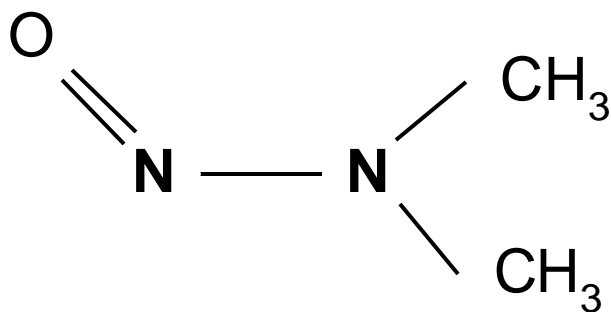


NDMA SOURCE CONTROL  
Sources of *n*-nitrosodimethylamine  
in the  
Orange County Sanitation District Service Area  
August 2000 - November 2001



Source Control Division  
Orange County Sanitation District, California  
March 27, 2002

# TABLE OF CONTENTS

---

	Page
<b>NDMA SOURCE CONTROL</b>	
Table of Contents .....	i
Table of Tables .....	iii
Table of Figures .....	iv
Table of Appendices .....	v
<b>chapter 1</b>	
<b>EXECUTIVE SUMMARY</b>	
1.1 ABSTRACT .....	1.1
1.2 BACKGROUND .....	1.1
1.3 PROJECT SUMMARY.....	1.2
<b>chapter 2</b>	
<b>PROJECT METHODS</b>	
2.1 PLANNING .....	2.1
2.2 COMMUNICATION.....	2.1
2.3 SAMPLE COLLECTION.....	2.1
2.4 SAMPLE ANALYSIS .....	2.2
<b>chapter 3</b>	
<b>TRUNKLINE SAMPLING</b>	
3.1 BACKGROUND .....	3.1
3.2 NEWHOPE / EUCLID TRUNK SAMPLING – AUGUST 8, 2000.....	3.1
3.3 AIRBASE TRUNK SAMPLING – SEPTEMBER 11, 2000.....	3.3
3.4 AIRBASE TRUNK MULTIPLE DAY SAMPLING – SEPTEMBER 24–29, 2000.....	3.4
3.5 AIRBASE TRUNK SAMPLING – MARCH 2001.....	3.5
3.6 TALBERT AND SUNFLOWER TRUNK SAMPLING – OCTOBER 2000.....	3.6
3.7 TALBERT AND SUNFLOWER TRUNK SAMPLING – MARCH 2001 .....	3.8

**TABLE OF CONTENTS (continued)**

---

	Page
<b>chapter 4</b>	
<b>INDUSTRIAL SAMPLING AND IRWD SAMPLING</b>	
4.1 SUMMARY.....	4.1
4.2 INDUSTRIAL SAMPLING – OCTOBER 2000.....	4.2
4.3 FOLLOW-UP INDUSTRIAL SAMPLING – MARCH–APRIL 2001 .....	4.4
4.4 NDMA CHARACTERIZATION AT A PRINTED CIRCUIT BOARD FACILITY.....	4.7
4.5 SAMPLING AT IRVINE RANCH WATER DISTRICT.....	4.10
 <b>chapter 5</b>	
<b>DOMESTIC BACKGROUND SAMPLING</b>	
5.1 DOMESTIC SAMPLING – OCTOBER 2000.....	5.1
5.2 DOMESTIC SAMPLING – NOVEMBER 2001 .....	5.2
 <b>chapter 6</b>	
<b>ROOT CONTROL SAMPLING</b>	
  <b>chapter 7</b>	
<b>CALCULATIONS</b>	
  <b>chapter 8</b>	
<b>REGULATORY AND OTHER ISSUES</b>	
  <b>chapter 9</b>	
<b>CONCLUSIONS AND RECOMMENDATIONS</b>	
9.1 CONCLUSIONS .....	9.1
9.2 RECOMMENDATIONS .....	9.2

## TABLE OF TABLES

---

	Page
Airbase Trunkline Survey – September 11–12, 2000.....	3.3
Airbase Trunkline Survey – September 24–29, 2000.....	3.4
Airbase Trunkline Survey – March 2001 .....	3.6
Comparison Among Plant 1 Trunklines .....	3.6
Talbert Trunkline Survey – October 8–11, 2000 .....	3.7
Sunflower Trunkline Survey – October 8–11, 2000 .....	3.7
Talbert Trunkline Survey – March 2001.....	3.9
Sunflower Trunkline Survey – March 2001 .....	3.9
Industrial Sampling – Average Concentrations, October–November 2000 .....	4.3
Industrial Sampling – Major Contributors Detail, October–November 2000.....	4.3
PCB Facility 1 – Flow-Weighted Mass Emissions, April 2001 .....	4.4
PCB Facility 2 – Flow-Weighted Mass Emissions, April 2001 .....	4.4
Industrial Point-Source NDMA Sampling – April 2001 .....	4.5
NDMA Characterization at a PCB Facility.....	4.9
IRWD Influent Sampling – October 09, 2000.....	4.10
Irvine Ranch Water District, Michelson Plant Influent.....	4.11
Irvine Ranch Water District, Michelson Plant Sludge Line.....	4.11
Domestic Background – Campus and Culver, Irvine (Turtle Rock).....	5.1
Domestic Background – Princeton, Costa Mesa (College Park) .....	5.1
Domestic Background Sampling – October 2000–November 2001 .....	5.2
Domestic Background Sampling – Raw Data for October 2000 and November 2001 .....	5.3
NDMA Sampling of Foaming Fumigant – June 2001 .....	6.1
Plant 1 Trunkline Daily Average Mass (lb/day) .....	7.1

## TABLE OF FIGURES

---

	Page
May/June 2000 Trunkline Sampling Results, Maximum Concentrations .....	3.1
Newhope / Euclid Trunk Sampling – August 8, 2000 .....	3.2
Airbase Trunk Comparison .....	3.3
Airbase Trunk Sampling – June 26, September 11 and September 24–29, 2000 .....	3.5
Airbase Trunk – Trend from Sept. 2000 to Mar. 2001 .....	3.5
Talbert Trunk – Trend from Oct. 2000 to Mar. 2001 .....	3.8
Sunflower Trunk – Trend from Oct. 2000 to Mar. 2001 .....	3.8
Oct/Nov 2000 Industry Sampling Locations by Trunkline .....	4.2

## **TABLE OF APPENDICES**

---

- Appendix A – Example Project Job Plan
- Appendix B – Project Task Force Members
- Appendix C – Letter To DTC Users, January 4, 2000
- Appendix D – OCSD Analysis Method for NDMA
- Appendix E – Newhope / Euclid Project – Meeting Minutes, August 2000
- Appendix F – Metam Sodium (DTC) – MSDS and Regulations
- Appendix G – Analysis Method Detection Limits and the California Toxics Rule
- Appendix H – MP&M Proposed Regulations, P. 446 – DTC Reference

## chapter 1

# EXECUTIVE SUMMARY

---

### 1.1 ABSTRACT

In August 2000, the Source Control Division of the Orange County Sanitation District (OCSD) was asked to assist in determining the sources of *n*-nitrosodimethylamine, or NDMA, entering OCSD Plant 1. The primary goal of the project was to reduce or eliminate concentration spikes of NDMA in the secondary effluent sent to the Orange County Water District for further treatment and reclamation. Investigation methods used between May 2000 and November 2001 included literature review, discussions with other wastewater agencies, industry inspections, sewer trunkline sampling, point source sampling, and drinking water supply sampling. The identified point sources include circuit board manufacturing, carpet dyeing, domestic sources, and the chemicals used for control of roots in sewers.

Based on information provided by the Los Angeles County Sanitation District, OCSD conducted effluent sampling at several circuit board manufacturers. The results indicated that this group is a significant source of NDMA. OCSD conducted a waste characterization study at a large circuit board manufacturer to determine the causes and pathways for NDMA creation. The study found that the use of dithiocarbamate (DTC) solutions for waste treatment was the primary source of NDMA from those facilities. This result was not unexpected, but had not been previously confirmed. Two companies accounted for 86% of the industrial portion of the NDMA mass entering OCSD's Plant 1. The total industrial contribution was about 23% of the total influent mass, while the domestic contribution was about 27%. Carpet dye operations may also be significant sources, but further study is needed to identify control methods. Other industrial processes contributed minimal or non-detectable NDMA concentrations. The remaining 50% is from as yet unknown sources.

### 1.2 BACKGROUND

On May 18, 2000, the USEPA published 40 CFR 131, Water Quality Standards: Establishment of Numeric Criteria for Priority Toxic Pollutants for the State of California, generally known as the California Toxics Rule. This final rule had a profound effect on municipalities involved in water reclamation. One pollutant in particular, called *n*-nitrosodimethylamine, or NDMA, is a serious concern because of its potential cancer link and its extremely low discharge limit. Since the summer of 2000, the Orange County Sanitation District (OCSD), in coordination with other regional agencies, has been involved in projects to identify and reduce the sources of NDMA to the sewer.

NDMA is identified as a carcinogen under California's Health and Safety Code Section 25249.5, et seq., the Safe Drinking Water and Toxic Enforcement Act of 1986 ("Proposition 65"). In addition, the US Environmental Protection Agency (US EPA) identifies NDMA as a "probable human carcinogen" (US EPA, 1997), and the National Toxicology Program lists NDMA as "reasonably anticipated to be a human carcinogen" (NTP, 1998). Because NDMA historically has not been considered a common drinking water contaminant, it has no state or federal maximum contaminant level (MCL). There is currently no standard or approved analytical method for NDMA at very low levels. In the absence of drinking water standards, the California State Department of Health Services uses a drinking water "action level" for the protection of public health, currently set at 20 ppt.

During the course of the OCSD efforts, analytical methods were developed by the District's laboratory that enabled the detection of NDMA in wastewater near the State's action level. The laboratory at the Orange County Water District (OCWD) uses a similar method for detection of 2 ppt in drinking water. These advances were critical to the OCSD effort to identify the sources of NDMA. Doing these analyses in-house enabled OCSD to collect as many samples as needed for statistical usefulness, without extreme cost. From May 2000 to November 2001, the District conducted a study that included literature review, discussions with other wastewater agencies, industry inspections, trunkline sampling, point source sampling, and drinking water supply sampling. The project coordinated OCSD's efforts with the OCWD,

Los Angeles County Sanitation District, and Irvine Ranch Water District. Research was conducted to identify potential point sources of NDMA and its precursors.

### 1.3 PROJECT SUMMARY

In May 2000, the NDMA project was initiated between the OCWD and OCSD's Laboratory. These agencies are involved in a major water reclamation project that will eventually send 100 million gallons per day of secondary effluent from OCSD Plant 1 to new treatment facilities at OCWD. NDMA surfaced early on as an obstacle to meeting the new California Toxics Rule limits for the treated water that OCWD would use for groundwater replenishment. In order to construct sufficient capacity to treat NDMA, OCWD asked OCSD to control NDMA concentrations in the OCSD influent through source control or other means. The goal was to eliminate or reduce the large concentration spikes detected in the OCWD influent received from OCSD. OCWD currently takes up to 10 MGD of OCSD secondary effluent for use in greenbelt irrigation and injection in seawater barrier wells along the Orange County coast.

The project evolved into three principle tasks: trunkline monitoring, industrial sampling, and domestic background sampling. Trunkline monitoring was performed to determine which of the five main Plant 1 trunklines were responsible for the majority of influent NDMA. Trunkline flows were used to calculate influent NDMA mass. Mass values were used to determine which trunklines were contributing most of the NDMA. Once the "hot" trunklines were determined, additional sampling was conducted at industrial permittees on those trunklines. Locations were chosen through literature review on the types of industries that may discharge NDMA. The list eventually included printed circuit board manufacturers, carpet dye houses, chemical manufacturers, and sewer root-removal operations. Flow measurement was conducted at most of the industrial locations, and flow-weighted composite data was obtained from two major NDMA dischargers. Sampling of purely domestic neighborhoods was also conducted to determine the domestic background NDMA concentration. This data may be used to propose new local limits for industrial NDMA discharge.

#### Trunkline Sampling

Based on the preliminary work on Plant 1 trunklines, the Sunflower, Talbert and Airbase trunks were the subjects of this project, where most of the significant industrial NDMA sources were found. The remaining Plant 1 trunks, the Euclid and Newhope, were sampled early in the project and contained only low levels of NDMA. Trunk sampling at the headworks was done primarily to gauge the effects of source control at industries, and to provide data to the OCWD for planning purposes.

Grab sampling on large trunks was attempted on two occasions but were not very useful because the sources were extremely variable during each day. Automatic samplers could not be used due to the weight of the equipment. The requirement for ice and glass bottles rendered the equipment too heavy to safely hang on a manhole jack. Initial planning called for a systematic survey of the trunks, starting at Plant 1 and working out toward point sources. This plan was abandoned when a sufficient number of point sources were found without additional trunk sampling.

Definite NDMA concentration patterns emerged after several days of trunkline data became available, including the absence of NDMA concentration spikes during the weekends and low NDMA concentrations during early morning hours. This information helped to narrow down the scope of the project. It was now believed that the significant sources were associated with the standard 5-day work week, and that the sources were mainly of the batch discharge variety as opposed to constant flow. The goals of the project were refined to finding and removing the sources of large NDMA spikes, and providing an estimate of the background NDMA concentration from domestic sources.

Mass calculations at the influent trunks provided an estimate of the percentage of NDMA coming from known sources. Some companies were responsible for as much as 3% of NDMA mass entering Plant 1 on the tributary trunkline during one day. A large percentage of NDMA derives from non-point domestic sources.



## **Industrial Sampling**

Work on the industrial segment began with input from the Los Angeles County Sanitation District (LACSD), which had been conducting an NDMA study of its own for several months. LACSD identified printed circuit board operations as a source when routine organics analysis of a metal finisher discharge showed large concentrations of NDMA. LACSD also contributed information on the use of DTC-based foaming fumigants, which are widely used in the OCSD service area. Cooling towers and fabric dye houses were added to the sampling list after a literature review. Several potential NDMA sources were not investigated because they either do not exist in the service area or they are tributary to OCSD Plant 2.

Composite samples were collected at industrial discharges using automatic equipment. Samples were collected during regular operating hours. Sampling in March 2001 included hourly flows for two of the largest dischargers, providing flow-weighted mass data. Discharge mass was calculated to find the percentage of total NDMA contributed to Plant 1 by these sources. The total number of known DTC users at the time of the project was about 20. The overall contribution to the Plant 1 influent from all known industrial point sources was about 11%. NDMA was detected at all facilities that use DTC for pretreatment.

An NDMA characterization was conducted at a large printed circuit board (PCB) facility located in the City of Irvine. The company provided information on the manufacturing process layout and the pretreatment system. OCSD collected or supervised the collection of samples from every discharge point. At the time of the March 2001 sampling, this company was evaluating a new DTC product that claimed to reduce the amount of NDMA seen at the sample box, and was using the product in the Memtek system. The original product was used in the batch treatment system.

It is likely that the complex matrix of a printed circuit board wastestream contains NDMA precursors, but results showed that NDMA is created in significant amounts only in the presence of DTC. OCSD has encouraged the industrial users and their vendors to conduct research on the chemistry of NDMA in their systems.

## **Domestic Background**

There were three principle goals for domestic sampling. First was the initial request from OCWD to provide data with which to plan and construct treatment facilities for NDMA destruction. Another goal was then developed to reduce industrial point sources to domestic levels. Local limits on NDMA may eventually be generated using the domestic data.

Sampling was conducted at six locations throughout the County. Background concentrations varied widely over the service area, with a range from non-detected (ND) to about 600 ng/L, and an average of about 103 ng/L for detected amounts. This concentration accounts for about 27% of total influent NDMA at Plant 1. Two samples were collected from potable water distribution systems. NDMA was detected at 4.2 ng/L in the potable water sample collected in the Turtle Rock area, in the City of Irvine. Irvine potable water is provided by Metropolitan Water District. A sample collected in the College Park area of Costa Mesa was non-detect for NDMA. That water is a blend of MWD and local well water.

## chapter 2

# PROJECT METHODS

---

### 2.1 PLANNING

Planning was influenced by the goal of immediately reducing or eliminating influent NDMA concentration spikes above the domestic background. The project was conducted in discreet phases, each one developed and implemented only after preceding phases were complete. The job plans included an outline of the work to be accomplished, staffing requirements, lab support, and project duration. All affected division heads reviewed the job plans and provided input. The District's Laboratory in particular was consulted during the development of each phase, because the Lab performed all analyses in-house. See **appendix a** for sample job forms.

### 2.2 COMMUNICATION

The NDMA project group included OCSD staff from Source Control, Laboratory, Collections, and Operations. OCWD contributed members of their management, operations and laboratory. Meetings were held to present the collected data, assess the impacts of source control on NDMA influent concentrations, and to plan the next steps. Due to the large number of samples, the Lab and Source Control staffs were tightly integrated, with a set of operating procedures in place to ensure quality. The project group is listed in **appendix b**.

A number of discussions were held with chemical vendors. This proved to be a valuable resource, since the distributors and chemical manufacturers were in a position to make product changes in response to our needs. One result of these discussions was the reformulation of DTC to reduce or eliminate residual NDMA in the product. A second and more important outcome was the shift by environmental consultants and chemical suppliers from recommending DTC-based systems to other systems based on ion exchange or sulfide.

On January 4, 2001 the District sent a mass-mail letter to all Class I permittees in the Metal Finishing categories (**appendix c**). The letter requested the elimination of DTC as a treatment chemical for metals removal. Response to the letter was varied. A small number of facilities commented that DTC was the only method that ensured compliance with metal discharge limits, and that they would resist change if possible. More facilities and their vendors responded that DTC would be replaced but that additional time was needed for the transition.

All Source Control staff were briefed on the project and given a page of "frequently asked questions" for their use when they received calls. Companies were reminded of the obligation to be in compliance with OCSD's requirements at all times and to ensure that transition away from DTC usage did not cause non-compliant discharges.

An NDMA intranet site was established for use by all project staff. The site included links to background literature, analysis data, current announcements, frequently asked questions, forms, project history, and contacts.

### 2.3 SAMPLE COLLECTION

Samples collected by automatic equipment were time-composited in 24 discreet bottles, four samples per bottle, with samples at 15-minute intervals. Prior to extraction and analysis, bottles were combined into four-hour composites. This method was used for all trunkline monitoring at the Plant 1 headworks, at industrial discharges, and for domestic sampling. Grab samples were collected when sampling on the trunklines upstream from Plant 1 where composite sampling could not be safely performed. Grab samples were also collected from discreet industrial processes.

In general, it was found that the quality of NDMA analysis results at low ppt levels was highly influenced by variations in sampling and preservation technique. Temperature and holding time were the critical factors. The following procedures were used to ensure consistent quality.

- Glass bottles were cleaned by the Laboratory with soap and distilled water, then baked in a high-temp oven.
- New tygon pump tubing was used for each new sampling location.
- Automatic sampling equipment was installed with a full load of ice. Ice levels were checked and maintained during the sample intervals.
- Composite samples were collected in 24 discreet 300 mL glass bottles.
- At locations where composite samples were not possible, multiple grab samples were collected at regular intervals and kept on ice.
- Samples were delivered to the Lab within 24 hours of collection.

## 2.4 SAMPLE ANALYSIS

OCSD's Laboratory performed all NDMA analyses in-house, using State methods enhanced by OCSD analysts. All samples submitted to the Lab included a report form with information about the sample matrix, including source, pH, and other substances if known. Standard procedure for time-composite samples was to combine four hourly bottles into a four-hour composite. Sample start times were almost always on the hour, allowing for the creation of consistent data tables. In the case of Plant 1 influent trunkline monitoring, on-the-hour sampling allowed for calculation of influent NDMA mass.

Interferences were tackled by using an amine-specific capillary column and a pH range of 5 to 9 during extraction. The instrument was set up with chemical ionization using methane as a reagent gas. This technique virtually eliminated all interferences. Interference could occur if it had the same mass energy ratio as NDMA. It was unusual but it did happen with dithiocarbamate and the root chemical. In these cases the Lab did a dilution to separate the interference. Also, if necessary, different injection and temperature programs were employed.

The instrument had a routine calibration from 10 ppt to 10,000 ppt. Routine extractions used 1000 mL for sample volumes. Industrial source samples routinely used 500 mL for sample volume extractions. For samples with known NDMA present, sample volumes were diluted with reagent water and varied from 50 mL to 500 mL. A few of the samples were diluted at the sample extract stage in order to fit within the calibration range. This is a routine procedure for environmental samples where compounds in a single sample can range from ND to a high concentration. The use of the recovery surrogate NDMA-d6 enabled the Lab to monitor the efficiency of the extraction.

The State requires the use of NDMA-d6 as a recovery surrogate, and provides QAQC guidelines for spikes and duplicates. The use of an ion trap GCMS is recommended but not required. Chemical ionization was suggested but not required. Enhancements to the method were made by the District's Lab, including development of specific guides for injection, type of solvent used, chemical ionization parameters, type of capillary column, pH range for extraction, temperature program, and tuning parameters for the ion trap. Guidelines were developed for dilutions at the sample extract level. The Orange County Water District employed many of these enhancements, although they were analyzing semi-clean to clean water samples. A copy of the District's method is included as **appendix d**.

## chapter 3

# TRUNKLINE SAMPLING

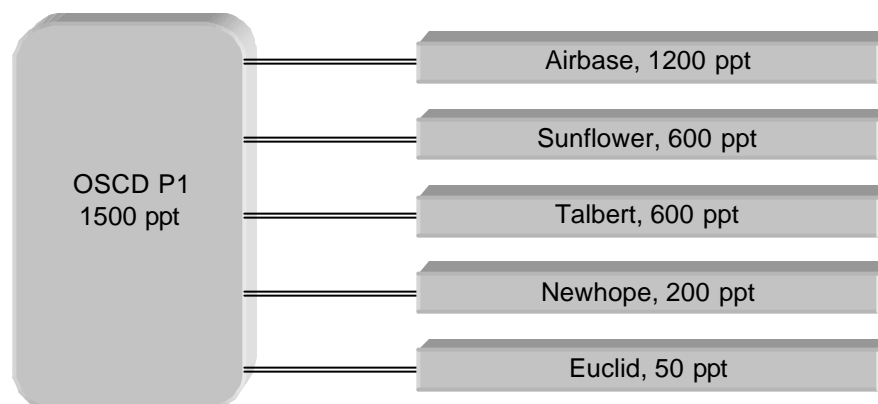
---

### 3.1 BACKGROUND

Prior to involvement by the Source Control Division, most of the initial research was conducted by the District's Laboratory. This work included coordination with the Orange County Water District, research on destruction methods, and sampling at the Plant 1 influent trunklines, AS influent and effluent, and Source Control sampling of a chemical manufacturer and a paper manufacturer. The industry samples were non-detect for NDMA. Results of the initial trunkline sampling conducted between May and June 2000 indicated that the Airbase Trunk had the highest NDMA concentration, followed by the Sunflower and Talbert trunks.

#### May/June 2000 Trunkline Sampling Results, Maximum Concentrations

Reference: Minutes of OCSD NDMA Taskforce, 08/17/2000 - appendix e



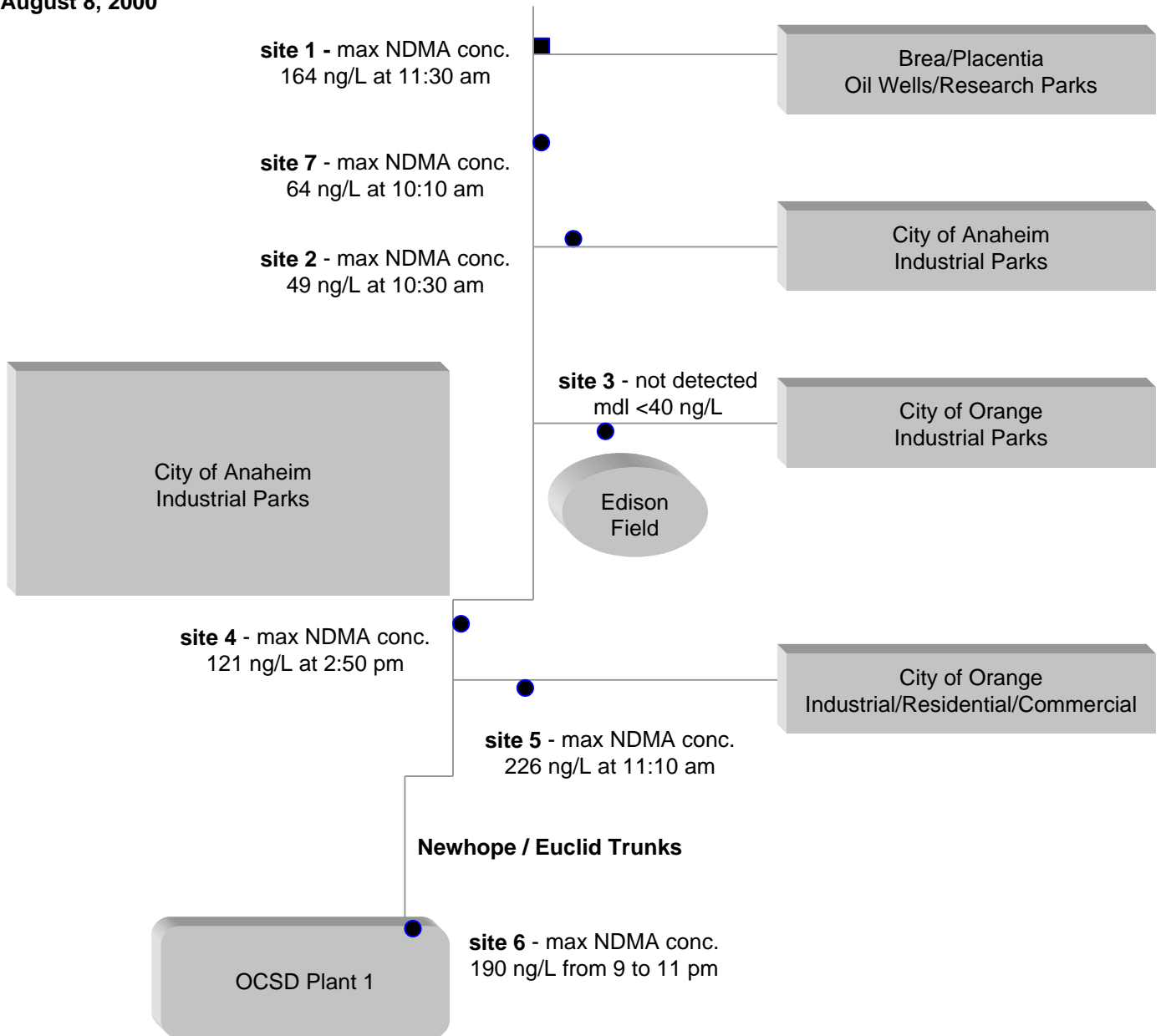
### 3.2 NEWHOPE / EUCLID TRUNK SAMPLING – AUGUST 8, 2000

Sampling was conducted on August 4, 2000 on the Newhope Trunk and its tributaries. The Newhope project also provided information on the Euclid Trunk, which runs parallel and is connected to the Newhope through numerous diversion structures. The sample data showed no NDMA concentrations above the domestic background, established later at a range of 0-600 ng/L. This result allowed Source Control to eliminate the Euclid and Newhope trunks from further investigation, concentrating efforts on the remaining trunklines.

The Newhope Trunk was the subject of a discussion on August 17, 2000 among the project members. Initial analyses of Newhope samples showed high NDMA concentrations. But the analysts also noticed that the peaks were “non-symmetrical”, indicating that the chromatographic column was not capable of separating the compounds from each other. A type of column specific for amine compounds was installed. The new column was able to separate NDMA from a previously undetected interfering substance. The results showed that the high concentrations seen previously were actually the interfering substance itself and not NDMA. **Appendix e** is a copy of the meeting minutes, with details of the new procedure.

### **Newhope / Euclid Trunk Sampling**

**August 8, 2000**



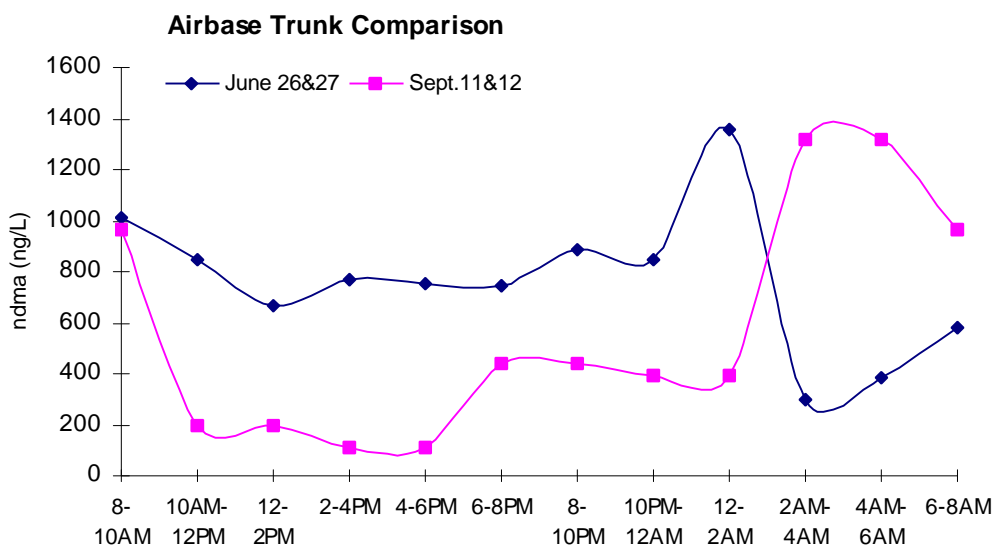
### 3.3 AIRBASE TRUNK SAMPLING – SEPTEMBER 11, 2000

On August 27, prior to the start of trunkline sampling, the Airbase Trunk was diverted from Plant 1 to Plant 2 by the Operations Division as a means of reducing NDMA delivered to OCWD in the secondary effluent. OCWD samples collected after the diversion showed that NDMA concentrations were reduced by about 50% from samples collected in June 2000. Therefore, the Airbase Trunk and its point sources were investigated, since the flow from Airbase might be required in Plant 1 in the future.

The Airbase Trunk was composite sampled on September 11, 2000. Three upstream trunkline locations were grab sampled. At this point in the investigation the Airbase Trunk was the only one with significant NDMA concentration “spikes”, so the initial effort was to confirm the June 2000 findings and begin to sample upstream locations on the trunkline. The data from the composite confirmed that the Airbase Trunk was a contributor of concentration spikes, which occurred between 2:30 am and 10:30 am on September 12. The pattern was different from June 2000, indicating that NDMA spikes would be a moving target. The upstream grab samples were all below detection limits. Review of the sample collection methods shows that the grab samples probably did not receive the amount of refrigeration required. The grab sample results are therefore not considered representative. The results of this phase showed that the pattern of influent NDMA concentrations varies from day to day.

**Airbase Trunkline Survey – September 11-12, 2000**

Date	Time	NDMA (ng/L)
09/11/2000	2:30-6:30pm	106
09/11/2000	6:30-10:30pm	437
09/12/2000	10:30pm-2:30am	390
09/12/2000	2:30-6:30am	1320
09/12/2000	6:30am-10:30am	967
09/12/2000	10:30-am-2:30pm	194



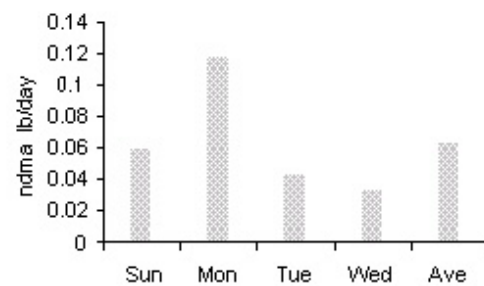
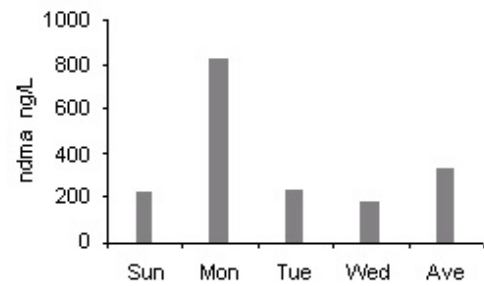
### 3.4 AIRBASE TRUNK MULTIPLE DAY SAMPLING – SEPTEMBER 24–29, 2000

Four consecutive composite samples were collected from the Plant 1 Airbase influent, starting on Sunday, September 24. The reason for continued sampling on the Airbase influent was the high variability, not only of NDMA concentration but also of concentration patterns during each day. The results of this phase showed that the NDMA concentrations continued to be lower than results from June 2000. Otherwise concentrations were relatively low. Hourly flows were recorded and used to calculate influent mass. The mass values tracked closely to the concentration. The data representing Sunday, September 24 shows NDMA at the domestic background level. The data confirms that a large point source (or sources), discharging once every few days, was probably responsible for the high concentration spikes. The average NDMA mass was 0.063 pounds per day, over four days. The data is presented in the table below.

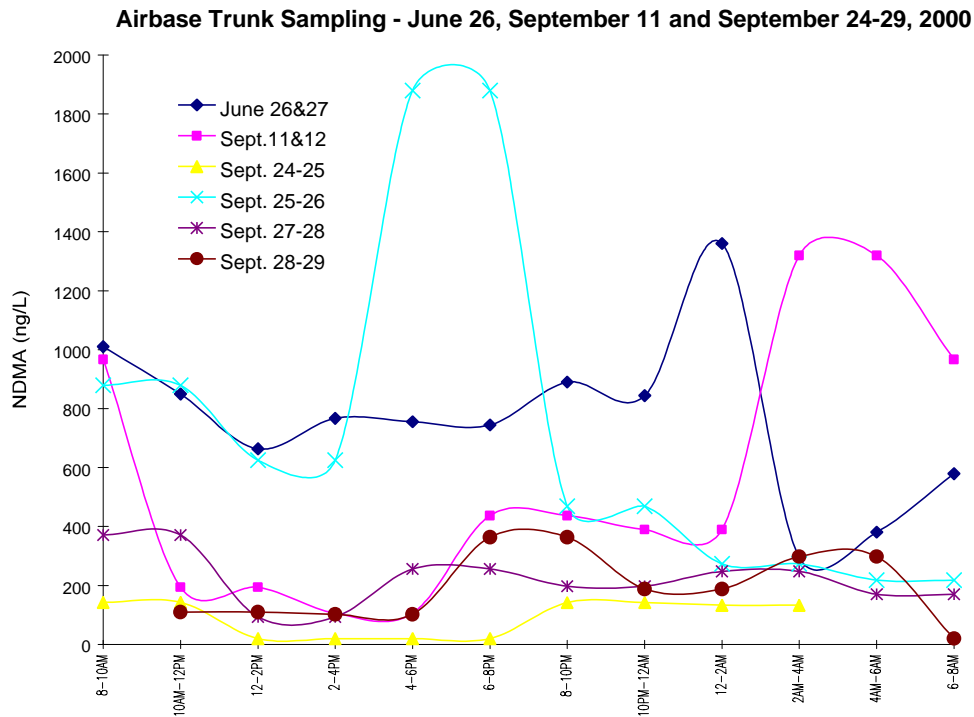
Combined with earlier results, the Airbase data shows that influent NDMA concentrations do not follow a narrow time pattern. General patterns include no high concentrations on weekends and isolated high concentrations occurring mid-week between 5 am and 10 pm. High concentration events occurred once every few days and lasted for two to four hours. The following graph compares the results from six 24-hour periods. Based on this information, the project group decided that composite sampling of main trunklines upstream from Plant 1 would not be the most efficient way to proceed. Instead, the remaining trunklines in the study area, the Sunflower and Talbert trunks, were sampled at Plant 1. Industrial point sources were sampled during the next phase of the project.

#### Airbase Trunkline Survey – September 24–29, 2000

Sample Date	Sample time	Flow (mg)	NDMA (ng/L)	NDMA (lb)
09/24/2000	0800-1200	3.52	143	0.004
09/24/2000	1200-1600	4.7	20	0.001
09/24/2000	1600-2000	4.2	20	0.001
09/24/2000	2000-2400	4.1	142	0.005
09/25/2000	2400-0400	2.7	133	0.003
09/25/2000	0900-1300	6.2	879	0.045
09/25/2000	1300-1700	5	625	0.026
09/25/2000	1700-2100	4.3	1880	0.067
09/25/2000	2100-0100	4	469	0.016
09/26/2000	0100-0500	2.4	273	0.005
09/26/2000	0500-0900	2.4	218	0.004
09/27/2000	0900-1300	4.7	371	0.015
09/27/2000	1300-1700	4.2	93	0.003
09/27/2000	1700-2100	4.1	256	0.009
9/27-28/00	2100-0100	4	198	0.007
09/28/2000	0100-0500	2.3	248	0.005
09/28/2000	0500-0900	2.4	170	0.003
09/28/2000	1000-1400	4.8	110	0.004
09/28/2000	1400-1800	4	102	0.003
09/28/2000	1800-2200	4.2	364	0.013
9/28-29/00	2200-0200	3.7	188	0.006
09/29/2000	0200-0600	1.9	298	0.005
09/29/2000	0600-1000	3	20	0.001

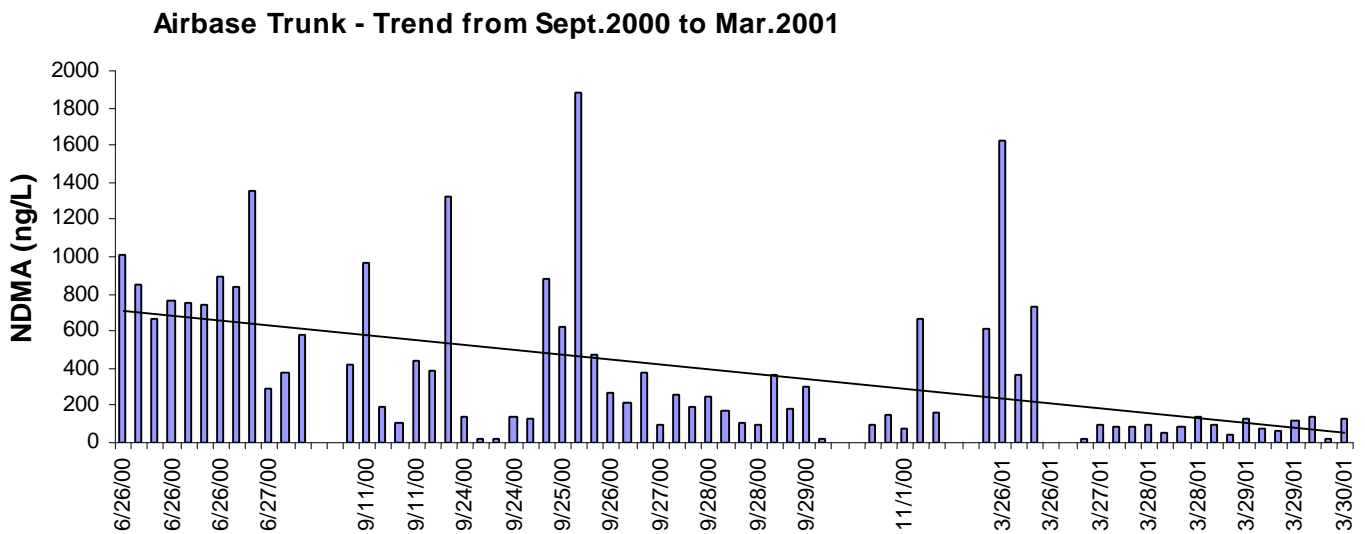


**Averages: 327 ng/L 0.063 lb/day**



### 3.5 AIRBASE TRUNK SAMPLING – MARCH 2001

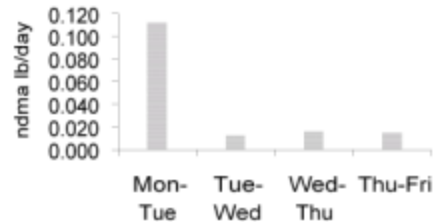
Composite samples were collected from the Airbase Trunk in March, 2001. The purpose was to determine whether product substitutions at major industrial dischargers were effective in reducing influent NDMA concentrations. Samples were also collected from 12 industrial dischargers, and a sample collected to determine if cooling towers are a significant NDMA source. A comparison of the trunkline data from September 2000 with the data from March 2001 shows a 38% reduction of influent mass on the Airbase Trunk. Printed circuit board facilities on the Airbase Trunk began conversions to non-DTC solutions in January 2001.





**Airbase Trunkline Survey – March 2001**

Sample Date	Sample Time	NDMA (ng/L)	Flow (mg)	NDMA(lb)
3/26/01	0800-12:00	612	3.81	0.019
3/26/01	1200-16:00	1625	4.38	0.059
3/26/01	16:00-20:00	362	3.73	0.011
3/26/01	20:00-24:00	727	3.61	0.022
3/26/01	24:00-04:00	ns		ns
3/26/01	04:00-08:00	ns		ns
3/27/01	0800-12:00	20	4.02	0.001
3/27/01	12:00-16:00	98	3.94	0.003
3/27/01	16:00-20:00	85	3.6	0.003
3/27/01	20:00-24:00	91	3.87	0.003
3/28/01	24:00-04:00	97	2.66	0.002
3/28/01	04:00-08:00	54	1.06	0.000
3/28/01	08:00 - 12:00	86	4.36	0.003
3/28/01	12:00 - 16:00	141	3.98	0.005
3/28/01	16:00 - 20:00	102	3.68	0.003
3/28/01	20:00 - 24:00	39	3.87	0.001
3/29/01	24:00 - 04:00	132	2.58	0.003
3/29/01	04:00 - 08:00	71	1.02	0.001
3/29/01	08:00 - 12:00	61	4.67	0.002
3/29/01	12:00-16:00	120	4.02	0.004
3/29/01	16:00-20:00	141	3.69	0.004
3/29/01	20:00-24:00	20	3.9	0.001
3/30/01	24:00-04:00	128	2.72	0.003



ns = no sample collected                      averages: 229 ng/L    0.039 lb/day

**3.6 TALBERT AND SUNFLOWER TRUNK SAMPLING – OCTOBER 2000**

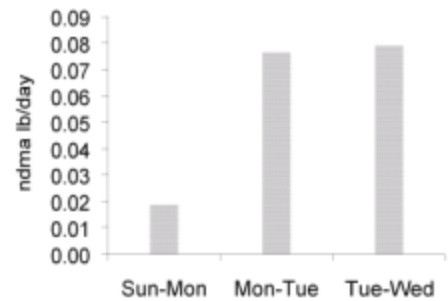
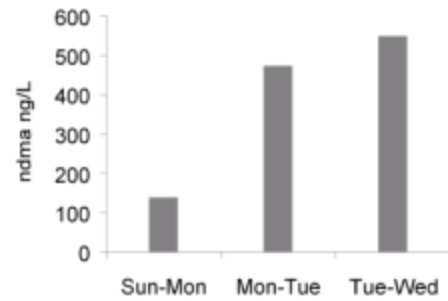
Three consecutive 24-hour composite samples were collected from the Talbert and Sunflower trunks at the Plant 1 headworks starting on Sunday, October 8. One of the objectives was to determine if NDMA spikes were observed on weekends. The results show that high concentration NDMA spikes are not observed on Sunday. The weekend readings were assumed to be coming mainly from domestic and other non-point sources. A diurnal pattern was observed on weekdays, with NDMA concentrations peaking at mid-morning on the Talbert Trunk and in the late evening on the Sunflower Trunk. Hourly flows were collected and used to calculate mass loading. The results showed that the average concentration of NDMA from the Airbase, Talbert, and Sunflower trunks was similar, with no trunkline obviously and consistently higher than the other. The charts on the following page present the data from this task.

**Comparison Among Plant 1 Trunklines**

Trunk	ng/L	lb/day	Sample Date
Airbase	327	0.063	09/2000
Talbert	387	0.058	10/2000
Sunflower	347	0.067	10/2000

**Talbert Trunkline Survey – October 08-11, 2000**

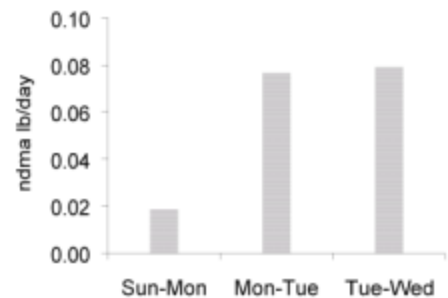
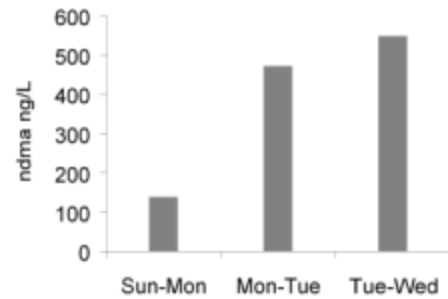
Sample Date	Sample Time	Flow (mg)	NDMA (ng/L)	NDMA (lb)
10/08/2000	9:00-13:00	3	208	0.005
10/08/2000	13:00-17:00	3.5	128	0.004
10/08/2000	17:00-21:00	3.25	75	0.002
10/8-9/2000	21:00-1:00	2.9	85	0.002
10/09/2000	1:00-5:00	1.8	143	0.002
10/09/2000	5:00-9:00	2.1	196	0.003
10/09/2000	9:00-13:00	3.35	515	0.014
10/09/2000	13:00-17:00	3.4	600	0.017
10/09/2000	17:00-21:00	3.6	711	0.021
10/9-10/2000	21:00-1:00	3.8	467	0.015
10/10/2000	1:00-5:00	1.9	351	0.006
10/10/2000	5:00-9:00	2.1	193	0.003
10/10/2000	9:00-13:00	3.5	380	0.011
10/10/2000	13:00-17:00	3.3	619	0.017
10/10/2000	17:00-21:00	3.4	845	0.024
10/10-11/00	21:00-1:00	3.5	240	0.007
10/11/2000	1:00-5:00	1.9	965	0.015
10/11/2000	5:00-9:00	2.3	242	0.005



**Averages: 387 ng/L 0.058 lb/day**

**Sunflower Trunkline Survey – October 08-11, 2000**

Sample Date	Sample Time	Flow (mg)	NDMA (ng/L)	NDMA (lb)
10/08/2000	9:00-13:00	3.8	377	0.012
10/08/2000	13:00-17:00	5.1	200	0.009
10/08/2000	17:00-21:00	4.4	148	0.005
10/8-9/2000	21:00-1:00	4.2	20	0.001
10/09/2000	1:00-5:00	2.4	54	0.001
10/09/2000	5:00-9:00	2.6	310	0.007
10/09/2000	9:00-13:00	4.6	321	0.012
10/09/2000	13:00-17:00	4.9	462	0.019
10/09/2000	17:00-21:00	4.8	391	0.016
10/9-10/2000	21:00-1:00	4.8	235	0.009
10/10/2000	1:00-5:00	2.6	201	0.004
10/10/2000	5:00-9:00	2.8	794	0.019
10/10/2000	9:00-13:00	4.85	415	0.017
10/10/2000	13:00-17:00	4.7	271	0.011
10/10/2000	17:00-21:00	4.5	426	0.016
10/10-11/00	21:00-1:00	4.7	354	0.014
10/11/2000	1:00-5:00	2.6	129	0.003
10/11/2000	5:00-9:00	2.8	1141	0.027

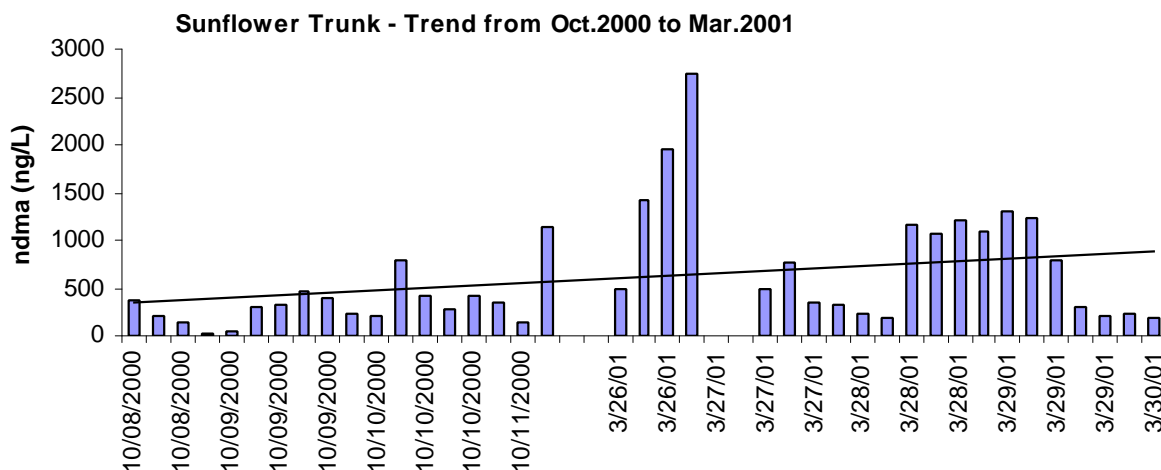
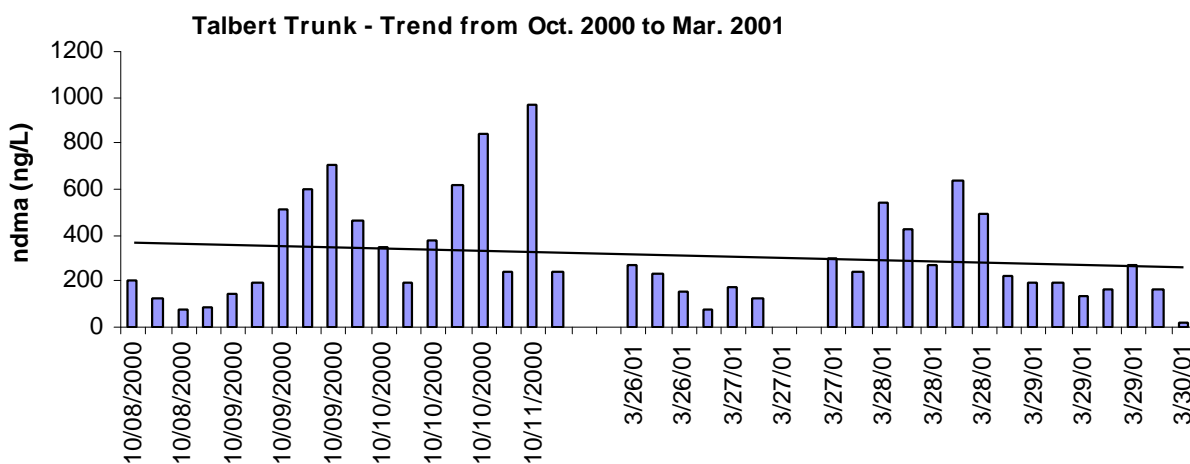


**Averages: 347 ng/L 0.067 lb/day**

### 3.7 TALBERT AND SUNFLOWER TRUNK SAMPLING – MARCH 2001

Composite samples were collected from the Talbert and Sunflower trunks in March, 2001. The purpose was to determine whether product substitutions and operational changes at major industrial dischargers were effective in reducing influent NDMA concentrations. A comparison of the trunkline data from October 2000 with the data from March 2001 shows a 35% reduction of influent mass on the Talbert trunk. The majority of facilities on the Talbert Trunk are relatively small printed circuit board operations.

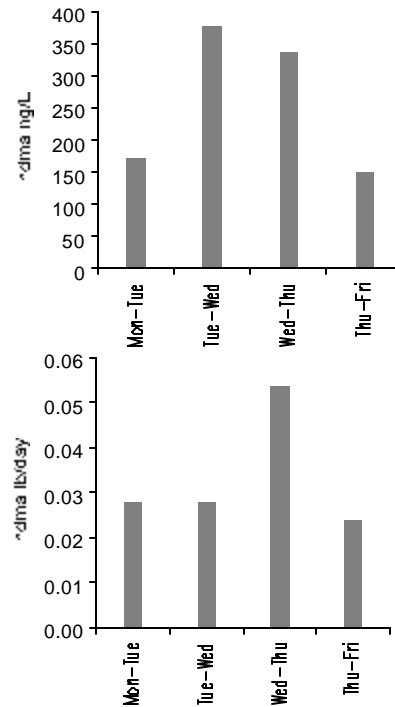
A comparison of the Sunflower trunkline data from October 2000 with the data from March 2001 shows a 130% increase. The increase on the Sunflower Trunk may be attributable to a single printed circuit board facility in Irvine. This facility was still using DTC as the principle agent for metals removal in both flow-through and batch treatment. The overall trends and the raw data are presented below and on the next page.



**Talbert Trunkline Survey: March 2001**

date	time	flow	ndma (ng/L)	mass
3/26/01	0800-12:00	3.68	271	0.008
3/26/01	12:00-16:00	3.78	233	0.007
3/26/01	16:00-20:00	3.34	153	0.004
3/26/01	20:00-24:00	3.61	79	0.002
3/27/01	24:00-04:00	2.41	177	0.004
3/27/01	04:00-08:00	1.97	121	0.002
3/27/01	08:00-12:00		ns	ns
3/27/01	12:00-16:00		ns	ns
3/27/01	16:00-20:00	3.23	300	0.008
3/27/01	20:00-24:00	3.32	242	0.007
3/28/01	24:00-04:00	2.07	543	0.009
3/28/01	04:00-08:00	1.06	425	0.004
3/28/01	08:00 - 12:00	3.37	272	0.008
3/28/01	12:00 - 16:00	3.6	641	0.019
3/28/01	16:00 - 20:00	3.57	493	0.015
3/28/01	20:00 - 24:00	3.87	226	0.007
3/29/01	24:00 - 04:00	2.23	196	0.004
3/29/01	04:00 - 08:00	0.85	194	0.001
3/29/01	08:00 - 12:00	3.72	140	0.004
3/29/01	12:00-16:00	3.93	162	0.005
3/29/01	16:00-20:00	3.88	268	0.009
3/29/01	20:00-24:00	3.86	166	0.005
3/30/01	24:00-04:00	2.53	20	0.000

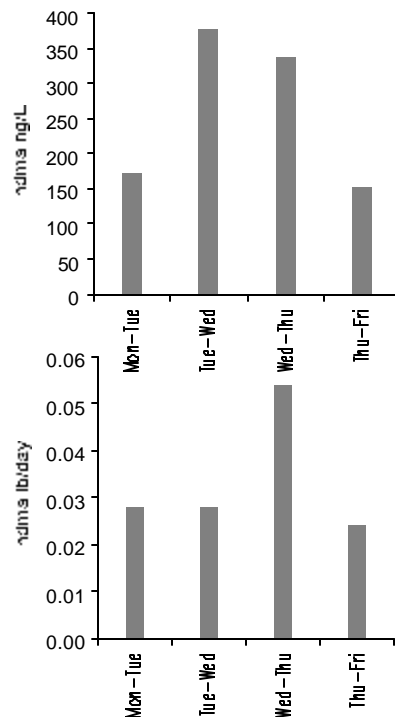
ns = no sample collected      averages:      253 ng/L      0.038 lb/day



**Sunflower Trunkline Survey: March 2001**

date	time	flow	ndma (ng/L)	mass
3/26/01	0800-12:00	4.44	494	0.018
3/26/01	12:00-16:00	4.82	1430	0.057
3/26/01	16:00-20:00	4.42	1950	0.072
3/26/01	20:00-24:00	4.8	2750	0.110
3/27/01	24:00-04:00		ns	ns
3/27/01	04:00-08:00		ns	ns
3/27/01	0800-12:00	4.54	485	0.018
3/27/01	12:00-16:00	4.71	774	0.030
3/27/01	16:00-20:00	4.34	340	0.012
3/27/01	20:00-24:00	4.82	331	0.013
3/28/01	24:00-04:00	2.91	238	0.006
3/28/01	04:00-08:00	2.51	195	0.004
3/28/01	08:00 - 12:00	4.4	1165	0.043
3/28/01	12:00 - 16:00	4.57	1074	0.041
3/28/01	16:00 - 20:00	4.36	1203	0.044
3/28/01	20:00 - 24:00	4.72	1101	0.043
3/29/01	24:00 - 04:00	2.97	1303	0.032
3/29/01	04:00 - 08:00	2.51	1232	0.026
3/29/01	08:00 - 12:00	3.9	784	0.026
3/29/01	12:00-16:00	6.86	309	0.018
3/29/01	16:00-20:00	4.38	217	0.008
3/29/01	20:00-24:00	4.74	240	0.009
3/30/01	24:00-04:00	2.97	193	0.005

ns = no sample      averages:      848 ng/L      0.159 lb/day



## chapter 4

# **INDUSTRIAL SAMPLING AND IRWD SAMPLING**

---

### **4.1 SUMMARY**

#### **Industrial Sampling**

During May and June 2000, OCSD and the Orange County Water District (OCWD) conducted literature searches and consulted with other sewerage agencies to identify potential sources of Nitrosodimethylamine (NDMA). One possible source identified was the reaction of chlorine products with other compounds to form NDMA. Two large manufacturers of paper and chemicals were identified that use chlorine products in their processes. Prior to the main sampling program initiated in October 2000, these two companies were composite sampled at their effluents in June 2000. No detectable NDMA was found, and no additional sampling was conducted on these types of discharger.

During the planning stages for industrial sampling, the Los Angeles County Sanitation District provided information that NDMA is found in the effluents from metal finishers and printed circuit board (PCB) operations that use dithiocarbamate, also known as DTC. DTC is used in these facilities for metals removal, particularly copper, lead and nickel. Research and planning for industrial sampling began in September 2000, including a search of OCSD files and databases for permittees using DTC. A list of PCB facilities was generated, including large and small shops tributary to OCSD Plant 1. Fabric dyes were known to be a potential NDMA source, so the sampling project included two large carpet dye facilities that are tributary to OCSD Plant 1.

Industrial sampling occurred in two phases. Sampling during the first phase, in October 2000, was conducted to measure the NDMA at known DTC users and at the two fabric dye facilities. The results of the sampling showed that DTC usage generates significant amounts of NDMA in the discharges from PCB facilities, and that fabric dye is also a potential source. OCSD then sent a letter in January 2001 to all metal finishers in the service area, asking them to reduce or eliminate the usage of DTC within two months. Feedback received from PCB facilities was mixed. Some facilities began the transition to other treatment chemistries. Others expressed concern that the deadline did not give enough time for changing chemistry. Others indicated that removal of DTC from the pretreatment process was causing non-compliance with discharge permit limits for metals.

The second sampling phase, conducted in April 2001, was meant to determine whether any reductions could be measured at previously sampled industries, and to sample newly identified industries. The results showed that the large PCB facilities were still using DTC and were experiencing difficulties implementing new chemistries. Most of the smaller facilities were having less trouble and several had successfully removed DTC from their systems. The majority of the smaller PCB facilities discharged NDMA near domestic background levels of approximately 150 ng/L, plus or minus 50 ng/L.

This chapter includes an in-depth study of NDMA formation in a full-service PCB facility, and concludes that NDMA formation is strongly linked to the use of DTC for metals removal in waste treatment.

#### **IRWD Sampling**

The industrial sampling project also targeted the flow into the OCSD system from a sewage treatment plant owned and operated by the Irvine Ranch Water District (IRWD). IRWD does not have sludge handling facilities of its own and sends its sludge to OCSD through a dedicated connection. Since at least one potential NDMA source was tributary to IRWD, sampling was conducted on the sludge disposal line and influent to the IRWD sewage treatment plant to determine whether any significant concentrations of NDMA were present. The IRWD sludge line had an NDMA concentration in the domestic range, while the IRWD Michelson Plant influent had NDMA concentrations as high as 1400 ng/L. Further study is needed to identify the fate of NDMA through the IRWD Michelson Plant.

## 4.2 INDUSTRIAL SAMPLING – OCTOBER 2000

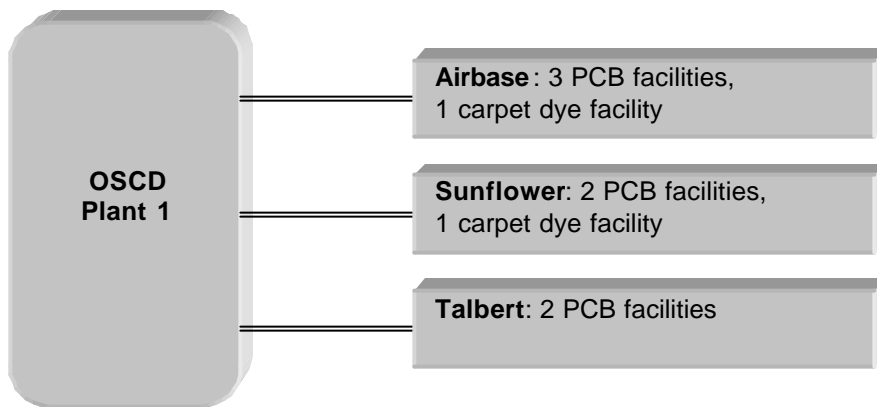
Composite samples were collected from the discharges of seven printed circuit board facilities and two carpet dye facilities during October and November 2000. Industries were chosen for sampling by Federal category, tributary trunkline, daily flow, file information on DTC usage, and literature review.

Two permittees tributary to the Airbase Trunk were sampled. One facility was chosen as a reference sample location, because it does not use DTC. This facility was either near or below the NDMA detection limit during the entire period. The second facility, which uses DTC products in flow-through and batch treatment, had high NDMA concentrations. A third facility, located on the Sunflower Trunk in Irvine, used DTC products for pretreatment and had readings similar to those from the second. Discharge concentrations increased after batch treatment at both companies. A fourth company, located in Santa Ana and tributary to the Talbert Trunk, uses DTC in batch treatment. No batches were released to the sewer from that facility during the sample period, and NDMA concentrations were low.

Samples were also collected from two carpet dye companies. Samples from a facility in Santa Ana, with an average flow of 0.5 million gallons per day (mgd), had an average NDMA concentration of 2500 ng/L. Samples from a second facility in Irvine were non-detect for NDMA. Due to limited resources, no additional samples were collected from these two dischargers. Further study is recommended on dye-related sources.

Note: NDMA sampling was conducted at OCSD permittees with their permission. The sample results that comprise this report were collected for research purposes only, and are not part of the enforcement records for these companies. Per their request, this report does not name the companies involved.

### October/November 2000 Industry Sampling Locations by Trunkline



Three dischargers out of a total of nine accounted for 94% of the NDMA mass detected during this test. NDMA concentrations comparable to the larger facilities were found at the smaller facilities, but the low flows from the small facilities resulted in a negligible NDMA mass. The carpet dye facility did not have the highest concentration but had by far the highest flow, resulting in the highest NDMA mass.

The cause of high concentration spikes at the Plant 1 headworks is believed to be the periodic release of batch-treated waste from PCB facilities, including the two examples in the table below. Note the difference between the low and high values at the PCB facilities, which vary by as much as a factor of ten. The carpet dye facility, by contrast, has a fairly consistent NDMA concentration.

**Industrial Sampling - Average Concentrations****Oct-Nov 2000**

<b>Company</b>	<b>Trunkline</b>	<b>Date</b>	<b>Ave. ndma (ng/L)</b>	<b>Flow (mgd)</b>	<b>Mass (lb)</b>
carpet dye 1	Sunflower	11/8-9/00	2477	0.5	0.0103
carpet dye 2	Airbase	11/8-9/00	nd	0.703	0.0000
PCB 1	Airbase	11/7-8/00	2980	0.0397	0.0010
PCB 2	Sunflower	10/31-1/00	9540	0.0375	0.0030
PCB 3	Airbase	10/31-1/00	16	0.0253	0.0000
PCB 4	Airbase	10/31-1/00	5663	0.1714	0.0081
PCB 5	Talbert	11/1-2/00	120	0.0361	0.0000
PCB 6	Talbert	11/8-9/00	137	0.0118	0.0000
PCB 7	Sunflower	11-8-9/00	2670	0.0127	0.0003

**Industrial Sampling - Major Contributors Detail****Oct-Nov 2000**

	<b>Trunk</b>	<b>Time</b>	<b>NDMA, ng/L</b>
<b>PCB facility</b>	Airbase	10:00-14:00	6900
24-hour		14:00-18:00	1500
composite		18:00-22:00	3730
on 10/31-11/2		22:00-02:00	5450
		02:00-06:00	2800
		06:00-10:00	13600
		<b>ave</b>	<b>5663</b>
<b>PCB facility</b>	Sunflower	09:30-13:30	4900
16-hour		13:30-17:30	7970
composite		17:30-21:30	15250
on 10/31-11/2		21:30-01:30	10040
		<b>ave</b>	<b>9540</b>
<b>carpet dye</b>	Sunflower	10:00-14:00	2480
24-hour		14:00-18:00	2460
composite		18:00-22:00	2620
on 11/8-11/11		22:00-02:00	2270
		02:00-06:00	2510
		06:00-10:00	2520
		<b>ave</b>	<b>2477</b>

### 4.3 FOLLOW-UP INDUSTRIAL SAMPLING – MARCH/APRIL 2001

Samples were collected from 12 industrial sources and a cooling tower during March and April 2001. Most of the facilities are the same ones sampled earlier. The industrial dischargers sampled during this phase were all printed circuit board facilities located tributary to the three subject trunklines.

Two companies accounted for 86% of the total NDMA mass discharged by the 12 industrial facilities. Neither company had completed any significant changes to their pretreatment chemistry. One company was evaluating an “NDMA-free” DTC product during the sample period. The product seemed to work well in a flow-through membrane system, but was not as effective for batch treatment. The other company had tried an alternative chemistry but could not maintain compliance with metal discharge limits and subsequently switched back to DTC. The discharges from these two companies included NDMA concentrations as high as 100 parts per billion, or about 1000 times higher than the domestic background.

Most of the other PCB facilities discharged NDMA at levels comparable to the domestic background. Some of these companies have reportedly switched to non-DTC treatment methods. A cooling tower was sampled at a large aluminum-forming facility, where a DTC-based chemical was used for algae control. The NDMA result was 44 ng/L, at the low end of the domestic range. According to information obtained from a company that services a large number of cooling towers in Orange County, DTC-based chemicals are used in only 2 or 3 cooling towers in the entire County. While this is not an in-depth study of cooling towers, the information was enough to delay any further work on this area indefinitely.

Two of the largest dischargers in terms of flow were flow-monitored on an hourly basis, providing a means to flow-weight the NDMA discharges. One facility uses a large amount of DTC in batch treatment, while the other uses DTC mainly in a flow-through system. The results are presented on the following pages.

#### PCB Facility 1 – Flow-Weighted Mass Emissions, April 2001

*Reported that batch treatment discharge occurred during the swing shift, from 1800 to 0200.*

Date	Time	NDMA (ng/L)	Flow (MG)	Mass (lb)
04/04/200	10:00 - 14:00	6300	0.029	0.0015
04/04/200	14:00 - 18:00	10000	0.034	0.0028
04/04/200	18:00 - 22:00	32600	0.034	0.0093
04/05/200	22:00 - 02:00	38700	0.020	0.0064
04/05/200	02:00 - 06:00	17200	0.043	0.0061
04/05/200	06:00 - 10:00	13900	0.030	0.0035
04/05/200	ndma-free DTC	ND		
<b>totals=</b>			<b>0.190</b>	<b>0.0297</b>

#### PCB Facility 2 – Flow-Weighted Mass Emissions, April 2001

Date	Time	NDMA (ng/L)	Flow (MG)	Mass (lb)
04/24/200	11:00 - 15:00	1450	0.038	0.0005
04/24/200	15:00 - 19:00	1285	0.046	0.0005
04/24/200	19:00 - 23:00	7050	0.022	0.0013
04/24/200	23:00 - 03:00	3960	0.025	0.0008
04/24/200	03:00 - 07:00	1460	0.028	0.0003
04/24/200	07:00 - 11:00	1130	0.045	0.0004
<b>totals=</b>			<b>0.204</b>	<b>0.0038</b>



**Industrial Point-Source NDMA Sampling, April 2001**

<b>Sample Date</b>	<b>Time</b>	<b>NDMA ng/L</b>	<b>Ave conc.</b>	<b>Flow (MGD)</b>	<b>Mass (lb/day)</b>
<b>company 1</b>					
04/25/2001	01:30 - 05:30	708	1435	0.01203	0.0001
04/25/2001	05:30 - 09:30	1540			
04/24/2001	09:30 - 13:30	1400			
04/24/2001	13:30 - 17:30	1770			
04/24/2001	17:30 - 21:30	1980			
04/24/2001	21:30 - 01:30	1210			
<b>company 2</b>					
04/18/2001	06:00-06:00	139	139	0.0104	0.00001
<b>company 3</b>					
04/18/2001	10:40 -14:40	1220	466	0.0409	0.00016
04/18/2001	14:40 -18:40	102			
04/18/2001	18:40 -22:40	173			
04/19/2001	22:40-10:40	368			
<b>company 4</b>					
04/19/2001	01:00-05:00	544	443	0.00995	0.00004
04/18/2001	05:00-09:00	95			
04/18/2001	09:00-13:00	279			
04/18/2001	13:00-17:00	522			
04/18/2001	17:00-21:00	611			
04/18/2001	21:00-01:00	606			
<b>company 5</b>					
04/25/2001	04:30 - 08:30	23600	56603	0.0423	0.01997
04/25/2001	08:30 - 12:30	4120			
04/24/2001	12:30 - 16:30	105000			
04/24/2001	16:30 - 20:30	94400			
04/24/2001	20:30 - 24:30	48900			
04/25/2001	24:30 - 04:30	63600			
<b>company 6</b>					
04/12/2001	03:00 - 07:00	186	158	0.007	0.00001
04/12/2001	07:00 - 11:00	138			
04/11/2001	11:00 - 15:00	65			
04/11/2001	15:00 - 19:00	109			
04/11/2001	19:00 - 23:00	215			
04/11/2001	23:00 - 03:00	235			
<b>company 7</b>					
04/12/2001	03:30 - 07:30	136	214	0.005	0.00001
04/12/2001	07:30 - 11:30	198			
04/11/2001	11:30 - 15:30	119			
04/11/2001	15:30 - 19:30	321			
04/11/2001	19:30 - 23:30	333			
04/11/2001	23:30 - 03:30	178			

**Industrial Point-Source NDMA Sampling, April 2001**

sample date	time	ng/L ndma	ave conc.	flow (MGD)	mass (lb/day)
<b>company 8</b>					
04/12/2001	03:30 - 07:30	67	134	0.016	0.00002
04/12/2001	07:30 - 11:30	89			
04/11/2001	11:30 - 15:30	45			
04/11/2001	15:30 - 19:30	151			
04/11/2001	19:30 - 23:30	314			
04/11/2001	23:30 - 03:30	140			
<b>company 9</b>					
04/25/2001	03:10 - 07:10	1460	2723	0.204	0.00463
04/25/2001	07:10 - 11:10	1130			
04/24/2001	11:10 - 15:10	1450			
04/24/2001	15:10 - 19:10	1285			
04/24/2001	19:10 - 23:10	7050			
04/24/2001	23:10 - 03:10	3960			
<b>company 10</b>					
04/23/2001	03:30 - 07:30	10	34	0.005	0.00000
04/23/2001	11:30 - 15:30	129			
04/23/2001	15:30 - 19:30	10			
04/23/2001	19:30 - 23:30	10			
04/23/2001	23:30 - 03:30	10			
<b>company 11</b>					
04/04/2001	09:00 - 13:00	6300	19783	0.1902	0.0314
04/04/2001	13:00 - 17:00	10000			
04/04/2001	17:00 - 21:00	32600			
04/05/2001	21:00 - 01:00	38700			
04/05/2001	01:00 - 05:00	17200			
04/05/2001	05:00 - 09:00	13900			
04/05/2001	"NDMA-free" DTC	ND			
<b>company 12</b>					
04/04/2001	10:00 - 14:00	1150	1872	0.0931	0.0015
04/04/2001	14:00 - 18:00	3590			
04/04/2001	18:00 - 22:00	1540			
04/05/2001	22:00 - 02:00	1250			
04/05/2001	02:00 - 06:00	590			
04/05/2001	06:00 - 10:00	3110			
04/24/2001	Cooling tower sample	44			

**Total ndma mass to the system = 0.0578 lb/day**

#### 4.4 NDMA CHARACTERIZATION AT A PRINTED CIRCUIT BOARD FACILITY

A principle goal of this project was to determine the extent that dithiocarbamate (DTC) is responsible for NDMA creation. OCSD received cooperation from an Orange County printed circuit board facility to conduct the study. This facility includes nearly every PCB process that is capable of generating wastewater. At the time of this project, starting in May 2001, a membrane filter system was used for low concentration wastewaters and a batch system for concentrated spent solutions. Both systems used DTC as an agent to remove copper and lead. The purpose of this project was to identify the sources of NDMA in the process area and pretreatment.



Samples are collected from a rinse water sump and pretreatment, April 2001



OCSD received comments from some vendors that processes in the facility such as stripper, electroless copper and developer solutions might contain NDMA or its precursors. Others commented that DTC was “used up” in the pretreatment process, leaving nothing for the creation of NDMA. During this study, OCSD staff observed the operation of the pretreatment systems. ORP meters in the reaction tanks controlled DTC in the flow-through membrane system. Samples from the membrane system effluent contained relatively low concentrations of NDMA. Samples collected from the batch system effluent contained high concentrations of NDMA. The system operators commented that the new “NDMA-free” DTC was not as effective for batch treatment as the original DTC product. At the time of this project the original DTC product was used for batch treatment. The operator poured DTC into the reaction tank one gallon at a time. Between additions the operator allowed the system to mix and react, using a portable ORP meter to measure treatment progress. A grab sample was collected periodically and analyzed onsite using a spectrophotometer to

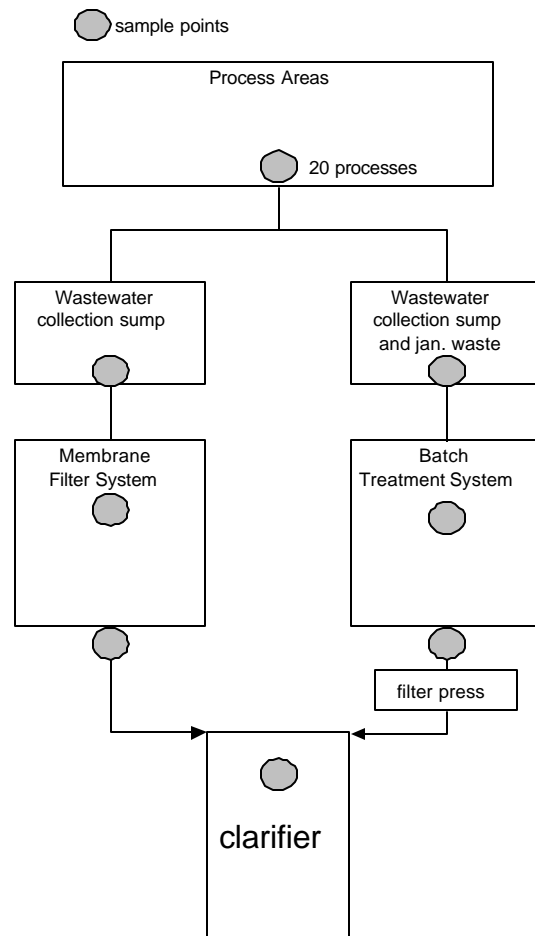
record copper and lead concentrations. The batch was released to the sewer when the metals concentrations were below the discharge limits.

A sample collected on an earlier date confirmed that a new “NDMA-free” DTC product does not contain detectable amounts of NDMA. The original product contained 4.6 mg/L (milligrams per liter) of NDMA, a concentration about 25 times higher than the value provided by the chemical supplier. As a point of reference, 4.6 mg/L is the same as 4,600,000 ng/L. This is the product commonly used for batch treatment. The facility's staff commented that it is common practice in the PCB industry to use more DTC than is required.

The chemical vendors agreed that “overdosing” is common with batch treatment. This facility's method of small increment additions was an exception to the common practice.

Samples were collected during May and June 2001 from every process or area with a discharge, and only while the processes were under normal usage. The goals of this phase were to determine whether any non-DTC related processes contributed NDMA to the discharge. Some chemical vendors believed that certain processes might include precursors to NDMA formation or NDMA itself. This study was performed in two phases due to the very large number of samples required and the need to attenuate the sample load on the laboratory.

The results of this study show that PCB manufacturing processes in general are not a significant source of NDMA. This work did not catalog potential NDMA precursors in these processes. In order to evaluate



potential reactions among spent process solutions, samples of mixed process waste were collected from the batch treatment tank and the membrane system prior to DTC addition. NDMA was below detection limits at the membrane system influent, indicating that the mixture of process wastewater entering the system was not reacting to form NDMA. The second stage reactor of the membrane system, where DTC is added, was also sampled and had NDMA at 320 ng/L. After filtration through the membrane, the effluent to the final clarifier was below the detection limit.

Sampling of the batch system in May 2001 showed a concentration of 4,400 ng/L NDMA before DTC addition. Due to this result, an inventory was taken of all waste streams tributary to batch treatment. We found that along with spent process solutions, the batch system was also treating spillage originating from the pretreatment area. Janitor waste and trench waste both contained wastewater from the area around batch treatment and the filter press. During June 2001 the batch treatment system was sampled again. The contents of the batch included janitor waste and trench waste from the area around the pretreatment system. Both wastestreams were sampled. The NDMA concentration of the janitor waste was a close match for the untreated batch sample, and indicates that NDMA was entering the batch system through recycling of collected spillage. Batch treatment using the original formula DTC resulted in NDMA concentration of 440,000 ng/L for the batch effluent, a seven-fold increase over the initial reading.

This project stopped short of finding the exact pathways of NDMA creation in the system. OCSD's goals were to identify processes linked to NDMA formation and to determine the role of DTC in NDMA formation, and that task was completed. The District has encouraged the chemical suppliers, consultants, and the permittees to conduct their own studies on NDMA formation, in an effort to better understand the chemistry and to enhance the likelihood of developing alternatives.

The following table includes the data from May and June 2001 sampling at the PCB facility. The District wishes to express its gratitude to the facility's management and staff for their assistance with this project.

**NDMA Characterization at a PCB Facility**

<b>May 2001</b>	<b>NDMA (ng/L)</b>
batch before treatment	4,400
batch after treatment	15,900
batch effluent after filter press	14,800
batch discharge at 1st stage clarifier	3,390
membrane filter 6 inch feed line, before DTC	ND
membrane filter 2nd stage, after DTC addition	320
membrane filter discharge to clarifier	ND
clarifier first stage, includes batch treat waste	392
solder strip rinse	40
screening	ND
electroless rinse	ND
soldermask rinse	ND
soldermask pumpout	ND
photo develop rinse	ND
immersion process	ND
resist strip rinse	ND
resist strip bath	ND
micro etch	ND
sulfuric -gold line	ND
sulfuric -electroless	ND
sulfuric -pattern line	ND
Electroless copper spent	ND
Electroless copper bath	ND
<b>June 2001</b>	<b>NDMA (ng/L)</b>
batch before treatment	62,000
batch after treatment	440,000
janitor containment	57,000
east trench waste	25,000
original formula DTC	4,600,000
"NDMA-Free" DTC (April 2001)	ND

ND = "Non-Detectable" or below detection limits

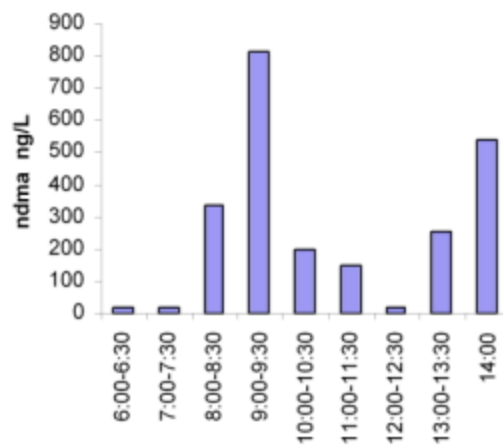
Sampling Notes: All of the above samples were grabs. Sample bottles were cleaned and prepared by the District's Lab. Sampling was conducted either by District staff or by the company's staff under our supervision. Samples were stored in ice immediately after collection and remained on ice until delivered to the extraction lab at the District.

### 4.5 SAMPLING AT IRVINE RANCH WATER DISTRICT

A composite sample was collected from the IRWD influent in October 2000. The purpose of the IRWD sample was to determine if high NDMA concentrations spikes were incident on the IRWD Michelson Plant influent. The result of the hourly analyses, run between 6 am and 2 pm, show a moderate increase at the IRWD influent occurring at about 9 am. NDMA concentrations were below detection limits for three hours during the test.

**Irvine Ranch Water District Influent Sampling – October 09, 2000**

Sample time	NDMA (ng/L)	Flow (MG)	Mass (lb/day)
06:00 - 06:30	nd	12	0.026
07:00 - 07:30	nd		
08:00 - 08:30	338		
09:00 - 09:30	814		
10:00 - 10:30	199		
11:00 - 11:30	146		
12:00 - 12:30	nd		
13:00 - 13:30	252		
1400	540		
	382		



nd = not detected at <20 ng/L mdl

Samples were collected from November 1 to November 3, 2000 from the IRWD influent, IRWD sludge line to OCSD. The IRWD sludge line contains waste solids from the Michelson Plant, which does not have solids handling facilities of its own. By agreement with OCSD, the sludge enters the Airbase Trunk for treatment at OCSD Plant 1. The pumps on automatic samplers cannot handle the high solids content, so grab samples were collected at half hour intervals for a period of 17 hours on November 1, 2000. NDMA values were elevated above domestic background levels from noon to 8 pm, with a peak concentration of 779 ng/L from 6 pm to 8 pm. This pattern indicates the presence of a point source tributary to the Michelson Plant. One large PCB facility is known to be tributary.

The average concentration of the IRWD sludge line was 364 ng/L. With an extrapolated daily flow of 0.969 MG, the daily mass of NDMA attributable to the IRWD sludge line is 0.003 lb/day. This value represents flow over several days, since sludge production and discharge occurs at a different rate from wastewater treatment. IRWD influent sampling was conducted on the following day, November 2, 2000. The average influent concentration was 824 ng/L, with a maximum value of 1466 ng/L. At a measured daily flow of 13.44 MG, the NDMA mass was 0.09 lb/day, about 300 times higher than the sludge line concentration. At some point in the future, OCSD and IRWD will attempt to answer the question: Where did the NDMA go? Tables on the next page present the data from this test.

**Irvine Ranch Water District, Michelson Plant Influent**

<b>Date</b>	<b>Time</b>	<b>NDMA (ng/L)</b>	<b>flow (MG)</b>	<b>mass (lb/day)</b>
11/02/2000	10:00-14:00	384	13.44	0.092
11/02/2000	14:00-18:00	416		
11/02/2000	18:00-22:00	468		
11/2-3/00	22:00-02:00	1313		
11/03/2000	02:00-06:00	895		
11/03/2000	06:00-10:00	1466		
		824		

**Irvine Ranch Water District, Michelson Plant Sludge Line**

<b>Date</b>	<b>Time</b>	<b>NDMA (ng/L)</b>	<b>Flow (MG)</b>	<b>Mass (lb)</b>
11/01/2000	0600-0800	259	0.087	0.00019
11/01/2000	0800-1000	109	0.083	0.00008
11/01/2000	1000-1200	241	0.082	0.00016
11/01/2000	1200-1400	594	0.082	0.00041
11/01/2000	1400-1600	425	0.076	0.00027
11/01/2000	1600-1800	360	0.072	0.00022
11/01/2000	1800-2000	779	0.085	0.00055
11/01/2000	2000-2200	143	0.079	0.00009

**average concentration = 364 ng/L**  
**effluent flow = 0.646 MG**  
**effluent mass = 0.002 lb**

**extrapolated daily flow = 0.969 MG**  
**extrapolated daily mass = 0.003 lb**

## chapter 5

### **DOMESTIC BACKGROUND SAMPLING**

---

#### 5.1 DOMESTIC SAMPLING – OCTOBER 2000

Twenty-four hour composite samples were collected from the Turtle Rock neighborhood in Irvine and the College Park area in Costa Mesa. Both locations are tributary to residential areas including several hundred homes. The hourly bottles were composited into four-hour batches for analysis. Potable water grab samples were collected from water well sample points to measure the NDMA in drinking water supplies in those neighborhoods. The results shown in the table below indicate an NDMA range from non-detect (at <20 ng/L) to 195 ng/L for the domestic wastewater samples. The two residential areas did not share a pattern of discharge concentrations, except that NDMA concentrations were in the same order of magnitude. The IRWD potable water sample contained 4.2 ng/L NDMA, based on analysis performed by the Orange County Water District. The Costa Mesa potable sample was non-detect for NDMA. There were two reasons to measure domestic background. First, the District needs the data in order to set local limits on NDMA. Second, the Water District can use the data to predict and plan for

##### **Domestic Background - Campus and Culver, Irvine (Turtle Rock)**

<b>Date</b>	<b>Time</b>	<b>NDMA (ng/L)</b>	<b>mdl (ng/L)</b>
10/25/2000	12:30-16:30	55	<20
10/25/2000	16:30-20:30	99	<20
10/25/2000	20:30-24:30	195	<20
10/26/2000	24:30-04:30	48	<20
10/26/2000	04:30-08:30	56	<20
10/26/2000	08:30-12:30	62	<20

*IRWD Potable Site #403, Turtle Rock = 4.2 ng/L (OCWD result)*

##### **Domestic Background - Princeton, Costa Mesa (College Park)**

<b>Date</b>	<b>Time</b>	<b>NDMA (ng/L)</b>	<b>mdl (ng/L)</b>
10/03/2000	9:00-13:00	88	<20
10/03/2000	13:00-17:00	nd	<20
10/03/2000	17:00-21:00	nd	<20
10/03/2000	21:00-1:00	24	<20
10/03/2000	1:00-5:00	nd	<20
10/03/2000	5:00-9:00	nd	<20

*CM Potable Site at Carnegie&Princeton = non-detect (OCWD result)*  
adequate NDMA treatment.



## 5.2 DOMESTIC SAMPLING – NOVEMBER 2001

Composite samples were collected from four additional domestic neighborhoods over a period of 48 hours from 0600 on Friday, November 9 to 0600 on Sunday, November 11, 2001. The selection of days was meant to characterize a “weekday” and a “weekend day”. Overall, no pattern was detected between weekdays and weekends. The highest concentration in any sample was found on Saturday morning, November 10, 2001, between 6 am and 10 am, at 604 ng/L. The average concentration for all samples, including those from October 2000, was 103 ng/L. The range between values at each sample point varied between 65 and 171 ng/L. A total of 49 samples were analyzed and used in the data analysis. The detection limit for domestic samples was between 20 and 30 ng/L.

The table below presents a summary of the data and calculated influent mass and concentration for OCSD Plant 1, including data from domestic sampling in October 2000. The statistics for the number of homes, persons/home and city populations were obtained from online city records. Influent mass calculations use the average of detectable results and a value of 88% for the fraction of total influent flow from domestic sources. A value of 246 mgd was used for the total influent flow (both plants). Plant 1 domestic mass was calculated using 90 mgd total influent, with 88% domestic. The calculation for pounds of NDMA / home / day is based on a daily flow of 240 gallons / home / day, a value taken from the OCSD Non-Industrial Source Control Report. Raw data is presented on the next page. A summary of the calculations is included in the appendix.

### Domestic Background Sampling – October 2000–November 2001

Location	NDMA ave. (ng/L)	Homes	Population	lb/house/day	Persons/home	lb/person/day
Orange	64.51	42,000	130,000	0.00000013	3.1	0.00000004
Costa Mesa	171.40	42,400	106,000	0.00000036	2.5	0.00000012
Huntington Beach	80.40	61,300	190,000	0.00000017	3.1	0.00000006
Garden Grove	114.40	45,800	170,000	0.00000024	3.7	0.00000008
Irvine	85.80	55,000	150,000	0.00000018	2.7	0.00000006
<b>averages</b>	<b>103.30</b>			<b>0.00000022</b>		<b>0.00000009</b>
<b>maximum</b>	<b>604.00</b>	(Costa Mesa location on Saturday, November 10, 2001, between 6 am and 10 am)				

**Domestic Background Sampling – Raw Data for October 2000 and November 2001**

<b>Location</b>	<b>Date</b>	<b>Day</b>	<b>Time</b>	<b>Result (ng/L)</b>
<b>Costa Mesa</b>	10/03/2000	Tue-Wed	0900-1300	88
	10/03/2000	Tue-Wed	1300-1700	nd
	10/03/2000	Tue-Wed	1700-2100	nd
	10/03/2000	Tue-Wed	2100-0100	24
	10/03/2000	Tue-Wed	0100-0500	nd
	10/03/2000	Tue-Wed	0500-0900	nd
	11/09/2001	Fri-Sat	0200-0600	50.3
	11/09/2001	Fri-Sat	0600-1000	100.0
	11/09/2001	Fri-Sat	1000-1400	113.0
	11/09/2001	Fri-Sat	1400-1800	182.0
	11/09/2001	Fri-Sat	1800-2200	68.0
	11/09/2001	Fri-Sat	2200-0200	45.5
	11/10/2001	Sat-Sun	0600-1000	604.0
	11/10/2001	Sat-Sun	1000-1400	99.3
	11/10/2001	Sat-Sun	1400-1800	193.0
	11/10/2001	Sat-Sun	1800-2200	246.0
	11/10/2001	Sat-Sun	2200-0200	391.0
11/10/2001	Sat-Sun	0200-0600	196.0	
<b>Garden Grove</b>	11/09/2001	Fri-Sat	0600-1000	73.8
	11/09/2001	Fri-Sat	1000-1400	155.0
<b>Huntington Beach</b>	11/09/2001	Fri-Sat	0130-0530	<20
	11/09/2001	Fri-Sat	0530-0930	135.0
	11/09/2001	Fri-Sat	0930-1330	119.0
	11/09/2001	Fri-Sat	1330-1730	121.0
	11/09/2001	Fri-Sat	1730-2130	104.0
	11/09/2001	Fri-Sat	2130-0130	76.7
	11/10/2001	Sat-Sun	0130-0530	52.2
	11/10/2001	Sat-Sun	0530-0930	81.9
	11/10/2001	Sat-Sun	0930-1330	49.8
	11/10/2001	Sat-Sun	1330-1730	37.0
	11/10/2001	Sat-Sun	1730-2130	81.9
	11/10/2001	Sat-Sun	2130-0130	25.9
<b>Orange</b>	11/10/2001	Fri-Sat	0200-0600	35.8
	11/10/2001	Fri-Sat	0600-1000	<20
	11/10/2001	Fri-Sat	1000-1400	53.5
	11/10/2001	Fri-Sat	1400-1800	<20
	11/10/2001	Fri-Sat	1800-2200	43.5
	11/10/2001	Fri-Sat	2200-0200	<20
	11/10/2001	Sat-Sun	0600-1000	50.6
	11/10/2001	Sat-Sun	1000-1400	108.0
	11/10/2001	Sat-Sun	1400-1800	94.4
	11/10/2001	Sat-Sun	1800-2200	78.5
	11/10/2001	Sat-Sun	2200-0200	51.8
<b>Irvine</b>	10/25/2000	Wed-Thu	1230-1630	55
	10/25/2000	Wed-Thu	1630-2030	99
	10/25/2000	Wed-Thu	2030-2430	195
	10/26/2000	Wed-Thu	2430-0430	48
	10/26/2000	Wed-Thu	0430-0830	56
	10/26/2000	Wed-Thu	0830-1230	62

## chapter 6 ROOT CONTROL SAMPLING

One of the benefits of collaboration with other agencies was information on new or undiscovered sources. The Los Angeles County Sanitation District (LACSD) had been working on the NDMA problem for several months prior to OCSD's effort. LACSD provided an MSDS sheet on a foaming fumigant used for



Vaporooter Application – Tustin, CA, June 2001

controlling roots in sanitary sewers. The MSDS described a specific brand name derivative called Sanafoam Vaporooter II. This compound is widely used in Orange County by independent plumbing contractors, city sewer maintenance divisions, specialty contractors, and large POTW's, including OCSD. **Appendix f** includes the material safety data sheet and regulations for metam-sodium, which is the common name for all brands of DTC-based foaming fumigants. The chemical name for Vaporooter is sodium methylthiocarbamate. This is the same base chemical (DTC) used in PCB facilities for waste treatment.



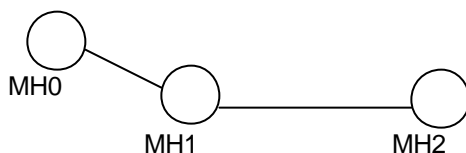
On June 11, 2001 the District conducted sampling for NDMA during a scheduled root-control job in the City of Tustin. The sewer was located in a residential area, with no industrial or commercial connections.

A sample of the mixed chemical was taken prior to injection. This sample contained 1,100,000 ng/L of NDMA, or about 1 ppm. This was the highest single reading obtained from a point source during the project. The tank volume was 100 gallons. A calculation performed on the mass of NDMA in this batch gives an estimate of a 50-100 ng/L impact at the District's headworks over a 1-2 hour time period. The NDMA mass from this application is equivalent to

the total NDMA mass discharged from 4,182 homes each day. As a result of this test, a notice was distributed to the cities in the District's service area, asking for voluntary cooperation to reduce or eliminate the use of metam-sodium products.

### NDMA Sampling of Foaming Fumigant – June 2001

Location	NDMA (ng/L)
Upstream blank (MH0)	ND
Undiluted DTC/foam mixture	1,100,000
Injection manhole during treatment (MH1)	490,000
Downstream - 20 minutes after injection (MH2)	1,850
Downstream - after 45 minutes	290,000
Downstream - after 65 minutes	200,000
Mass of NDMA in the Batch	0.00092 lb



Jacaranda Ave., City of Tustin

## chapter 7 CALCULATIONS

This section includes the summary data and calculations used in the report findings. Most of the data was obtained directly from the NDMA project. The remainder was obtained from OCSD annual records.

Assumptions	Source
<input type="checkbox"/> The percentage of domestic flow at the OCSD influent is 88% of the total.	<input type="checkbox"/> 2001 Source Control Annual Report
<input type="checkbox"/> Total flow tributary to Plant 1 is assumed to be 90 MGD.	<input type="checkbox"/> 2001 O&M Report
<input type="checkbox"/> Total flow tributary to both Plant 1 and Plant 2 is 246 MGD.	<input type="checkbox"/> 2001 O&M Report
<input type="checkbox"/> The average NDMA concentration in the Newhope and Euclid Trunks is 103 ng/L.	<input type="checkbox"/> NDMA Report
<input type="checkbox"/> Average daily flow per household is 240 gallons / day.	<input type="checkbox"/> NISC reports

### NDMA Mass per Household

For each home the mass of NDMA = (site average concentration, mg/L) x (average flow / home, MG) x (conversion factor) = pounds per day per home. Sample, for the site in the City of Orange:  
 $(64.51 \text{ ng/L NDMA}) \times (1 \text{ mg}/10^6 \text{ ng}) \times (0.00024 \text{ MGD}) \times (8.34) = 0.00000013 \text{ lb/day/home}$

### Plant 1 Domestic NDMA Mass

(domestic average concentration, mg/L) x (domestic flow, MG) x (conversion factor) = pounds per day  
 $(103 \text{ ng/L}) \times (1 \text{ mg}/10^6 \text{ ng}) \times (79 \text{ MG}) \times (8.34) = 0.068 \text{ lb/day}$

### Plant 1 Total NDMA Mass

Plant 1 total mass is calculated by averaging the daily mass readings for each trunk, and taking a sum of the averages. Mass on Euclid and Newhope Trunks is constant because they are assumed to have only domestic background concentrations of NDMA. Total NDMA mass at Plant 1 influent is 0.256 lb/day.

### Plant 1 Trunkline Daily Average Mass, lb/day

	talbert	airbase	sunflower	euclid	newhope	sum
	0.019	0.059	0.035	0.015	0.021	
	0.076	0.118	0.079	0.015	0.021	
	0.079	0.042	0.088	0.015	0.021	
	0.028	0.032	0.267	0.015	0.021	
	0.043	0.114	0.083	0.015	0.021	
	0.054	0.012	0.208	0.015	0.021	
	0.025	0.016	0.071	0.015	0.021	
		0.015				
range	316%	883%	663%			
max	0.079	0.118	0.267			
min	0.025	0.012	0.071			
<b>average</b>	<b>0.046</b>	<b>0.056</b>	<b>0.119</b>	<b>0.015</b>	<b>0.021</b>	<b>0.256</b>

### Plant 1 Industrial NDMA Contribution

The industrial NDMA fraction was calculated using the sum of the masses found in Chapter 4, pages 4.5 and 4.6. Twelve companies were composite sampled in April 2001. Flow readings were taken and masses were calculated. These companies were selected because they were tributary to Plant 1 and because they presently use DTC in their treatment processes or used DTC at some point in the past.

The total mass from these sources was 0.05785 lb/day, representing 22.6% of the total influent mass of 0.256 lb/day.

### Root Control

This calculation provides the mass and downstream concentration resulting from a single routine application of metam-sodium (DTC) in a residential sewer. The solution tank on the OCSD truck has a 100-gallon capacity. The NDMA concentration of that solution is 1,100,000 ng/L, or 1.1 mg/L.

The NDMA mass in 100 gallons of solution is:  $(1.1 \text{ mg/L}) \times (8.34) \times (0.0001 \text{ MG}) = 0.00092 \text{ lb NDMA}$ . This mass is equivalent to the daily average discharge from 4,182 homes.

For the purpose of the next calculation, it is assumed that the metam-sodium “slug” will take about one hour to pass any point in the sewer system. At Plant 1, one hour of flow at mid-day is about 5 million gallons.

The mass fraction of NDMA contributed by one application is:  
 $(0.00092 \text{ lb} / 0.256 \text{ lb}) \times (100) = 0.4\%$ .

The concentration at the Plant 1 headworks contributed by one application is:  
 $(0.00092 \text{ lb}) \times 10^6 / ((8.34) \times (5 \text{ MG})) = 22 \text{ ng/L}$

### NDMA Mass Balance in the Plant 1 System

Sampling conducted at the Plant 1 influents for the three subject trunklines (Airbase, Sunflower, Talbert) indicate that the total NDMA mass coming from these sources was 0.221 lb/day. Including the Euclid/Newhope system increases the mass to 0.256 lb/day, assuming the domestic concentration and average flow for those systems.

The domestic contribution is 0.068 lb/day, or about 27% of the total influent mass. Industrial sources existing at the time of sampling in April 2001 contributed 0.058 lb/day, or another 23%. The application of DTC for root control may account for another 0.4% for each application performed each day. These reasonably well-known sources account for about 50% of influent NDMA. Other point sources include dye operations that were not sampled during the project, NDMA potentially created in the sewer system by reactions among precursors, and all commercial sources.

## chapter 8

# **REGULATORY AND OTHER ISSUES**

---

Metal finishers using DTC for waste treatment are affected by three important initiatives that happen to be occurring at the same time. They are the California Toxics Rule, the MP&M regulations, and the District's GWR project. Taken together, these initiatives create a very challenging regulatory environment.

### **California Toxics Rule**

In May 2000, the USEPA issued the final rule: **Water Quality Standards: Establishment of Numeric Criteria for Priority Toxic Pollutants for the State of California, 40 CFR Part 131**. Portions of the rule are included in **appendix i**. The intent of the rule is "...to fill a gap in California water quality standards that was created in 1994 when a State court overturned the State's water quality control plans, which contained water quality criteria for priority toxic pollutants. Thus the State of California has been without numeric water quality criteria for many priority toxic pollutants as required by the Clean Water Act, necessitating this action by EPA." EPA acknowledged that POTW's and the industries that discharge to them were potentially affected by this rule. NDMA was assigned a value of 0.69 ng/L as a Human Health standard. The State of California responded by setting an "action level" of 20 ng/L. A limit closer to the EPA value is under consideration. The Orange County Water District is answerable to this new standard.

One of the early concerns with the California Toxics Rule (40 CFR Part 131) was that the numerical limit for NDMA is below the Method Detection Limit (mdl) of most analytical laboratories. The EPA responded in the final rule that "Analytical detection limits have never been an acceptable basis for setting water quality criteria since they are not related to actual environmental impacts. Setting the criteria at levels that reflect adequate protection tends to be a forcing mechanism to improve analytical detection methods." (Full text in **appendix g**). In fact that prediction was correct. In response to the need for low mdl's and a quick turnaround, the District's Lab started with the State-approved method and developed improvements that removed interferences and improved recovery. While the method has not yet been certified by the State, it has proven to be accurate and dependable. A full description of the method is included in **appendix d**.

### **MP&M**

During the same period of time as the publishing of 40 CFR 131, the USEPA published the proposed rule for the new Metal Products and Machinery (MP&M) category. Printed circuit board facilities and platers who use DTC for waste treatment are potentially affected. Page 446 of the proposed rule document, included as **appendix h**, includes a statement that EPA is basing estimated costs and pollutant removals on the use of DTC. This puts metal finishers in a bind, since a basis for EPA's limits may no longer be an allowable alternative in the future.

### **GWR**

Orange County Sanitation District has joined forces with the Orange County Water District to develop the largest water reclamation project in Southern California. Known as the Groundwater Replenishment (GWR) project, the goal is to reclaim up to 100 million gallons per day of secondary effluent from OCSD by sending it to OCWD for advanced tertiary treatment. The water will then be sent to existing spreading basins for percolation into the aquifer. The issue of concern to NDMA dischargers is the 20 ng/L action level set in the CTR for the Water District effluent. Water reclamation is currently the main force driving the need to reduce NDMA concentrations at the District's influent.

### **Analysis Cost**

Cost is a major concern for industrial point sources trying to control and measure NDMA in their discharge. At this time, commercial laboratories charge from \$400 to \$1200 per sample, a cost that most small companies cannot support. The District may eventually establish local limits on NDMA, along with sample requirements. The cost of sampling and analysis will be considered when self-monitoring guidelines are developed. The District made the decision to collect and analyze all samples connected with this project, including many samples collected in a large PCB facility to characterize the creation,

transport and fate of NDMA inside the facility. The benefits to the District were consistency in sample collection and analytical methods, fast turnaround, and quality assurance.

### **NDMA Control vs. Discharge Compliance**

In January 2001 the District sent a mass-mail to all affected permittees, informing them that DTC was a known source and precursor of NDMA, and that DTC users should find other chemistries for metal waste treatment. A small number of companies responded that they had no viable alternatives, or needed more time to implement new treatment chemistries. The District responded that compliance with discharge limits was the first priority, and that any changes must be made responsibly to prevent non-compliant discharges. At the time this report was published, the District was still asking for voluntary cooperation.

### **Safety of Alternative Methods**

One of the principle alternative pretreatment methods is sulfide precipitation. While this is not a new technology, it has earned new recognition as a safe and effective alternative to DTC. Local vendors and consultants have successfully used sulfide at a few of Orange County's smaller facilities, and those facilities will be evaluated later this year. District inspectors and permit engineers will receive additional training on sulfide pretreatment systems.

### **Foaming Fumigants and Root Control**

The revelation that root control may result in NDMA formation has many possible consequences. A large number of private and public entities use these chemicals to prevent roots from clogging sanitary sewers. In coastal areas especially, there is much attention focused on preventing sewer overflows. Prohibiting the use of metam-sodium will reduce NDMA levels in the sewer, but it may also increase the cost of sewer maintenance since alternative chemical methods must be applied more frequently. Our sampling shows that using DTC for root control may contribute about 0.4% of the total influent NDMA for each application. This number is insignificant unless the applications occur too frequently. Discussions on this topic will likely include private firms, local agencies, and the Regional Water Quality Control Board.

## chapter 9

# **CONCLUSIONS AND RECOMMENDATIONS**

---

### **9.1 CONCLUSIONS**

#### **NDMA Reductions at Plant 1**

Voluntary efforts by some industrial users of DTC have made a measurable difference at the OCSD Plant 1 influent. One major DTC user recently tested a non-DTC method for batch treatment. A sample from this facility showed a ten-fold decrease in the NDMA discharge.

#### **NDMA and Printed Circuit Board Manufacturing**

DTC is the only significant source of NDMA in a full service printed circuit board operation. The highest NDMA concentrations were observed at the effluent from batch treatment. Flow-through treatment contributes additional smaller amounts. This conclusion comes after a thorough examination of every process and wastestream at a full-service printed circuit board facility.

#### **Root Control and DTC**

DTC is a major ingredient in foaming fumigants used by many municipal agencies and private companies to control root growth in sewers. NDMA concentrations immediately downstream from a treated sewer were the highest found during the entire project. DTC-based fumigants may be a possible major source of NDMA if used at a high enough frequency.

#### **Carpet Dye Operations**

NDMA concentrations were high at one carpet dye operation and non-detect at the other. This project did not address this manufacturing process in depth, but a preliminary conclusion can be made that NDMA concentration is tied to the type or color of dye being used. These facilities discharge large flows in excess of 0.5 mgd, and have the potential for high NDMA concentration and mass loadings.

#### **NDMA in Cooling Towers**

DTC is used in a small number of Orange County cooling towers. Most towers use other chemistries. A cooling tower that uses DTC as an algicide tested at 44 ppt in the blowdown. This is not considered a significant amount, and efforts expended on product substitution would not yield a measureable improvement at the Plant 1 influent. Cooling towers therefore are not considered to be a significant source of NDMA at this time.

#### **Treatment Alternatives**

Several manufacturers and distributors of treatment chemistries for the printed circuit board industry have participated in this study by attending meetings with District staff to discuss DTC/NDMA chemistry, other possible sources of NDMA, and alternatives to the use of DTC for metal removal. As a result, a number of vendors now offer effective treatment alternatives. The printed circuit board industry in Orange County should be able to change treatment chemistries with no more difficulty than installation of existing systems, although some long-term costs may be higher.

#### **Domestic NDMA**

The average NDMA concentration from purely domestic sources is 103 ng/L. This value is based on samples collected from six locations throughout the service area.

#### **Stringfellow**

The Stringfellow Pretreatment Facility discharged NDMA at 120 ng/L, approximately the domestic background level.



**Irvine Ranch Water District**

The Irvine Ranch Water District sludge line contributes 0.003 lb/day to the Airbase Trunk, while the IRWD influent was measured at 0.09 lb/day. Further study is needed to discover the transport path and fate of NDMA in the IRWD wastewater. The mass of NDMA from IRWD accounts for about 1.4% of total NDMA in the OCSD Plant 1 influent.

**9.2 RECOMMENDATIONS**

<b>Regulatory</b>	<ul style="list-style-type: none"> <li>• Consider developing a local limit for NDMA discharges using the data generated on influent, domestic, and industrial NDMA concentrations tributary to OCSD Plant 1.</li> <li>• Monitor progress toward the final version of MP&amp;M regulations with regard to DTC, and communicate with USEPA concerning the use of DTC as a standard for metals removal.</li> <li>• Set a goal of achieving a 200 ng/L instantaneous maximum at the combined Plant 1 influent, in response to the needs of the Orange County Water District. Develop a long term sampling strategy for the Plant 1 influent trunklines.</li> <li>• Develop a strategy within Source Control to reduce or eliminate the use of the current formulation of DTC in printed circuit board operations, and develop standard practices for its use in treating wastewater. It is anticipated that many companies will need extended periods to finance and build the necessary changes. The Enforcement Compliance Schedule Agreement (ECSA) system should be used to accommodate them whenever possible.</li> <li>• Include NDMA as a constituent in the Sample Requirements Book, with a frequency to be influenced in part by available Lab resources. Include SAWPA Green River and Stringfellow for routine NDMA sampling. NDMA should not be a required constituent for routine self-monitoring, due to the extreme high cost of this analysis.</li> </ul>
<b>Research</b>	<ul style="list-style-type: none"> <li>• Conduct follow up work on known significant NDMA dischargers. Conduct further study on NDMA control at carpet dye facilities, due to their high flow and potential for high NDMA concentrations. Assign an inspector/engineer team to each facility and work with that facility to develop alternatives to reduce NDMA concentrations.</li> <li>• Provide limited NDMA analysis support for permittees evaluating new chemistries. This support would not be long term and would be limited to transition periods only.</li> </ul>
<b>Training</b>	<ul style="list-style-type: none"> <li>• Hold a workshop for affected permittees and other businesses that use dithiocarbamate (DTC) products. The purpose of the workshop will be to inform DTC users about the new regulations, present the results of the NDMA project, and offer alternative guidelines. Treatment vendors should be invited to attend, both to inform them and to allow them to offer their services.</li> <li>• Provide training for Source Control inspectors and permit engineers on NDMA issues, including treatment alternatives, and how they will impact permitting and enforcement.</li> </ul>
<b>Root Control</b>	<ul style="list-style-type: none"> <li>• Work with the Collections Division to self-regulate the use by OCSD of DTC-based root control products. Conduct research on alternatives.</li> <li>• Develop a District outreach program to educate other Orange County municipalities and private companies about the creation of NDMA during root control operations. Attempt to quantify the amounts of DTC-based root control products used on an annual basis in the District's service area.</li> </ul>

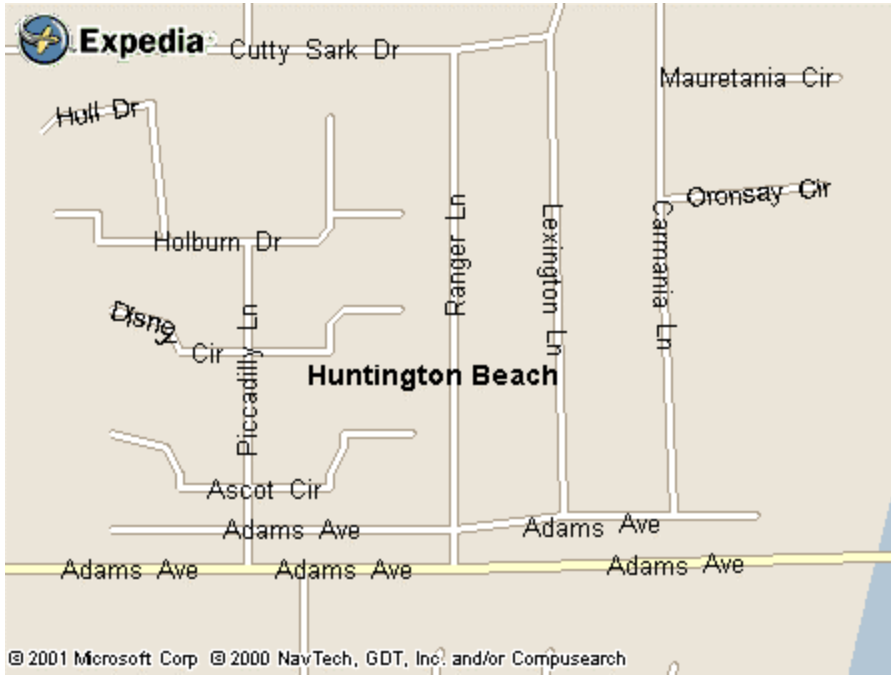
**appendix a**  
**EXAMPLE PROJECT JOB PLAN**

---



**Sample Locations:**

#1 Huntington Beach Adams Ave. at Ranger Lane



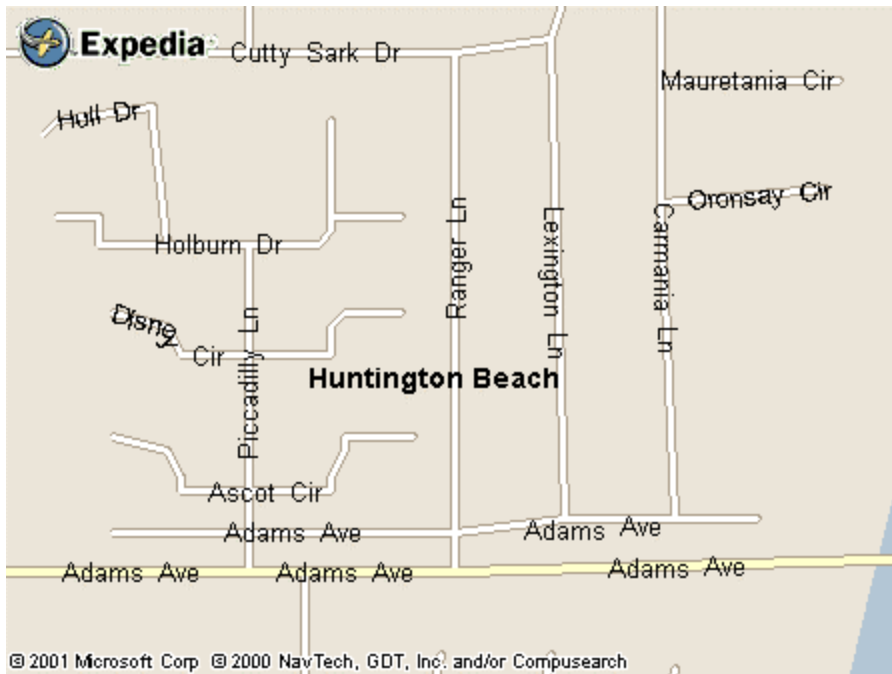
#2 Costa Mesa Redwood Ave.



April 10, 2002

**Sample Locations:**

**#3 Garden Grove**



**#4 Orange**





**appendix b**  
**PROJECT TASK FORCE MEMBERS**

---

**appendix b**  
**Project Task Force Members**

<b>Jim Wybenga</b>	Project Leader	(714) 593-7430	jwybenga@ocsd.com
<b>Kelly Christensen</b>	Project Coordinator	(714) 593-7420	kchristensen@ocsd.com
<b>Mahin Talebi</b>	Source Control Manager	(714) 593-7410	mtalebi@ocsd.com
<b>Sam Mowbray</b>	Lab Manager	(714) 593-7500	smowbray@ocsd.com
<b>Canh Nguyen</b>	Organics Lab Analyst	(714) 593-7506	cqnguyen@ocsd.com
<b>Kim Christensen</b>	Organics Lab Supervisor	(714) 593-7494	kimchristensen@ocsd.com
<b>Ron Dewitt</b>	Source Control Inspector	(714) 593-7446	rdewitt@ocsd.com
<b>Darrell Ennis</b>	Source Control Inspector	(714) 593-7447	dennis@ocsd.com
<b>Tim Foley</b>	Source Control Inspector	(714) 593-7421	tfoley@ocsd.com
<b>Mike Wehner</b>	OC Water District	(714) 378-3200	mwehner@ocwd.com
<b>Bill Dunivin</b>	OC Water District	(714) 378-3200	wdunivin@ocwd.com
<b>Suzanne Wienke</b>	Los Angeles CSD	(562) 699-7411	swienke@lacsds.org
<b>Jim Hyde</b>	Irvine Ranch WD	(949) 453-5866	hyde@irwd.com



**appendix c**

**LETTER TO DTC USERS, JANUARY 4, 2000**

---

## appendix c

### January 4, 2000 Letter to DTC Users

January 4, 2001

For All Metal Finishers

Subject: IMPORTANT NOTICE - ELIMINATION OF DTC

The Orange County Sanitation District (OCSD) requests your assistance to control the level of a newly identified contaminate known as n-nitrosodimethylamine, or NDMA into the sewer system. In early 1999, the U.S. EPA passed a new regulation called the California Toxics Rule (40 CFR 131). This rule sets regulations on priority pollutants, such as NDMA, that may affect public health by contact with drinking or recreational waters and threaten water reuse in Orange County.

Water from OCSD's treatment Plant No. 1 is reclaimed by the Orange County Water District (OCWD) for injection into a seawater intrusion barrier in Fountain Valley, in order to protect the groundwater basin. Therefore, controlling the quality of industrial waste into the OCSD sewer system is an important part of the water reclamation process that may affect the usability of the groundwater.

Earlier this year, NDMA was identified in the wastewater entering the OCSD sewer facilities, as well as the reclaimed water produced by OCWD. NDMA is classified as a probable human carcinogen with an interim action limit of 20 parts per trillion for drinking water. This action limit has also been applied to the reclaimed water injected into the seawater barrier. To achieve the limit, OCWD and OCSD are investigating every option to control and treat NDMA.

It has come to our attention that certain chemicals may be responsible for formation of NDMA in the sewer system. Among those chemicals is a compound known as dithiocarbamate, or DTC, which is sometimes used for treatment of metal finishing wastewater. The mechanisms of NDMA formation are not well understood and the water industry is investing in research to better understand how NDMA is formed and how it can be prevented. However, we already have information implicating DTC as one of the most efficient precursors of NDMA formation.

Therefore, we request your assistance in eliminating the use of DTC as a treatment chemical in an effort to control precursors to NDMA formation. Based on the recent information obtained from manufacturers, there are treatment chemicals that can easily be substituted for DTC usage. If you are using DTC, we are requesting that your company eliminate the usage of DTC by **February 28, 2001**. Please be reminded that you have an obligation to be in compliance with the District's requirements at all times and take all the necessary steps to ensure that elimination of DTC will not cause noncompliant discharges.

OCSD and OCWD greatly appreciate your effort in this matter, which is an important step to assure that our reclaimed water is of the highest quality possible and to have reliable water resources in the future. If you have any questions, please call Kelly Christensen at (714) 593-7420.

Robert P. Ghirelli, D.Env.

Director of Technical Services

RPG:mb

H:\wp.dta\ts\3590\talebi\OCWD NDMA draft.doc

**appendix d**

**OCSD ANALYSIS METHOD FOR NDMA**

---



## EXTRACTION AND ANALYSIS OF NDMA

Kimberly C. Christensen Laboratory Supervisor	Dr. Samuel L. Mowbray Laboratory Manager

# **EXTRACTION AND INSTRUMENTAL ANALYSIS OF N-NITROSODIMETHYLAMINE**

## **1.0 SCOPE AND APPLICATION**

This method covers the extraction and concentration required for the determination of N-Nitrosodimethylamine (NDMA). This method describes the analytical conditions for extraction of wastewater, industrial wastewater, and deionized water samples.

## **2.0 SUMMARY OF METHOD**

3.1 A measured volume of sample, approximately 1000 mL, is extracted with dichloromethane at a pH between 5 and 9 using a separatory funnel. A surrogate compound, NDMA-d6, is spiked into the sample extraction prior to extraction in order to correct for recovery and to ensure reliable results. The dichloromethane extract is concentrated by rotoevaporation and nitrogen gas. The resulting sample extract is transferred into a 2mL autosampler vial for injection. The extract is separated by gas chromatography using ion trap mass spectrometry and chemical ionization.

3.2 Samples shall be extracted within seven days of collection and completely analyzed within 40 days of extraction.

## **3.0 PREVENTION OF INTERFERENCES**

3.1 Solvents, glassware, glass sample collection containers, and other processing hardware must be free of any contaminants. Refer to LOPM 600 for glassware cleaning procedures.

3.2 With each sample batch, a water blank (deionized water) will be analyzed to demonstrate the absence of any method interferences.

3.3 High purity solvents will be used to minimize interferences.

3.4 Matrix interferences may be caused by contaminants that are co-extracted from the sample. The extent of matrix interferences will vary considerably from source to source, depending upon the nature and diversity of the industrial complex or municipality being sampled.

## **4.0 SAFETY**

4.1 It is mandatory to wear a laboratory coat, closed toe shoes, and safety glasses while in the fumehood area.

4.2 All extractions, glassware cleaning, and sample cleanup techniques involving any solvents shall take place in a fumehood. Use of appropriate safety gloves is required during solvent use.

4.3 Material Safety Data Sheets (MSDS) are on file in the Organic Chemistry

Section and are available to all personnel involved in the use of hazardous materials during a chemical analysis.

- 4.4 Extreme caution, awareness, and the proper use of safety equipment are required during the handling of any hazardous material. If the analyst has any questions regarding safety, contact the Supervisor prior to the start of this procedure.

## 5.0 APPARATUS AND MATERIALS

### 5.1 Sample collection and preparation

- A. Amber glass sample bottles with Teflon-lined screw cap, 1.2 liter
- B. Glass sampler container with Teflon-lined screw cap. If the sampler used is collecting a single 24 hour composite sample, a 10 liter container is required. If the sampler used is collecting 24 separate one hour composites, a 300 mL glass container is required.

### 5.2 Separatory funnel extraction

- A. Separatory funnel with Teflon stopcock, 1 or 2 liter
- B. Filtering funnel, large
- C. Flat bottom boiling flask, 500 mL, 24/40 joint, with stopper

### 5.3 Concentration setup

- A. Rotoevaporator with plastic spring clamp and water bath, set at  $35 \pm 5$  °C
- B. Distillation trap, 250 mL, 24/40 joint
- C. Tube adapter, enlarger, 24/40 to 14/20
- D. Chiller unit, set at  $0 \pm 5$  °C
- E. Vacobox
- F. Glass disposable pasteur pipette
- G. Pipette bulb for pasteur pipette

### 5.4 Miscellaneous

- A. Fumehood
- B. Graduated cylinder, 1000mL

- C. Glass beaker, 1000mL
- D. Constant temperature oven, set at  $200 \pm 20$  °C
- E. Ultrasonic bath/cleaner
- F. Refrigerator,  $4 \pm 2$  °C
- G. Gastight volumetric syringe, 1.0mL and 0.5mL
- H. Teflon-coated stirring rod
- I. Heavy duty aluminum foil
- J. Volumetric flask, 25mL
- K. Glasswool, precleaned
- L. Centifuge tubes, 10mL
- M. Autosampler vial, 2mL

5.5 Thermo-Finnigan GCQ Ion Trap MS/MS equipped with Trace 2000 Series Gas Chromatograph, and AS2000 CE Autosampler

- A. Split/splitless injector with 5 mm glass insert for injector and graphite sealing ring
- B. Thermolite septa for SPI injector, 17mm
- C. Phenyl-methyl deactivated fused silica guard column, 5-meter, 0.32mm ID
- D. Restek RTx-5 Amine capillary column, 30 meters long, 0.25mm ID and 0.5 microns film thickness
- F. Press fit glass connector
- G. Ultra-high purity helium for carrier gas, 80 psi
- H. Gas purifer for helium gas
- I. Ultra-high pure methane for chemical ionization gas, 40 psi
- J. Ion source for chemical ionization
- K. Ferrules, 0.5mm M-4 for injector and 0.4mm vespel for detector

5.6 Data handling system

## 6.0 REAGENTS

6.1 Deionized water

6.2 Hot and cold tap water

6.3 Capillary grade dichloromethane and methanol

6.4 Sodium sulfate, anhydrous granular, 12-60 mesh, pesticide grade

6.5 NDMA-d6, Cambridge

6.6 NDMA, Ultra Scientific

## 7.0 CALIBRATION AND MAINTENANCE

7.1 The GCQ GC/MS/MS instrument operating conditions are set at:

A. AS2000 autosampler

1. Sample volume = 2  $\mu$ L
2. Air volume = 1  $\mu$ L
3. Injection delay = 2 sec
4. Pullout delay = 2 sec
5. Injection speed = 5  $\mu$ L/sec
6. Sample cleans = 0
7. Pull-up pumps = 2
8. Pull-up volume = 2.0  $\mu$ L
9. Pull-up delay = 1 sec
10. Pre-Injection washes = 2
11. Pre-Injection volume = 10  $\mu$ L
12. Pre-injection solvent = A
13. Post injection washes = 2
14. Post injection volume = 10  $\mu$ L
15. Post injection solvent = A
16. Solvent vial = A
17. Solvent volume = 2  $\mu$ L
18. Air volume = 1  $\mu$ L
19. Air before solvent = NO

B. Injector temperature = 250 °C. Splitless mode. Split time = 0.5 min. Split flow = 40 mL/min. Surge pressure OFF for 0.5 min. Surge pressure = 5 psi. Constant purge OFF for 0.5 min.



- C. Set carrier flow at 1.5 mL/min. Constant flow.
- D. Set temperature program: Initial column temperature is 45°C; hold 2.0 minutes; ramp temperature to 150°C at 20°C/min; hold for 0 minutes, ramp temperature to 275°C at 50°C/min, hold for 0.25 minutes. The total run time is 10 minutes.
- E. MS parameters.
  - 1. Acquisition time = 6.0 min. Source temperature = 180 °C. Transfer line = 275 °C.
  - 2. Start time = 4.2 min. Polarity = POS. Mult. Offset = 0 V. Tune file = db\_ci.
  - 3. Scan event 1. Micro scans = 5. Max ion time = 50. Scan Mode = Full scan. First mass = 40. Last Mass = 95.
  - 4. Optimal reagent gas flow will register approximately 90m Torr on the convectron and approximately 1.1-004 Torr on the ionization gauge.

7.2 The gas chromatography system is calibrated using an internal standard calibration method.

- A. Calibration curve is linear and forced through the origin.
- B. There are five or more different concentration levels due to differing standard concentrations. Calibration standard is prepared by a stock solution. Calibration standard includes an internal standard (NDMA-d6) at a known constant amount.
- C. Using an injection volume of 2.0 microliters, inject and analyze the calibration standards according to the GC operating conditions. Calculate the area response of the standard against the concentration for each compound and internal standard. Calculate the relative response factor (RRF) for each compound for one of the internal standards.
- D. Calculate the mean RRF from the calibration standard. Calculate the standard deviation (STDDEV) and the relative standard deviation (RSD) from each mean.
- E. For the initial calibration to be acceptable, the RSD of the mean RRF must be below 10%. If the acceptance criteria is not met, a new calibration curve must be prepared.
- F. The working calibration curve or the RRF shall be verified on each

working day by injecting one (or more) calibration standard(s) or one (or more) check standard(s) with each sample set. By definition, a check standard differs from the calibration standard by source and supplier. The results for the calibration standards for all constituents must fall within  $\pm 25\%$  from the predicted response. Any result that falls outside of the range is cause for an evaluation of the instrument. Preventive maintenance of the instrument and/or recalibration of the constituent is necessary. Any sample analysis must be repeated using a new calibration standard or a new calibration curve.

- 7.3 An instrument maintenance schedule is maintained for the GCQ system. Dates and initials are recorded in a notebook located in the instrument area.
- A. Replace the injector glass insert, graphite sealing ring, and septa after approximately 50 injections. Clean injector parts if necessary. Replace guard column when necessary. After injector maintenance, perform column evaluation.
  - B. Refill solvent module with capillary grade dichloromethane when solvent module is approximately half full.
  - C. Replace capillary column after approximately once per year. Perform column evaluation.
  - D. Replace carrier gas gas purifier approximately once per year.
  - E. Clean lens components, ion source and inspect filament when necessary. Replace filament if necessary. After cleaning source components, retune for EI positive. Then turn on reagent methane gas to achieve mass 17 maximum height and retune under CI positive. Perform mass calibration under EI and CI.
  - F. Replace pump oil approximately once per year.
  - G. Replace injector syringe on autosampler when necessary.

## 8.0 QUALITY CONTROL

- 8.1 QA/QC records are maintained to document the quality of data generated by the method. Control charts of water spike percent recovery and matrix percent recovery are generated through ongoing data quality checks.
- 8.2 All samples prior to extraction are spiked with 0.5mL of 1  $\mu\text{g/mL}$  NDMA-d6. The solution is contained in dichloromethane.

- 8.3 Each sample batch includes extraction of a water blank for analysis to demonstrate that interferences from the analytical system are under control. For each sample batch, a water sample is spiked with NDMA and analyzed to determine the concentration of the spike compound. Calculate the percent recovery for NDMA.
- 8.4 If sample volume allows, for each sample batch, one to two samples are spiked with NDMA and analyzed to determine the concentration of the spiked compound. If two samples are spiked, the RPD between the replicate spikes is calculated to determine the precision of the spike technique and method. The percent recovery is calculated for each spike. A nonspiked sample of the replicate set is analyzed to determine background concentrations for each parameter of interest.
- 8.5 Evaluation of the method procedure and instrumentation must be completed for evidence of any atypical performance. If there is evidence of any atypical performance of the method procedure and/or instrumentation, the problem must be immediately identified and corrected. A respike must be analyzed and procedure/instrumentation reevaluated. If possible, unspiked samples must be reanalyzed under corrected method conditions.

## **9.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING**

All samples are kept refrigerated at  $4 \pm 2^\circ\text{C}$  from the time of collection until extraction.

## **10.0 PROCEDURE**

- 10.1 Sodium sulfate cleaning procedure. Clean sodium sulfate by transferring into a 1000 mL beaker and place in the constant temperature oven. Bake at a minimum of  $200 \pm 20^\circ\text{C}$  for a minimum of 12 hours. Remove sodium sulfate and cool. Label with date, contents, and initials.
- 10.2 Glass wool cleaning procedure. Cut four inch sections of glass wool and place inside a 400 mL beaker. Fill beaker with a 1:1 solution of methanol and dichloromethane and place in an ultrasonic bath. Sonicate for a minimum of 30 minutes. Decant 1:1 solution, allow glass wool to air dry inside a fumehood and store in aluminum foil until use. Label with date, contents, and initials.
- 10.3 Sample extraction by separatory funnel.
- A. Bring samples to room temperature. Samples extracted shall have a pH range of 5 to 9. Adjustments to the pH by the addition of either concentrated sulfuric acid or sodium hydroxide 10N, may be necessary. Record the volume of acid or base used on the laboratory datasheet. Tighten Teflon stopcocks on one or two liter separatory funnels. Use the 2 liter funnels if the sample volume is 500 to 1000

mL. Use the one liter funnel if the sample volume is 500mL or less. Set up 500 mL flat bottom flask with filtering funnels. Line the inside of the filtering funnel with cleaned glass wool and add sodium sulfate. Place the 500 mL flask with filtering funnel set-up under the separatory funnel. Label each flask with tape by sample ID.

- B. Mix sample and measure volume using a solvent rinsed 1000 mL graduated cylinder. Record the sample volume on the laboratory datasheet. Pour the sample into a separatory funnel. Rinse the empty sample jar with 60 mL dichloromethane, swirl and transfer the solvent into its corresponding separatory funnel.
- C. Spike 500  $\mu$ L of 1  $\mu$ g/mL of NDMA-d6 into each sample within the extraction set. NDMA-d6 shall be at room temperature prior to use. Using a gastight volumetric syringe, pipet NDMA-d6 directly into the sample contained within the separatory funnel. Record the sample ID, volume of spike, followed by the preparation date/initials of the spikes, onto the laboratory datasheet.
- D. QA/QC spikes of NDMA is introduced into specified samples. The spike shall be at room temperature prior to use. Using a gastight volumetric syringe, pipet the spike directly into the sample contained within the separatory funnel. Record the sample ID, volume of spike, followed by the preparation date/initials of the spikes, onto the laboratory datasheet.
- E. Invert the separatory funnel and vent it to release vapor pressure. Extract the sample by shaking the separatory funnel for a minimum of two minutes. Continue to vent the separatory funnel as needed.
- F. Allow the organic layer to separate from the water phase. Use a Teflon-coated stirring rod to aid with the separation. Drain the organic layer through the filter funnel set-up and into the 500 mL flask. When the organic/emulsion layer has completely passed through the filter funnel set-up, rinse the filter with two 15 mL portions of dichloromethane.
- G. Repeat twice the addition of 60 mL of dichloromethane and shaking of the sample for 2 minutes. After the third and final shake, drain the organic layer and the remaining emulsion into the labeled 500 mL flask.
- H. Rinse the filtering funnel containing the glass wool and sodium sulfate with an additional 30 mL of dichloromethane. The final volume of dichloromethane in the 500 mL flask should be approximately 300 mL. Cap the boiling flask with a ground glass stopper. Keep the extracted sample refrigerated at  $4 \pm 2$  °C, until time to concentrate.

#### 10.4 Sample concentration by rotoevaporation

- A. Remove boiling flask containing extracted sample from the refrigerator and allow the sample to come to room temperature.
  - B. Prepare the roto-evaporator for concentration by turning on chiller and maintain the chiller temperature at  $0 \pm 5$  °C. Turn on the waterbath at a temperature of  $35 \pm 5$  °C.
  - C. Attach a distillation trap to the steam duct on the roto-evaporator. Secure the trap with a plastic spring clip.
  - D. Attach the round bottom flask containing the extracted sample to the distillation trap. Secure the flask with a plastic spring clip.
  - F. Use the servo-jack arm to lower the sample flask into the water bath. Turn on the roto-evaporator motor, and adjust the rotation so no solvent flashes back into the distillation trap. Turn on vacobox and adjust pressure to 600 mbar.
  - G. Concentrate sample to approximately 5.0 mL. Release internal pressure by switching off the vacobox, raise arm, and remove sample flask from trap. Remove flask from roto-evaporator.
- 10.5 Transfer the sample extract to a labeled 10 mL centrifuge tube and rinse the 500 mL flask with dichloromethane. Using nitrogen gas, concentrate the extract to approximately 1 mL.
- 10.6 Transfer the extract into a labeled 2 mL autosampler vial. Rinse the 10mL tube and add the rinse to autosampler vial. Using nitrogen gas, concentrate the extract to 1mL.

## **11.0 SAMPLE ANALYSIS PROCEDURE**

- 11.1 Load the autosampler vials into the autosampler carousel. Add dichloromethane rinse vials for every 2 to 3 samples. Analytical calibration standards are injected first. At the end of the samples, add a check standard.
- 11.2 If the response for a peak exceeds the working range of the system, dilute the extract and reanalyze.
- 11.3 Using chemical ionization, the identification of NDMA-d6 uses mass 81 at 4.72 minutes. NDMA uses mass 75 at 4.74 minutes. Identification relies on spectrum of each component.

## **12.0 CALCULATIONS**

- 12.1 An internal standard procedure is used for determining the unknown sample concentration. The data system calculates the relative response factor

(RRF) for NDMA by using NDMA-d6 as the internal standard from each calibration standard. The calibration standard concentrations of NDMA varies from 10 ng to 10,000 ng per liter. NDMA-d6 remains constant at 500ng/L for all levels of the calibration standards. The following equation is used:

$$RRF = \frac{(A_x)(C_{is})}{(A_{is})(C_x)}$$

Where:

$A_x$  = Peak area response of the NDMA  
 $C_{is}$  = Quantity of the internal standard (concentration, 500 ng/L)  
 $A_{is}$  = Peak area response of the NDMA-d6  
 $C_x$  = Quantity of the NDMA (concentration, ng/L)

- 12.2 The concentration (ng/L) of NDMA in the unknown sample utilizes NDMA-d6 that was spiked into the sample prior to extraction as an internal standard. Because NDMA-d6 was added prior to extraction, the concentration is recovery-corrected for NDMA. The following equation is used:

$$conc = \frac{(A_x)(C_{is})}{(A_{is})(SV)(RRF)}$$

Where:

$A_x$  = Peak area response of NDMA  
 $C_{is}$  = Total mass of NDMA-d6 added prior to sample extraction (500 ng)  
 $A_{is}$  = Peak area response of NDMA-d6  
 $SV$  = Volume of sample extracted (L)  
 $RRF$  = Relative response factor

- 12.3 Relative standard deviation, RSD, is calculated by the following equation:

$$RSD = \frac{100 * STDEV}{Mean RRF}$$

- 12.4 The method detection limit (MDL) is defined as the minimum concentration of a compound that can be measured and reported with 99% confidence that

the value is reported above zero. The MDL for NDMA is 10ng/L and was obtained using reagent water.

**appendix e**  
**NEWHOPE / EUCLID PROJECT —**  
**MEETING MINUTES, AUGUST 2000**

---



Minutes of OCSD NDMA Taskforce: August 17, 2000

Reported by Sam Mowbray

The meeting was called primarily to discuss the data from the investigation of the NDMA levels in the Newhope Trunkline. That purpose was changed to discuss strategy for pursuing the sources NDMA in the plant 1 influent. The following summarizes points in the discussion.

1. Sam presented a summary of the current status of the investigation:
  - a) It does not appear that NDMA is being produced within the P1 treatment plant in processes involved in producing WF21 water. That includes the ferric process, polymer for advanced primary, peroxide for odor control, primary and advanced primary, and activated sludge.
  - b) The P1 influent has been monitored over a 24 hour time period on three different occasions. There are significant differences in concentrations at each of these events, but a general conclusion is that NDMA levels peak at about 2 parts per billion, and the maximum concentrations occur from about noon until about 10PM.
  - c) The five trunklines coming into P1 have been monitored over 24 hours once. It was erroneously reported earlier that the Newhope trunkline had the highest NDMA levels. This issue will be discussed in more detail below. On the basis of the single study the Airbase trunkline has the highest concentration of NDMA (800 to 1200 parts per trillion). Euclid has the lowest at 50 ppt or less. Sunflower and Talbert are about 400 to 600 ppt. In one analysis, Newhope had several spikes of about 200 ppt, but in many instances was below detection limits of 40 ppt.
  
2. There was a significant discussion of interferences in the method of analysis for NDMA by Kim Christensen and Sam Mowbray. The low detection limit (5-10 parts per trillion) analysis for NDMA uses a non-certified method that was developed for analyzing clean water matrices for drinking water. It has been recommended by the Department of Health Services, but there have been no in-depth studies that are normally required for method certification. Moreover, at OCSD, the sample is wastewater that has a very different matrix composition from drinking water. The issue of variability of results from laboratory to laboratory is a major issue in the drinking water industry, and that variability can only be magnified with a dirty sample matrix.

In the analysis of samples in several of the trunkline studies, the organic chemistry group at OCSD noted non-symmetrical peaks in the chromatographic analysis. Eventually, a chromatographic column was found that had an enhanced ability to separate compound of the NDMA type (amines). This column was able to separate the interfering material from NDMA itself. Earlier samples were reanalyzed, and it was determined that the earlier results on the Newhope trunkline were erroneous. It had been earlier reported that up to 12,000 ppt NDMA was present. If any of you want more detail on this complex issue, see Kim Christensen. I thank her for discovering this problem and for her diligence in resolving the situation. Her professionalism shines through. A lesson here is that when a non-certified method is used with a complex,

undefined matrix a professional, heads-up approach in analyzing the results is absolutely required.

3. Kim Christensen has reanalyzed several of the previously generated samples both within the treatment plant and in the influent and trunkline samples. The chromatographic interference does not appear to influence results other than for the Newhope trunkline. In particular, the AS effluent feed to WF21 does not appear to contain interferences and that data appears to be reliable.
4. The group agreed that we need more data on the variability of NDMA levels in the P1 trunklines. Kelly Christensen and Jim Wybenga of Source Control took on the task of developing a comprehensive monitoring plan and a general workplan for evaluating the upstream feeds into the various trunklines. A study was discussed of monitoring over a 4 or 5 day period with 15 minute grabs taken over a 24 hour period and composited into 4 to 6 hour time intervals. This will generate four to six samples per day per trunkline for analysis or as many as a total of 150 samples for analysis. This study will likely be initiated the week of September 10. Following this study, a decision will be made on additional upstream trunkline studies.
5. Tom Dawes stated that the GWRS project will move forward with a plan to increase the UV intensity in the disinfection process in order to remove NDMA. Some concern was expressed about reformation of NDMA from precursors. Tom expressed his appreciation for the work done by OCSD to reduce the NDMA levels in the feedwater to GWRS to a minimum, and encouraged continuation of the investigation.

The meetings of the OCSD NDMA task force currently scheduled for 8/24 and 8/31 will be cancelled. We will meet on September 7 at the regularly scheduled time to discuss the Source Control workplan.

Sam Mowbray

**appendix f**  
**METAM SODIUM (DTC) —**  
**MSDS AND REGULATIONS**

---

**MATERIAL SAFETY DATA SHEET.**  
Database and format copyright © 2000 by  
C&P Press. All rights reserved.

## METAM SODIUM

**FOR CHEMICAL EMERGENCY, SPILL,  
LEAK,  
FIRE, EXPOSURE, OR ACCIDENT, CALL  
CHEMTREC—DAY OR NIGHT 1-800-424-  
9300**

**MANUFACTURER**  
**PLATTE CHEMICAL CO.**  
150 South Main Street  
Fremont, NE 68025-5697  
**EMERGENCY TELEPHONE NO.:**  
CHEMTREC  
(800) 424-9300 (24 Hours)

### SECTION I—IDENTIFICATION OF

#### PRODUCT

**TRADE NAME AND SYNONYMS:** CLEAN  
CROP  
METAM SODIUM  
**CHEMICAL NAME AND SYNONYMS:**  
Metam, Metam  
Sodium: Sodium methylthiocarbamate.  
**CHEMICAL FAMILY:** Dithiocarbamate Soil  
Fumigant.  
**EPA REGISTRATION NUMBER:** 5481-  
350-34704

### SECTION II—PRODUCT COMPONENTS

**COMPONENT: %  
THRESHOLD LIMIT  
VALUE (Units):**  
Sodium methylthiocarbamate  
(CAS:  
137-42-8)  
32.7 None established  
Inert Ingredients 67.3

### SECTION III—PHYSICAL INFORMATION

**APPEARANCE AND ODOR:** Olive green to  
light yellow  
liquid with fairly strong sulfur-like odor.  
**BOILING POINT (°C):** 110°C (230°F)  
**BULK DENSITY:** 9.7 - 9.8 lbs./gal.  
**EVAPORATION RATE (BUTYL ACETATE  
= 1):** Not  
available.  
**PERCENT VOLATILE (BY VOLUME):** Not  
available.  
**pH:** 9.0 - 10.5  
**SOLUBILITY IN WATER:** Miscible in water.  
**SPECIFIC GRAVITY (WATER = 1):** 1.16 -  
1.18 at  
68°F (20°C)  
**VAPOR DENSITY (AIR = 1):** Not available.  
**VAPOR PRESSURE (MM OF MERCURY):**  
21 mmHg  
at 77°F (25°C)  
**VISCOSITY:** 4.7 - 5.0 cp

### SECTION IV—FIRE AND EXPLOSION HAZARD INFORMATION

**FLASH POINT (SPECIFY METHOD—°C):**  
>94°C  
(200°F) TCC  
**FLAMMABLE LIMITS (PERCENT BY  
VOLUME):**  
None available.  
**FIRE EXTINGUISHING MEDIA:** Not defined  
as  
flammable or combustible. However, the  
product may  
support combustion under fire conditions to  
give off  
toxic materials. Use Water spray, dry  
chemical, or  
carbon dioxide. Avoid use of heavy water  
stream.  
**SPECIAL FIRE FIGHTING PROCEDURES:**  
Smoke  
and fumes from fire may contain hazardous  
components.

Use self-contained breathing apparatus and full  
protective clothing. Fight fire from upwind side.  
Avoid  
runoff. Keep nonessential personnel away from  
immediate  
fire area and out of any fallout or runoff areas.  
Evacuate people downwind from fire.

#### UNUSUAL FIRE AND EXPLOSION HAZARDS:

If water  
is used to fight fire or cool containers, contain  
runoff  
by diking to prevent contamination of water  
supplies.  
Containers in fire may burst or explode from  
excessive  
heat. Stay well back from fire area.

#### NFPA HAZARD RATING:

0 Least  
1 Slight  
2 Moderate  
3 High  
4 Severe  
2 Health  
1 Flammability  
0 Reactivity

### SECTION V—REACTIVITY INFORMATION

**STABILITY:** Stable.

**CONDITIONS TO AVOID:** Excessive heat.

**INCOMPATIBILITY (Avoid contact with):** Acids.  
Product gradually decomposes when exposed to  
air.

Corrosive to brass, copper, zinc, and aluminum.

**HAZARDOUS DECOMPOSITION PRODUCTS:**  
Methyl isothiocyanate. Oxides of sulfur, oxides of  
nitrogen, and other unknown hazardous materials  
may  
be formed in a fire situation. Incomplete  
combustion  
may lead to formation of carbon monoxide and/or  
other asphyxiants.

**HAZARDOUS POLYMERIZATION:** Will not  
occur.

**CONDITIONS TO AVOID:** None known.

### SECTION VI—HEALTH INFORMATION

#### TOXICOLOGICAL TEST DATA:

**(Source of Information—Registry of Toxic  
Effects**

**of Chemical Substances):**

**For Metam Sodium:** Acute Oral LD<sub>50</sub> (rat): 450  
mg/kg; Acute Dermal LD<sub>50</sub> (rabbit): 800 mg/kg

**EFFECTS OF OVEREXPOSURE:**

**Routes of Entry:** Ingestion, inhalation, eye and  
skin  
contact. Most Likely Route of Entry: Inhalation  
and  
dermal. This product is considered slightly toxic if  
ingested  
or absorbed by skin. Primary hazard from use  
of this product is mild to extreme irritation of skin,  
respiratory  
tract, and eyes. Prolonged or repeated exposure  
may lead to reddening of skin, rash, dermatitis,  
or other skin reactions.

#### EMERGENCY AND FIRST AID PROCEDURES:

**Call a physician immediately in all cases of  
suspected  
poisoning.**

**Ingestion:** Immediately give several glasses of  
water  
by DO NOT induce vomiting. If vomiting does  
occur,  
give fluids again. Have a physician determine if  
condition of patient will permit induction of  
vomiting or  
evacuation of stomach. Do not give anything by  
mouth  
to an unconscious or convulsing person. Get  
medical  
attention.

**Eyes:** Flush with running water for at least 15  
minutes  
while holding eyelids open to flush out material.  
Get  
medical attention.

**Skin:** Immediately remove all contaminated  
clothing  
and wash skin thoroughly with soap and  
water, paying  
attention to hair, areas under fingernails and  
other hard

to reach places. Get medical attention.

**Inhalation:** Remove to fresh air. If breathing  
is difficult,  
administer oxygen; if breathing stops  
administer artificial  
respiration. Get medical attention  
immediately.

#### MEDICAL CONDITIONS AGGRAVATED BY EXPOSURE:

None known. Preexisting skin or respiratory  
disorders may be aggravated by excessive  
exposure  
to this material.

#### POTENTIAL CARCINOGEN STATUS

**(Source of Information—Registry of**

**Toxic Effects**

**of Chemical Substances):**

Not known. None of the components in this  
product is  
listed by IARC, NTP or OSHA as a potential  
carcinogen.

#### SECTION VII

**—SPILL OR LEAK PROCEDURES**

**STEPS TO BE TAKEN IN CASE**

**MATERIAL IS RELEASED**

**OR SPILLED:** Use appropriate clothing and  
safety equipment to protect against  
exposure. Contain  
spill; absorb liquids by covering with clay or  
other

absorbent material; then vacuum or scoop  
and sweep

up wastes and place in container for

disposal. Generously

cover area with a slurry of common

household

detergent and water, brush into cracks and

crevices,

allow to stand 2 or 3 minutes, and flush with

water.

Repeat if necessary.

**WASTE DISPOSAL METHOD:** Material

which cannot

be used at the site should be disposed of in

an approved

waste disposal facility following all

applicable

Federal, State, and local regulations.

**METAL:** Triple

rinse empty containers and offer for

recycling or reconditioning,

or puncture and dispose of in a sanitary

landfill, or by other procedures approved by

state and

local authorities. **PLASTIC:** Triple rinse

empty containers

and puncture and dispose of in a sanitary

landfill,

or by incineration, or, if allowed by state and

local authorities,

by burning. If burned, stay out of smoke. Do

not contaminate water supplies by disposal

of wastes

or containers.

### SECTION VIII—SPECIAL PROTECTION INFORMATION

#### PROTECTIVE CLOTHING:

**Eye Protection (Type):** Nonventing

chemical goggles

or full face shield.

**Gloves (Type):** Chemical-resistant gloves.

**Respiratory Protection:** FIT TESTED

NIOSH- or

MSHA-approved half-face respirator with

organic vapor

cartridges plus non-venting chemical

goggles or

a NIOSH- or MSHA-approved full-face respirator with organic vapor cartridges.  
**Other Clothing:** Long pants, long-sleeved shirt, chemical-resistant gloves and boots. When a closed system is not use, mixers and loaders must also wear a chemical-resistant apron or cloth coverall.  
**VENTILATION:**  
**Local Exhaust:** Use if aerosol is generated.  
**Mechanical (General):** Use if ventilation is not adequate.  
**Special:** Not normally required.  
**Other:** Work in well-ventilated area.

#### **SECTION IX—SPECIAL PRECAUTIONS**

**HANDLING AND STORAGE:** Store in a cool, dry place away from children, domestic animals, food and feed products, seed, and fertilizer. Do not contaminate other stored products or the storage area by handling or storage of this product. Immediately clean up any spills which occur during handling and storage. Store above 0°F.  
**OTHER PRECAUTIONS:** Do not contaminate water supplies by handling or storage of product, cleaning of equipment, or disposal of wastes. Keep work and storage areas clean. Toxic to fish and other aquatic organisms. Read and follow precautionary measures on product label.

#### **SECTION X—REGULATOR INFORMATION**

**SARA TITLE III HAZARD CATEGORY:**

**IMMEDIATE:** Y

**DELAYED:** Y

**FIRE:** N

**REACTIVE:** N

**SUDDEN RELEASE OF PRESSURE:** N

**SUBSTANCES REGULATED UNDER**

**SARA, TITLE**

**III, SECT. 313:** None.

**DATE OF ISSUE:** 05/20/92

**SUPERSEDES:** 08/21/91

All information contained in this Material Safety Data

Sheet is furnished free of charge and is intended for

your evaluation. In our opinion the

information is, as

of the date of this Material Safety Data

Sheet, reliable,

however, it is your responsibility to

determine the suitability

of the information for your use. You are

advised

not to construe the information as absolutely complete

since additional information may be

necessary or desirable

when particular, exceptional, or variable

conditions

or circumstances exist or because of

applicable

laws or government regulations. Therefore,

you should

use this information only as a supplement to

other information

gathered by you, and you must make

independent

determinations of the suitability and

completeness

of the information from all sources to assure both proper use of the material described herein and the safety and health of employees. Accordingly, no guarantee expressed or implied is made by Platte Chemical Co. as to the results to be obtained based upon your use of the information, nor does Platte Chemical Co. assume any liability arising out of your use of the information.

**Metam-Sodium  
Information Sheet  
March 2000**

This Information Sheet has been prepared to answer common questions about the soil fumigant metam-sodium and its use.

**Overview:**

Metam-sodium (also known as Sodium N-methyldithiocarbamate) is an agricultural use soil fumigant developed in the 1950s. Specifically, it acts as a nematocide (controls worms), a fungicide (controls fungi), and a herbicide (controls weeds). It is used extensively by farmers as a pre-plant soil treatment in many parts of the United States, including California, for a wide variety of fruit and vegetable crops, including, but not limited to, melons, peppers, tomatoes, potatoes, strawberries, grapes, artichokes, asparagus, and carrots. Metam-sodium is transported as a liquid, generally either by train in tanker cars or by trucks in bulk liquid containers. The use of metam-sodium helps to ensure more bountiful yields for farmers and wholesome and affordable foods for the consumer.

Metam-sodium is not an ozone-depleting compound and is fast replacing the use of methyl bromide, a known ozone depleter. Under the Montreal Protocol, ozone depleters are to be phased out of worldwide use and production in the coming years. The U.S. Environmental Protection Agency (EPA), under the authority of the Clean Air Act, has established a ban on the use and manufacture of methyl bromide effective 2005, subject to very limited exceptions.

**Regulation Of Metam-Sodium Products:**

EPA and numerous state agencies regulate the use of metam-sodium within the United States. All manufacturers of metam-sodium must register their products with EPA and obtain EPA approval of the terms and conditions of use. The labels of metam-sodium products must specify the EPA-approved terms and conditions of registration, including, among other things, application methods, rates of application, applicator and handler precautions, precautionary statements, applicator and handler protective clothing and equipment, use restrictions, storage and disposal requirements, entry restrictions, worker notification, and other measures designed to minimize exposure to humans and the environment. It is a violation of federal law to use metam-sodium in a manner that is inconsistent with its product label.

**Protective Measures For Workers And Bystanders:**

The current labels for metam-sodium products require adherence to very specific personal protective equipment for applicators and other handlers. These requirements are designed to minimize the potential for dermal exposure to on-site personnel. For example, applicators and other handlers performing direct contact tasks must use the following personal protective equipment: coveralls over long-sleeved shirt and long pants; waterproof gloves; chemical-resistant footwear, plus socks; chemical-resistant headgear for overhead exposure; chemical-resistant apron when cleaning equipment, or when mixing, loading, or transferring the material with dry-disconnect fittings; face-sealing goggles, unless a full-face respirator is worn; and a respirator with either an organic vapor-removing cartridge with a prefilter approved for pesticides or a canister approved for pesticides. The California Technical Information Bulletin also requires that all mixing and loading of metam-sodium be performed using a closed system. Entry into fields treated with metam-sodium, without required personal protective equipment, is restricted and is not allowed for 48 hours from the last application. During this period, workers in the area must be verbally notified and the treated area must be posted at the entrances with the following:

- "DANGER/PELIGRO";
- "Area under fumigation - DO NOT ENTER/NO ENTRE";
- "Metam-sodium Soil Fumigant in use";
- The date and time of fumigation; and
- The name, address, and telephone number of the applicator.

In addition, states and local Agricultural Commissions may impose additional restrictions on the use of metam-sodium. As an example, a state may impose a "buffer zone" that restricts the use of the product within a certain distance of inhabited dwellings. The intent of the buffer zone is to prevent or limit potential exposure to people, especially children or the elderly who may live or be present in the area of application. Buffer zones may vary depending on the application method and local requirements. Under federal law, when used in agricultural applications, metam-sodium

is not a restricted use pesticide and does not have to be applied by a certified applicator. Under California law, however, metam-sodium is a restricted use chemical when applied in an agricultural setting, which means that only certified applicators may lawfully apply metam-sodium and that special precautions must be followed.

States also impose additional warning requirements to minimize the likelihood of entry to treated fields before the designated reentry times. California posting requirements consist of a skull and cross bones symbol that can be viewed at a minimum distance of 25 feet. Other states require the posting of a symbol representing a stern-faced individual with a raised hand to warn people not to enter a treated area.

**Health Effects:**

Metam-sodium users should carefully adhere to label directions and state requirements. As noted above, individuals, especially children and the elderly, should not remain in areas that have been recently treated and are still posted with warnings of “no entry.” Once metam-sodium is applied and MITC, the primary breakdown product of metam-sodium, is produced, drift of MITC may occur. Measurable drift may be the result of unusual weather conditions or improper application. Individuals exposed to sufficient levels of MITC may smell strong odors and experience symptoms that may include eye, nose, and throat irritation, headaches, nausea, and vomiting. When concentrations are sufficient to cause an odor, the odor is usually noticed immediately. The detection of an odor should be treated as a warning sign for individuals to immediately vacate the affected area. The symptoms generally go away in a few hours once an individual is removed from the point of exposure. Nonetheless, medical attention should be sought if one suspects that an exposure has occurred or if symptoms persist. Hydrogen sulfide is also a breakdown product of metam-sodium. The odor of hydrogen sulfide is characteristic of rotten eggs and at sufficient levels of exposure can produce some of the same symptoms noted above for MITC exposure. As with MITC, removal from exposure should alleviate the symptoms. From an acute toxicity perspective, metam-sodium can be harmful or fatal if a high enough dose is obtained by ingestion, inhalation, or absorption through the skin. Metam-sodium can potentially irritate any part of the body with which it comes into contact. At high concentrations it is known to cause redness, swelling, inflammation, and sensitization to the skin (a person becomes more sensitive to subsequent exposures after the first exposure and often at lower exposure concentrations). Prolonged or frequent exposure to metamsodium may cause allergic reactions in some individuals.

On the basis of evidence in laboratory animals, EPA has classified metam-sodium as a probable human carcinogen. California has identified metam-sodium as a carcinogen and reproductive toxicant. These carcinogenic determinations are based on lifetime continuous exposures of test animals to high metamsodium concentrations, and not on short-term or acute exposures over a period of several hours or days. Exposures to metam-sodium are limited, and thus the Task Force believes the potential risk of carcinogenicity is very low.

**Who To Contact:**

In the event an individual notices strong odors of “horseradish or rotten eggs,” or experiences any of the symptoms noted above, the individual should immediately remove himself or herself from the affected area and contact local health and agricultural authorities.

Companies involved in the production of metam-sodium have formed the Metam-Sodium Task Force to steward all aspects of the proper and effective use of metam-sodium. The members of the Task Force are Amvac Chemical Corporation, Tessengerlo Kerley, Inc., and UCB Chemicals Corporation. Metamsodium products manufactured by Task Force member companies include Amvac Metam Sodium®, Metam CLR® 32.7%, Metam CLR® 42%, Sectagon 42®, and Vapam® and may differ as to formulation, percentage of active ingredient, application information, and technical data. The differences among the various metam-sodium products are noted on the individual product labels. To find out more about metam-sodium, contact the Metam-Sodium Task Force at 1-800-311-0198, or the website at [www.metampsc.com](http://www.metampsc.com).

**appendix g**

**ANALYSIS METHOD DETECTION LIMITS AND THE  
CALIFORNIA TOXICS RULE**

---



## Excerpt from the full document

ENVIRONMENTAL PROTECTION AGENCY

40 CFR Part 131

**Water Quality Standards;**

**Establishment of Numeric Criteria for Priority Toxic Pollutants for the State of California**

AGENCY: Environmental Protection Agency.

ACTION: Final rule.

EPA is aware that the criteria promulgated today for some of the priority toxic pollutants are at concentrations less than EPA's current analytical detection limits. Analytical detection limits have never been an acceptable basis for setting water quality criteria since they are not related to actual environmental impacts. The environmental impact of a pollutant is based on a scientific determination, not a measuring technique which is subject to change. Setting the criteria at levels that reflect adequate protection tends to be a forcing mechanism to improve analytical detection methods. See 1985 Guidelines, page 21. As the methods improve, limits based on the actual criteria necessary to protect aquatic life and human health become measurable. The Agency does not believe it is appropriate to promulgate criteria that are not sufficiently protective. EPA discusses this issue further in its Response to Comment Document for today's final rule. EPA does believe, however, that the use of analytical detection limits are appropriate for assessing compliance with National Pollutant Discharge Elimination System (NPDES) permit limits. This view of the role of detection limits was first articulated in guidance for translating dioxin criteria into NPDES permit limits. See "Strategy for the Regulation of Discharges of PHDDs and PHDFs from Pulp and Paper Mills to Waters of the U.S." Memorandum from the Assistant Administrator for Water to the Regional Water Management Division Directors, May 21, 1990. This guidance presented a model for addressing toxic pollutants which have criteria less than current detection limits. EPA, in more recent guidance, recommends the use of the "minimum level" or ML for reporting sample results to assess compliance with WQBELs (TSD page 111). The ML, also called the "quantification level," is the level at which the entire analytical system gives recognizable mass spectra and acceptable calibration points, i.e., the point at which the method can reliably quantify the amount of pollutant in the sample. States can use their

## Excerpt from the full document

own procedures to average and otherwise account for monitoring data, e.g., quantifying results below the ML. These results can then be used to assess compliance with WQBELs. (See 40 CFR part 132, Appendix F, Procedure 8.B.) This approach is applicable to priority toxic pollutants with criteria less than current detection limits. EPA's guidance explains that standard analytical methods may be used for purposes of assessing compliance with permit limits, but not for purposes of establishing water quality criteria or permit limits. Under the CWA, analytical methods are appropriately used in connection with NPDES permit limit compliance assessments. Because of the function of water quality criteria, EPA has not considered the sensitivity of analytical methods in deriving the criteria promulgated today.

**ENVIRONMENTAL PROTECTION AGENCY**

**40 CFR Part 131**

[FRL-6587-9]

RIN 2040-AC44

**Water Quality Standards; Establishment of Numeric Criteria for Priority Toxic Pollutants for the State of California**

**AGENCY:** Environmental Protection Agency.

**ACTION:** Final rule.

**SUMMARY:** This final rule promulgates: numeric aquatic life criteria for 23 priority toxic pollutants; numeric human health criteria for 57 priority toxic pollutants; and a compliance schedule provision which authorizes the State to issue schedules of compliance for new or revised National Pollutant Discharge Elimination System permit limits based on the federal criteria when certain conditions are met.

EPA is promulgating this rule based on the Administrator's determination that numeric criteria are necessary in the State of California to protect human health and the environment. The Clean Water Act requires States to adopt numeric water quality criteria for priority toxic pollutants for which EPA has issued criteria guidance, the presence or discharge of which could reasonably be expected to interfere with maintaining designated uses.

EPA is promulgating this rule to fill a gap in California water quality standards that was created in 1994 when a State court overturned the State's water quality control plans which contained water quality criteria for priority toxic pollutants. Thus, the State of California has been without numeric water quality criteria for many priority toxic pollutants as required by the Clean Water Act, necessitating this action by EPA. These Federal criteria are legally applicable in the State of California for inland surface waters,

enclosed bays and estuaries for all purposes and programs under the Clean Water Act.

**EFFECTIVE DATE:** This rule shall be effective May 18, 2000.

**ADDRESSES:** The administrative record for today's final rule is available for public inspection at the U.S. Environmental Protection Agency, Region 9, Water Division, 75 Hawthorne Street, San Francisco, California 94105, between the hours of 8:00 a.m. and 4:30 p.m. For access to the administrative record, call Diane E. Fleck, P.E., Esq. at 415 744-1984 for an appointment. A reasonable fee will be charged for photocopies.

**FOR FURTHER INFORMATION CONTACT:** Diane E. Fleck, P.E., Esq. or Philip Woods, U.S. Environmental Protection Agency, Region 9, Water Division, 75 Hawthorne Street, San Francisco, California 94105, 415-744-1984 or 415-744-1997, respectively.

**SUPPLEMENTARY INFORMATION:** This preamble is organized according to the following outline:

- A. Potentially Affected Entities
  - 1. Introduction
  - 2. Overview
  - 3. Statutory and Regulatory Background
  - 4. California Water Quality Standards Actions
    - 1. California Regional Water Quality Control Board Basin Plans, and the Inland Surface Waters Plan (ISWP) and the Enclosed Bays and Estuaries Plan (EBEP) of April 1991
    - 2. EPA's Review of California Water Quality Standards for Priority Toxic Pollutants in the ISWP and EBEP, and the National Toxics Rule
    - 3. Status of Implementation of CWA Section 303(c)(2)(B)
    - 4. State-Adopted, Site-Specific Criteria for Priority Toxic Pollutants
      - a. State-Adopted Site-Specific Criteria Under EPA Review
      - b. State-Adopted Site-Specific Criteria With EPA Approval
  - E. Rationale and Approach For Developing the Final Rule
    - 1. Legal Basis
    - 2. Approach for Developing this Rule

- F. Derivation of Criteria
  - 1. Section 304(a) Criteria Guidance Process
  - 2. Aquatic Life Criteria
    - a. Freshwater Acute Selenium Criterion
    - b. Dissolved Metals Criteria
    - c. Application of Metals Criteria
    - d. Saltwater Copper Criteria
    - e. Chronic Averaging Period
    - f. Hardness
  - 3. Human Health Criteria
    - a. 2,3,7,8-TCDD (Dioxin) Criteria
    - b. Arsenic Criteria
    - c. Mercury Criteria
    - d. Polychlorinated Biphenyls (PCBs) Criteria
    - e. Excluded Section 304(a) Human Health Criteria
    - f. Cancer Risk Level
- G. Description of Final Rule
  - 1. Scope
  - 2. EPA Criteria for Priority Toxic Pollutants
  - 3. Implementation
  - 4. Wet Weather Flows
  - 5. Schedules of Compliance
  - 6. Changes from Proposed Rule
- H. Economic Analysis
  - 1. Costs
  - 2. Benefits
- I. Executive Order 12866, Regulatory Planning and Review
- J. Unfunded Mandates Reform Act of 1995
- K. Regulatory Flexibility Act
- L. Paperwork Reduction Act
- M. Endangered Species Act
- N. Congressional Review Act
- O. Executive Order 13084, Consultation and Coordination With Indian Tribal Governments
- P. National Technology Transfer and Advancement Act
- Q. Executive Order 13132 on Federalism
- R. Executive Order 13045 on Protection of Children From Environmental Health Risks and Safety Risks

**A. Potentially Affected Entities**

Citizens concerned with water quality in California may be interested in this rulemaking. Entities discharging pollutants to waters of the United States in California could be affected by this rulemaking since water quality criteria are used by the State in developing National Pollutant Discharge Elimination System (NPDES) permit limits. Categories and entities that ultimately may be affected include:

Category	Examples of potentially affected entities
Industry .....	Industries discharging pollutants to surface waters in California or to publicly-owned treatment works.
Municipalities .....	Publicly-owned treatment works discharging pollutants to surface waters in California

This table is not intended to be exhaustive, but rather provides a guide for readers regarding entities likely to be affected by this action. This table lists the types of entities that EPA is now aware could potentially be affected by this action. Other types of entities not

listed in the table could also be affected. To determine whether your facility might be affected by this action, you should carefully examine the applicability criteria in § 131.38(c). If you have questions regarding the applicability of this action to a

particular entity, consult the persons listed in the preceding **FOR FURTHER INFORMATION CONTACT** section.

## B. Introduction and Overview

### 1. Introduction

This section introduces the topics which are addressed in the preamble and provides a brief overview of EPA's basis and rationale for promulgating Federal criteria for the State of California. Section C briefly describes the evolution of the efforts to control toxic pollutants; these efforts include the changes enacted in the 1987 CWA Amendments, which are the basis for this rule. Section D summarizes California's efforts since 1987 to implement the requirements of CWA section 303(c)(2)(B) and describes EPA's procedure and actions for determining whether California has fully implemented CWA section 303(c)(2)(B). Section E provides the rationale and approach for developing this final rule, including a discussion of EPA's legal basis for this final rule. Section F describes the development of the criteria included in this rule. Section G summarizes the provisions of the final rule and discusses implementation issues. Sections H, I, J, K, L, M, N, O, P, and Q briefly address the requirements of Executive Order 12866, the Unfunded Mandates Reform Act of 1995, the Regulatory Flexibility Act, the Paperwork Reduction Act, the Endangered Species Act, the Congressional Review Act, Executive Order 13084, Consultation and Coordination with Indian Tribal Governments, the National Technology Transfer and Advancement Act, and Executive Order 13132, Federalism, respectively.

The proposal for this rulemaking was published in the **Federal Register** on August 5, 1997. Changes from the proposal are generally addressed in the body of this preamble and specifically addressed in the response to comments document included in the administrative record for this rulemaking. EPA responded to all comments on the proposed rule, including comments received after the September 26, 1997, deadline. Although EPA is under no legal obligation to respond to late comments, EPA made a policy decision to respond to all comments.

Since detailed information concerning many of the topics in this preamble was published previously in the **Federal Register** in preambles for this and other rulemakings, references are frequently made to those preambles. Those rulemakings include: Water Quality Standards; Establishment of Numeric Criteria for Priority Toxic Pollutants for the State of California; Proposed Rule, 62 FR 42159, August 5, 1997 (referred

to as the "proposed CTR"); Water Quality Standards; Establishment of Numeric Criteria for Priority Toxic Pollutants, 57 FR 60848, December 22, 1992 (referred to as the "National Toxics Rule" or "NTR"); and the NTR as amended by Administrative Stay of Federal Water Quality Criteria for Metals and Interim Final Rule, Water Quality Standards; Establishment of Numeric Criteria for Priority Toxic Pollutants; States' Compliance—Revision of Metals Criteria, 60 FR 22228, May 4, 1995 (referred to as the "National Toxics Rule [NTR], as amended"). The NTR, as amended, is codified at 40 CFR 131.36. A copy of the proposed CTR and its preamble, and the NTR, as amended, and its preambles are contained in the administrative record for this rulemaking.

EPA is making this final rule effective upon publication. Under the Administrative Procedure Act, 5 U.S.C. 553(d)(3), agencies must generally publish a rule no more than 30 days prior to the effective date of the rule except as otherwise provided for by the Agency for good cause. The purpose of the 30-day waiting period is to give affected parties a reasonable time to adjust their behavior before the final rule takes effect. See *Omnipoint Corp. v. F.C.C.*, 78 F.3d 620, 630–631 (D.C. Cir. 1996); *Riverbend Farms, Inc. v. Madigan*, 958 F.2d 1479, 1485 (9th Cir. 1992).

In this instance, EPA finds good cause to make the final rule effective upon publication. In order to find good cause, an Agency needs to find that the 30-day period would be: (1) Impracticable, (2) unnecessary, or (3) contrary to the public interest. Here EPA is relying on the second reason to support its finding of good cause. EPA also notes that the State has requested EPA to make the rule immediately effective.

EPA finds that in this instance, waiting 30 days to make the rule effective is unnecessary. As explained in further detail elsewhere in this preamble, this rule is not self implementing; rather it establishes ambient conditions that the State of California will implement in future permit proceedings. These permit proceedings will, by regulation, take longer than 30 days to complete. This means that although the rule is immediately effective, no discharger's conduct would be altered under the rule in less than 30 days, and therefore the 30-day period is unnecessary.

### 2. Overview

This final rule establishes ambient water quality criteria for priority toxic pollutants in the State of California. The

criteria in this final rule will supplement the water quality criteria promulgated for California in the NTR, as amended. In 1991, EPA approved a number of water quality criteria (discussed in section D), for the State of California. Since EPA had approved these criteria, it was not necessary to include them in the 1992 NTR for these criteria. However, the EPA-approved criteria were subsequently invalidated in State litigation. Thus, this final rule contains criteria to fill the gap created by the State litigation.

This final rule does not change or supersede any criteria previously promulgated for the State of California in the NTR, as amended. Criteria which EPA promulgated for California in the NTR, as amended, are footnoted in the final table at 131.38(b)(1), so that readers may see the criteria promulgated in the NTR, as amended, for California and the criteria promulgated through this rulemaking for California in the same table. This final rule is not intended to apply to waters within Indian Country. EPA recognizes that there are possibly waters located wholly or partly in Indian Country that are included in the State's basin plans. EPA will work with the State and Tribes to identify any such waters and determine whether further action to protect water quality in Indian Country is necessary.

This rule is important for several environmental, programmatic and legal reasons. Control of toxic pollutants in surface waters is necessary to achieve the CWA's goals and objectives. Many of California's monitored river miles, lake acres, and estuarine waters have elevated levels of toxic pollutants. Recent studies on California water bodies indicate that elevated levels of toxic pollutants exist in fish tissue which result in fishing advisories or bans. These toxic pollutants can be attributed to, among other sources, industrial and municipal discharges.

Water quality standards for toxic pollutants are important to State and EPA efforts to address water quality problems. Clearly established water quality goals enhance the effectiveness of many of the State's and EPA's water programs including permitting, coastal water quality improvement, fish tissue quality protection, nonpoint source controls, drinking water quality protection, and ecological protection. Numeric criteria for toxic pollutants allow the State and EPA to evaluate the adequacy of existing and potential control measures to protect aquatic ecosystems and human health. Numeric criteria also provide a more precise basis for deriving water quality-based effluent limitations (WQBELs) in

National Pollutant Discharge Elimination System (NPDES) permits and wasteload allocations for total maximum daily loads (TMDLs) to control toxic pollutant discharges. Congress recognized these issues when it enacted section 303(c)(2)(B) to the CWA.

While California recognizes the need for applicable water quality standards for toxic pollutants, its adoption efforts have been stymied by a variety of factors. The Administrator has decided to exercise her CWA authorities to move forward the toxic control program, consistent with the CWA and with the State of California's water quality standards program.

Today's action will also help restore equity among the States. The CWA is designed to ensure all waters are sufficiently clean to protect public health and/or the environment. The CWA allows some flexibility and differences among States in their adopted and approved water quality standards, but it should be implemented in a manner that ensures a level playing field among States. Although California has made important progress toward satisfying CWA requirements, it has not satisfied CWA section 303(c)(2)(B) by adopting numeric water quality criteria for toxic pollutants. This section was added to the CWA by Congress in 1987. Prior to today, the State of California had been the only State in the Nation for which CWA section 303(c)(2)(B) had remained substantially unimplemented after EPA's promulgation of the NTR in December of 1992. Section 303(c)(4) of the CWA authorizes the EPA Administrator to promulgate standards where necessary to meet the requirements of the Act. The Administrator determined that this rule was a necessary and important component for the implementation of CWA section 303(c)(2)(B) in California.

EPA acknowledges that the State of California is working to satisfy CWA section 303(c)(2)(B). When the State formally adopts, and EPA approves, criteria consistent with statutory requirements, as envisioned by Congress in the CWA, EPA intends to stay this rule. If within the applicable time frame for judicial review, the States' standards are challenged, EPA will withdraw this rule after such judicial review is complete and the State standards are sustained.

### C. Statutory and Regulatory Background

The preamble to the August 5, 1997, proposed rule provided a general discussion of EPA's statutory and regulatory authority to promulgate water

quality criteria for the State of California. See 62 FR 42160–42163. EPA is including that discussion in the record for the final rule. Commenters questioned EPA's authority to promulgate certain aspects of the proposal. EPA is responding to those comments in the appropriate sections of this preamble, and in the response to comments document included in the administrative record for this rulemaking. Where appropriate, EPA's responses expand upon the discussion of statutory and regulatory authority found in the proposal.

### D. California Water Quality Standards Actions

#### 1. California Regional Water Quality Control Board Basin Plans, and the Inland Surface Waters Plan (ISWP) and the Enclosed Bays and Estuaries Plan (EBEP) of April 1991

The State of California regulates water quality through its State Water Resources Control Board (SWRCB) and through nine Regional Water Quality Control Boards (RWQCBs). Each of the nine RWQCBs represents a different geographic area; area boundaries are generally along watershed boundaries. Each RWQCB maintains a Basin Plan which contains the designated uses of the water bodies within its respective geographic area within California. These designated uses (or "beneficial uses" under State law) together with legally-adopted criteria (or "objectives" under State law), comprise water quality standards for the water bodies within each of the Basin areas. Each of the nine RWQCBs undergoes a triennial basin planning review process, in compliance with CWA section 303. The SWRCB provides assistance to the RWQCBs.

Most of the Basin Plans contain conventional pollutant objectives such as dissolved oxygen. None of the Basin Plans contains a comprehensive list of priority toxic pollutant criteria to satisfy CWA section 303(c)(2)(B). The nine RWQCBs and the SWRCB had intended that the priority toxic pollutant criteria contained in the three SWRCB statewide plans, the Inland Surface Waters Plan (ISWP), the Enclosed Bays and Estuaries Plan (EBEP), and the Ocean Plan, apply to all basins and satisfy CWA section 303(c)(2)(B).

On April 11, 1991, the SWRCB adopted two statewide water quality control plans, the ISWP and the EBEP. These statewide plans contained narrative and numeric water quality criteria for toxic pollutants, in part to satisfy CWA section 303(c)(2)(B). The water quality criteria contained in the SWRCB statewide plans, together with

the designated uses in each of the Basin Plans, created a set of water quality standards for waters within the State of California.

Specifically, the two plans established water quality criteria or objectives for all fresh waters, bays and estuaries in the State. The plans contained water quality criteria for some priority toxic pollutants, provisions relating to whole effluent toxicity, implementation procedures for point and nonpoint sources, and authorizing compliance schedule provisions. The plans also included special provisions affecting waters dominated by reclaimed water (labeled as Category (a) waters), and waters dominated by agricultural drainage and constructed agricultural drains (labeled as Category (b) and (c) waters, respectively).

#### 2. EPA's Review of California Water Quality Standards for Priority Toxic Pollutants in the ISWP and EBEP, and the National Toxics Rule

The EPA Administrator has delegated the responsibility and authority for review and approval or disapproval of all new or revised State water quality standards to the EPA Regional Administrators (see 40 CFR 131.21). Thus, State actions under CWA section 303(c)(2)(B) are submitted to the appropriate EPA Regional Administrator for review and approval.

In mid-April 1991, the SWRCB submitted to EPA for review and approval the two statewide water quality control plans, the ISWP and the EBEP. On November 6, 1991, EPA Region 9 formally concluded its review of the SWRCB's plans. EPA approved the narrative water quality criterion and the toxicity criterion in each of the plans. EPA also approved the numeric water quality criteria contained in both plans, finding them to be consistent with the requirements of section 303(c)(2)(B) of the CWA and with EPA's national criteria guidance published pursuant to section 304(a) of the CWA.

EPA noted the lack of criteria for some pollutants, and found that, because of the omissions, the plans did not fully satisfy CWA section 303(c)(2)(B). The plans did not contain criteria for all listed pollutants for which EPA had published national criteria guidance. The ISWP contained human health criteria for only 65 pollutants, and the EBEP contained human health criteria for only 61 pollutants for which EPA had issued section 304(a) guidance criteria. Both the ISWP and EBEP contained aquatic life criteria for all pollutants except cyanide and chromium III (freshwater only) for which EPA has CWA section

304(a) criteria guidance. The SWRCB's administrative record stated that all priority pollutants with EPA criteria guidance were likely to be present in California waters. However, the SWRCB's record contained insufficient information to support a finding that the excluded pollutants were not reasonably expected to interfere with designated uses of the waters of the State.

Although EPA approved the statewide selenium objective in the ISWP and EBEP, EPA disapproved the objective for the San Francisco Bay and Delta, because there was clear evidence that the objective would not protect the designated fish and wildlife uses (the California Department of Health Services had issued waterfowl consumption advisories due to selenium concentrations, and scientific studies had documented selenium toxicity to fish and wildlife). EPA restated its commitment to object to National Pollutant Discharge Elimination System (NPDES) permits issued for San Francisco Bay that contained effluent limits based on an objective greater than 5 parts per billion (ppb) (four day average) and 20 ppb (1 hour average), the freshwater criteria. EPA reaffirmed its disapproval of California's site-specific selenium objective for portions of the San Joaquin River, Salt Slough, and Mud Slough. EPA also disapproved of the categorical deferrals and exemptions. These disapprovals included the disapproval of the State's deferral of water quality objectives to effluent dominated streams (Category a) and to streams dominated by agricultural drainage (Category b), and the disapproval of the exemption of water quality objectives to constructed agricultural drains (Category c). EPA found the definitions of the categories imprecise and overly broad which could have led to an incorrect interpretation.

Since EPA had disapproved portions of each of the California statewide plans which were necessary to satisfy CWA section 303(c)(2)(B), certain disapproved aspects of California's water quality standards were included in EPA's promulgation of the National Toxics Rule (NTR) (40 CFR 131.36, 57 FR 60848). EPA promulgated specific criteria for certain water bodies in California.

The NTR was amended, effective April 14, 1995, to stay certain metals criteria which had been promulgated as total recoverable. Effective April 15, 1995, EPA promulgated interim final metals criteria as dissolved concentrations for those metals which had been stayed (Administrative Stay of Federal Water Quality Criteria for Metals and Interim Final Rule, Water

Quality Standards; Establishment of Numeric Criteria for Priority Toxic Pollutants; States' Compliance—Revision of Metals Criteria; 60 FR 22228, 22229, May 4, 1995 [the NTR, as amended]). The stay was in response to a lawsuit against EPA challenging, among other issues, metals criteria expressed as total recoverable concentrations. A partial Settlement Agreement required EPA to stay specific metals criteria in the NTR. EPA then promulgated certain metals criteria in the dissolved form through the use of conversion factors. These factors are listed in the NTR, as amended. A scientific discussion of these criteria is found in a subsequent section of this preamble.

Since certain criteria have already been promulgated for specific water bodies in the State of California in the NTR, as amended, they are not within the scope of today's final rule. However, for clarity in reading a comprehensive rule for the State of California, these criteria are incorporated into 40 CFR 131.38(d)(2). Footnotes to the Table in 40 CFR 131.38(b)(1) and 40 CFR 131.38(d)(3) clarify which criteria (and for which specific water bodies) were promulgated by the NTR, as amended, and are therefore excluded from this final rule. The appropriate (freshwater or saltwater) aquatic life criteria which were promulgated in the NTR, as amended, for all inland surface waters and enclosed bays and estuaries include: chromium III and cyanide. The appropriate (water and organism or organism only) human health criteria which were promulgated in the NTR, as amended, for all inland surface waters and enclosed bays and estuaries include:

antimony  
thallium  
asbestos  
acrolein  
acrylonitrile  
carbon tetrachloride  
chlorobenzene  
1,2-dichloroethane  
1,1-dichloroethylene  
1,3-dichloropropylene  
ethylbenzene  
1,1,2,2-tetrachloroethane  
tetrachloroethylene  
1,1,2-trichloroethane  
trichloroethylene  
vinyl chloride  
2,4-dichlorophenol  
2-methyl-4,6-dinitrophenol  
2,4-dinitrophenol  
benzidine  
bis(2-chloroethyl)ether  
bis(2-ethylhexyl)phthalate  
3,3-dichlorobenzidine  
diethyl phthalate  
dimethyl phthalate  
di-n-butyl phthalate

2,4-dinitrotoluene  
1,2-diphenylhydrazine  
hexachlorobutadiene  
hexachlorocyclopentadiene  
hexachloroethane  
isophorone  
nitrobenzene  
n-nitrosodimethylamine  
n-nitrosodiphenylamine

Other pollutant criteria were promulgated in the NTR, as amended, for specific water bodies, but not all inland surface waters and enclosed bays and estuaries.

### 3. Status of Implementation of CWA Section 303(c)(2)(B)

Shortly after the SWRCB adopted the ISWP and EBEP, several dischargers filed suit against the State alleging that it had not adopted the two plans in compliance with State law. The plaintiffs in a consolidated case included: the County of Sacramento, Sacramento County Water Agency; Sacramento Regional County Sanitation District; the City of Sacramento; the City of Sunnyvale; the City of San Jose; the City of Stockton; and Simpson Paper Company.

The dischargers alleged that the State had not adopted the ISWP and EBEP in compliance with the California Administrative Procedures Act (Gov Code, Section 11340, *et seq.*), the California Environmental Quality Act (Pub. Re Code, Section 21000, *et seq.*), and the Porter-Cologne Act (Wat. Code, Section 13200, *et seq.*). The allegation that the State did not sufficiently consider economics when adopting water quality objectives, as allegedly required by Section 13241 of the Porter Cologne Act, was an important issue in the litigation.

In October of 1993, the Superior Court of California, County of Sacramento, issued a tentative decision in favor of the dischargers. In March of 1994, the Court issued a substantively similar final decision in favor of the dischargers. Final judgments from the Court in July of 1994 ordered the SWRCB to rescind the ISWP and EBEP. On September 22, 1994, the SWRCB formally rescinded the two statewide water quality control plans. The State is currently in the process of readopting water quality control plans for inland surface waters, enclosed bays and estuaries.

CWA section 303(c)(2)(B) was fully implemented in the State of California from December of 1992, when the NTR was promulgated, until September of 1994, when the SWRCB was required to rescind the ISWP and EBEP. The provisions for California in EPA's NTR together with the approved portions of

A		B Freshwater		C Saltwater		D Human Health (10 <sup>-6</sup> risk for carcinogens) For consumption of:	
# Compound	CAS Number	Criterion Maximum Conc. <sup>d</sup> B1	Criterion Continuous Conc. <sup>d</sup> B2	Criterion Maximum Conc. <sup>d</sup> C1	Criterion Continuous Conc. <sup>d</sup> C2	Water & Organisms ( $\mu$ g/L) D1	Organisms Only ( $\mu$ g/L) D2
1. Antimony	7440360					14 a,s	4300 a,t
2. Arsenic <sup>b</sup>	7440382	340 i,m,w	150 i,m,w	69 i,m	36 i,m		
3. Beryllium	7440417					n	n
4. Cadmium <sup>b</sup>	7440439	4.3 e,i,m,w,x	2.2 e,i,m,w	42 i,m	9.3 i,m	n	n
5a. Chromium (III)	16065831	550 e,i,m,o	180 e,i,m,o			n	n
5b. Chromium (VI) <sup>b</sup>	18540299	16 i,m,w	11 i,m,w	1100 i,m	50 i,m	n	n
6. Copper <sup>b</sup>	7440508	13 e,i,m,w,x	9.0 e,i,m,w	4.8 i,m	3.1 i,m	1300	
7. Lead <sup>b</sup>	7439921	65 e,i,m	2.5 e,i,m	210 i,m	8.1 i,m	n	n
8. Mercury <sup>b</sup>	7439976	[Reserved]	[Reserved]	[Reserved]	[Reserved]	0.050 a	0.051 a
9. Nickel <sup>b</sup>	7440020	470 e,i,m,w	52 e,i,m,w	74 i,m	8.2 i,m	610 a	4600 a
10. Selenium <sup>b</sup>	7782492	[Reserved] p	5.0 q	290 i,m	71 i,m	n	n
11. Silver <sup>b</sup>	7440224	3.4 e,i,m		1.9 i,m			
12. Thallium	7440280					1.7 a,s	6.3 a,t
13. Zinc <sup>b</sup>	7440666	120 e,i,m,w,x	120 e,i,m,w	90 i,m	81 i,m		
14. Cyanide <sup>b</sup>	57125	22 o	5.2 o	1 r	1 r	700 a	220,000 a,j
15. Asbestos	1332214					7,000,000 fibers/L k,s	
16. 2,3,7,8-TCDD (Dioxin)	1746016					0.00000013 c	0.00000014 c
17. Acrolein	107028					320 s	780 t
18. Acrylonitrile	107131					0.059 a,c,s	0.66 a,c,t
19. Benzene	71432					1.2 a,c	71 a,c
20. Bromoform	75252					4.3 a,c	360 a,c
21. Carbon Tetrachloride	56235					0.25 a,c,s	4.4 a,c,t
22. Chlorobenzene	108907					680 a,s	21,000 a,j,t
23. Chlorodibromomethane	124481					0.401 a,c	34 a,c
24. Chloroethane	75003						
25. 2-Chloroethylvinyl Ether	110758						

26. Chloroform	67663					[Reserved]	[Reserved]
27. Dichlorobromomethane	75274					0.56 a,c	46 a,c
28. 1,1-Dichloroethane	75343						
29. 1,2-Dichloroethane	107062					0.38 a,c,s	99 a,c,t
30. 1,1-Dichloroethylene	75354					0.057 a,c,s	3.2 a,c,t
31. 1,2-Dichloropropane	78875					0.52 a	39 a
32. 1,3-Dichloropropylene	542756					10 a,s	1,700 a,t
33. Ethylbenzene	100414					3,100 a,s	29,000 a,t
34. Methyl Bromide	74839					48 a	4,000 a
35. Methyl Chloride	74873					n	n
36. Methylene Chloride	75092					4.7 a,c	1,600 a,c
37. 1,1,2,2-Tetrachloroethane	79345					0.17 a,c,s	11 a,c,t
38. Tetrachloroethylene	127184					0.8 c,s	8.85 c,t
39. Toluene	108883					6,800 a	200,000 a
40. 1,2-Trans-Dichloroethylene	156605					700 a	140,000 a
41. 1,1,1-Trichloroethane	71556					n	n
42. 1,1,2-Trichloroethane	79005					0.60 a,c,s	42 a,c,t
43. Trichloroethylene	79016					2.7 c,s	81 c,t
44. Vinyl Chloride	75014					2 c,s	525 c,t
45. 2-Chlorophenol	95578					120 a	400 a
46. 2,4-Dichlorophenol	120832					93 a,s	790 a,t
47. 2,4-Dimethylphenol	105679					540 a	2,300 a
48. 2-Methyl-4,6-Dinitrophenol	534521					13.4 s	765 t
49. 2,4-Dinitrophenol	51285					70 a,s	14,000 a,t
50. 2-Nitrophenol	88755						
51. 4-Nitrophenol	100027						
52. 3-Methyl-4-Chlorophenol	59507						
53. Pentachlorophenol	87865	19 f,w	15 f,w	13	7.9	0.28 a,c	8.2 a,c,j
54. Phenol	108952					21,000 a	4,600,000 a,j,t
55. 2,4,6-Trichlorophenol	88062					2.1 a,c	6.5 a,c
56. Acenaphthene	83329					1,200 a	2,700 a
57. Acenaphthylene	208968						
58. Anthracene	120127					9,600 a	110,000 a



59. Benzidine	92875					0.00012 a,c,s	0.00054 a,c,t
60. Benzo(a)Anthracene	56553					0.0044 a,c	0.049 a,c
61. Benzo(a)Pyrene	50328					0.0044 a,c	0.049 a,c
62. Benzo(b)Fluoranthene	205992					0.0044 a,c	0.049 a,c
63. Benzo(ghi)Perylene	191242						
64. Benzo(k)Fluoranthene	207089					0.0044 a,c	0.049 a,c
65. Bis(2-Chloroethoxy)Methane	111911						
66. Bis(2-Chloroethyl)Ether	111444					0.031 a,c,s	1.4 a,c,t
67. Bis(2-Chloroisopropyl)Ether	39638329					1,400 a	170,000 a,t
68. Bis(2-Ethylhexyl)Phthalate	117817					1.8 a,c,s	5.9 a,c,t
69. 4-Bromophenyl Phenyl Ether	101553						
70. Butylbenzyl Phthalate	85687					3,000 a	5,200 a
71. 2-Chloronaphthalene	91587					1,700 a	4,300 a
72. 4-Chlorophenyl Phenyl Ether	7005723						
73. Chrysene	218019					0.0044 a,c	0.049 a,c
74. Dibenzo(a,h)Anthracene	53703					0.0044 a,c	0.049 a,c
75. 1,2 Dichlorobenzene	95501					2,700 a	17,000 a
76. 1,3 Dichlorobenzene	541731					400	2,600
77. 1,4 Dichlorobenzene	106467					400	2,600
78. 3,3'-Dichlorobenzidine	91941					0.04 a,c,s	0.077 a,c,t
79. Diethyl Phthalate	84662					23,000 a,s	120,000 a,t
80. Dimethyl Phthalate	131113					313,000 s	2,900,000 t
81. Di-n-Butyl Phthalate	84742					2,700 a,s	12,000 a,t
82. 2,4-Dinitrotoluene	121142					0.11 c,s	9.1 c,t
83. 2,6-Dinitrotoluene	606202						
84 Di-n-Octyl Phthalate	117840						
85. 1,2-Diphenylhydrazine	122667					0.040 a,c,s	0.54 a,c,t
86. Fluoranthene	206440					300 a	370 a
87. Fluorene	86737					1,300 a	14,000 a
88. Hexachlorobenzene	118741					0.00075 a,c	0.00077 a,c
89. Hexachlorobutadiene	87683					0.44 a,c,s	50 a,c,t
90. Hexachlorocyclopentadiene	77474					240 a,s	17,000 a,j,t
91. Hexachloroethane	67721					1.9 a,c,s	8.9 a,c,t

92. Indeno(1,2,3-cd) Pyrene	193395					0.0044 a,c	0.049 a,c
93. Isophorone	78591					8.4 c,s	600 c,t
94. Naphthalene	91203						
95. Nitrobenzene	98953					17 a,s	1,900 a,j,t
96. N-Nitrosodimethylamine	62759					0.00069 a,c,s	8.1 a,c,t
97. N-Nitrosodi-n-Propylamine	621647					0.005 a	1.4 a
98. N-Nitrosodiphenylamine	86306					5.0 a,c,s	16 a,c,t
99. Phenanthrene	85018						
100. Pyrene	129000					960 a	11,000 a
101. 1,2,4-Trichlorobenzene	120821						
102. Aldrin	309002	3 g		1.3 g		0.00013 a,c	0.00014 a,c
103. alpha-BHC	319846					0.0039 a,c	0.013 a,c
104. beta-BHC	319857					0.014 a,c	0.046 a,c
105. gamma-BHC	58899	0.95 w		0.16 g		0.019 c	0.063 c
106. delta-BHC	319868						
107. Chlordane	57749	2.4 g	0.0043 g	0.09 g	0.004 g	0.00057 a,c	0.00059 a,c
108. 4,4'-DDT	50293	1.1 g	0.001 g	0.13 g	0.001 g	0.00059 a,c	0.00059 a,c
109. 4,4'-DDE	72559					0.00059 a,c	0.00059 a,c
110. 4,4'-DDD	72548					0.00083 a,c	0.00084 a,c
111. Dieldrin	60571	0.24 w	0.056 w	0.71 g	0.0019 g	0.00014 a,c	0.00014 a,c
112. alpha-Endosulfan	959988	0.22 g	0.056 g	0.034 g	0.0087 g	110 a	240 a
113. beta-Endosulfan	33213659	0.22 g	0.056 g	0.034 g	0.0087 g	110 a	240 a
114. Endosulfan Sulfate	1031078					110 a	240 a
115. Endrin	72208	0.086 w	0.036 w	0.037 g	0.0023 g	0.76 a	0.81 a,j
116. Endrin Aldehyde	7421934					0.76 a	0.81 a,j
117. Heptachlor	76448	0.52 g	0.0038 g	0.053 g	0.0036 g	0.00021 a,c	0.00021 a,c
118. Heptachlor Epoxide	1024573	0.52 g	0.0038 g	0.053 g	0.0036 g	0.00010 a,c	0.00011 a,c
119-125. Polychlorinated biphenyls (PCBs)			0.014 u		0.03 u	0.00017 c,v	0.00017 c,v
126. Toxaphene	8001352	0.73	0.0002	0.21	0.0002	0.00073 a,c	0.00075 a,c
Total Number of Criteria <sup>h</sup>		22	21	22	20	92	90

**Footnotes to Table in Paragraph (b)(1):**

a. Criteria revised to reflect the Agency q1\* or RfD, as contained in the Integrated Risk Information System (IRIS) as of October 1, 1996. The fish tissue bioconcentration factor (BCF) from the 1980 documents was retained in each case.

b. Criteria apply to California waters except for those waters subject to objectives in Tables III-2A and III-2B of the San Francisco Regional Water Quality Control Board's (SFRWQCB) 1986 Basin Plan, that were adopted by the SFRWQCB and the State Water Resources Control Board, approved by EPA, and which continue to apply.

c. Criteria are based on carcinogenicity of 10 (-6) risk.

d. Criteria Maximum Concentration (CMC) equals the highest concentration of a pollutant to which aquatic life can be exposed for a short period of time without deleterious effects. Criteria Continuous Concentration (CCC) equals the highest concentration of a pollutant to which aquatic life can be exposed for an extended period of time (4 days) without deleterious effects. ug/L equals micrograms per liter.

e. Freshwater aquatic life criteria for metals are expressed as a function of total hardness (mg/L) in the water body. The equations are provided in matrix at paragraph (b)(2) of this section. Values displayed above in the matrix correspond to a total hardness of 100 mg/l.

f. Freshwater aquatic life criteria for pentachlorophenol are expressed as a function of pH, and are calculated as follows: Values displayed above in the matrix correspond to a pH of 7.8.  $CMC = \exp(1.005(pH) - 4.869)$ .  $CCC = \exp(1.005(pH) - 5.134)$ .

g. This criterion is based on 304(a) aquatic life criterion issued in 1980, and was issued in one of the following documents: Aldrin/ Dieldrin (EPA 440/5-80-019), Chlordane (EPA 440/5-80-027), DDT (EPA 440/5-80-038), Endosulfan (EPA 440/5-80-046), Endrin (EPA 440/5-80-047), Heptachlor (440/5-80-052), Hexachlorocyclohexane (EPA 440/5-80-054), Silver (EPA 440/5-80-071). The Minimum Data Requirements and derivation procedures were different in the 1980 Guidelines than in the 1985 Guidelines. For example, a "CMC" derived using the 1980 Guidelines was derived to be used as an instantaneous maximum. If assessment is to be done using an averaging period, the values given should be divided by 2 to obtain a value that is more comparable to a CMC derived using the 1985 Guidelines.

h. These totals simply sum the criteria in each column. For aquatic life, there are 23 priority toxic pollutants with some type of freshwater or saltwater, acute or chronic criteria. For human health, there are 92 priority toxic pollutants with either "water + organism" or "organism only" criteria. Note that these totals count chromium as one pollutant even though EPA has developed criteria based on two valence states. In the matrix, EPA has assigned numbers 5a and 5b to the criteria for chromium to reflect the fact that the list of 126 priority pollutants includes only a single listing for chromium.

i. Criteria for these metals are expressed as a function of the water-effect ratio, WER, as defined in paragraph (c) of this section. CMC

= column B1 or C1 value x WER; CCC = column B2 or C2 value x WER.

j. No criterion for protection of human health from consumption of aquatic organisms (excluding water) was presented in the 1980 criteria document or in the 1986 Quality Criteria for Water. Nevertheless, sufficient information was presented in the 1980 document to allow a calculation of a criterion, even though the results of such a calculation were not shown in the document.

k. The CWA 304(a) criterion for asbestos is the MCL.

l. [Reserved]

m. These freshwater and saltwater criteria for metals are expressed in terms of the dissolved fraction of the metal in the water column. Criterion values were calculated by using EPA's Clean Water Act 304(a) guidance values (described in the total recoverable fraction) and then applying the conversion factors in § 131.36(b)(1) and (2).

n. EPA is not promulgating human health criteria for these contaminants. However, permit authorities should address these contaminants in NPDES permit actions using the State's existing narrative criteria for toxics.

o. These criteria were promulgated for specific waters in California in the National Toxics Rule ("NTR"), at § 131.36. The specific waters to which the NTR criteria apply include: Waters of the State defined as bays or estuaries and waters of the State defined as inland, i.e., all surface waters of the State not ocean waters. These waters specifically include the San Francisco Bay upstream to and including Suisun Bay and the Sacramento-San Joaquin Delta. This section does not apply instead of the NTR for this criterion.

p. A criterion of 20 ug/l was promulgated for specific waters in California in the NTR and was promulgated in the total recoverable form. The specific waters to which the NTR criterion applies include: Waters of the San Francisco Bay upstream to and including Suisun Bay and the Sacramento-San Joaquin Delta; and waters of Salt Slough, Mud Slough (north) and the San Joaquin River, Sack Dam to the mouth of the Merced River. This section does not apply instead of the NTR for this criterion. The State of California adopted and EPA approved a site specific criterion for the San Joaquin River, mouth of Merced to Vernalis; therefore, this section does not apply to these waters.

q. This criterion is expressed in the total recoverable form. This criterion was promulgated for specific waters in California in the NTR and was promulgated in the total recoverable form. The specific waters to which the NTR criterion applies include: Waters of the San Francisco Bay upstream to and including Suisun Bay and the Sacramento-San Joaquin Delta; and waters of Salt Slough, Mud Slough (north) and the San Joaquin River, Sack Dam to Vernalis. This criterion does not apply instead of the NTR for these waters. This criterion applies to additional waters of the United States in the State of California pursuant to 40 CFR 131.38(c). The State of California adopted and EPA approved a site-specific criterion for the Grassland Water District, San Luis National Wildlife Refuge, and the Los Banos

State Wildlife Refuge; therefore, this criterion does not apply to these waters.

r. These criteria were promulgated for specific waters in California in the NTR. The specific waters to which the NTR criteria apply include: Waters of the State defined as bays or estuaries including the San Francisco Bay upstream to and including Suisun Bay and the Sacramento-San Joaquin Delta. This section does not apply instead of the NTR for these criteria.

s. These criteria were promulgated for specific waters in California in the NTR. The specific waters to which the NTR criteria apply include: Waters of the Sacramento-San Joaquin Delta and waters of the State defined as inland (i.e., all surface waters of the State not bays or estuaries or ocean) that include a MUN use designation. This section does not apply instead of the NTR for these criteria.

t. These criteria were promulgated for specific waters in California in the NTR. The specific waters to which the NTR criteria apply include: Waters of the State defined as bays and estuaries including San Francisco Bay upstream to and including Suisun Bay and the Sacramento-San Joaquin Delta; and waters of the State defined as inland (i.e., all surface waters of the State not bays or estuaries or ocean) without a MUN use designation. This section does not apply instead of the NTR for these criteria.

u. PCBs are a class of chemicals which include aroclors 1242, 1254, 1221, 1232, 1248, 1260, and 1016, CAS numbers 53469219, 11097691, 11104282, 11141165, 12672296, 11096825, and 12674112, respectively. The aquatic life criteria apply to the sum of this set of seven aroclors.

v. This criterion applies to total PCBs, e.g., the sum of all congener or isomer or homolog or aroclor analyses.

w. This criterion has been recalculated pursuant to the 1995 Updates: Water Quality Criteria Documents for the Protection of Aquatic Life in Ambient Water, Office of Water, EPA-820-B-96-001, September 1996. See also Great Lakes Water Quality Initiative Criteria Documents for the Protection of Aquatic Life in Ambient Water, Office of Water, EPA-80-B-95-004, March 1995.

x. The State of California has adopted and EPA has approved site specific criteria for the Sacramento River (and tributaries) above Hamilton City; therefore, these criteria do not apply to these waters.

**General Notes to Table in Paragraph (b)(1)**

1. The table in this paragraph (b)(1) lists all of EPA's priority toxic pollutants whether or not criteria guidance are available. Blank spaces indicate the absence of national section 304(a) criteria guidance. Because of variations in chemical nomenclature systems, this listing of toxic pollutants does not duplicate the listing in Appendix A to 40 CFR Part 423-126 Priority Pollutants. EPA has added the Chemical Abstracts Service (CAS) registry numbers, which provide a unique identification for each chemical.

2. The following chemicals have organoleptic-based criteria recommendations that are not included on this chart: zinc, 3-methyl-4-chlorophenol.

**appendix h**  
**MP&M PROPOSED REGULATIONS, P. 446 —**  
**DTC REFERENCE**

---

## **Metal Products and Machinery Effluent Guidelines and Standards - Proposed Rule**

### **Summary**

*EPA is proposing Effluent Limitations Guidelines and Standards for the Metal Products and Machinery (MP&M) Point Source Category. This proposed regulation would establish technology-based effluent limitations and pretreatment standards for wastewater discharges associated with the operation of new and existing metal products and machinery facilities.*

### **Background on Effluent Guidelines**

Effluent limitations guidelines are national regulations that control the discharge of pollutants to surface waters and to publicly-owned treatment works (POTWs). Effluent guidelines are specific to each industry. Although the effluent limitations are based on specific process or treatment technologies to control pollutant discharges, EPA does not require dischargers to use a specific technology. Individual facilities may meet the requirements by adopting treatment technologies and processes that best suit their needs. The effluent guidelines program is one of EPA's most successful environmental protection programs. Effluent guidelines reduce the discharge of pollutants that have serious environmental impacts, including pollutants that kill or impair fish and other aquatic organisms; cause health problems through contaminated water, fish, or shellfish; and degrade aquatic ecosystems. Since 1974, EPA has promulgated effluent limitations guidelines and standards for more than 50 industrial categories.

### **Summary of the Proposed Rule**

The MP&M proposed regulation would establish technology-based effluent limitations and pretreatment standards for wastewater discharges for new and existing facilities that manufacture, rebuild, or maintain finished metal products, parts, or machines in one of the following industrial sectors: Aerospace; Aircraft; Bus and Truck; Electronic Equipment; Hardware; Household Equipment; Instruments; Job Shops; Mobile Industrial Equipment; Motor Vehicle; Office Machine; Ordnance; Precious Metals and Jewelry; Printed Wiring Boards; Railroad; Ships and Boats; Stationary Industrial Equipment; and Miscellaneous Metal Products.

This proposal will divide the MP&M industrial category into the following eight subcategories: General Metals; Metal Finishing Job Shops; Printed Wiring Boards; Non-Chromium Anodizing; Steel Forming and Finishing; Oily Wastes; Railroad Line Maintenance; and Shipbuilding Dry Docks. This proposed regulation establishes effluent limitations for direct dischargers for all 8 subcategories and establishes pretreatment standards for indirect dischargers (those that discharge wastewater to POTWs) for five of the eight subcategories. EPA is not proposing pretreatment standards for the Non-Chromium Anodizing, the Railroad Line Maintenance, and the Shipbuilding Dry Dock subcategories based on the low levels of pollutants discharged by the facilities in these subcategories. Further, wastewater discharges from facilities in these subcategories do not cause biological inhibition or sludge contamination at POTWs. This proposed regulation reflects extensive engineering and economic analysis of a wide range of regulatory alternatives, and a thorough environmental assessment. This proposal incorporates a variety of pollution prevention and water conservation techniques.

### **Benefits and Costs**

The proposed regulation covers 10,000 facilities, and will improve water quality on more than 1,100 streams. Nearly 20 pollutants would be controlled. The rule will reduce the discharge of conventional pollutants by at least 115 million pounds per year, priority pollutants by 12 million pounds per year, and nonconventional metal and organic pollutants by 43 million pounds per year. These pollutant reductions provide significant human health benefits and will improve the quality and value of water-based recreation. The annualized cost of this rule is \$1.9 billion, and the value of annual benefits is \$0.7 billion.

economic impacts for the Shipbuilding Dry Dock subcategory.

## VII. Water Use and Wastewater Characteristics

### A. Wastewater Sources and Characteristics

EPA classified the MP&M unit operations into the following three groups depending on their water use and discharge: (1) Unit operations that typically use process water and discharge process wastewater; (2) unit operations that typically either do not use process water or use process water but do not discharge wastewater; and (3) miscellaneous operations reported in the MP&M questionnaires by fewer than five respondents.

Process wastewater includes any water that, during manufacturing or processing, comes into direct contact with or results from the production or use of any raw materials, intermediate products, finished products, by-products, or waste products. Process wastewater includes wastewater from wet air pollution control devices. For the purposes of the MP&M regulation, EPA does not consider non-contact cooling water or storm water a process wastewater nor does it consider non-aqueous wastes used as processing liquids, such as spent solvents or quench oil, as process wastewater. (See Section III for detailed discussion on general applicability of today's proposed rule).

Wastewater from the operations that use process water have different characteristics depending on the unit operation from which they are derived. EPA discusses the five different types of MP&M process wastewater below. First, oil-bearing wastewater is typically generated from the use of metal shaping coolants and lubricants, surface preparation solutions used to remove oil and dirt from components, and associated rinses. Some examples of oil-bearing wastewater are: Machining and grinding coolants and lubricants; pressure and impact deformation lubricants; dye penetrant and magnetic flux testing; and alkaline cleaning solutions and rinses used to remove oil and dirt. This wastewater typically requires preliminary treatment to remove oil and grease. The most common type of treatment for oil-bearing wastewater is chemical emulsion breaking followed by gravity separation and oil skimming. EPA also identified MP&M facilities that used membrane separation technologies for oil and grease removal.

Second, hexavalent chromium-bearing wastewater typically consists of

concentrated surface preparation or metal deposition solutions, sealants, and associated rinses. Some examples of hexavalent chromium-bearing wastewater are: Chromic acid treatment solutions and rinses; chromate conversion coating solutions and rinses; and chromium electroplating solutions and rinses. This wastewater typically requires preliminary treatment to reduce the hexavalent chromium to trivalent chromium for subsequent chemical precipitation and settling. Typically, MP&M facilities use sodium metabisulfite or gaseous sulphur dioxide as reducing agents in the reduction of hexavalent chromium-bearing wastewater.

Third, many surface preparation or metal deposition solutions and their associated rinses generate process wastewater that contains cyanide. Two examples of cyanide-bearing wastewater are: Cyanide-bearing alkaline treatment solutions and rinses (typically used as a surface treatment step prior to electroplating with cyanide solutions) and cyanide-bearing electroplating solutions and rinses. This wastewater typically requires preliminary treatment to destroy cyanide and facilitate subsequent chemical precipitation and settling. MP&M facilities most often use sodium hypochlorite for the destruction of cyanide by alkaline chlorination.

Fourth, concentrated surface preparation or metal deposition solutions and their associated rinses can generate process wastewater that contain complexed or chelated metals. In particular, electroless plating operations and their rinses typically produce this type of wastestream. This wastewater requires preliminary treatment to break and/or precipitate the complexes for subsequent chemical precipitation and settling. MP&M facilities typically use sodium borohydride, hydrazine, sodium hydrosulfite, or sodium dimethyldithiocarbamate (DTC) as reducing and precipitating agents in this preliminary treatment process.

For the MP&M proposal, EPA based the estimated costs and pollutant removals associated with the treatment of chelated or complexed metals on the use of DTC. When DTC is used appropriately, it may effectively enhance the removal of some difficult to treat pollutants without impacting the environment or POTW operations. However, DTC is toxic to aquatic life and to activated sludge and thus can upset POTW operations. DTC can combine to form, or break down to, a number of other toxic chemicals, including thiram and ziram (both EPA registered fungicides) and other

thiurams, other dithiocarbamates, carbon disulfide, and dimethylamine. EPA's pollutant of concern list (see below for a description of the development of this list) contained ziram, carbon disulfide, and N-nitrosodimethylamine. Ziram is known to be toxic to aquatic life at the following levels: LC50 less than 10 ug/L (parts per billion) for several varieties of bluegill and trout; LC 50 between 10 and 100 ug/L in other studies (AQUIRE data base at <http://www.epa.gov/medecotx/quicksearch.htm>.) EPA solicits comment on the use of DTC for the treatment of chelated wastewater and its potential harmful effects on the environment and on POTW operations. The Agency is particularly interested in receiving data and information on alternative treatments for wastewater containing chelated or complexed metals.

Finally, virtually all MP&M process wastewater contains some metallic pollutants. Metal shaping solutions, surface preparation solutions, metal deposition solutions, and surface finishing solutions typically produce the most concentrated metal-bearing wastewater. MP&M facilities most commonly use chemical precipitation (usually with either lime or sodium hydroxide) and settling for metals removal. Many facilities also use coagulants and flocculants to assist chemical precipitation and settling.

As discussed in Section V.C, EPA conducted wastewater sampling episodes at 71 MP&M facilities to obtain data on the characteristics of MP&M wastewater and solid wastes, and to assess the following: the loading of pollutants to surface waters and POTWs from MP&M sites; the effectiveness of technologies designed to reduce and remove pollutants from MP&M wastewater; and the variation of MP&M wastewater characteristics across unit operations, metal types processed in each unit operation, and sectors. Although EPA analyzed the wastewater from these facilities for approximately 324 pollutant parameters (including conventional, nonconventional, and priority pollutants), it did not consider all of these pollutants for potential regulation. Rather, EPA reduced the list to 132 pollutants (referred to as pollutants of concern or POCs) for further consideration by retaining only those pollutants that met the following criteria:

- EPA detected the pollutant parameter in at least three samples collected during the MP&M sampling program.
- The average concentration of the pollutant parameter in samples of