2, nitrification did not occur. Here, though, the measurements of the amount of metham sodium were a little clearer. In some, the amount of metham sodium was greater than what would be expected based on the measured concentration in the raw sewage. It is possible, then, that some amount of metham sodium had been adsorbed onto the organic material in the raw sewage during shaking with PAC, then subsequently released.

**Table 8 - Bench Scale Reactors Characteristics and Results
For Experiment Performed February 14-15, 1995**

Raw Sewage Characteristics

Date and Time Obtained	February 14, 1995 11:30 am
TSS, mg/L	290
TVSS, mg/L	260
Percent Volatile Material	89%
Imhoff Test, ml/L	20
pH	7.1
Initial NH ₃ -N, mg/L	15

Activated Sludge Characteristics

Date Obtained	February 14, 1995
MLSS*, mg/L	2470
MLVSS*, mg/L	2090
Percent Volatile Material*	85%
Initial pH	7.1

Results of 4 Hour Shaking of Raw Sewage, Metham Sodium and PAC Mixture

	Reactor			
	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>
Initial metham, mg/L	0	200	400	800
PAC, mg/L	0	500	500	500
Final metham, mg/L	0	0.7	4.6	19.8
X/M, mg/mg	-	0.40	.79	1.56
Final pH	7.4	8.6	9.4	9.9
Adjusted pH**	7.4	6.6	7.4	7.3

Results of Batch Reactors - Overnight Test

	Reactor			
	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>
Initial pH	7.6	7.6	7.6	7.5
Final pH	7.1	7.7	7.9	8.0
Added NH ₄ -N, mg/L	0	0	0	0
Final NH ₄ -N, mg/L	0	10.2	12.5	16.0
Initial metham, mg/L	0	0.1	0.9	4.0
Final metham, mg/L	0	1.8	<1	2.9

* As occurred in batch reactor

** sulfuric acid added to lower pH to achieve better settling

V. DISCUSSION

A. Degradation of Metham Sodium

Metham sodium was found to be fairly stable in solution over a period of twenty four hours. While hydrolysis was occurring even at near neutral conditions, evaporation was the most likely source of loss of metham sodium in open containers.

At pH levels below 5, only 25% of the metham sodium degraded over a period of eight hours, as shown in Figure 2. Insignificant degradation occurred after 10 hours, up to 46 hours. The mechanism for this degradation was most likely hydrolysis, which, according to Draper and Wakeham⁴, will occur under acidic conditions and will produce methyl amine and carbon disulfide. During this degradation, acid was consumed at a proportion of one mole of hydrogen ions per one mole of metham sodium. Therefore, as acid was consumed, pH increased and the reaction rate decreased. When a pH of about 6 was reached, the reaction stopped. This is seen in Figure 2 where with an initial pH of 4, the concentration of metham sodium steadily decreased for ten hours, then only showed a slow loss rate afterwards. With an initial pH of 5, the loss rate was slower, the concentration declined steadily over a period of about 30 hours, then declined at a slower rate. At an initial pH of 6 to 7, little loss was

seen.

Similar results were seen at alkaline conditions, as shown in Figure 3. Reactions of metham sodium with hydroxide ions produce methyl isothiocyanate. At an initial solution pH of 11, degradation occurred steadily over a period of about 20 hours, then slowed to a very slow rate. Solutions with an initial pH of 8 to 10 showed insignificant degradation. This is consistent with assertions reported by Draper and Wakeham⁴ that this reaction is thermodynamically unfavorable below pH 9.5. As with the reaction with acid, the reaction of metham sodium under alkaline conditions drove the solution towards neutral pH conditions. The reaction therefore only proceeded as long as pH remains above 10. Once this pH was obtained, the reaction stopped.

Figure 12 illustrates the effect pH has on the chemical degradation rate of metham sodium. The data for this figure was derived from the data in Figures 2 and 3. The percent amount of degradation which occurred from 0 to 7.25 hours was calculated, then divided by 7.25 hours. (The only exception was for a pH of 6 which used data at 0 and 21 hours, as the 7.25 hour reading was lower than later values, and is therefore anomalous.) Rates above 1% per hour occur only above a pH of 11 or below a pH of 4. Even at these pH values, though, the degradation rate is only 2.5 to 3.3% per hour. The implication is that chemical degradation of

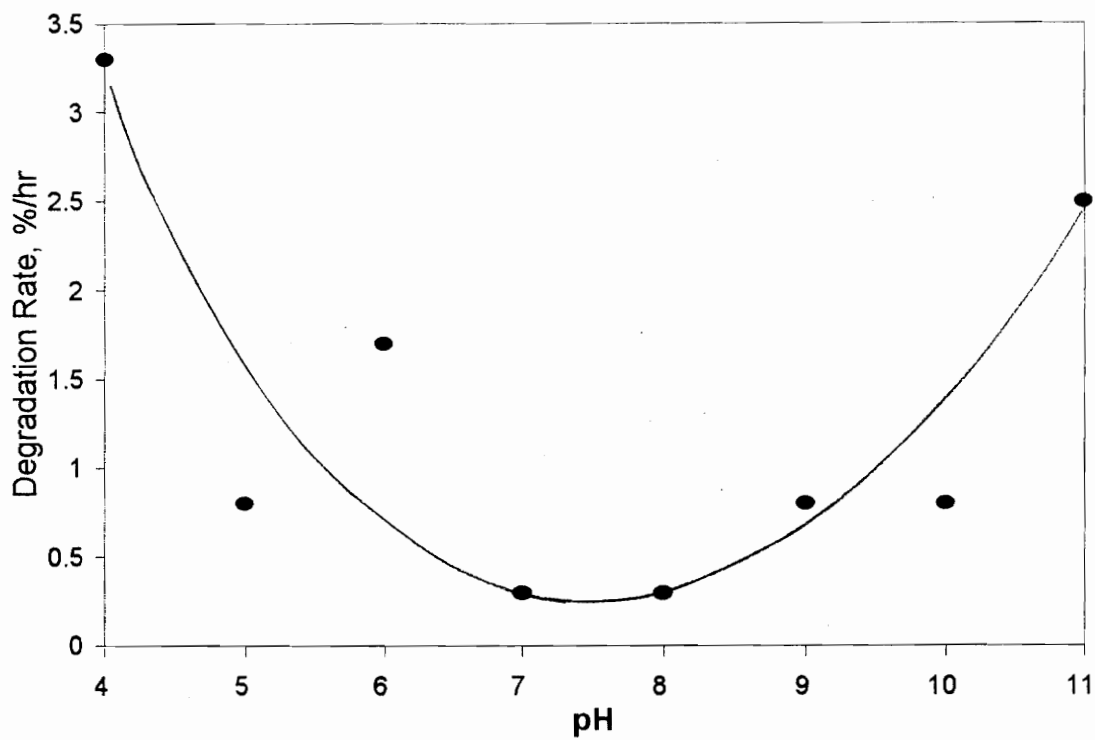


Figure 12. Effect of pH on Degradation Rate of Metham in Water

metham sodium due to high or low pH conditions is a minor consideration. Even if a means was introduced to maintain pH below 4 or above 11, and if the sewage had an 8 hour transit time through the lines of a collection system, only about one-fourth of the metham sodium would degrade.

The results of this study show that since sewer lines are typically near neutral pH, it is unlikely that acid or alkaline driven decomposition occurs while metham sodium is flowing through the collection system. These experiments also point out that trying to drive a degradation of metham sodium to methyl amine in a collection system by applying acid would be a cumbersome project. Not only would enough acid have to be applied to convert the metham, but enough would have to be added to overcome natural buffers in the system. Also, the pH would have to be much lower than 5 to achieve substantial degradation in the several hours sewage typically spends in the collection lines. Such a pH level would probably cause damage to the pipes.

Degradation to MITC by alkaline addition faces similar problems. Natural buffers would tend to keep the pH below 10. Also, data in Figure 7 showed that MITC is more toxic to nitrifying bacteria as is metham sodium, so nothing would be gained by this conversion.

The presence or absence of air in solution had no

apparent effect on the decomposition of metham sodium. This is seen in Figure 4. For the first sixty hours (about two and a half days), the amount of metham sodium in an oxygen free solution and in a solution with normal amounts of dissolved oxygen were the same. The experiment was allowed to continue for several more days. After a few more days, the solution open to the atmosphere showed a somewhat lower concentration. This was most likely due to increased evaporation as compared to the more tightly capped oxygen free bottle.

The implication of this experiment is that metham sodium could be expected to behave similarly in an anaerobic environment, such as occurs in a sewage collection system, as it would in an aerobic environment, such as in a storm water collection system.

These first two experiments raised the question as to what drives the chemical change from metham sodium to methyl isothiocyanate when Vapam is applied to soils. Apparently this change is driven neither by pH conditions in the soil nor the exposure of Vapam to air. This question was pertinent to this research because there is a need to know whether metham sodium or a degradation product is the most likely chemical specie at the discharge from the collection system. To help answer this, this researcher talked by

telephone to a chemist at Zeneca, the manufacturer of Vapam. In August, 1994, discussions were held with John Ericson of Zeneca's Western Research Center in Richmond, California. He was unable to provide much insight to this question. While he had much information about degradation rates, he knew of no studies which examined the driving mechanism for the reaction.

In an attempt to answer this question, an experiment was run exposing a metham sodium solution to ferric oxide (Fe_2O_3). Ferric oxide was chosen simply because it is a common compound found in most soils. Metham was found to degrade rapidly in its presence. The result of this is shown in Figure 5. The degradation is first order with a half life of four hours.

The implication of this is that apparently chemicals in the soil are primarily responsible for the degradation of Vapam to MITC. (According to Reference 2, the degradation is not by microbial action). These results inspired another set of experiments wherein a metham sodium solution was exposed to iron powder and aluminum powder. No degradation occurred because of exposure to these metals.

While these experiments did not fully explain the mechanisms by which Vapam degrades to MITC, on a whole they do indicate that metham sodium, and not MITC, is the chemical specie of primary concern at the end of the

collection system. Metham sodium is fairly stable in solution over a period of several hours, is stable at the pH values expected in collection systems, and is not influenced by the presence or absence of air.

During soil application, chemicals in the soil apparently act as catalysts in the degradation process. This theory, while it has merit, is beyond the scope of this research project.

B. Impact on Nitrification of Metham Sodium, MITC and Dichlobenil

Both metham sodium and MITC are effective agents in killing a wide range of microorganisms in soils. It is reasonable to assume they would have a similar effect in aeration basins at waste treatment plants. Experiments were made to determine at what concentrations nitrification is impacted by the presence of these two chemical species.

First, an experiment was performed which gave an indication of the concentrations at which all biological activity would be impacted by the presence of metham sodium. It is noted here, though, that this was not the initial intent of the experiment.

Hach BOD bottles were used to determine oxygen consumption in activated sludge. To individual portions of this sludge in the bottles was added a known amount of

chemical ammonia in the form of ammonium chloride (NH_4Cl), and various concentrations of metham sodium. The intent was that when ammonia was added to the activated sludge, higher oxygen uptake rates would be measured if nitrification occurred. The inhibition of nitrification caused by the various concentrations of metham sodium could be measured by observing oxygen uptake rates.

These experiments failed for two main reasons. First, the amount of oxygen consumed by the nitrifiers was small compared to that consumed by the heterotrophs. Because nitrifying bacteria only constitute about 3 to 5% of all activated sludge bacteria, even with their higher oxygen consumption levels the differences could not be seen between bottles with and without added ammonia. Secondly, there was a good deal of mechanical failure of the apparatus. The commonest problem was the separation of mercury in the manometer column. This was occurring in about one out of every five experiments. This problem made accurate readings impossible.

However, one viable piece of data was obtained from these experiments. In bottles where metham sodium levels were 10 mg/L or less, heterotrophic activity apparently was not impacted. At a concentration of 100 mg/L, no biological activity was evident. This is consistent with the concentrations reported in Appendix A for impacting

biological activity at sewage treatment plants.

This data gave a range of metham sodium concentrations to examine for nitrification inhibition. As 100 mg/L apparently stopped all activity, further experiments investigated dose ranges at less than 50 mg/L. Also, since metham sodium concentrations in sewer lines could be over 100 mg/L, it can be assumed that no biological activity is occurring in the collection lines which might consume or degrade metham sodium.

Batch reactors were operated to determine at what concentrations of metham sodium nitrification was impacted. The results are summarized in Figure 6. Below 4 mg/L of metham sodium, nitrification occurred without disruption. At concentrations of 8 mg/L and greater, nitrification ceased. This was determined by chemically adding 20 mg/L of ammonia nitrogen to the activated sludge, letting the reactor operate overnight, then checking for the presence of ammonia in the morning. All nitrogen was consumed when concentrations were less than 4 mg/L. At concentrations greater than 8 mg/L, all ammonia was still present. At 4 mg/L, some tests showed full nitrification, repeat experiments shows about 4 mg/L ammonia still present. Likewise at 8 mg/L metham sodium, some experiments showed all ammonia present, repeat experiments showed about 12 mg/L ammonia nitrogen. This indicates that in the range of 4 to

8 mg/L, nitrification is significantly impacted, but not totally stopped.

Similar experiments were run to determine the impact of MITC on nitrification. Laboratory grade MITC was obtained and used in these experiments. The results are shown in Figure 7. The concentrations at which nitrification was impacted were essentially the same as for metham sodium. Below 2 mg/L, nitrification was not impacted. Above 8 mg/L, nitrification ceased.

The end results of these two experiments show that both metham sodium and MITC can inhibit nitrification at concentrations as low as 4 mg/L.

Another set of experiments looked at the impact of dichlobenil on nitrification. This substance did not have an impact at the concentrations of concern here. At 36 mg/L dichlobenil, full nitrification was still seen.

As dichlobenil is used at only one-tenth the amount of metham sodium in the Vaporooter II process, only a small concentration would reach the waste treatment plant. Also, dichlobenil is used because it largely clings to the pipe even when wet, and so helps provide residual effectiveness. Dichlobenil's ability to cling to surfaces was observed while handling it in the laboratory. Dichlobenil powder, when added to water, did not readily dissolve, but mostly stayed as soggy lumps in solution. Much of it stuck to the

sides of the beaker, and only came off with vigorous washing. In the nitrification test, care was made to add dry powder directly into the middle of the reactor, where it would be thoroughly mixed by the agitating action of the diffusing air. This method would keep the dichlobenil largely dissolved or suspended in solution. Little dichlobenil was seen clinging to the sides of the beakers at the end of these experiments.

The end result of this series of experiments was that the data indicate that metham sodium is the chemical causing the disruption of nitrification in waste treatment plants. Dichlobenil is not present in sufficient quantity to cause a problem, and apparently metham sodium does not degrade to MITC in the collection system fast enough to form a significant quantity of MITC before the flow reaches the wastewater treatment plant.

C. Adsorption of Metham Sodium by Powdered Activated Carbon (PAC)

The ability of PAC to adsorb metham sodium from a waste stream was experimentally determined, and the results shown in Freundlich isotherms in Figures 10 and 11. The first figure shows adsorption in a water solution, the latter shows adsorption from raw sewage.

The PAC chosen for these experiments was Nuchar-SA from

Westvaco. The specifications and properties of this material are given in Appendix B. This PAC was very good at adsorbing metham sodium from both water and raw sewage. In water, at X/M values (mass of metham sodium adsorbed to mass of PAC) below 1.0 mg/mg, typically 99% of the metham can be removed from solution. This percentage, though, decreases as X/M increases. At X/M of 2 mg/mg, about 50% of the metham is removed from solution, and at 4 mg/mg about 30% is removed.

Nuchar-SA was also very good at removing metham sodium from raw sewage. As seen when Figure 11 is compared to Figure 10, a lower final concentration was achievable for the same X/M value in raw sewage than in water. This was due to the fact that metham sodium was also being adsorbed by the organic material in the sewage. This is consistent with what is seen during soil application of metham sodium, where humic material readily adsorbs metham sodium⁵.

The amount of metham sodium adsorbed by organic material, while small compared to the overall amount of metham sodium in the system, can be significant in terms of its impact on biological activity. At X/M = 1.0 mg/mg, the organic material adsorbed the equivalent of 10 mg/L from solution. As the volatile suspended solids concentration in the sewage was about 280 mg/L, the suspended solids then had a metham sodium concentration of about 3.6%. This means the

organic material contained about 36000 ppm metham sodium. This concentration may seriously impact biological activity of any organism trying to consume the organic material. Also, this metham sodium may be re-released as the organic material is consumed by the activated sludge.

One very important parameter when using the data in Figures 10 and 11, is the time required to reach equilibrium. Figures 8 and 9 show test results of X/M versus time for water solutions and raw sewage solutions. Generally, the lower the higher the ratio of carbon to metham sodium, the quicker equilibrium was reached. Also, equilibrium was reached faster in water solutions than in raw sewage, due to more competition for adsorption sites on the carbon particles. Care must be given in knowing the concentration remaining in solution, not just the adsorbed fraction. For example, for an experiment with 400 mg/L metham sodium and 1000 mg/L PAC, the X/M equaled 0.380 mg/mg after one hour and 0.396 mg/mg after four hours. There was little difference in the measured X/M. However, the concentration still in solution was 20 mg/L after one hour and 4 mg/L after 4 hours. This is significant if the goal is to reduce the final concentration to a very low value.

In raw sewage at higher X/M values, the time to reach equilibrium was longer. At an initial metham sodium concentration of 3200 mg/L and PAC concentration of 1000

mg/L, the X/M was 3.14 mg/mg after 5 hours, and after 20.5 hours was 3.20 mg/mg. The values of X/M were not too different at these two times, but the metham sodium concentration in solution after five hours was 65 mg/L and after 20.5 hours was 3 mg/L. This is a very significant difference if the goal is to achieve a No Observable Effect Level (NOEL) of metham sodium.

D. Achievement of No Observable Effect Level

The bench scale reactors showed that a ratio of about 10 to 1 of PAC to metham sodium quantities is required to achieve a true NOEL. The amount is higher than would be predicted by determining X/M for a residual concentration of about 2 mg/L from Figure 11. There are two reasons for this. First, an equilibrium concentration was not reached after 4 hours. Secondly, some metham sodium that had been adsorbed onto the organic material in sewage was released into the activated sludge. The high dose of PAC is necessary so that the metham sodium will preferentially sorb to the PAC over the organic matter.

These results were not unexpected. Metham sodium was developed to be a killing agent for a wide range of soil organisms. Its most desirable purpose is that it kills virtually any type of microorganism, and can do so at low concentrations. It is natural to conclude, then, that it

would be equally effective in a biological waste treatment environment. As nitrifiers are generally much less hardy than heterotrophs, and are present in much smaller numbers, disruption of nitrification would be the first effect seen when metham sodium is introduced into a system. This is the effect seen in these experiments.

It is recommended that when the data generated during this study is used to prevent the disruption of nitrification in waste treatment plants, that safety factors be applied.

The NOEL for metham sodium was no greater than 4 mg/L in these controlled experiments. In practice, the NOEL will vary significantly due to differing concentrations of suspended solids, temperature and pH in various aeration basins. A more generic NOEL is probably 2 mg/L at 2000 mg/L MLVSS. In terms of herbicide concentration to MLVSS concentration, this NOEL is 7.8×10^{-6} moles metham per gram MLVSS.

Also, the amount of PAC actually required will be close to five times the amount predicted by Figure 11. According to this figure, an X/M of 0.5 should have been sufficient to lower the metham sodium concentration to desired levels. However, experiments showed an X/M of 0.1 was required. This overdosing is necessary so that the metham sodium preferentially adsorbs to PAC over organic material in the

sewage.

Also, it should be assumed that all interaction between PAC and metham sodium occurs in the collection system, as there is little agitation in the primary clarifier. As such, assuming that only 80% of equilibrium may be achieved is a reasonable yet conservative assumption.

VI. CONCLUSIONS AND RECOMMENDATIONS

1. Metham sodium is the chemical responsible for the loss of nitrification in activated sludge waste treatment plants after its application in the sewers to destroy roots.
2. Metham is fairly stable in solution at the times, temperatures and pH levels normally encountered in sewage collection systems.
3. Dichlobenil occurs at a much lower concentration than metham sodium, and does not appear to impact nitrification processes.
4. PAC is very a vert effective adsorbent for metham.
5. The adsorption of metham after PAC dosing is much greater in sewage than in water, implying that metham is adsorbed by the suspended solids in sewage.

Recommendation

A suggested method of using the data generated in this report is:

°use a target concentration in the activated sludge of no more than 2 mg/L of metham sodium at 2000 mg/L MLVSS, (equivalent to 7.8×10^{-6} moles metham per gram MLVSS) .

°assume all adsorption of metham sodium to PAC occurs in the collection system (the lack of agitation in the clarifier would preclude much interaction between PAC

and metham sodium)

°assume that the metham sodium would reach no more than 80% of its equilibrium value in the collection system after the application of PAC

°use five times the amount of PAC as determined from the data in Figure 11 so that the metham sodium preferentially adsorbs to PAC over the organic material in sewage

References

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- 10) Weed Society of America, *Herbicide Handbook*, Monograph 3, 2nd edition, WF Humphrey Press, Geneva NY. 1970. (SB611 W34)
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Appendix A - Anlab Report

SANAFOAM™ VAPOROOTER® II

WASTEWATER MICROORGANISM TOXICITY TESTS

**CONDUCTED BY ANLAB ANALYTICAL LABORATORY
A DIVISION OF DEWANTE & STOWELL
1990**



**ANALYTICAL LABORATORY
A DIVISION OF DEWANTE & STOWELL**

RESULTS:

Test results show that there is little or no impact on the biological process of either activated sludge or pond wastewater treatment systems when the dosing concentration of SY-II is 40 ppm or lower.

However, when SY-II dosing rates reach 50 ppm and higher the biological activity of these plants can be dramatically affected.

When a biological process was extended to the nitrification mode the process still operated normally at lower dosages. As the dosage rate approached 50 ppm, biological activity was affected as in conventional plants.

Ponds were studied and were also affected at rates around 50 ppm.

In conclusion, the no-observable-effect concentration (NOEC) of foamed SY-II in activated wastewater samples was found to be 40 ppm. Wastewater treatment plants can be affected by use of SY-II used in treatment of roots in sewers lines at high dosage levels. Under normal conditions the dosage used to treat sewer lines have no adverse effect on the treatment plant; however, with extremely small plants under 1 mgd caution should be exercised.

CHEMICALS USED

SANAFoAM VAPORoOTER II (SV II):

This material is mainly composed of two active ingredients; which accomplish the derooting task, Metham Sodium, and Dichlobenil.

Both Metham Sodium & Dichlobenil are registered by EPA for this use.

Metham Sodium is a common name for Sodium Methylidithiocarbamate a non-selective contact herbicide which acts as a fumigant in sewer lines.

Dichlobenil is the common name for 2,6-Dichlorobenzonitrile, a herbicide which controls the regrowth of roots from 1 to 4 years depending on the condition in the sewer line.

Together they give a fast acting and long lasting control of roots in a waste water collection system.

DOSING SOLUTION PROCEDURE:

A 50,000 parts per million mixture of SV-II in water was foamed through an AEC Minifoamer. The foam was allowed to collapse for a period of 45 minutes, then collected and taken to the laboratory for further dilution in waste water samples.

The above foamed mixture was used to prepare a 1,000 ppm nominal concentration of SV-II in raw sewage. This sample was mixed for 30 minutes with gentle agitation to simulate the dilution/mixing action that occurs in sewer lines.

This 1,000 ppm SV-II mixture was used for the final dosing of wastewater samples being studied.

ANALYSES METHODS:

Biochemical Oxygen Demand

Standard Methods, 16th Edition
Method 507

Chlorine Demand

Standard Methods, 16th Edition
Method 409

Total Coliform Bacteria

Standard Methods, 16th Edition
Method 908

Sludge Volume Index

Standard Methods, 16th Edition
Method 213

Microscopic

EPA Methods of Identification
of Microorganisms, 1976

**Appendix B - Health and Safety Information on
Metham Sodium and Dichlobenil**



SEWER ROOT CONTROL SPECIALISTS

April 28, 1994

Dr. Clifford W. Randall
Department of Civil Engineering
Virginia Tech
Blacksburg, VA 24061

RE: Safety Information on Metham Sodium and Dichlobenil

Dear Dr. Randall,

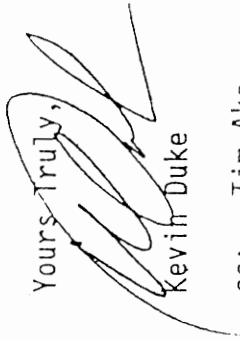
Sorry for this delay in getting back to you. After our meeting, I was in Michigan on business and I didn't return until this week.

I have enclosed the safety and health information we discussed.

I have heard of a new study which found that metham-sodium has tetragenic effects. I have not seen this study myself. To be safe, keep all pregnant women away from metham-sodium.

On another matter, we have asked our attorney, Larry Bousquet, to draft an agreement. Larry may be contacting you directly to determine the University's interests. We hope to get things rolling as soon as possible.

Yours Truly,



Kevin Duke

cc: Tim Ake

Encl.

DUKE'S SALES & SERVICE, INC.
1020 HIAWATHA BLVD., WEST
SYRACUSE, NEW YORK 13204-1131
CALL TOLL FREE 1-800-44-ROOTS
(315) 472-4781 FAX (315) 475-4203

MATERIAL SAFETY DATA SHEET

(Updated 2/1/93)

Airrigation Engineering Company, Inc.
1279 Quarry Lane
Easanton, CA 94566
(510) 462-6606

Duke's Sales & Service, Inc.
1020 Hiawatha Blvd. West
Syracuse, NY 13204-1131
(315) 472-4781

Product Identification

Trade Names: SANAFOAM[®] VAPOROOTER[®] II

EPA Registration: 9993-3

Labels: Sodium methyldithiocarbamate (anhydrous) 24.25%
2,6 - dichlorobenzonitrile 1.95%
Inert ingredients 73.80%
100.00%

Chemical Names: Sodium methyldithiocarbamate, metam-sodium CAS 137-42-8
2,6 - dichlorobenzonitrile, dichlobenil CAS 1194-65-6
also contains a small amount of isopropyl alcohol CAS 67-63-0

Product Description: The fiberboard box holds two containers: a 30 ounce plastic bag containing dichlobenil POWDER and a 5 gallon plastic container of the metam-sodium/foaming agent solution. Where applicable, the plastic container contents will be referred to as the LIQUID and the plastic bag contents as the POWDER.

<u>Physical Properties</u>	<u>Liquid</u>	<u>Powder</u>
Appearance	Light green to yellow	tan powder
Odor	Sulfur-like	slight aromatic
Boiling point	ND	NA
Specific gravity	1.15 (H ₂ O = 1)	NA
Vapor density	ND	NA
Melting Point	NA	NA
Vapor pressure	NA	NA
pH	7.5-9.5	NA
Evaporation rate	ND	NA
Water solubility	miscible	insoluble, dispersible

(ND - not determined, NA - not applicable)

Fire Data

Flashpoint: 150°F(Pensky-Martins CC)

This flashpoint results from the presence of a small quantity of isopropyl alcohol (less than 1%); the product is nonflammable.

Extinguishing Media: Water

Fire Fighting Techniques: Wear full face, self-contained breathing apparatus and impervious protective clothing. Evaluate non-essential personnel from the area. The fiberboard boxes contain plastic containers, so cool with a water spray to avoid container rupture. The breakdown products resulting from high heat are irritating to the respiratory tract and may cause breathing difficulty and pulmonary edema. Run off from fire control or dilution with water may cause pollution or contamination of building, grounds and equipment.

Health Hazard Information

The principal routes of exposure are skin contact, eye contact or inhalation. Irritation may result from skin or eye contact with either the LIQUID or the POWDER.

No data have been identified which address medical conditions that are generally recognized as being aggravated by exposure to this product.

FIRST AID:

eye Contact: flush eyes with water for at least 15 minutes and get medical attention if eye irritation persists.

Skin Contact: Immediately remove contaminated clothing or shoes, and flush with plenty of water to avoid skin irritation.

Inhalation in Confined Spaces, such as tanks and manholes: remove to fresh air. If breathing has stopped, start artificial respiration procedures, and get medical attention immediately.

Ingestion: Give several glasses of water. Do not induce vomiting. Get medical attention immediately. These materials are not listed in accepted cancer registries, such as NTP or IARC.

Reactivity

These products are stable under normal storage conditions.

Avoid mixing with acidic material as evolution of Hydrogen Sulfide may occur.

The POWDER may decompose on exposure to bases.

The LIQUID is corrosive to brass, copper, zinc and aluminum.

The product will decompose in extreme heat. There is no indication of hazardous polymerization.

Special Handling Information

Eye Protection: Avoid eye contact with this material. Use of face shield and glasses or goggles is recommended.

Respiratory Protection: Avoid breathing vapor or mist. Use a self-contained breathing apparatus in confined spaces, such as tanks and manholes. Ensure good ventilation in manufacturing and use areas. A NIOSH/MSHA-approved pesticide respirator with pre-filter is useful to avoid mists or dust fumes. Examples of NIOSH/MSHA respirators for this use are:

- Wilson TC-23C-751, TC-23C-747, TC-23C-791 and TC-23C-792
- North TC-23C-74/190
- Easi-Care(3M) TC-23C-860

This equipment must be worn if a pungent sulfurous odor persists.

Skin Protection: Avoid skin contact with this material for it can be a severe skin irritant if not washed off. Use gauntlet-type unlined rubber gloves and long-sleeved shirts.

Other: A large amount of water (10 gallons or more) should be available to wash any spills off personnel.

Spill, Leak and Disposal

Use appropriate safety equipment when dealing with spills or leaks. Add absorptive granules such as litter, and sweep up the absorbents. Place in a waste disposal container for safe, legal disposal. Then clean area with a minimum amount of water.

For container disposal, triple rinse the containers and place rinse water into the application equipment solution tank or sanitary sewer manholes. Puncture or cut container in three places and dispose of container in a sanitary landfill. Ensure that all federal, state and local regulations for disposal are followed.

Do not hose spillage onto adjacent planted areas. These herbicides may adversely affect desirable lawns, shrubs or trees. Foam should be shoveled off of planted areas immediately.

Special Precautions

- Keep out of reach of children.
- Do not store near food or foodstuffs.
- This LIQUID portion of the product is toxic to fish.
- Keep children and pets out of storage and treatment areas.

The information and statements on this Material Safety Data Sheet are believed to accurately reflect the scientific evidence used in making the hazard determination, but is not to be construed as a warranty or representation for which we assume legal responsibility.

Storage

To extend product quality:

- Avoid prolonged exposure to temperatures below 33°F to prevent package damage.
- Avoid prolonged exposure to temperatures above 90°F to protect foam quality. Never store near heat source or in direct sunlight.

**Appendix C - Specifications for Nuchar-SA Powdered
Activated Carbon**

NUCHAR® S-A powdered activated carbon

Description and Typical Applications

Nuchar S-A is a high activity powdered activated carbon with a large preponderance of pores in the transitional and macro pore range. It is specifically designed for the adsorption of large quantities of high molecular weight substances such as color bodies. The filtering speed and acidic pH make *Nuchar S-A* particularly effective for the treatment of corn syrups. The efficient purification of other food products, chemicals, pharmaceuticals, and municipal and industrial wastes may also be assured with *Nuchar S-A*. *Nuchar S-A* meets the food grade quality of activated carbons as defined in the Third Edition, Food Chemicals Codex (1981).

Specifications*

Iodine Number (mg/g)	900 min
Molasses Decolorizing Index	14.0 min
Filtering Time (sec)	50-100
Moisture, As Packed (%)	10 max
pH	4-6

Product Data Bulletin P-102

Typical Properties*†

Apparent Density (lbs/cu ft)	21-23
Apparent Density (kg/m ³)	337-369
Ash (%)	3-6
Surface Area (Nitrogen BET Method) (m ² /g)	1400-1800
Total Pore Volume (cm ³ /g)	2.2-2.5
Water Solubles (%)	1-3
Sieve Analysis:	
Thru 100 mesh (%)	95-100
Thru 200 mesh (%)	85-95
Thru 325 mesh (%)	65-85

Packaging

Nuchar S-A is available in bulk trucks, bulk rail cars or in individually shrink-wrapped, 45-pound multiwall paper bags on nonreturnable, wood pallets.

*Specifications and typical property data as produced using Westvaco procedures.

†Typical properties are for general information and are not to be construed as purchase specifications.

CAS Registry #7440-44-0

The information contained herein is believed to be accurate, but no warranty is given nor is freedom from any patent to be inferred.

The Seller warrants only that this product will meet the above described published specifications. The Seller makes no other warranties of any kind either expressed or implied, by operation of law or otherwise including but not limited to warranties of merchantability or fitness for a particular purpose or application. The Buyer assumes all risk and tort liabilities arising from the use of this product.

CAUTION: Never enter tanks or other confined areas containing wet, activated carbon. Wet, activated carbon will adsorb oxygen and asphyxiation may result.

4-92 Supersedes all previous *Nuchar S-A* Data Bulletins

Printed on STERLING Line Paper

Appendix D - Tabulation of Data from Figures

Figures 2 and 3 - Acid and Alkaline Degradation of Metham Sodium

<u>Hours</u>	<u>pH4</u>	<u>pH5</u>	<u>pH6</u>	<u>pH7</u>
0	50	50	50	50
2	46	47	47	49
4	43	47	47	54
7.25	38	47	44	49
21	38	43	47	49
24	34	37	44	46
28	36	41	46	46
32	32	38	46	47
46	34	40	46	47

<u>Hours</u>	<u>pH8</u>	<u>pH9</u>	<u>pH10</u>	<u>pH11</u>
0	50	50	50	50
2	50	50	50	46
4	54	49	50	46
7.25	49	47	47	41
21	49	44	49	34
24	44	46	46	29
28	46	46	47	29
32	46	46	49	31
46	46	46	46	29

Figure 4 - Effect of DO on the Chemical Degradation of Metham

<u>Hours</u>	<u>Air</u>	<u>Sealed</u>
0	50	50
1.25	53	47
2.2	44	44
3.5	45	43
7.3	40	41
10.0	39	40
23.4	40	41
23.7	38	39
25.1	37	39
29.7	37	39
48.0	39	40
121.4	29	36
148.5	28	36

Figure 5 - Metham Sodium Degradation by Ferric Oxide

<u>Hours</u>	<u>mg/l</u>
0	50
0.5	43
4.5	23
8.5	11
22.5	0.9

Figure 8 - PAC Adsorption of Metham Sodium in Water
(1000 mg/l PAC)

<u>Hours</u>	<u>X/M for:</u>			
	<u>400mg/l</u>	<u>800mg/l</u>	<u>1000mg/l</u>	<u>3200mg/l Metham</u>
0	0	0	0	0
0.5				1.62
1	0.38	0.77	1.78	
2	0.39	0.78		2.54
3	0.393	0.79	1.97	
4	0.396	0.79		2.9
6.1			1.98	3.15
7.7			1.98	
17.75				3.2

Figure 9 - PAC Adsorption of Metham Sodium in Raw Sewage
(1000 mg/l PAC)

<u>Hours</u>	<u>X/M for:</u>		
	<u>1600mg/l</u>	<u>3200mg/l</u>	<u>6400mg/l Metham</u>
0	0	0	0
4	1.58	2.38	3.50
5.5	1.58	3.14	4.66
7.2	1.59	3.16	5.98
18.7	1.59	3.19	6.26
20.5	1.59	3.20	6.31

Figure 10 PAC Adsorption of Metham in Water

<u>C_e (mg/l)</u>	<u>X/M</u>
13	0.77
6	0.39
4	0.08
36	1.50
9	0.79
3	0.16
6.1	0.99
3.8	0.49
0.6	0.10
10.4	0.99
4.7	0.50
1.1	0.10
20	1.98
15	1.97

Figure 11 PAC Adsorption of Metham in Raw Sewage

<u>C_e (mg/l)</u>	<u>X/M</u>
3.7	0.99
0.6	0.50
0.6	0.10
4.4	1.00
1.3	0.50
0.2	0.10
9.8	1.99
7.6	1.98
1.3	0.40
2.6	0.80
5.7	1.59
9.8	3.20
1.0	0.20
1.9	0.40
4.3	0.80
10.0	1.59

Figure 12 - Effect of pH on the Chemical Degradation Rate of Metham

<u>pH</u>	<u>%/hr</u>
4	3.3
5	0.8
6	1.7
7	0.3
8	0.3
9	0.8
10	0.8
11	2.5

Appendix E - Tabulation of Data from Chemical Degradation Studies of Metham Sodium in the Presence of Iron and Aluminum Powders

<u>Time</u> <u>Hours</u>	<u>Concentration of Metham Sodium</u> <u>With Iron</u>	<u>With Aluminum</u>
0	48	48
0.5	48	47
1	47	47
4.7	46	47
8.7	46	47
20.9	44	46
30.3	44	46

The Evaluation of Metham Sodium and Dichlobenil Impacts on
Activated Sludge Nitrification

by

Timothy Nelson Ake

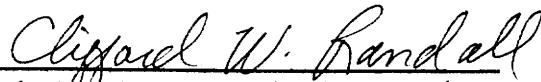
Thesis submitted to the Faculty of the
Virginia Polytechnic Institute and State University
in partial fulfillment of the requirements for the degree of

MASTERS OF SCIENCE

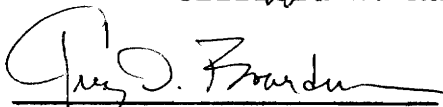
IN

ENVIRONMENTAL ENGINEERING

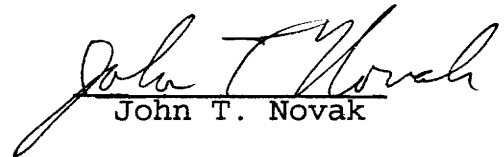
APPROVED



Clifford W. Randall, chair



Gregory D. Boardman



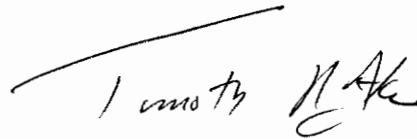
John T. Novak

May 1995

Blacksburg, Virginia

Key words: metham, vapam, dichlobenil, nitrification

Timothy Nelson Ake is a licensed professional engineer in the Commonwealth of Virginia. He graduated in 1973 from the University of Maryland with a BS degree in Nuclear and Mechanical Engineering, and earned an MS degree from the University of Cincinnati in 1975. He spent eighteen years working for Babcock and Wilcox in Lynchburg, Virginia as a nuclear analyst. His responsibilities included the performance of analyses required for the licensing and design of nuclear reactors and nuclear fuel. He has authored several papers in the nuclear field. Currently he is residing in Lynchburg, Virginia.

A handwritten signature in black ink that reads "Timothy N. Ake". The signature is written in a cursive style with a long horizontal line above the name.