

Technical Report Documentation Page

1. REPORT No.

2. GOVERNMENT ACCESSION No.

3. RECIPIENT'S CATALOG No.

4. TITLE AND SUBTITLE

Environmental Evaluation of Calcium Magnesium Acetate
(CMA)

5. REPORT DATE

1985

6. PERFORMING ORGANIZATION

7. AUTHOR(S)

Winters, Gidley, Hunt

8. PERFORMING ORGANIZATION REPORT No.

9. PERFORMING ORGANIZATION NAME AND ADDRESS

10. WORK UNIT No.

11. CONTRACT OR GRANT No.

12. SPONSORING AGENCY NAME AND ADDRESS

13. TYPE OF REPORT & PERIOD COVERED

14. SPONSORING AGENCY CODE

15. SUPPLEMENTARY NOTES

16. ABSTRACT

The purpose of this study is to evaluate, by means of a literature survey and a limited laboratory study, how calcium magnesium acetate (CMA) interacts with the environment, and to identify CMA's beneficial or detrimental environmental impacts.

In recent years transportation agencies have endeavored to improve the safety and convenience of winter travel by attempting to keep roadways free of ice and snow. Therefore, over the last twenty years, the use of sodium chloride (NaCl) for snow and ice removal has risen dramatically. Large scale use of NaCl has significant negative economic and environmental impacts. NaCl corrodes metal and degrades pavement, thereby damaging bridges, road surfaces, and vehicles. Heavy NaCl use damages or kills roadside vegetation, degrades aquatic ecosystems, and pollutes domestic water supplies (1,2). The damage done by NaCl is ultimately paid for by the public.

Because of the negative aspects of NaCl use, research is underway to identify agents which are effective deicers, but which are less deleterious than NaCl. Recent research by Bjorksten Research Inc. (3), conducted for the Federal Highway Administration identified CMA as a potential alternative to NaCl as a deicing agent. The Bjorksten research showed that CMA is effective in removing snow and ice from pavement. Bjorksten's limited environmental analysis of CMA found no significant negative environmental impacts for CMA. However, a more thorough environmental analysis of CMA was necessary to make sure that CMA would have no deleterious environmental impacts, and to identify any positive impacts that this chemical might have.

17. KEYWORDS

18. No. OF PAGES:

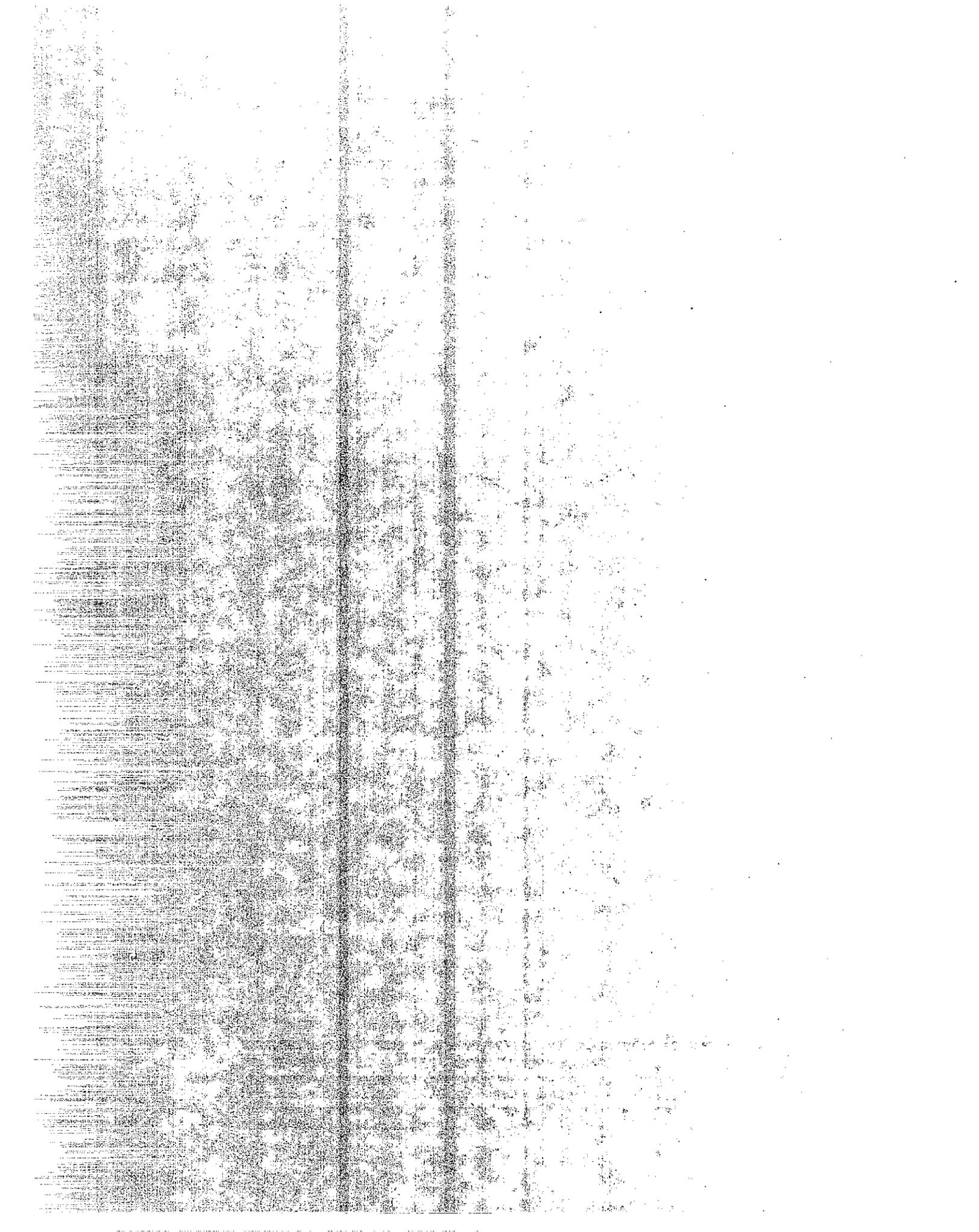
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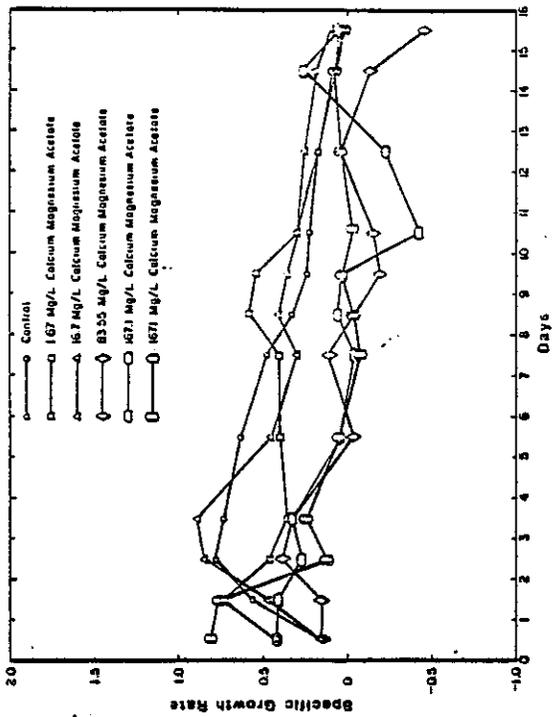
19. DRI WEBSITE LINK

<http://www.dot.ca.gov/hq/research/researchreports/1981-1988/RD84-094.pdf>

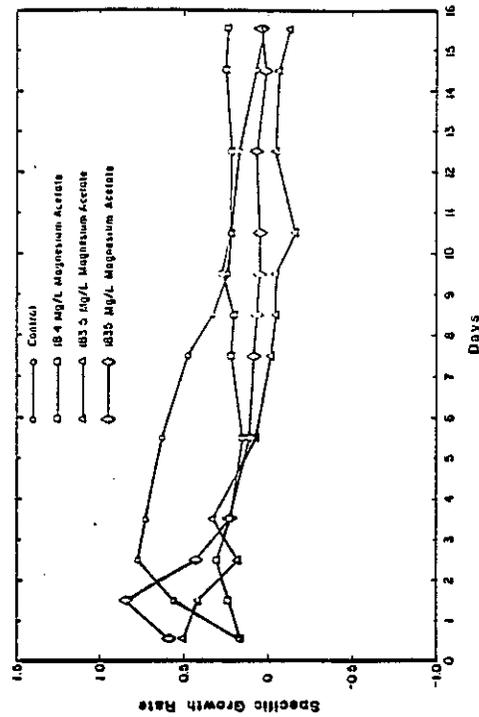
20. FILE NAME

RD84-094.pdf

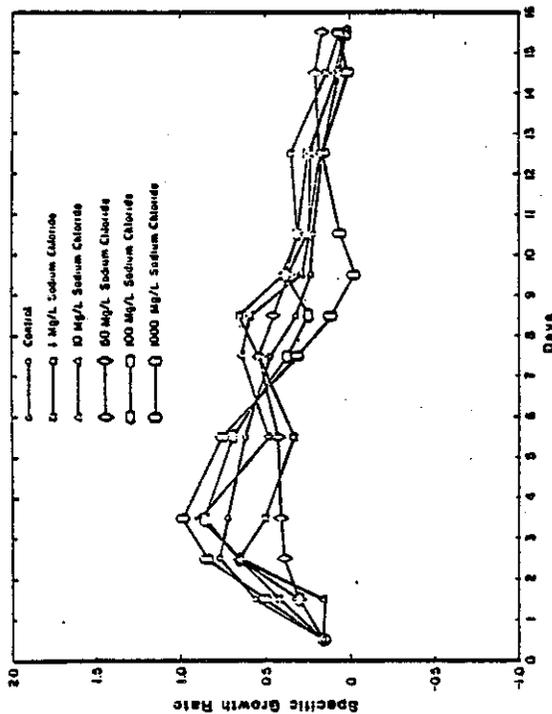




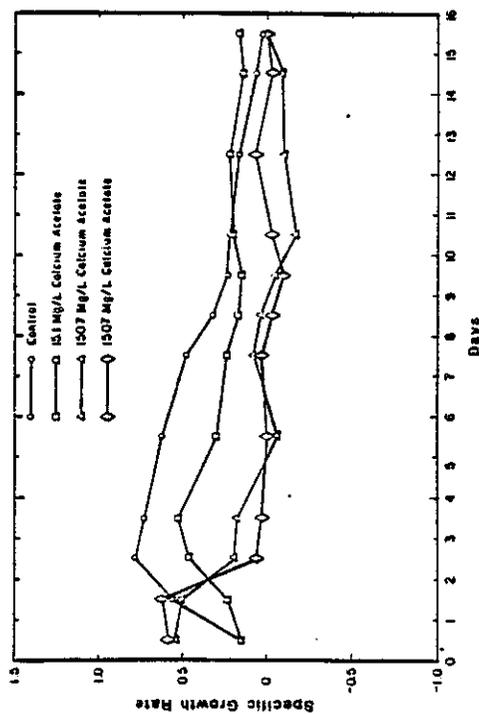
THE SPECIFIC GROWTH RATE (Two Day Moving Average) OF *ANABAENA FLOS-AQUAE* GROWN IN CALCIUM MAGNESIUM ACETATE COMPARED TO A CONTROL. (7/12/82-7/28/82)



THE SPECIFIC GROWTH RATE (Two Day Moving Average) OF *ANABAENA FLOS-AQUAE* GROWN IN MAGNESIUM ACETATE COMPARED TO A CONTROL. (7/12/82-7/28/82)



THE SPECIFIC GROWTH RATE (Two Day Moving Average) OF *ANABAENA FLOS-AQUAE* GROWN IN SODIUM CHLORIDE COMPARED TO A CONTROL. (7/12/82-7/28/82)



THE SPECIFIC GROWTH RATE (Two Day Moving Average) OF *ANABAENA FLOS-AQUAE* GROWN IN CALCIUM ACETATE COMPARED TO A CONTROL. (7/12/82-7/28/82)

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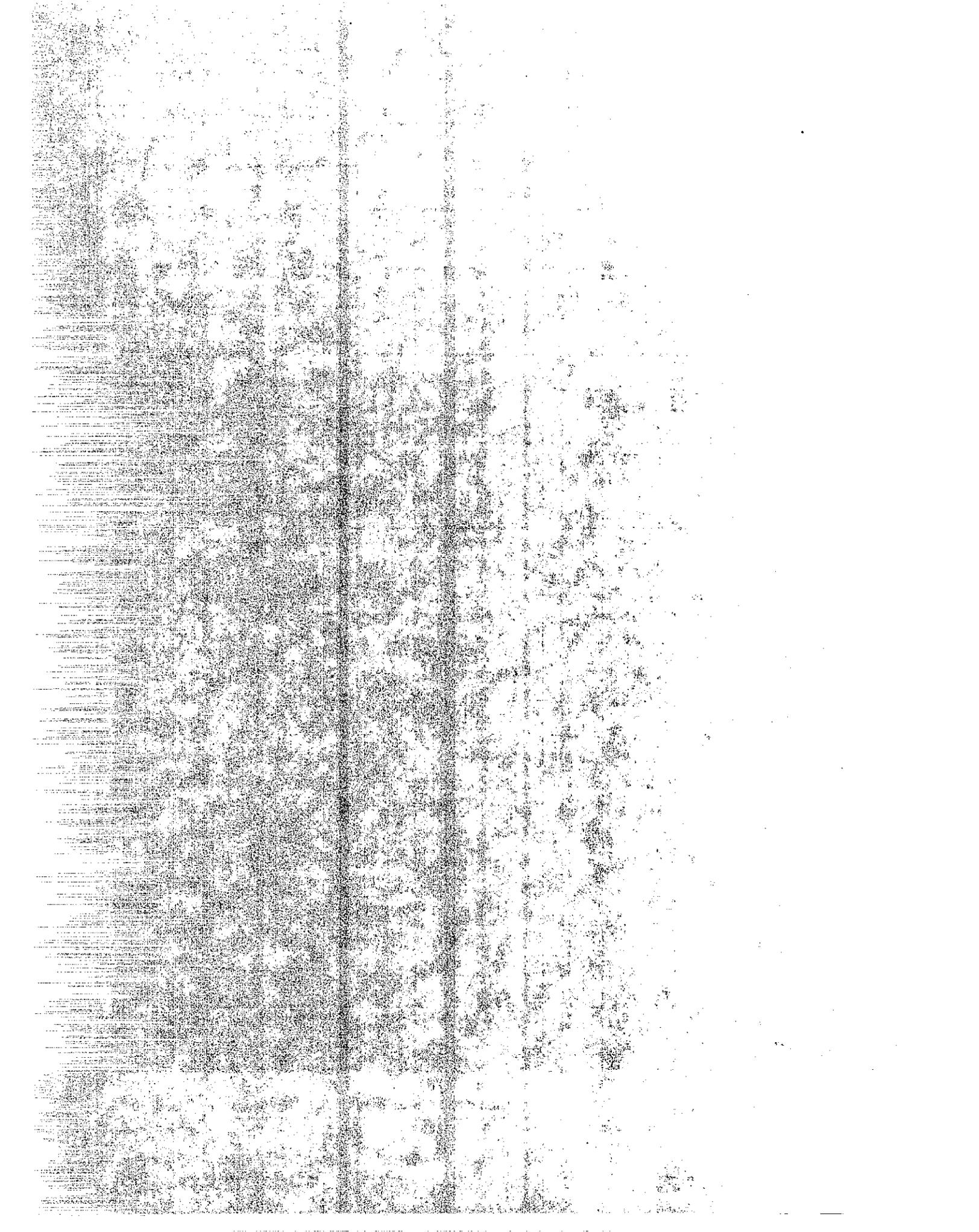


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EXECUTIVE SUMMARY

I. PURPOSE OF THIS STUDY

The purpose of this study is to evaluate, by means of a literature survey and a limited laboratory study, how calcium magnesium acetate (CMA) interacts with the environment, and to identify CMA's beneficial or detrimental environmental impacts.

II. INTRODUCTION

In recent years transportation agencies have endeavored to improve the safety and convenience of winter travel by attempting to keep roadways free of ice and snow. Therefore, over the last twenty years, the use of sodium chloride (NaCl) for snow and ice removal has risen dramatically. Large scale use of NaCl has significant negative economic and environmental impacts. NaCl corrodes metal and degrades pavement, thereby damaging bridges, road surfaces, and vehicles. Heavy NaCl use damages or kills roadside vegetation, degrades aquatic ecosystems, and pollutes domestic water supplies (1,2). The damage done by NaCl is ultimately paid for by the public.

Because of the negative aspects of NaCl use, research is underway to identify agents which are effective deicers, but which are less deleterious than NaCl. Recent research by Bjorksten Research Inc. (3), conducted for the Federal Highway Administration identified CMA as a potential alternative to NaCl as a deicing agent. The Bjorksten research showed that CMA is effective in removing snow and ice from pavement. Bjorksten's limited environmental analysis of CMA found no significant negative environmental impacts for CMA. However, a more thorough environmental analysis of CMA was necessary to make sure that CMA would have no deleterious environmental impacts, and to identify any positive impacts that this chemical might have.

This report is a more comprehensive examination of the impacts of CMA on surface water quality, groundwater quality, air quality, aquatic ecology, and soils. These areas were studied in varying degrees of detail. A literature search was performed for each subject, and in some areas a limited laboratory analysis was performed. While more extensive than the earlier environmental work on CMA, this study does not address the long term impacts of CMA on the environment.

A 1:1 equivalent weight mixture of analytical grade calcium acetate and magnesium acetate was used to manufacture CMA for this study. This was essentially a pure material which contained no byproducts. The by-products which may be present in industrially produced CMA are unknown. The by-products resulting from various manufacturing processes can sometimes pose environmental hazards even when the pure compound is innocuous. Consequently, the environmental impacts of industrially produced CMA were not determined in this study.

III. ENVIRONMENTAL EVALUATION

A. Surface Water Quality, Groundwater Quality, and Air Quality

The impacts of CMA on surface water quality, groundwater quality, and air quality were determined by means of a literature survey. The literature data bases surveyed included: Aqualine, Aquatic Sciences and Fisheries Abstracts, Air Pollution Technical Information Center, Biological Abstracts (Biosis Previews), CAB Abstracts, Enviroline, Environmental Bibliography, Life Sciences Collection, Instructional Resources Information System (IRIS), National Technical Information Service (NTIS), and Pollution Abstracts (TRISNET).

No source specifically identifying the impacts of calcium acetate, magnesium acetate, or CMA on surface water quality, groundwater quality or air quality was found during the literature search. Up to the present time, it seems that not enough of these materials are being used to generate much environmental information about them. Some transportation agencies have reported dust problems while using CMA. Consequently, the impacts of CMA on these resources is unknown. Some estimates of the impact of CMA on surface water quality are discussed below.

The addition of calcium and magnesium to a water body could result in an increase of water hardness. However, this would not be expected to be significant unless a relatively large amount of CMA entered a water body. There would probably be no other significant effect from slightly elevated calcium and magnesium levels.

While the acetate ion is mildly toxic to some fish, it is readily decomposed and would probably not reach toxic levels. The decomposition of acetate could result in localized oxygen depletion in water bodies, however, the acetate concentrations necessary for this would probably not be reached during deicing operations.

B. Aquatic Ecology

The potential impacts of CMA on aquatic ecosystems were investigated by a literature review and by laboratory bioassays. A bioassay is a toxicity procedure in which living organisms are exposed to known concentrations of a potentially toxic substance for a standardized period of time. The following organisms were used in the bioassays conducted for this study: Rainbow Trout (Salmo gairdneri) Fathead Minnow (Pimephales promelas) Waterflea (Daphnia magna), Green Algae (Selenastrum capricornutum), and Blue Green Algae (Anabaena flos-aquae). These organisms are commonly used in bioassays, and represent different groups of organisms in the aquatic food web.

Fish occupy the highest trophic level in the waterbodies most likely to receive CMA runoff. Rainbow trout (Salmo gairdneri) and Fathead Minnows (Pimephales promelas) were used to represent this trophic level. Short term static bioassays and long term renewal bioassays were performed.

The short term static bioassays were used to determine the acute toxicities of calcium acetate, magnesium acetate, and CMA to Rainbow Trout and Fathead Minnow fingerlings. The results are expressed as 96 hour LC₅₀'s. The 96 hour LC₅₀ is that concentration of a substance which kills 50% of the exposed test organisms in a period of 96 hours. The methods used in the static fish bioassays were the standard methods developed by the California Department of Fish and Game. The results of these bioassays are summarized below:

Short Term Fish Bioassay

	LC ₅₀ (mg/liter)			
	<u>NaCl</u>	<u>CMA</u>	<u>Ca Acetate</u>	<u>Mg Acetate</u>
Rainbow trout	12,200	18,700	16,200	4,300
Fathead minnow	11,400	21,000	14,300	9,000

The long term renewal bioassays were used to determine the impacts of CMA on the development of Rainbow Trout eggs. The long term bioassays developed problems which made analyzing the results difficult. However, the long term bioassays indicated that continuously maintained CMA concentrations >5,000 mg/liter could reduce Rainbow trout hatching success.

Zooplankton are small aquatic animals which occupy an intermediate position in the food web between aquatic plants and fish. To address the effects of CMA on the zooplankton component of the food web acute short-term

static and long-term static bioassays were conducted on waterfleas (Daphnia magna). The ability of Waterfleas to tolerate low dissolved oxygen levels, limited genetic variability among parthenogenetic offspring, high susceptibility to pollution, and ease of culture makes them ideal for bioassays.

Short-term static bioassays were used to determine the acute median lethal concentrations (96 hr LC₅₀'s) for CMA, calcium acetate, magnesium acetate, and NaCl (kiln-dried, road salt). The methods used in the Waterflea short-term static bioassays were adapted from Greenberg et al (4). The results are summarized below:

Short Term Daphnia magna Bioassays 96 hr LC₅₀'s
(mg/liter)

CMA when bacteria are present	<384
CMA when bacteria are absent	1421
Ca acetate when bacteria are present	482
Mg acetate when bacteria are absent	127
NaCl	4500

Long-term chronic bioassays were used to determine the No Observable Effects Concentration (NOEC). Reproductive success was used as the measure of the chronic effects of the tested chemicals on waterfleas. The assumption inherent in this testing is that the toxicant level which causes no reproductive impairment will have no chronic effects on individuals or populations in natural environments. The results of the long-term Waterflea bioassays are shown below:

Long Term Daphnia magna Bioassays No Observed Effects
Concentration (mg/liter)

CMA	125
Ca acetate	100
Mg acetate	100
NaCl	500

Green Algae (Selenastrum capricornutum) and Blue Green Algae (Anabaena flos-aquae) were used to determine the impacts of CMA, calcium acetate, magnesium acetate, and NaCl (kiln-dried, road salt) on primary producers. The method used for the algae tests was a modification of the EPA bottled algal assay test. Both types of algae were grown in natural water, and in artificial algae growth medium. Algal growth was determined by measuring the fluorescence of samples by using a Turner Model III fluorometer. A conservative estimate of the maximum concentration at which little effect from CMA, calcium acetate, or magnesium acetate would probably be less than 50 mg/L; for NaCl S. capricornutum was not affected by 1000 mg/L concentrations, similarly, A. flos-aquae was not affected by any

concentration of NaCl tested.

C. Terrestrial Ecology

The impacts of CMA on terrestrial ecology were examined by limited laboratory studies on vegetation and soil. The limited time spent on this project and the lack of industrially produced CMA precluded an in depth field evaluation on vegetation or soils. The vegetation study for this investigation measured the impacts of CMA on selected plants when applied in the irrigation water, or in foliar sprays. The soils study measured the nutrients and metals that leached out of selected soils when 1 N solution of CMA was passed through the soil.

There have been many studies measuring the impacts of NaCl on roadside vegetation. There have been no similar studies on CMA. During this study, it was assumed that CMA applied to highway would leave the highway either as runoff or as traffic generated aerosols, both of which would impact vegetation. Therefore, selected plant species were irrigated with a CMA solution. The species selected for this study are listed in Table 1. NaCl (kiln dried, road salt) was also applied in irrigation water and as a foliar spray so that a comparison could be made between CMA and NaCl. The irrigation water contained 5, 10, 50 or 100 milliequivalents of CMA or NaCl. The foliar sprays were 0.1, 0.5, 1.0, 2.0 N solutions of CMA or NaCl. These levels were selected because they bracket the concentrations of NaCl and CMA expected within 25 feet of a highway. The results of the vegetation study are summarized in Table 1.

Whenever there are long term additions of chemicals to the soil, there is always a question of whether or not the addition of the chemicals will reduce soil fertility. Various acetates, ammonium, sodium, and calcium are used for extractive purposes in soil chemistry procedures. Therefore, it is possible that long term CMA use might result in a disruption of the soil chemistry and a loss of soil fertility. To investigate the potential effects of CMA laden water might have on soil chemistry, a 1N solution was passed through seven selected soil samples. The liquid that leached through the soils was chemically analyzed to determine if significant amounts of metals or plant nutrients were removed from the soil. As a control, deionized water was passed through other samples of the same soils. The liquid that leached through these samples was chemically analyzed to determine if significant amounts of heavy metals or plant nutrients were removed from the soil. The results of the samples of the control series were compared with the results of the CMA series. It appears that 1 N CMA has the potential to remove significant amounts of iron, aluminum, sodium potassium and hydrolyzable orthophosphate from soil.

IV CONCLUSIONS AND RECOMMENDATIONS

A. Conclusions

1. CMA is less toxic to rainbow trout (Salmo gairdneri) and fathead minnows (Pimephales promelas) than NaCl, calcium acetate, or magnesium acetate. Magnesium acetate is slightly more toxic to rainbow trout and fathead minnows than NaCl. Calcium acetate is less toxic to these two fish species than NaCl. A continuously maintained concentration of 5000 mg/liter of CMA slightly delays the hatching of rainbow trout, but does not influence the number of eggs that hatch.

2. Waterflea (Daphnia magna) bioassays indicate that the 96 hr LC₅₀ CMA is 304 mg/liter when the CMA is associated with bacteria, and 1421 mg/liter when the CMA is bacteria free. The 96 hr LC₅₀ is that concentration of a chemical which kills 50% of the test animals within 96 hrs. The long term chronic bioassays indicated that waterflea reproduction was significantly inhibited at 250 mg/liter of CMA. The 96 hr LC₅₀ was for NaCl determined to be 4500 mg/liter. Waterflea reproduction was significantly inhibited at 125 mg/liter of NaCl.

3. The algae bioassays indicate that CMA, calcium acetate, and magnesium acetate are more toxic to algae than NaCl. It is estimated a concentration of less than 50 mg/liter of CMA is necessary to eliminate any deleterious effects of CMA on algae.

4. CMA leached through soil resulted in some removal of iron, aluminum, and selected nutrients from the tested soils.

5. In general NaCl is more injurious to plants than CMA. Only one species of plant, the Russian Olive (Elaeagnus angustifolia) was damaged more by CMA than by NaCl.

6. At the present time CMA's impacts on the public health and safety aspects of surface water quality, ground water quality and air quality are unknown. An extensive literature search found no information relating to these areas.

7. At the CMA concentrations likely to be generated by the use of CMA in snow and ice control, CMA may be less environmentally damaging than NaCl.

8. Workers exposed to CMA dust should wear dust masks.

B. Recommendations

CMA appears to be less deleterious to aquatic and terrestrial ecosystems than NaCl. However, these results are based on a literature search and limited laboratory study, and as such suffer the limitations inherent in such evaluations.

Based on the results of this study, it is recommended that:

1. Additional laboratory studies be conducted on the way and the rate by which bacteria degrades CMA under various soil and temperature conditions.
2. Controlled field testing should be conducted to determine the fate of CMA in the soil and vegetation and its impacts on ground water quality, aquatic ecosystems (particularly the lower trophic levels), and soil chemistry and physics over an extended period of time. These studies should be performed in climate zones where CMA is likely to be used.
3. Research should be conducted into how to reduce the dust problem associated with CMA.

TABLE I CMA/NaCl Damage to Plant Species

	Calcium Magnesium Acetate (CMA)		Sodium Chloride (NaCl)	
	<u>Soil</u>	<u>Spray</u>	<u>Soil</u>	<u>Spray</u>
<u>Abies concolor</u> (white-fir)	Low	Low	High	High
<u>Acer saccharum</u> (sugar maple)	Low	Low	Moderate	Moderate
<u>Amelanchier canadensis</u> (June berry)	Low	Low	High	High
<u>Arctostaphylos patula</u> (G. manzanita)	None	None	High	High
<u>Betula papyrifera</u> (paperbark birch)	Very low	Very low	Moderate- high	Moderate- high
<u>Calodecrus decurrens</u> (Incense cedar)	Low	Low	Moderate	Moderate
<u>Cornus florida</u> (flowering dogwood)	Moderate	None	High	High
<u>Elaeagnus angustifolia</u> (Russian Olive)	High	Moderate	Low- moderate	Moderate
<u>Fraxinus pennsylvanica</u> (white ash)	Low	Low	Moderate	Moderate
<u>Malix 'Hopa'</u> (flowering crab)	Moderate	Low	Moderate	High
<u>Pinus jefferyi</u> (Jeffery Pine)	Low	None	High	High
<u>Pinus lambertiana</u> (sugar pine)	Low	Low	High	High
<u>Quercus alba</u> (white oak)	Low-moderate	Low-moderate	Moderate- High	Moderate- high
<u>Quercus rubra</u> (red oak)	Low-moderate	Low-moderate	High	High
<u>Salix</u> sp. (willow)	None	None	None	None
<u>Thuja occidentalis</u> (American arborvitac)	Low	Low	Moderate	Moderate
<u>Viburnum lantana</u> (wayfaring tree)	Low	Low	High	High

Low = 0%-25% treatment related damage,
 Moderate = 26%-75% treatment related damage
 High = 76%-100% treatment related damage

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I INTRODUCTION

The use of Sodium Chloride (NaCl) for snow and ice removal in the United States has risen dramatically during the last 20 years. Currently, between nine and ten million tons of NaCl are used annually (1). In some areas as much as 25 tons of NaCl per lane mile are applied each winter. Many highway departments have adopted a bare pavement policy in snowy areas and this results in high NaCl use. Bare, i.e., snow and ice free, pavement is safer and allows higher speeds than snow covered pavements.

Highway departments rely on NaCl rather than abrasives for snow and ice control because the deicing salt melts the snow and ice, thereby breaking the bond between the ice and the pavement. Abrasives do not melt the snow and ice on the road, rather they coat the snow and ice covered road. Abrasives are more readily blown from the roadway, take longer to apply, require more cleanup, and are more expensive than NaCl. An abrasive coated ice pack is a less fuel efficient road surface than bare pavement, and traffic speeds are reduced.

The use of NaCl for highway snow and ice control has serious drawbacks. NaCl damages vehicles, pavement, structures, vegetation, wildlife, and domestic water supplies. (2, 3). Therefore, the Federal Highway Administration is researching alternatives to NaCl.

The recent study "Alternative Highway Deicing Chemicals", by Bjorksten Research Inc., has identified calcium magnesium acetate (CMA) as a potential alternative to NaCl as a deicing agent. This research showed that CMA is effective in melting ice and snow, is easily stored, can be dispersed with existing equipment, and unlike NaCl is noncorrosive and environmentally acceptable.

Bjorksten's research included a limited environmental evaluation of CMA, consequently a more thorough analysis of CMA's interactions with the environment was necessary. The study reported here is a literature and limited laboratory study which addresses the potential impacts of CMA on surface water quality, ground water quality, aquatic ecology, terrestrial ecology and soils. These areas were studied in varying degrees of detail.

No commercial source of CMA existed when this research was conducted. The CMA used in this study was prepared by mixing analytical grade calcium acetate and magnesium acetate in a 1:1 equivalent weight ratio. NaCl used for comparison with CMA during testing was kiln-dried, road salt.

The impacts of CMA on surface water quality, ground water quality and air quality were studied via a literature search. The impacts of CMA on aquatic ecosystems were evaluated via a literature search and via a series of bioassays. A bioassay is a toxicity test in which living organisms are exposed to known concentrations of a potentially toxic substance for a standardized period of time.

Standard static fish bioassay procedures were used to determine the effects of CMA on rainbow trout (Salmo gairdneri) and fathead minnows (Pimephales promelas). Both short term acute and long term chronic bioassays were conducted.

CMA's impacts on aquatic producers were studied by means of algae bioassays. The method used for the algae was a modification of the U.S. Environmental Protection Agency's (EPA) bottled algal bioassay test (4). The test determines the effects of a substance on the maximum growth rate and the maximum standing crop of selected algae species. Single species tests were performed with the green algae Selenastrum capricornutum, and the blue green algae Anabaena flos-aquae. Natural water and an artificial medium were both used.

CMA's impacts on zooplankton were studied by means of waterflea (Daphnia magna) bioassays. Both short term acute and long term chronic D. magna bioassays were performed. Both CMA and NaCl were tested.

CMA's impacts on terrestrial ecology were studied by means of limited vegetation and soil studies. In the vegetation study, eighteen common highway landscaping plant species were tested. Both NaCl and CMA were tested. Plants were subjected to either irrigation water containing one of the tested chemicals, or to a foliar spray containing one of the tested chemicals. The plants subjected to the chemicals were compared to controls to determine if the plants were damaged by the chemicals.

Whenever there are long term additions of chemicals to the soil, there is always a question of whether or not the addition of the chemicals will reduce soil fertility. Various acetates of ammonium, sodium, and calcium are used for extractive purposes in soil chemistry procedures. Therefore, it is possible that long term CMA use might result in a disruption of the soil chemistry and a loss of soil fertility. To investigate the potential effects that CMA laden water might have on soil chemistry, a 1 N solution was passed through seven selected soil samples. The liquid that leached through the soils was chemically analyzed to determine if significant amounts of metals or plant nutrients were removed from the soil. As a control, deionized water was passed through other samples of the same soils. The liquid that leached through these samples was chemically analyzed to determine if significant amounts of metals or plant nutrients were removed from the soil. The results of the samples of the control series were compared with the results of the CMA series.

II CONCLUSIONS AND RECOMMENDATIONS

A. Conclusions

1. CMA is less toxic to rainbow trout (Salmo gairdnerii) and fathead minnows (Pimephales promelas) than NaCl, calcium acetate, or magnesium acetate. Magnesium acetate is slightly more toxic to rainbow trout and fathead minnows than NaCl. Calcium acetate is less toxic to these two fish species than NaCl. A continuously maintained concentration of 5000 mg/liter of CMA slightly delays the hatching of rainbow trout, but does not influence the number of eggs that hatch.
2. Waterflea (Daphnia magna) bioassays indicate that the 96 hr LC₅₀ CMA is 304 mg/liter when the CMA is associated with bacteria, and 1421 mg/liter when the CMA is bacteria free. The 96 hr LC₅₀ is that concentration of a chemical which kills 50% of the test animals within 96 hrs. The long term chronic bioassays indicated that waterflea reproduction was significantly inhibited at 250 mg/liter of CMA. The 96 hr LC₅₀ was for NaCl determined to be 4500 mg/liter. Waterflea reproduction was significantly inhibited at 125 mg/liter of NaCl.
3. The algae bioassays indicate that CMA, calcium acetate, and magnesium acetate are more toxic to algae than NaCl. It is estimated a concentration of less than 50 mg/liter of CMA is necessary to eliminate any deleterious effects of CMA on algae.
4. CMA leached through soil resulted in some removal of iron, aluminum, and selected nutrients from the tested soils.
5. In general NaCl is more injurious to plants than CMA. Only one species of plant, the Russian Olive (Elaeagnus angustifolia) was damaged more by CMA than by NaCl.
6. At the present time CMA's impacts on the public health and safety aspects of surface water quality, groundwater quality and air quality are unknown. An extensive literature search found no information relating to these areas.
7. At the CMA concentrations likely to be generated by the use of CMA in snow and ice control, CMA may be less environmentally damaging than NaCl.
8. Workers exposed to CMA dust should wear dust masks.

B. Recommendations

CMA appears to be less deleterious to aquatic and terrestrial ecosystems than NaCl. However, these results are based on a literature search and limited laboratory study, and as such suffer the limitations inherent in such evaluations.

Based on the results of this study, it is recommended that:

1. Additional laboratory studies be conducted on the way and the rate by which bacteria degrades CMA under various soil and temperature conditions.
2. Controlled field testing should be conducted to determine the fate of CMA in the soil and vegetation and its impacts on groundwater quality, aquatic ecosystems (particularly the lower trophic levels), and soil chemistry and physics over an extended period of time. These studies should be performed in climate zones where CMA is likely to be used.
3. Research should be conducted into how to reduce the dust problem associated with CMA.

III ENVIRONMENTAL EVALUATION

A. Surface Water Quality, Groundwater Quality and Air Quality

This study addressed the impacts of CMA on surface water quality and groundwater quality, air quality, aquatic ecology, terrestrial ecology and soils in varying depths.

The surface water quality, groundwater quality and air quality investigations were limited to literature surveys. Databases searched included: Aqualine, Aquatic Sciences and Fisheries Abstracts, Air Pollution Technical Information Center, Biological Abstracts (Biosis Previews), CAB Abstracts, Claims/vs. Patent Abstracts, Enviroline, Environmental Bibliography, Life Sciences Collection, Instructional Resources Information System (IRIS), National Technical Information Service (NTIS) and Pollution Abstracts.

No information on calcium acetate's, magnesium acetate's, or CMA's impacts on surface water quality, or groundwater quality was found during the literature search.

During field tests conducted by Iowa and Michigan significant amounts of fine CMA dust were generated during deicing operations (5,6). The dust may be due to the small CMA particle size used during the testing. No information concerning the medical implications of a CMA dust inhalation was discovered during our literature search. However, inhalation of any dust can potentially damage lung tissue. Further research should be conducted into how the CMA dust problem can be resolved. Until effective dust control can be achieved, workers using CMA should wear dust masks.

An increased input of calcium and magnesium in a waterbody could lead to an increase in water hardness. However, this would not be expected unless relatively large amounts of CMA enter a small waterbody. With the exception of an increase in water hardness, it is difficult to envision significant deleterious effects from slightly elevated calcium and magnesium levels.

The acetate ion, while mildly toxic to some fish, will probably be decomposed by bacteria before it accumulates to troublesome levels. The decomposition of acetate could result in localized dissolved oxygen depletion within water bodies, however, it is anticipated the levels necessary for this to occur probably will not be reached during deicing procedures.

B. Aquatic Ecology

1. Fish Bioassays

CMA, when used as a roadway deicer, will find its way in runoff to streams and lakes. Because fish occupy the highest trophic level in the water bodies most likely to receive CMA laden runoff, two species of fish were tested to observe the effects

of CMA, calcium acetate, and magnesium acetate. The two species chosen were a cold water species, the Rainbow Trout (Salmo gairdneri), and warm water species, the fathead minnow (Pimephales promelas). The effect of CMA on eyed eggs of rainbow trout was also tested.

Short-term, static bioassays and long-term, renewal bioassays were performed. The static bioassays were performed on both fathead minnow fingerlings and rainbow trout fingerlings to determine the acute toxicity of CMA, calcium acetate and magnesium acetate. The chronic bioassays were performed on eyed eggs of rainbow trout to determine the effect of CMA on egg development, hatching, and larval development. The bioassays and interpretation of results were performed by personnel from the California Department of Fish and Game, Water Pollution Control Laboratory.

a. Materials and Methods

1) Short-term Static Bioassays - Standardized methods developed by the California Department of Fish and Game were used (7). The results were expressed as 96 hr LC₅₀'s. The 96 hour LC₅₀ is that concentration of a toxicant which kills 50% of the test organisms during a 96 hour period.

The Rainbow Trout were acquired from the Nimbus Fish Hatchery in Rancho Cordova, CA. The fathead minnows were acquired from the Chico Fish Farm in Chico, CA.

The water used for testing was sand filtered water from the American River in Rancho Cordova, CA. Prior to testing, all fish were acclimated for seven days in American River water.

Preliminary range finding bioassays were conducted to establish the chemical concentration ranges which would later be tested in the definitive bioassays. In the range finding bioassays 1 gallon wide mouthed jars containing 21 liters of solution were used. Two to four fish were placed in each jar for 24 hours.

Definitive bioassays were conducted using 20 liter aquariums containing 10 liters of solution. For each concentration tested, there were three replicates. Ten fish were added to each replicate, so that a total of 30 fish were exposed to each concentration of toxicant.

CMA was tested on rainbow trout, while calcium acetate and magnesium acetate were tested on both Rainbow Trout and Fathead Minnow.

Rainbow Trout (Fig. 1) were tested at 15°C + 1°C while Fathead Minnow were tested at 20°C + 1°C. The aquariums were checked daily for dead fish which were immediately removed. The dissolved oxygen level, pH, and water temperature were also measured. All results were

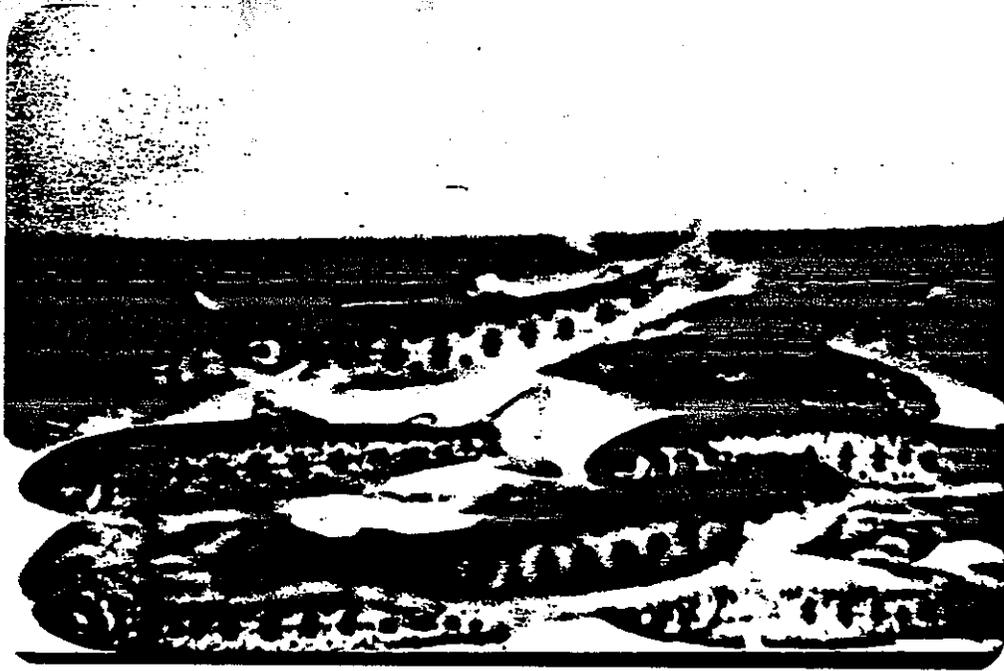


Figure 1. Young rainbow trout (*salmo gairdneri*)
used in static acute toxicity bioassays.



Figure 2. Test aquaria with eyed-egg cups, toxicant at
noted concentratoin and net screen chamber
for transfer of just hatched alvins.

recorded daily. At the end of 96 hours the total number of fish that died at each concentration was determined. The LC50 values were calculated by linear interpolation of mortality vs. concentration data plotted on probability paper.

2. Long-term Renewal Bioassay - A long-term bioassay was used to test the impacts of CMA on rainbow trout eggs and larva (Fig. 2). Eyed rainbow trout eggs were obtained from the American River Fish Hatchery in Rancho Cordova, CA.

Thirty eggs were placed in each of specially constructed egg cups for part of the bioassay. The egg cups were constructed from 38mm diameter acrylic tubing (Figure 3). The tubing was cut into segments that were 80mm long. Nylon netting was secured to one end of each tube with silicone sealant. The egg cups were attached by nylon monofilament fishing line and fishing tackle swivel snaps to oscillating arms driven by an electric motor (7). The whole apparatus was placed in 20 liter glass aquariums which contained 10 liters of test solution. The egg cups were adjusted so that the top of the egg cup did not become submerged, while the eggs remained submerged. Air was bubbled through the solution through 1 ml. milk pipettes.

After hatching the alevins were transferred to open topped nylon screen alevin chambers. The chambers were cuboidal with sides approximately 10 cm. long and an open top. The alevin chambers were placed in the same aquariums which contained the egg cups. The open tops of the alevin chambers were kept above the surface of the water.

When the fish reached the swim up fry stage they were transferred to a nylon net enclosure suspended in the test aquarium. The nylon net enclosure facilitated the daily exchange of the test solution (Figure 4).

Two egg cups, containing a total of 60 eggs, were placed in each of the following test concentrations of CMA: 1 mg/liter, 50 mg/liter, 1000 mg/liter, and 5000 mg/liter, and the control 0 mg/liter. Three egg cups, containing a total of 90 eggs, were placed in each of the following test concentrations of CMA: 100 mg/liter and 550 mg/liter.

The test solutions were changed daily. This was accomplished by moving the test animals to aquariums containing fresh solution. After use, the aquariums were rinsed with American River water and filled with fresh test solution. Proper amounts of dry calcium acetate and magnesium acetate were added to water to make up the 500 mg/liter, 1000 mg/liter, and 5000 mg/liter test concentrations. A stock solution of 10 mg/ml of CMA was used to make up the 1 mg/liter, 50 mg/liter, and 100 mg/liter test solutions.

Each day the number of dead eggs, hatched alevins, dead

alevins, living swim up fry and dead swim up fry were recorded. The dissolved oxygen level, pH, and water temperature were also measured daily. The air temperature in the environmental chamber was continuously recorded and remained at 9° + 1°C throughout the test period.

b. Results

1. Short Term Static Bioassays - Results of the static acute bioassays are shown in Table 1. CMA and calcium acetate are less toxic to Rainbow Trout than NaCl. Magnesium acetate is more toxic to Rainbow Trout than NaCl. For Fathead Minnows, magnesium acetate is more toxic than NaCl, while calcium acetate is less toxic than NaCl.

Table 1. Results of the Short Term Fish Bioassays (LC₅₀'s in mg/liter)

	NaCl	CMA	Ca Acetate	Mg Acetate
Rainbow Trout	12,200	18,700	16,200	4,300
Fathead Minnow	11,400	21,000	14,300	9,000

2. Long Term Bioassays - A fungal infection persisted in the 100 mg/liter and 500 mg/liter concentrations despite repeated treatment efforts. It is well known that fungi can affect survival and development in fish. Additionally, disruption of the air supply in the 100 mg/liter tank caused 10 alevins to die. Consequently, the results are not quantitative.

Despite the problems, some results were obtained. Some difficulty in hatching due to egg membrane hardening, was observed in the 5000 mg/liter concentration. The larval fish appeared to be less able to free themselves completely from the egg shell for several days. Two of the developing fish were unable to penetrate the egg membranes. Healthy alevins were released from these eggs by rupturing the egg membrane with slight pressure from a glass rod.

c. Conclusions

Magnesium acetate is slightly more toxic and calcium acetate is slightly less toxic to Fathead Minnows and Rainbow Trout than NaCl. CMA is less toxic to Rainbow Trout than NaCl or either acetate tested separately.

A continuously maintained concentration of 5000 mg/liter of CMA impacts the membranes of Rainbow Trout eggs. This suggests that slightly higher CMA levels could cause increased hatching mortality. However, a sustained concentration of this level during snow and ice removal is unlikely.

Because this was a laboratory study, it does not completely reflect the actual conditions in the field. A scientifically designed field study should be performed.



Figure 3. Acrylic egg cups.



Figure 4. Open topped nylon screen chambers with alvins.

2. Zooplankton Bioassays

a. Introduction

Zooplankton are small aquatic animals that occupy a position in the food web that is intermediate between some microbes of the lower trophic levels and the carnivores of the higher trophic levels. The Waterfleas of the Order Cladocera form a significant portion of the zooplankton in many waters, and are an important source of food for both aquatic insects and fish (9).

Daphnia magna is a fresh Waterflea found primarily in ponds containing large amounts of suspended organic matter. It feeds on algae, protozoa, bacteria, and organic detritus. D. magna is tolerant of low oxygen levels, and is generally more sensitive to pollutants than fish. It is also relatively easy to culture. If the proper conditions are maintained, females will naturally clone giving rise to parthenogenetic young which are genetically identical to their mother, and to each other.

The ease of culture, sensitivity to pollution, and the ability to produce large numbers of identical test animals makes Daphnia magna an ideal organism for bioassays. D. magna has been used in toxicity studies for many years.

b. Materials and Methods

Daphnia magna were purchased from a biological supply company. D. magna was mass cultured in a 20 gallon aquarium and in three liter jars. The individuals actually used in the toxicity tests were cultured in 125 ml wide mouth flint glass bottles (Figure 5). All cultures were kept at room temperature. The culture medium was made by mixing 15 mg of dried sheep manure, 75 gm of dried garden soil, and 3 liters of dechlorinated tap water. This mixture was allowed to stand for 2 days, filtered through cheese cloth, and through a .100 mesh filtering cloth. The filtrate was allowed to stand for one week before use. The culture medium consisted of 250 ml of the original filtrate added to 650 ml of dechlorinated tap water. The original filtrate was kept until the supply was exhausted, then a new supply was made up. Three times a week .01 mg of yeast and about 100,000 Selenastrum capricornutum cells were added to each culture jar.

The young produced in the 125 ml flint glass jars were removed daily (Figure 6). Neonates to be used in bioassays were placed in a common vessel containing fresh medium from the same batch of medium used in the bioassay. If not needed for a bioassay, the young were either cultured or discarded.

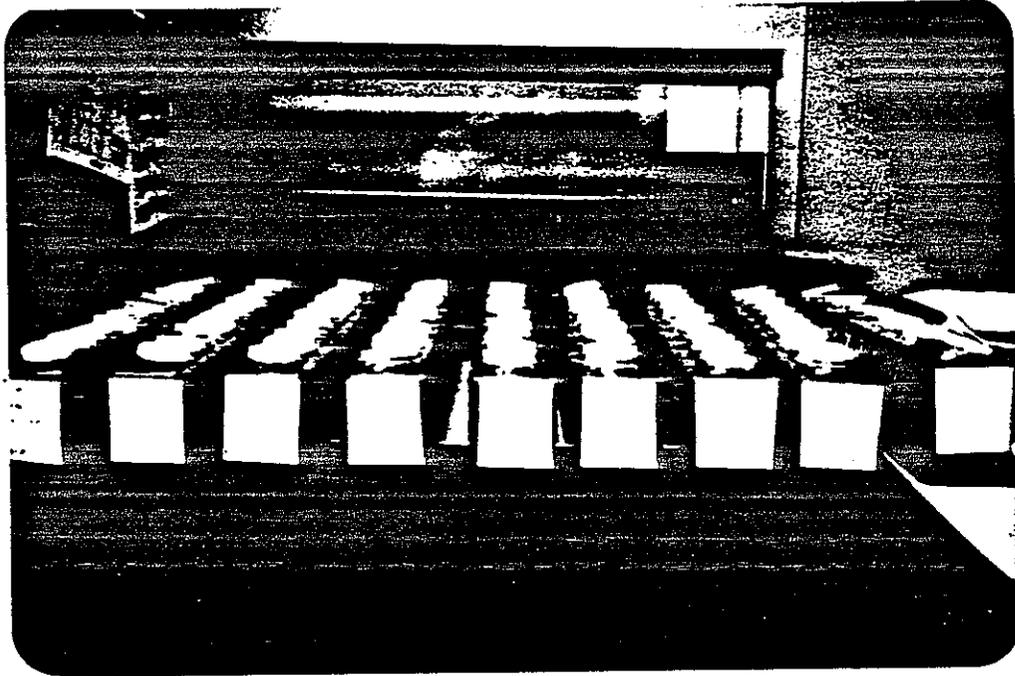


Figure 5. Individual 125 ml wide mouth jars used for raising individual Daphnia and conducting tests. Large aquarium in background used for mass culturing.

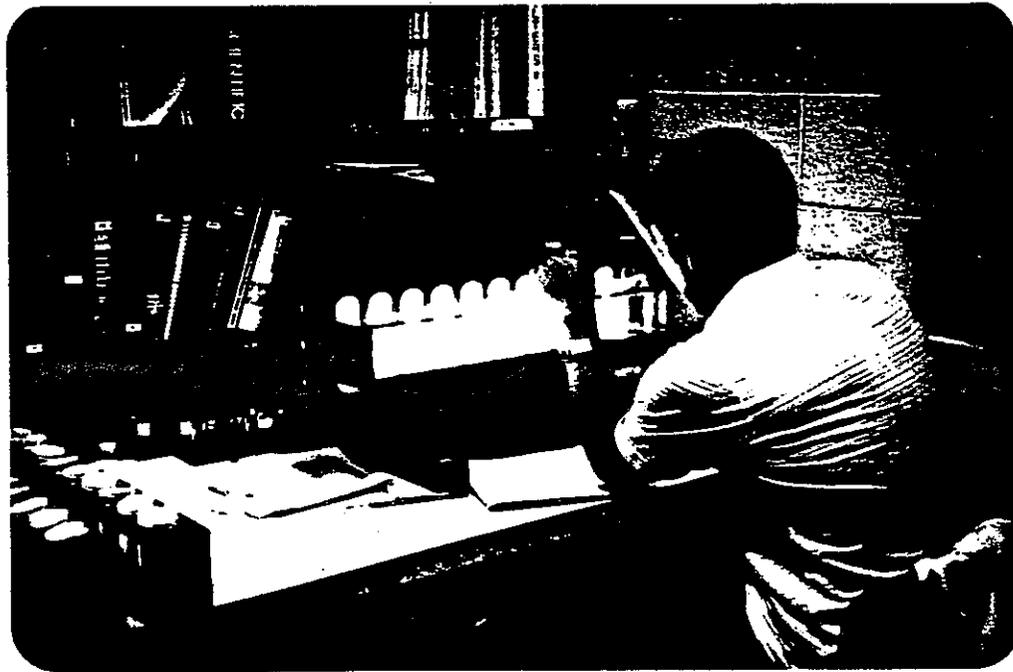


Figure 6. Background light source used to view Daphnia during testing.

1. Short-term Bioassays - Short-term static bioassays were used to determine the median lethal concentration (96 hr LC₅₀) for CMA, calcium acetate, magnesium acetate, and NaCl. The LC₅₀ is that concentration of toxicant which kills 50% of the test animals in 96 hours. Tables 3, 4, 5, and 6 shows the concentrations for each deicer that was tested. In every test each concentration and each control was run in triplicate.

The individual tests were conducted in 125 ml wide-mouth flint glass jars to which 100 ml of test solution or control solution was added. The control solution consisted of the growth medium. The test solution consisted of growth medium plus a measured amount of deicer.

After the various deicer concentrations and the control were prepared, 10 neonates <24 hr. old were transferred to each bottle using a large bore pipette (Figure 6). The number of nonmotile test animals was determined every 24 hours. The test animals were not fed during the test procedure. After 96 hours the LC₅₀ was calculated using the binomial moving average and probit methods.

In the initial short-term bioassays large amounts of bacteria grew in the higher concentrations of CMA, calcium acetate, and magnesium acetate. Tentative results indicated that the bacterial blooms could have been killing the D. magna.

To determine if the bacterial blooms were killing the test animals, the test procedure was modified to minimize the potential for bacterial blooms to develop. All glassware was washed with phosphorus free detergent, rinsed with a 10% solution of hydrochloric acid, rinsed with deionized water, autoclaved for 30 minutes and dried overnight at 110 C. The test medium was autoclaved for 45 minutes either prior to the addition of the tested deicer, or in one case after the addition of the deicer. The D. magna neonates were washed in dechlorinated water, and transferred to sterile medium prior to placement in the test medium. Table 3 shows those tests in which the bacterial growth reducing techniques were used.

2. Long-term Bioassays - Long-term bioassays were used to test the chronic effects of CMA, calcium acetate, magnesium acetate, and NaCl. Reproductive success was used as a measure of chronic effects in the long-term bioassays because it was assumed that the toxicant level which has no reproductive impairment will have no detectable chronic effects on the individual on the population.

The test medium for the long term bioassays was prepared in the same way that the test medium for the short term bioassays was prepared. The concentrations for deicer tested were chosen based on the results of the short-term bioassays. Table 2 shows the concentrations of the various deicers that

Table 2 - CMA, NaCl, Calcium Acetate, and Magnesium Acetate Concentrations Tested in Long-Term Static Bioassays (Concentrations in mg/liter)

CMA Run 1	CMA Run 2	CaAcetate
500	500	1000
100	250	100
4	125	10
0.8	62.5	1
0 (Control)	0 (Control)	0 (Control)

MgAcetate	NaCl
1000	2500
100	500
10	100
1	20
0 (Control)	0 (Control)

Table 3 - Results of short-term Daphnia magna bioassays using Calcium Magnesium Acetate

Test Run 1 - Non-sterile media

Concentrations mg/liter	Number of test organisms	Number of test organisms nonmotile at:			
		24 hrs	48 hrs	72 hrs	96 hrs
8355	30	30	30	30	30
1671	30	15	18	22	25
167	30	2	5	6	6
17	30	2	5	8	11
0 (Control)	30	1	1	2	13

Test Run 2 - Non-sterile media

Concentrations mg/liter	Number of test organisms	Number of test organisms nonmotile at:			
		24 hrs	48 hrs	72 hrs	96 hrs
1000	15	1	7	14	15
500	15	0	2	3	5
100	15	0	0	0	0
0 (Control)	15	0	0	0	0

LC₅₀ estimated by:

binomial method	-	-	653.0	572.2
95% confidence limits	-	-	500-1000	100-1000
moving average method	-	-	653.0	-
95% confidence limits	-	-	533.5-767.0	-
probit method	-	-	641.4	-
95% confidence limits	-	-	525.2-785.2	-

Test Run 3 - Non-sterile media

Concentrations mg/liter	Number of test organisms	Number of test organisms nonmotile at:			
		24 hrs	48 hrs	72 hrs	96 hrs
2000	30	0	10	19	30
400	30	1	1	3	25
80	30	0	4	12	12
16	30	0	0	0	0
0 (Control)	30	0	0	0	1

LC₅₀ estimated by:

binomial method	-	-	1386.9	113.5
95% confidence limits	-	-	400-2000	16-400
moving average method	-	-	1386.9	149.4
95% confidence limits	-	-	943.7-2430.3	28.3-222.7
probit method	-	-	1337.4	152.9
95% confidence limits	-	-	0-∞	0-∞

Test Run 4 - Sterile media

Concentrations mg/liter	Number of test organisms	Number of test organisms nonmotile at:			
		24 hrs	48 hrs	72 hrs	96 hrs
10,000	30	30	30	30	30
2,000	30	0	8	9	14
400	30	0	0	4	4
80	30	0	0	1	1
0 (Control)	30	0	0	0	0

LC₅₀ estimated by:

binomial method	-	3001.4	2861.0	2148.1
95% confidence limits	-	2000-10,000	2000-10,000	2000-10,000
moving average method	-	-	2149.5	1421.4
95% confidence limits	-	-	1551.3-3002.6	993.2-2113.3
probit method	-	-	1971.3	1526.6
95% confidence limits	-	-	0-∞	0-∞

Test Run 5 - Sterile media

Concentrations mg/L	Number of test organisms	Number of test organisms nonmotile at:			
		24 hrs	48 hrs	72 hrs	96 hrs
6000	30	24	30	30	30
2400	30	2	2	2	9
960	30	1	1	1	1
384	30	0	0	0	0
0(control)	30	0	0	0	0

LC₅₀ estimated by:

binomial method	4222.9	3519.4	2942.6
95% confidence limits	2400-6000	2400-6000	2400-6000
moving average method	4223-0	3290.4	2946.6
95% confidence limits	3661.9-4982.3	2801.8-3966.4	2259.1-3125.5
probit method	4138.4	3289.9	2706.2
95% confidence limits	0-∞	0-∞	2264.9-3239.3

Test Run 6 - Modified growth reducing method/seeding.

A. Modified bacterial growth reducing techniques.

Concentrations mg/L	Number of test organisms	Number of test organisms nonmotile at:			
		24 hrs	48 hrs	72 hrs	96 hrs
6000	30	20	30	30	30
2400	30	13	27	29	29
960	30	0	8	17	19
384	30	0	0	0	0
154	30	0	0	0	0
0(control)	0	0	0	0	0

LC₅₀ estimated by:

binomial method	3109.3	1317.9	887.9	830.5
95% confidence limits	2400-6000	960-2400	384-2400	384-960
moving average method	3412.4	1322.6	1001.1	958.5
95% confidence limits	2699.9	1062.1-1683.0	805.5-1209.9	777.4-1227.0
probit method	3647.4	1305.1	949.2	899.1
95% confidence limits	2860.4-4941.8	1086.4-1567.7	792.9-1136.4	750.8-1075.8

B. Modified bacterial growth reducing technique and seeding with unsterilized culture medium.

Concentrations mg/L	Number of test organisms	Number of test organisms nonmotile at:			
		24 hrs	48 hrs	72 hrs	96 hrs
6000	30	24	30	30	30
2400	30	21	24	29	30
960	30	1	11	13	14
384	30	0	0	0	0
154	30	0	0	0	0
0 (Control)	30	0	0	0	0

Test Run 7 - Mixed Bioassay

A. Bacterial growth reducing techniques.

Concentrations mg/L	Number of test organisms	Number of test organisms nonmotile at:			
		24 hrs	48 hrs	72 hrs	96 hrs
6000	30	30	30	30	30
2400	30	26	30	30	30
960	30	0	4	25	25
384	30	0	0	1	10
0 (Control)	30	0	0	0	0

LC₅₀ Estimated by:

binomial method	721.9	1338.1	676.2	514.3
95% confidence limits	960-2400	960-2400	384-960	384-960
moving average method	-	1220	676.2	514.3
95% confidence limits	-	1041.6-1459.2	596.5-780.0	370.4-644.0
probit method	-	1242.4	699.5	508.1
95% confidence limits	-	0-∞	589.4-813.9	385.4-628.0

B. Unsterilized culture medium.

Concentrations mg/L	Number of test organisms	Number of test organisms nonmotile at:			
		24 hrs	48 hrs	72 hrs	96 hrs
6000	30	30	30	30	30
2400	30	29	30	30	30
960	30	18	27	30	30
384	30	27	28	28	28
0 (Control)	30	0	0	0	0

LC₅₀ estimated by:

binomial method	1891.6	1259.5	1054.5	999.9
95% confidence limits	960-2400	384-2400	384-2400	384-2400
moving average method	1891.6	1259.5	1054.2	-
95% confidence limits	1625.2-2321.7	808.0-1641.2	899.8-1244.6	-
probit method	2426.7	1315.0	1058.3	-
95% confidence limits	817.2-11071.9	1070.1-1616.0	877.1-1264.9	-

Table 4 - Results of short-term Daphnia magna bioassays using Calcium Acetate

Test Run 1 - Non-sterile medium

Concentrations mg/L	Number of test organisms	Number of test organisms nonmotile at:			
		24 hrs	48 hrs	72 hrs	96 hrs
1500	30	21	28	30	30
500	30	0	1	19	21
100	30	0	1	2	2
20	30	0	0	0	0
0 (Control)	40	0	0	2	15

Test Run 2 - Non-sterile medium

Concentrations mg/L	Number of test organisms	Number of test organisms nonmotile at:			
		24 hrs	48 hrs	72 hrs	96 hrs
1000	30	13	19	28	30
500	30	2	5	16	16
250	30	0	0	0	1
125	30	0	0	0	1
62.5	30	0	0	0	1
0 (Control)	30	0	0	0	1

LC ₅₀ estimated by:	-	48 hrs	72 hrs	96 hrs
binomial method	-	828.6	484.8	481.7
95% confidence limits	-	>500.	250-1000	250-1000
moving average method	-	828.6	519.5	481.7
95% confidence limits	-	691.4-1117.7	457.3-592.5	411-643
probit method	-	834.5	520.0	441.4
95% confidence limits	-	705.8-1051.0	450.4-600.7	0-∞

Table 5. - Results of short-term *Daphnia magna* bioassays using Magnesium-Acetate

Test Run 1 - Non-sterile media

Concentrations in mg/L	Number of test organisms	Number of test organisms nonmotile at:			
		24 hrs	48 hrs	72 hrs	96 hrs
1500	30	8	15	30	30
500	30	0	0	8	9
100	30	0	0	0	0
20	30	0	0	0	0
0 (Control)	30	0	0	2	15

Test Run 2 - Non-sterile media

Concentrations in mg/L	Number of test organisms	Number of test organisms nonmotile at:			
		24 hrs	48 hrs	72 hrs	96 hrs
1000	30	1	1	1	20
500	30	0	0	0	0
250	30	0	0	0	0
125	30	0	0	0	0
62.5	30	0	0	0	0
0 (Control)	30	0	0	0	0

LC ₅₀ estimated by					96 hrs
binomial method	-	-	-	-	857.1
95% confidence limits	-	-	-	-	500-1000

Test Run 3 - Non-sterile media

Concentrations in mg/L	Number of test organisms	Number of test organisms nonmotile at:			
		24 hrs	48 hrs	72 hrs	96 hrs
2000	30	4	12	20	27
400	30	0	6	7	28
80	30	2	9	9	9
16	30	0	0	0	0
0 (Control)	30	0	0	0	1

LC ₅₀ estimated by:	-	-	72 hrs	96 hrs
binomial method	-	-	1090.0	126.6
95% confidence limits	-	-	400-2000	80-400
moving average method	-	-	1090.0	139.8
95% confidence limits	-	-	665.1-2173.5	91.6-208.2
probit method	-	-	898.7	154.6

Table 6 - Results of short-term *Daphnia magna* bioassays using Sodium Chloride (NaCl)

Test Run 1 - Non-sterile technique

Concentrations in mg/L	Number of test organisms	Number of test animals nonmotile at:	
		24 hrs	48 hrs
10,000	10	10	10
1,000	10	0	0
100	10	0	0
0 (Control)	10	0	0

Test Run 2 - Non-sterile technique

Concentrations in mg/L	Number of test organisms	Number of test organisms nonmotile at:			
		24 hrs	48 hrs	72 hrs	96 hrs
10,000	30	30	30	30	30
5,000	30	27	30	30	30
2,000	30	1	1	4	11
500	30	0	1	4	13
0 (Control)	30	0	1	1	11

Test Run 3 - Non-sterile technique

Concentrations in mg/L	Number of test organisms	Number of test organisms nonmotile at:			
		24 hrs	48 hrs	72 hrs	96 hrs
5,000	15	12	14	15	15
3,000	15	0	3	8	10
0 (Control)	15	0	0	0	1

Test Run 4 - Sterile technique

Concentrations in mg/L	Number of test organisms	Number of test organisms nonmotile at:			
		24 hrs	48 hrs	72 hrs	96 hrs
10,000	30	30	30	30	30
2,000	30	0	0	0	0
400	30	0	0	0	0
80	30	0	0	0	0
0 (Control)	30	0	0	0	0

Test Run 5 - Sterile technique

Concentrations in mg/L	Number of test organisms	Number of test organisms nonmotile at:			
		24 hrs	48 hrs	72 hrs	96 hrs
6,000	30	30	30	30	30
2,400	30	0	0	0	0
960	30	0	0	0	0
384	30	0	0	0	0
0 (Control)	60	0	0	0	0

Test Run 6 - Sterile technique

Concentrations in mg/L	Number of test organisms	Number of test organisms nonmotile at:			
		24 hrs	48 hrs	72 hrs	96 hrs
4,000	30	4	5	5	6
3,500	30	0	2	2	2
3,000	30	0	0	0	1
2,500	30	0	0	0	0
2,000	30	0	1	1	1
0 (Control)	30	0	0	0	0

Test Run 7 - Sterile technique

Concentrations mg/L	Number of test organisms	Number of test organisms nonmotile at:			
		24 hrs	48 hrs	72 hrs	96 hrs
5,000	30	17	26	29	29
4,500	30	3	7	8	15
4,000	30	1	3	5	7
3,500	30	0	0	0	0
3,000	30	0	2	3	3
0 (Control)	30	1	1	1	1

LC ₅₀ estimated by:	48 hrs	72 hrs	96 hrs
binomial method	- 4697.3	4640.9	4500
95% confidence limits	- 4500-5000	4500-5000	4000-5000
moving average method	- 4697.3	4640.9	4500
95% confidence limits	- 4588.4-4793.2	4542.9-4718.5	4272.7-4619.1
probit method	- 4666.4	4511.4	4317.6
95% confidence limits	- 0-∞	0-∞	0-∞

were tested.

Ten replicates were used for each concentration and control in every test. A neonate *D. magna* <24 hrs old was introduced into each test bottle, and allowed to mature during the course of the experiment. The test was concluded when the controls produced at least six broods of young. The total number of young produced at each test concentration and in the controls was determined. Single factor analysis of variance and the Student-Newman-Keuls test were used to determine if there was any difference among the test concentrations and the control (10, 11). The hypothesis tested in all cases was H_0 : the mean number of young produced in the control test bottles equals the mean number of young produced in the test concentrations. All significance tests were done at the .05 level.

c. Results

Short-term Bioassays - The results of the short-term bioassays used to determine the acute median lethal concentration (LC 50) for CMA, calcium acetate, magnesium acetate, and NaCl are shown in Tables 3-6. The following is a summary of these results:

- <384 mg/liter - CMA when bacteria are present.
- 1421 mg/liter - CMA when bacteria are reduced
- 482 mg/liter - Calcium acetate when bacteria are present.
- 127 mg/liter - Magnesium acetate when bacteria are present
- 4500 mg/liter - NaCl

Long-term Bioassays - The results of the CMA, calcium acetate, magnesium acetate, and NaCl long term bioassays are shown in Table 7, 8, and 9. The maximum concentrations at which no significant decrease in reproduction was noted were:

- 125 mg/liter - for CMA
- 500 mg/liter - for NaCl
- 100 mg/liter - for Calcium acetate
- 100 mg/liter - for magnesium acetate

These levels are the No Observed Effects Concentrations for the various deicers.

d. Discussion

CMA is readily used as a nutrient by a variety of bacteria. The tests indicate that the bacterial blooms which occur in CMA solutions at room temperature are deleterious to *Daphnia magna*. *D. magna* in test jars with bacterial bloom experienced heavy and usually complete mortality. The mortality may have been due to oxygen depletion caused by the high oxygen demand of the bacterial bloom. The high bacterial growth rate made it necessary to establish two distinct LC₅₀ values, one for CMA and one for the bacterial

Table 7 - Daphnia magna Long-Term CMA Test Results

CMA Test Run #1 - The number of young produced in each replicate during the bioassay.

Concentrations(mg/liter)	Jar Number	1	2	3	4	5	6	7	8	9	10	Mean	St.Dev.
500		0	0	0	4	1	0	0	9	0	0	1.4	2.95
100		53	46	67	53	59	53	52	53	65	62	56.3	6.65
20		53	44	44	49	42	47	48	44	40	55	46.6	4.76
4.0		32	54	47	55	52	61	49	20	52	21	44.3	14.61
0.8		59	37	46	58	40	18	38	51	30	34	41.1	12.75
0 (Control)		30	62	30	31	42	36	47	28	46	53	40.51	11.45

Comparisons of the means of young produced at each concentration.

Concentration (mg/Liter)	500	100	20	4	0.8	0
mean # of <u>D. magna</u> born	1.5*	56.3*	46.6	44.3	41.1	40.5

*significant difference from Control at the 0.05 level.

CMA Test Run #2 - The number of young produced in each replicate during the second CMA long-term bioassay.

Concentrations(mg/L)	Jar Number	1	2	3	4	5	6	7	8	9	10	Mean	St.Dev.
500		0	0	0	0	0	0	0	0	0	0	0	0
250		0	3	0	42	0	0	0	0	0	0	4.5	13.21
125		106	119	130	77	113	53	86	0	108	92	88.4	38.27
62.5		5	105	65	82	80	87	59	89	96	63	73.1	28.12
9(Control)		121	73	104	96	95	81	74	93	90	86	91.3	14.34

Comparisons of the means of young produced at each concentration.

Concentration (mg/liter)	500	250	125	62.5	0
	0*	4.5*	88.4	73.1	91.2

*Significant difference from control at the 0.05 level.

Table 8 - Daphnia Long-Term NaCl Test results.

Jar Number	1	2	3	4	5	6	7	8	9	10	Mean	St. Dev.
2500	57	77	42	62	48	68	30	74	106	42	60.6	36.35
500	120	82	89	91	127	81	129	104	115	82	102	19.00
100	105	90	104	96	75	83	100	71	102	82	90.8	13.70
20	97	106	103	107	88	80	69	111	90	70	92.1	16.60
0	121	73	104	96	95	81	74	93	90	86	91.3	15.71

Comparisons of the means of the number of D. magna born at each concentration during the NaCl long-term bioassay.

Concentration (mg/liter)	2500	500	100	20	0
Mean # of <u>D. magna</u> born	60.6*	102	90.8	92.1	91.3

*Significant difference from control at the 0.05 level.

Table 9 - Daphnia magna Long-Term Ca Acetate and Mg Acetate test results

The number of young produced in each replicate during the Ca acetate and Mg acetate long-term bioassay.

Jar Number	1	2	3	4	5	6	7	8	9	10	Mean	St.Dev.
Ca Acetate												
1000	13	25	0	0	0	3	0	0	0	0	4.1	8.40
100	75	62	66	66	0	66	73	80	95	88	67.1	25.84
10	45	58	67	65	69	25	32	42	39	88	53	19.58
1	59	58	60	49	45	56	60	79	50	48	56.4	9.67
Mg Acetate												
1000	0	0	0	11	1	13	11	133	109	8	28.6	49.29
100	89	49	75	92	80	91	79	71	73	81	78	12.58
10	70	38	60	67	61	49	61	63	64	53	58.6	9.49
1	60	57	69	53	67	59	61	0	56	42	52.4	19.87
Control												
0	57	62	62	48	44	47	71	58	72	0	52.1	20.63

Comparisons of the means of young produced at each concentration.

Concentration (mg/liter)	MgAcet 1000	CaAcet 1000	MgAcet 100	CaAcet 100	MgAcet 10	CA Acet 10	Mg/Acet 1	CaAcet 1	Control 0
mean # of <u>D.magna</u> born	28.6*	4.1*	78	67.1	58.6	53	52.4	56.4	52.1

*Significant difference of control at the 0.05 level.

blooms that occur in CMA solutions.

The laboratory data must be carefully applied to known field conditions before hypotheses about how CMA will affect aquatic ecosystems can be made. In the field, CMA can be expected to behave similarly to NaCl. Because CMA melts snow and ice as it is applied, it will create its own solution which will rapidly flow into the aquatic environment. The amounts of CMA and NaCl required for effective deicing are similar, therefore, similar concentrations of CMA and NaCl should be expected in the aquatic ecosystems.

Goldman and Hoffman (12) measured the levels of chloride entering the aquatic ecosystem due to salt use in deicing operations in the Lake Tahoe basin in California and Nevada. Their measurements indicate that large amounts of chlorides are transported into the aquatic ecosystem during the winter, but the amounts vary tremendously with time and place. Runoff samples collected from areas near roads receiving NaCl during the winter had a mean concentration of 270 mg of Cl^- /liter with a maximum concentration of 2051 mg Cl^- /liter concentrations. Concentrations at the entrance to Donner Lake were as high as 163 mg Cl^- /liter. The winter average in Donner Lake was 12 mg Cl^- /liter.

If CMA were used for deicing, concentrations of acetate similar to those of chloride may be expected to occur in the immediate vicinity of the road. Thus, in rare instances, concentrations approaching the LC_{50} 's for CMA to Daphnia magna could occur in the immediate vicinity of the road. The amount of acetate that would likely be found in streams directly affected by road deicing is above that required to produce bacterial blooms under laboratory conditions. However, because of low winter temperature bacterial growth should be retarded long enough for the acetate to be diluted to concentrations at which a bacterial bloom would not occur. In the cold water, the acetate would be slowly decomposed by bacteria. The amount of bacteria in the receiving waters may increase providing additional food for other organisms.

Use of CMA for deicing would raise the calcium and magnesium levels in receiving waters, thereby increasing water hardness. Increasing the hardness in some streams could cause a change in what species of animals live in the stream. Some organisms live only in soft water, while others live in hard water. Some organisms live in either. No generalized hypothesis can be made concerning the impacts of the increase in water hardness on aquatic biota, due to the diversity of water conditions, probable differing application rates of CMA, and different species found in different geographical areas.

The results of this study are not exhaustive, due to the limitations inherent in single species laboratory studies.

The results of this study simply indicate that CMA is probably not highly toxic to zooplankton. Carefully controlled field studies should be done to more thoroughly determine the impacts of CMA on zooplankton.

3. Phytoplankton Bioassays

a. Introduction

Phytoplankton are the microscopic algae of the aquatic environment. These algae form part of the producer trophic level and provide energy to the higher trophic levels. To determine the impacts of CMA, calcium acetate, magnesium acetate, and NaCl, both unialgal and natural water algae bioassays were performed. Algae bioassays test for both stimulatory and toxic effects of a substance on algae, because they measure the algal growth rate and the maximum standing crop. The unialgal bioassay is a standardized test of growth response of a well characterized organism under standardized laboratory conditions. The method used for this test was a modification of the EPA bottle algal assay test (4) using an artificial growth medium rather than natural receiving water. This method was used so regional water characteristics could be disregarded. The natural water bioassay used natural water with indigenous algae and other naturally occurring micro organisms. This allowed assessment of the deicers on one particular assemblage of organisms.

b. Materials and Methods

The bioassays were conducted using both the Green Algae Selenastrum capricornutum and the Blue Green Algae Anabaena flos-aquae. Cultures of both species of algae were obtained from the U.S. Environmental Protection Agency, the Environmental Research Laboratory in Corvallis, OR. After reception, the cultures were checked for authenticity and purity. Both species of algae were maintained in 500 ml erlenmeyer flasks which contained 200 ml of algae medium (Figure 1). Every 7-10 days the S. capricornutum was recultured, while A. flos-aquae was recultured every 2-3 weeks. Additionally, both species were placed on 1% agar so new cultures could be started if the cultures maintained in the liquid medium became contaminated.

The synthetic culture medium that was used for algae cultures and some of the bioassays, was that characterized by the EPA (4). Table 10 shows the nutrient concentrations in the medium. The pH of the medium was 7.5+0.1.

To insure that the cultures and bioassays were bacteria free, the medium was autoclaved. All glassware was washed in a phosphate free detergent, rinsed in hydrochloric acid, rinsed in deionized water, autoclaved, and oven-dried at 100 C prior to use. All transfers of algae were performed using aseptic technique.

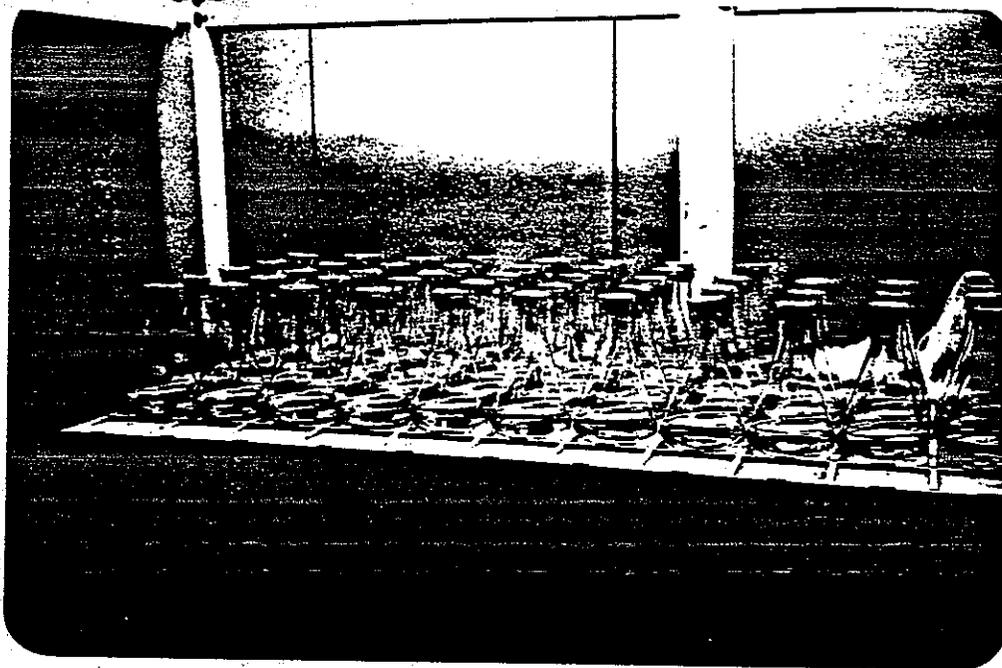


Figure 7. Algae flask replicates placed on oscillating table with environmental chamber.



Figure 8. Turner Fluorometer and a single replicate of flask used in determining algal growth rates and biomass.

Table 10. Final Concentration of Macronutrients in Algae Culture Medium as Salts and Elemental Concentrations

<u>Compound</u>	<u>Concentration (µg/liter)</u>	<u>Element</u>	<u>Concentration (µg/liter)</u>
NaNO ₃	25.50	N	4.20
		Na	11.00
NaHCO ₃	15.00	C	2.14
K ₂ HPO ₄	1.04	K	0.469
		P	0.186
MgSO ₄ ·7H ₂ O	14.70	S	1.91
		Mg	2.90
MgCl ₂ ·6H ₂ O	12.164		
CaCl ₂ ·2H ₂ O	4.41	Ca	1.20
H ₃ BO ₃	185.51	B	32.46
MnCl ₂ ·4H ₂ O	415.61	Mn	115.37
ZnCl ₂	3.27	Zn	1.57
CoCl ₂ ·6H ₂ O	1.428	Co	0.35
CuCl ₂ ·2H ₂ O	0.012	Cu	0.004
NaMoO ₄ ·2H ₂ O	7.26	Mo	2.88
FeCl ₃ ·6H ₂ O	160.0	Fe	33.05
Na ₂ EDTA·2H ₂ O	300.0	--	

Table 11 shows the concentrations of NaCl, calcium acetate, magnesium acetate, and CMA in each test run. All test concentrations and controls were run in triplicate. The concentrations for testing were equivalent weights (e.g. 1g NaCl is equivalent to 1.67 g CMA).

The bioassays were conducted in an environmental chamber. The temperature was maintained at 24 C ± 1 C, and the relative humidity was maintained at about 50%. Test flasks were 500 ml pyrex erlemeyer flasks which contained 200 ml of test solution. Loose fitting aluminium foil was used for flask closures (Figure 7). The flasks were continually shaken by 100 RPM. The cultures were grown under continuous cool white fluorescent light, the light was maintained at 400 ft. candles + 10% 0.5 inches above the shaker table. The Anabaena flos-aquae was covered with cheese cloth to reduce light intensity by 50%.

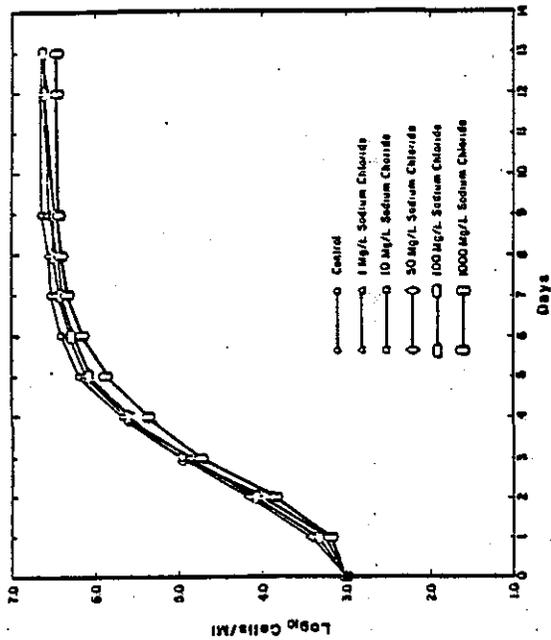
Algal growth was measured by fluorescence using a Turner Model III fluorometer (Figure 8). Both the specific growth rate and the maximum standing crop were measured. The specific growth rate was calculated by using the equation:

$$G = \frac{n(x_2/x_1)}{T_x - T_1} \text{ day}^{-1}$$

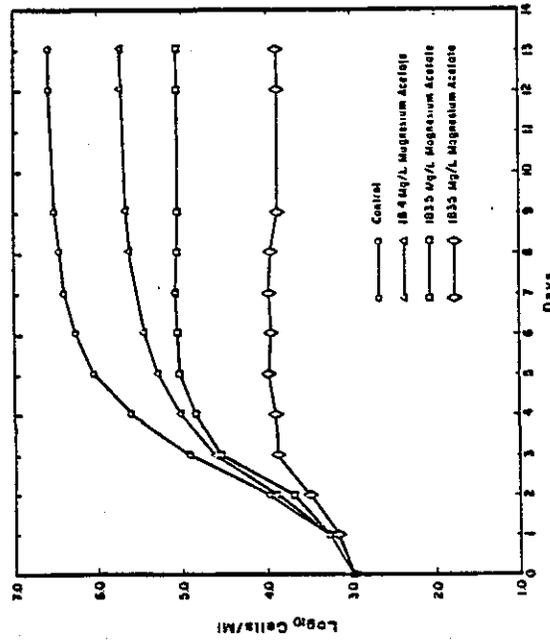
where G = Growth Rate
X1 = biomass at time one
X2 = biomass at time X

Table 11. The Concentration of NaCl, CMA and Calcium and Magnesium Acetate used for each bioassay:

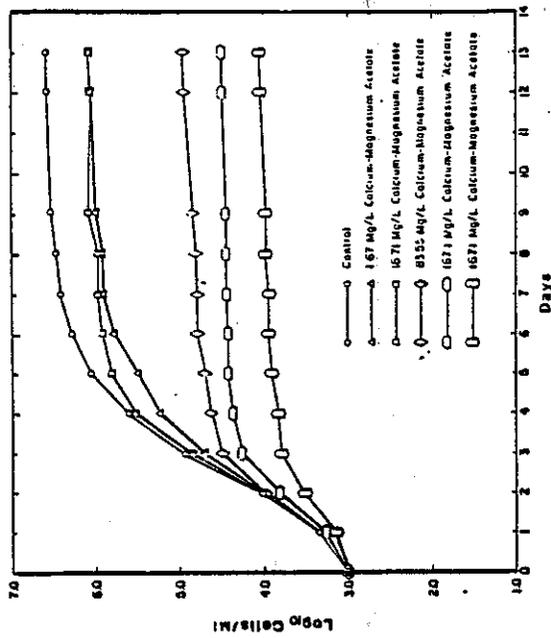
<u>Flask #</u>	<u>Test Toxicant</u>	<u>Concentrations</u>
1	Control	0
2	NaCl	1 mg/L
3	NaCl	10 mg/L
4	NaCl	50 mg/L
5	NaCl	100 mg/L
6	NaCl	1000 mg/L
7	CMA	1.67 mg/L
8	CMA	16.71 mg/L
9	CMA	83.55 mg/L
10	CMA	167.1 mg/L
11	CMA	1671 mg/L
12	Control	0
13	Ca Acetate	15.07 mg/L
14	Ca Acetate	150.7 mg/L
15	Ca Acetate	1507 mg/L
16	Mg Acetate	18.35 mg/L
17	Mg Acetate	183.5 mg/L
18	Mg Acetate	1835 mg/L
19	Control	0



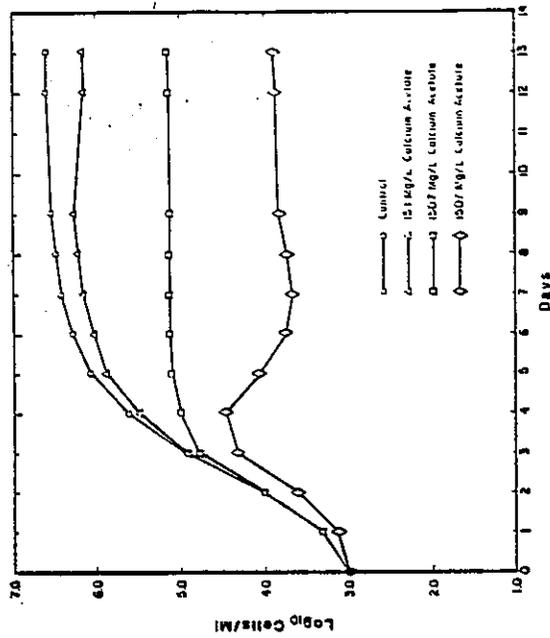
RESPONSE OF SELENASTRUM CAPRICORNUTUM TO NaCl COMPARED TO A CONTROL. (3/13/82-3/25/82)



RESPONSE OF SELENASTRUM CAPRICORNUTUM TO Mg ACETATE COMPARED TO A CONTROL. (3/13/82-3/25/82)

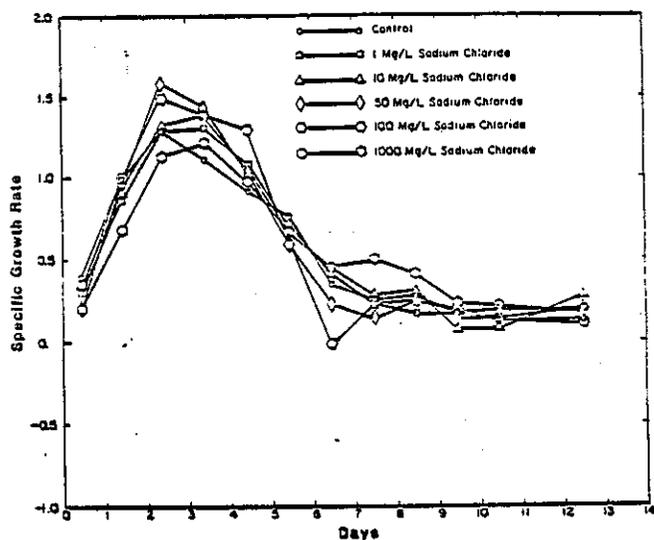


RESPONSE OF SELENASTRUM CAPRICORNUTUM TO Ca ACETATE COMPARED TO A CONTROL. (3/13/82-3/25/82)

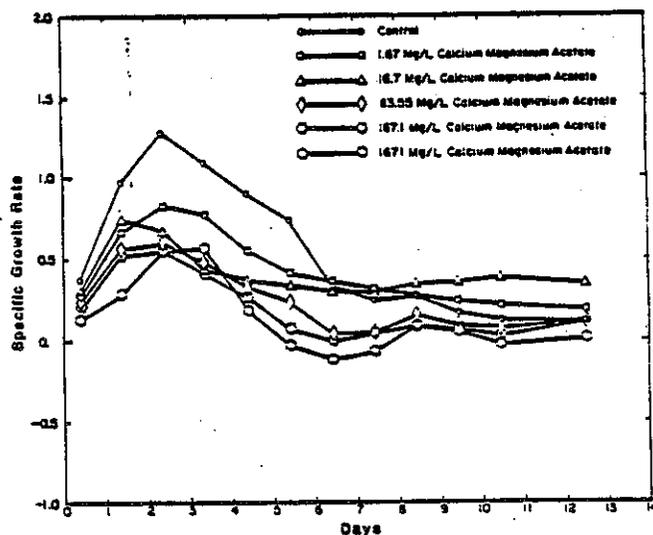


RESPONSE OF SELENASTRUM CAPRICORNUTUM TO Ca ACETATE COMPARED TO A CONTROL. (3/13/82-3/25/82)

Figure 9.. The growth of Selenastrum capricornutum in various concentrations of NaCl, CMA, calcium acetate and magnesium acetate (1/19/82 - 2/1/82).

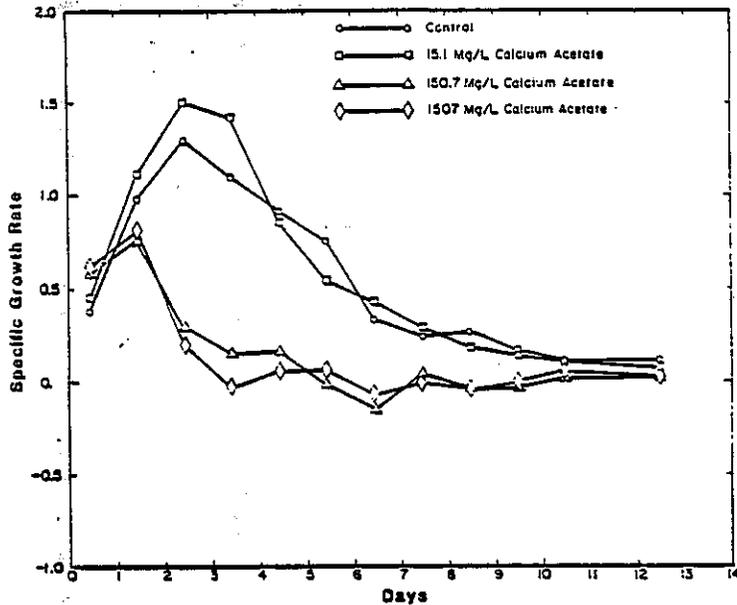


THE SPECIFIC GROWTH RATE (Two Day Moving Avg.) OF SELENASTRUM CAPRICORNUTUM GROWN IN SODIUM CHLORIDE COMPARED TO A CONTROL. (1/19/82-2/1/82)

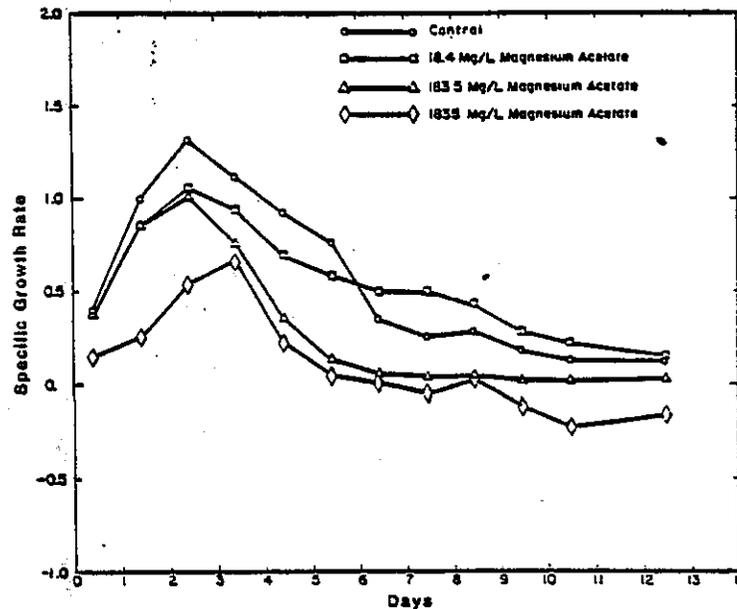


THE SPECIFIC GROWTH RATE (Two Day Moving Avg.) OF SELENASTRUM CAPRICORNUTUM GROWN IN CALCIUM MAGNESIUM ACETATE COMPARED TO A CONTROL. (1/19/82-2/1/82)

Figure 10. The specific growth rate (two-day moving average) of Selenastrum capricornutum grown in various concentrations of NaCl and CMA (1/19/82 - 2/1/82).



THE SPECIFIC GROWTH RATE (Two Day Moving Avg.) OF SELENASTRUM CAPRICORNUTUM GROWN IN CALCIUM ACETATE COMPARED TO A CONTROL (1/19/82-2/1/82)



THE SPECIFIC GROWTH RATE (Two Day Moving Avg.) OF SELENASTRUM CAPRICORNUTUM GROWN IN MAGNESIUM ACETATE COMPARED TO A CONTROL (1/19/82-2/1/82)

Figure 11. The specific growth rate (two-day moving average) of Selenastrum capricornutum grown in various concentrations of calcium acetate and magnesium acetate (1/19/82 - 1/1/82).

The maximum standing crop is the maximum biomass occurring during the test run. Practically, the maximum standing crop is assumed to be achieved when the biomass increases less than 5% per day. The maximum specific growth rate is the largest rate in growth occurring at any time during the incubation period.

The fluorescence readings were converted to the g/liter of chlorophyll and the number of cells/ml. Replicate means and the standard deviation of each series of replicates was calculated. A one-way analysis of variance was performed for each test run to determine if significant differences existed among treatments. For each treatment the specific growth rate and standing crop were calculated for each day.

The purpose of the natural-water, algae-bioassays was to determine if algae in natural receiving water, with an established bacterial population, would be affected differently by the various chemicals tested than was algae in the artificial medium. The algae bioassay test method was modified so that natural water was used rather than artificial medium. Water from the American and Bear Rivers of California was used. Nutrients and an inoculum of S. capricornutum were added to the water. The concentrations tested are shown in Table 11.

c. Results

Unialgal Bioassays - Four Selenastrum capricornutum bioassays and three Anabaena flos-aquae bioassays were run. Of these, two S. capricornutum and two A. flos-aquae bioassays were successful. The other tests were rejected because the controls did not grow properly. The results of the successful bioassays were used to assess the effects of CMA on the environment. Each successful bioassay will be reported individually.

S. capricornutum bioassay of 1/19/82 - 2/1/82. The growth of S. capricornutum in various concentrations of NaCl, CMA, calcium acetate, and magnesium acetate are shown in Figure 9. Figures 10 and 11 show the specific growth rates observed. A two day moving average was used to decrease the effect of sampling error.

None of the NaCl concentrations caused a significant difference in growth during the bioassay. Growth depressions occurred in all CMA concentrations tested. Both the calcium acetate and the magnesium acetate treatments showed a growth rate depression similar to that of CMA. In both treatments, the observable differences occurred later in time than CMA treatment.

S. capricornutum bioassay of 3/13/82 - 3/25/82. The growth of S. capricornutum in various concentrations of NaCl, CMA, calcium acetate, and magnesium acetate are shown in Figure

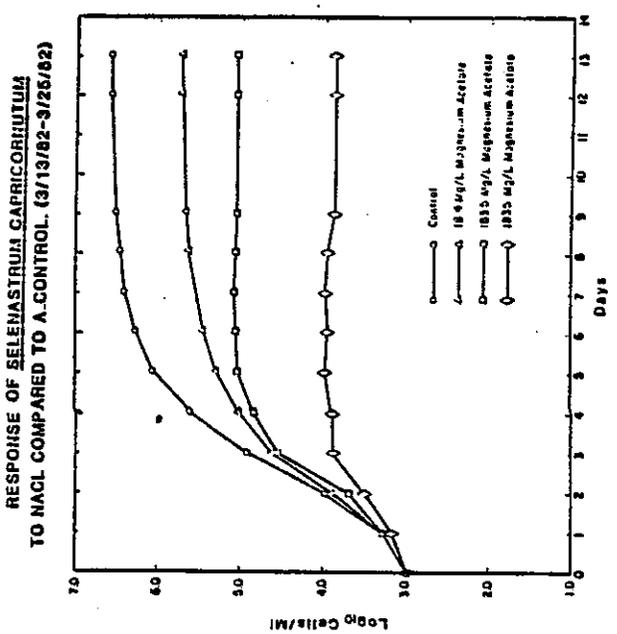
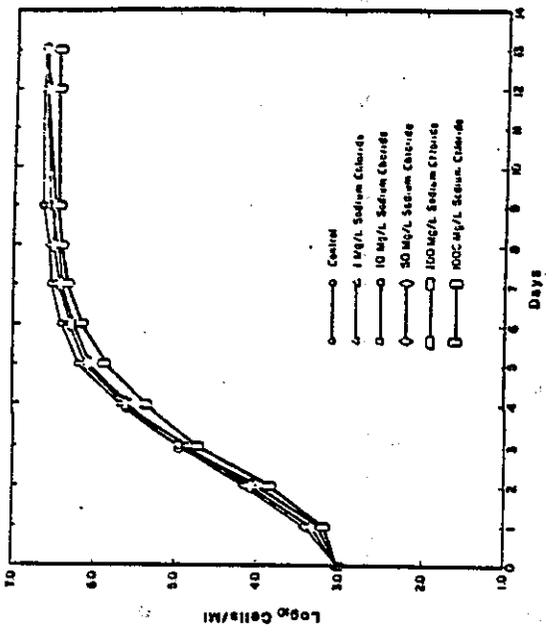
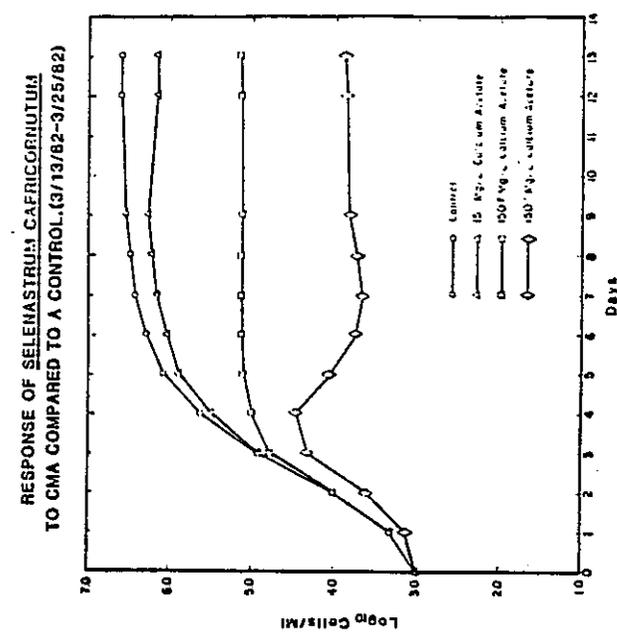
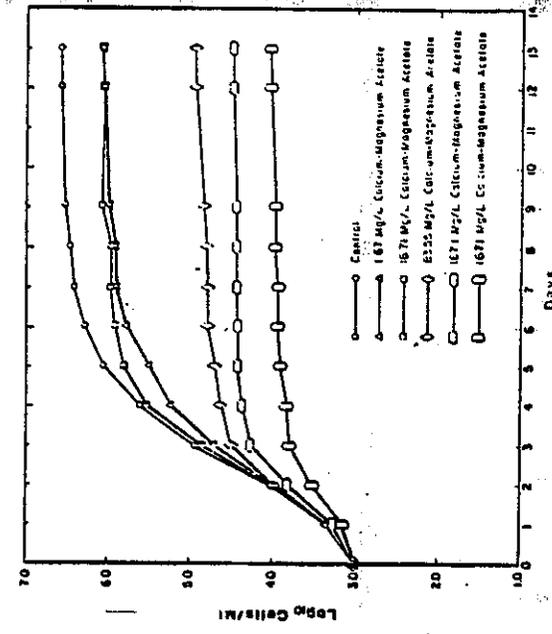
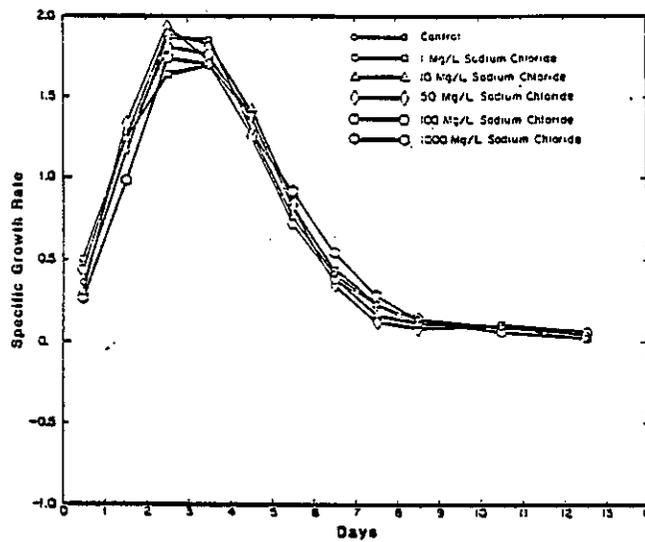
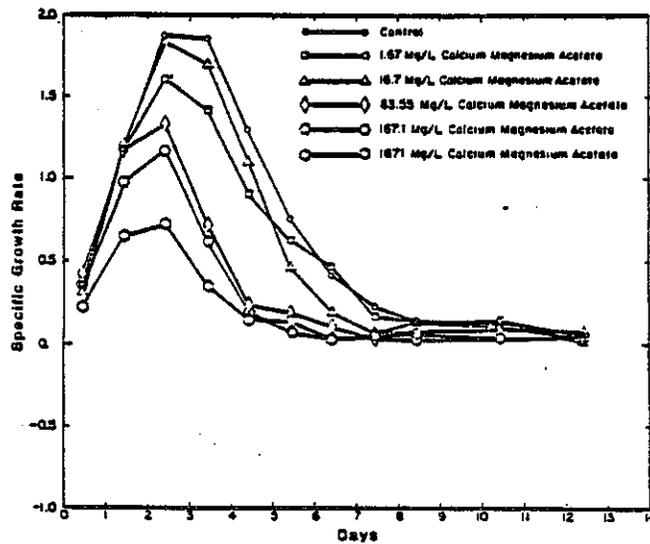


Figure 12. The growth of Selenastrum capricornutum in various concentrations of NaCl, CMA, calcium acetate and magnesium acetate (3/13/82 - 3/25/82).

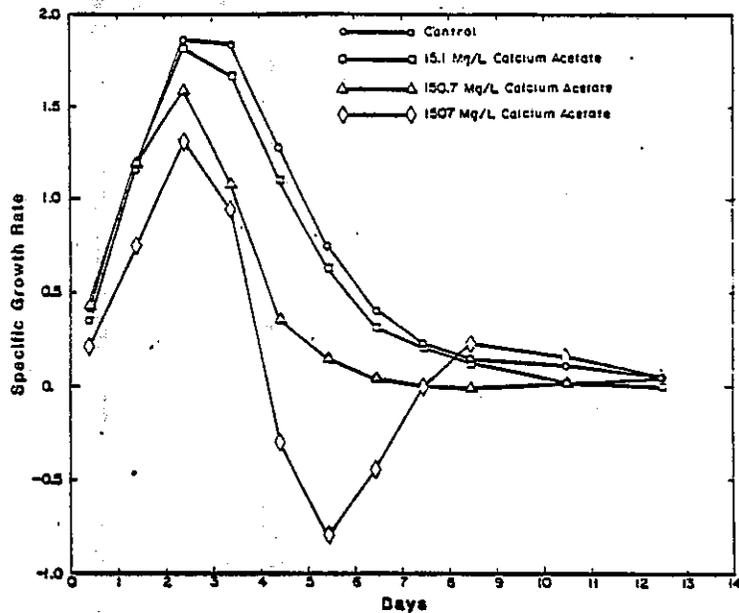


THE SPECIFIC GROWTH RATE (Two Day Moving Avg.) OF SELENASTRUM CAPRICORNUTUM GROWN IN SODIUM CHLORIDE COMPARED TO A CONTROL (3/13/82-3/25/82)

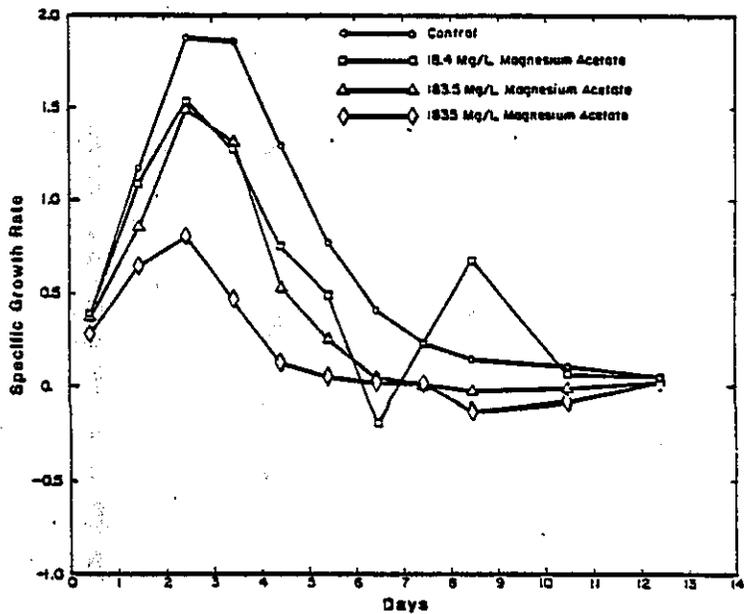


THE SPECIFIC GROWTH RATE (Two Day Moving Avg.) OF SELENASTRUM CAPRICORNUTUM GROWN IN CALCIUM MAGNESIUM ACETATE COMPARED TO A CONTROL (3/13/82-3/25/82)

Figure 13. The specific growth (two-day moving average) of Selenastrum capricornutum grown in various concentrations of NaCl and CMA (3/13/82 - 3/25/82).



THE SPECIFIC GROWTH RATE (Two Day Moving Avg.) OF SELENASTRUM CAPRICORNUTUM GROWN IN CALCIUM ACETATE COMPARED TO A CONTROL. (3/13/82-3/25/82)



THE SPECIFIC GROWTH RATE (Two Day Moving Avg.) OF SELENASTRUM CAPRICORNUTUM GROWN IN MAGNESIUM ACETATE COMPARED TO A CONTROL. (3/13/82-3/25/82)

Figure 14. The specific growth rate (two-day moving average) of Selenastrum capricornutum grown in various concentrations of calcium acetate and magnesium acetate (3/13/82 - 3/25/82).

12. The specific growth rate (two-day moving average) is shown in Figures 13 and 14 for the different treatments.

Except for the first day, the growth of all NaCl concentrations were not statistically different (at the .05 level of significance) from the control. All concentrations of CMA exhibited depressed growths.

The specific growth rates for NaCl were indistinguishable from the controls. CMA treatments showed a consistent pattern of depressed growth rates. The most severe depression occurred at the highest concentration. Although less regular than the CMA results, both the calcium acetate and the magnesium acetate treatments showed growth rate depressions. Generally, the higher concentrations were more depressed than the lower concentrations.

A. flos-aquae bioassay (7/13/82 - 7/28/82). The A. flos-aquae bioassays grew more slowly than the S. capricornutum bioassays, and the maximum standing crop and the daily growth rates attained were lower. The results are shown in Figure 15. The daily specific growth rates (two-day moving average) for the treatments are shown in Figure 16.

The maximum standing crop in the NaCl treatments was not significantly different from that of the controls. Despite some inconsistencies in the data the higher concentrations of CMA had a lower standing crop than the controls.

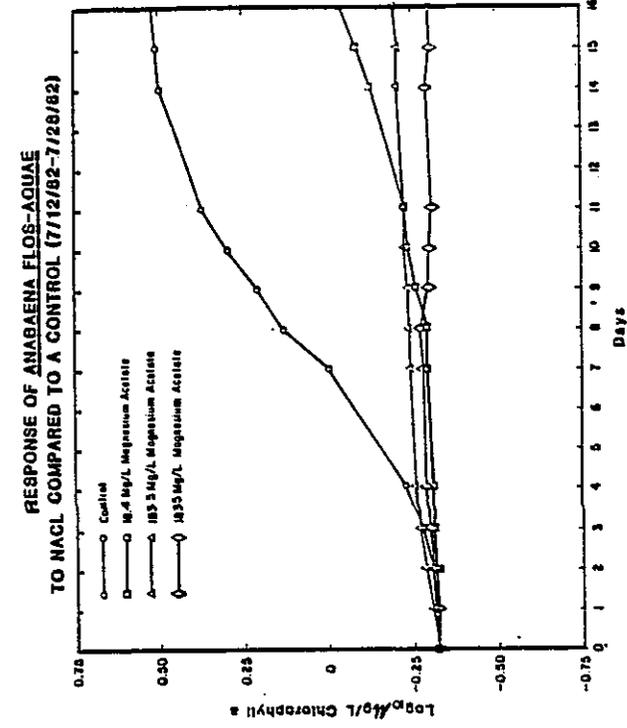
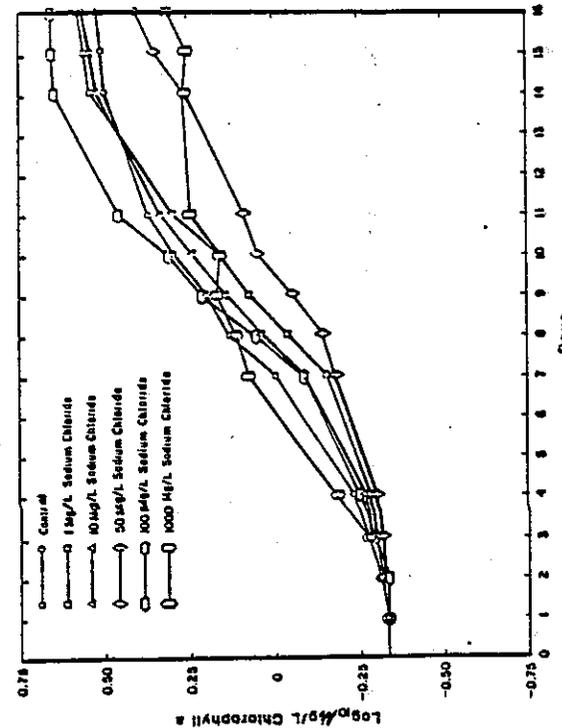
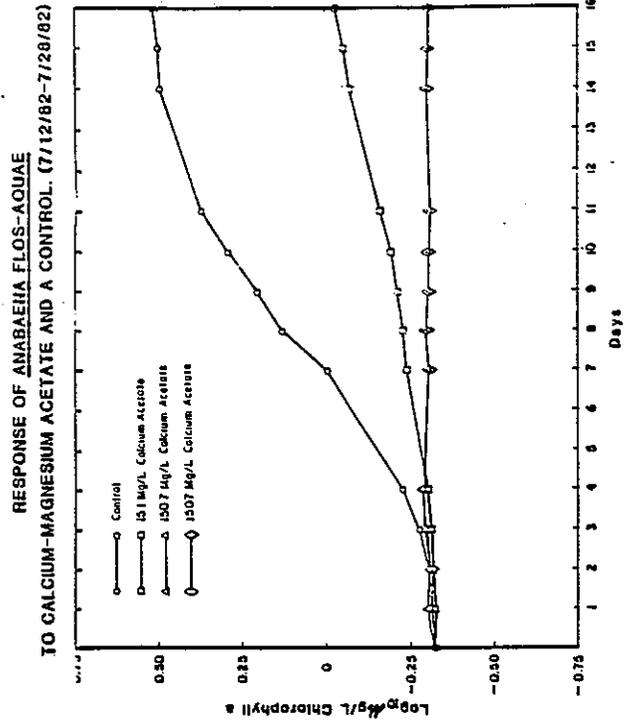
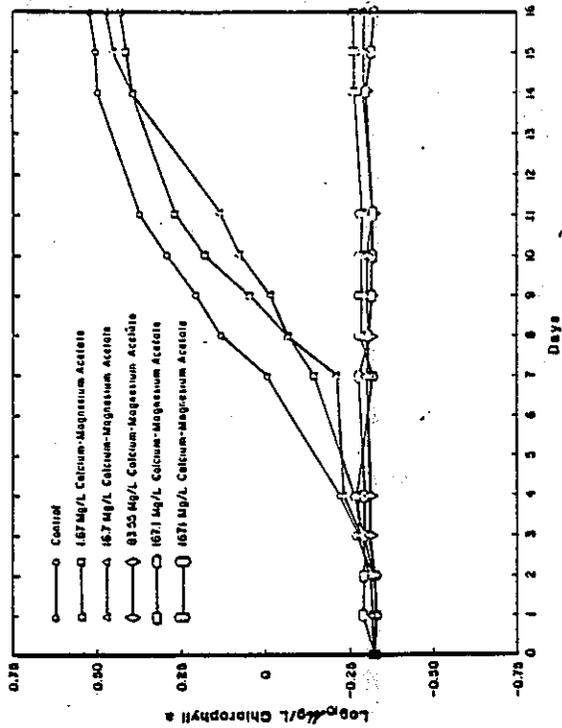
The data for calcium acetate and magnesium acetate are more consistent than those for CMA. All concentrations of both calcium acetate and magnesium acetate exhibited a significantly smaller standing crop than the controls.

The data on specific growth rates is too inconsistent to draw any conclusions.

A. flos-aquae bioassay (1/18/83 - 2/7/83). The standing crop and the daily specific growth rate of various concentrations of NaCl, CMA, calcium acetate and magnesium acetate are shown in Figures 17 and 18.

The NaCl treatments showed a growth pattern similar to the previous A. flos-aquae bioassay. By the end of the experiment the highest NaCl concentration had a significantly smaller standing crop than the controls and the lower NaCl concentrations.

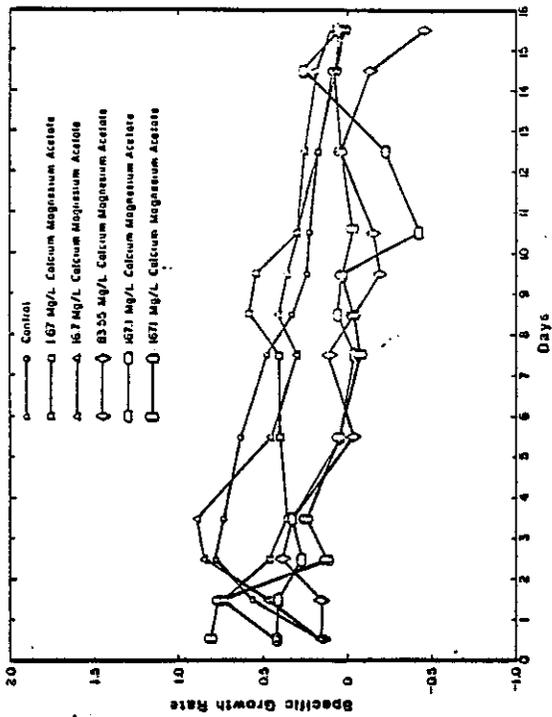
The CMA treatments showed a similar reduction in standing crop at the higher concentrations to the reductions seen in other algae bioassays. By the end of the bioassay the standing crop in the control, the 1.67 mg/liter and the 16.71 mg/liter were all significantly larger than the 167.1 mg/Liter and 1671 mg/liter concentrations.



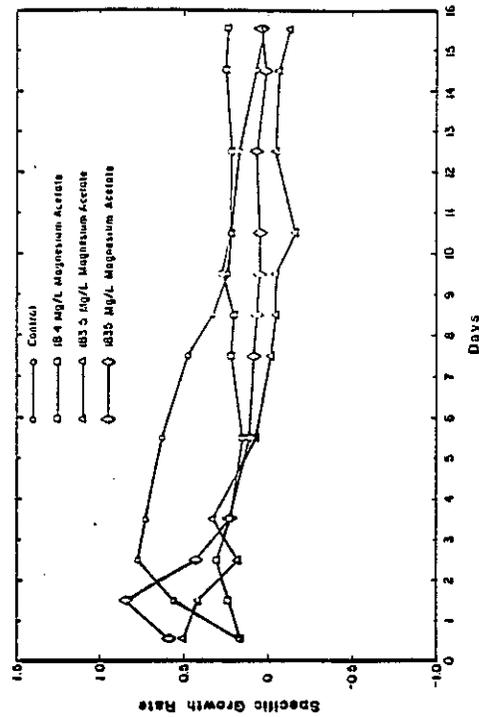
RESPONSE OF ANABAENA FLOS-AQUAE TO CMA COMPARED TO A CONTROL. (7/12/82-7/28/82)

RESPONSE OF ANABAENA FLOS-AQUAE TO MAGNESIUM ACETATE COMPARED TO A CONTROL. (7/12/82-7/28/82)

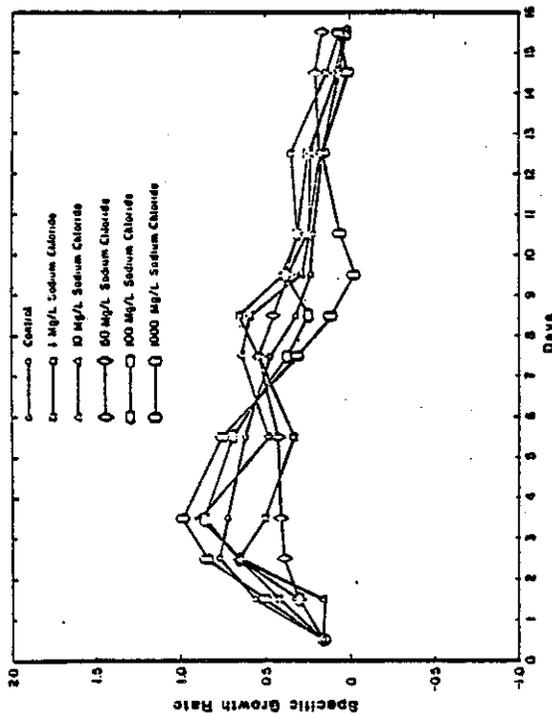
Figure 15. The growth in Anabaena flos-aquae in various concentrations of NaCl, CMA, calcium acetate and magnesium acetate (7/12/82 - 7/28/82).



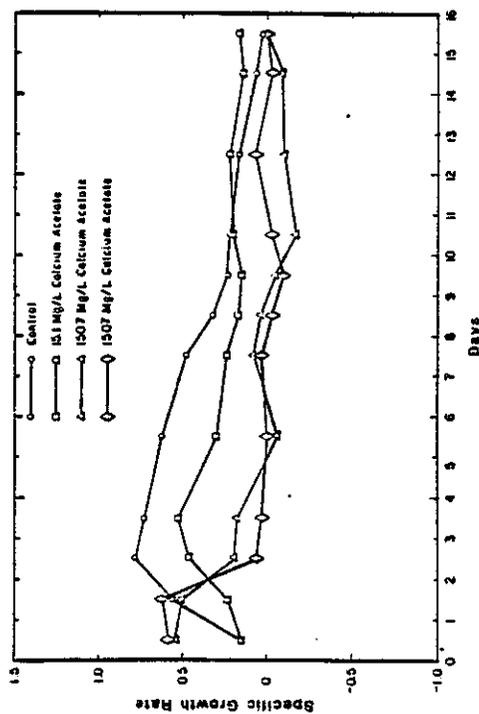
THE SPECIFIC GROWTH RATE (Two Day Moving Average) OF ANABAENA FLOS-AQUAE GROWN IN CALCIUM MAGNESIUM ACETATE COMPARED TO A CONTROL. (7/12/82-7/28/82)



THE SPECIFIC GROWTH RATE (Two Day Moving Average) OF ANABAENA FLOS-AQUAE GROWN IN MAGNESIUM ACETATE COMPARED TO A CONTROL. (7/12/82-7/28/82)



THE SPECIFIC GROWTH RATE (Two Day Moving Average) OF ANABAENA FLOS-AQUA GROWN IN SODIUM CHLORIDE COMPARED TO A CONTROL. (7/12/82-7/28/82)



THE SPECIFIC GROWTH RATE (Two Day Moving Average) OF ANABAENA FLOS-AQUAE GROWN IN CALCIUM ACETATE COMPARED TO A CONTROL. (7/12/82-7/28/82)

Figure 16. The specific growth rate (two-day moving average) of *Anabaena flos-aquae* ride, CMA, calcium acetate and magnesium acetate (7/12/82 - 7/28/72).

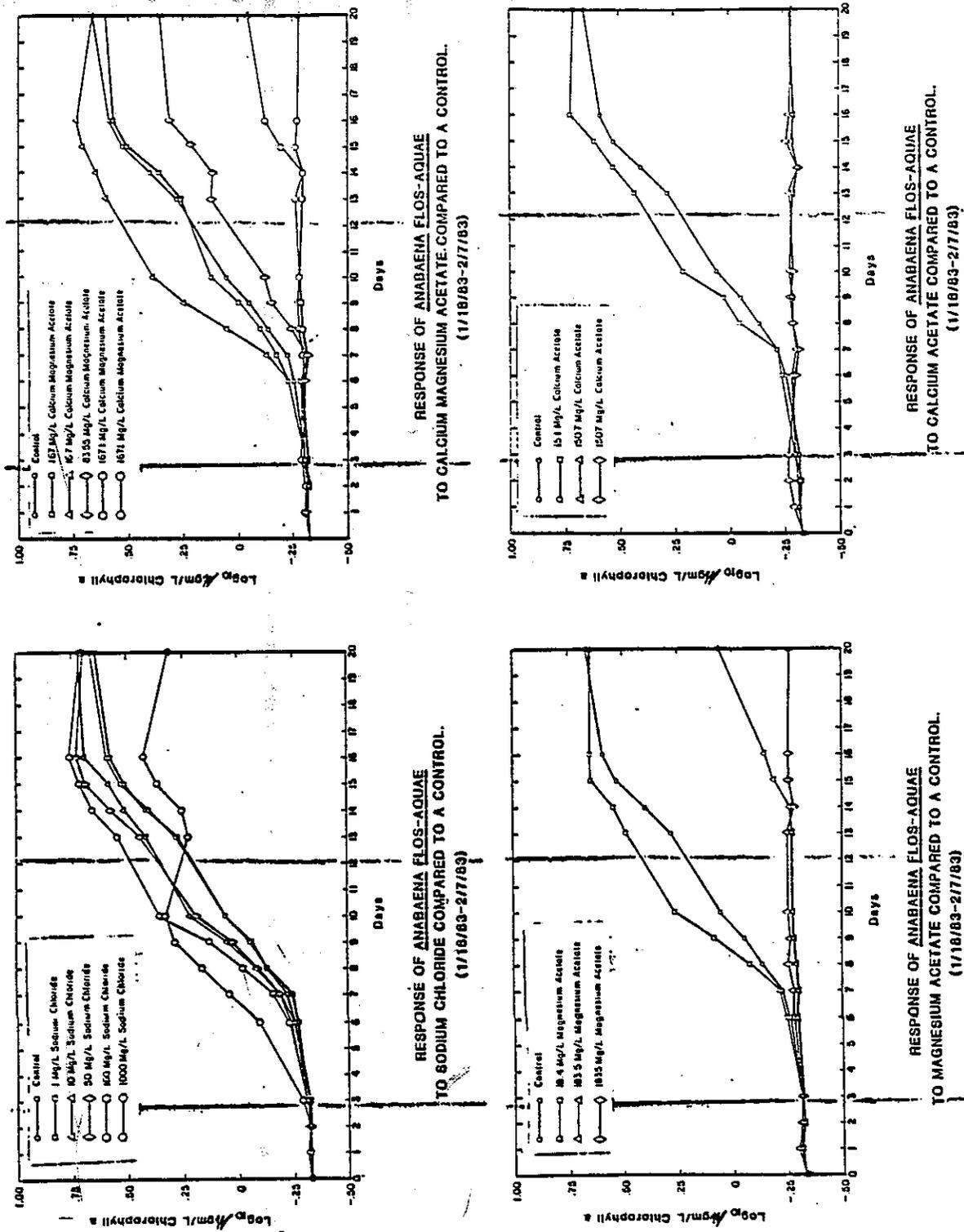
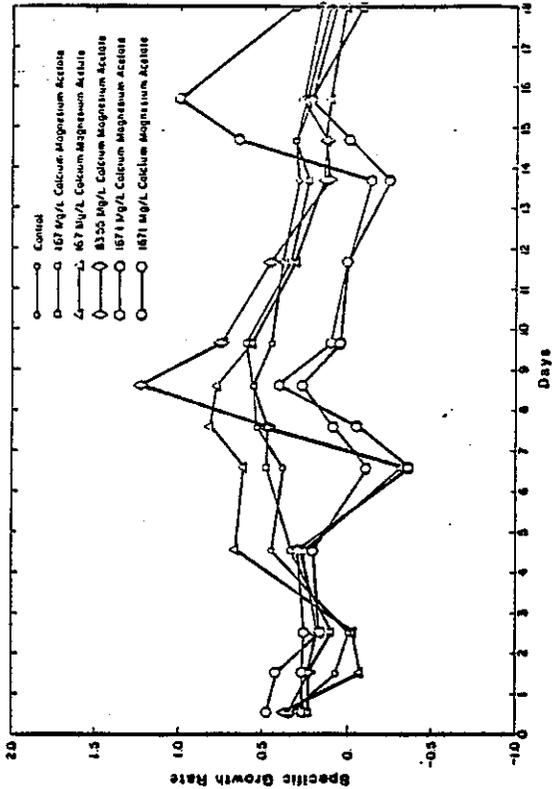
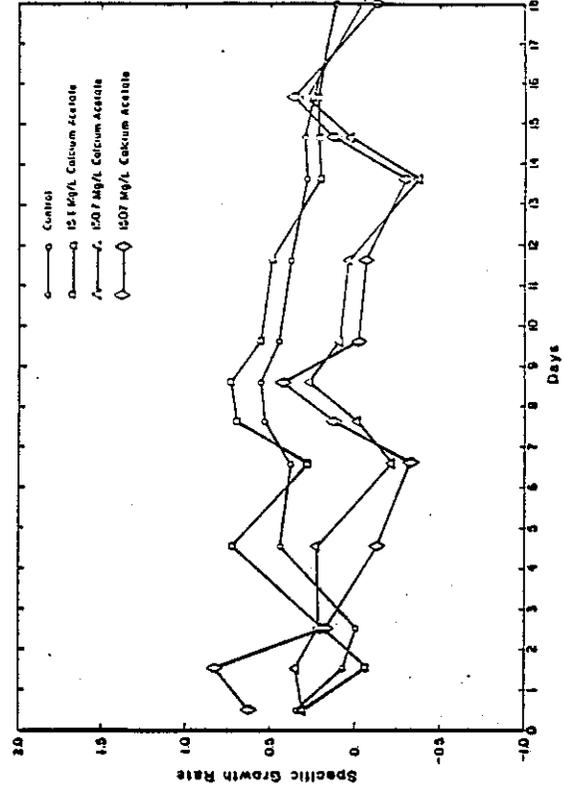


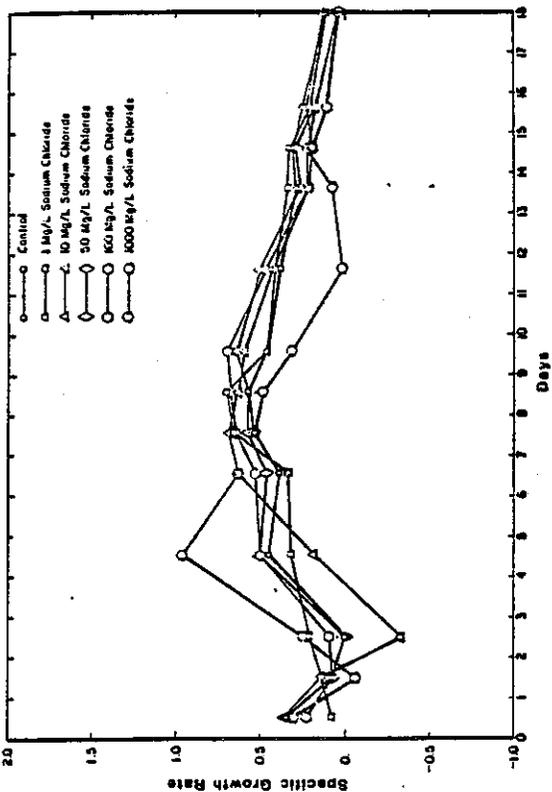
Figure 17. The growth of *Anabaena flos-aquae* in various concentrations of NaCl, CMA, calcium acetate and magnesium acetate (1/18/83 - 2/7/83).



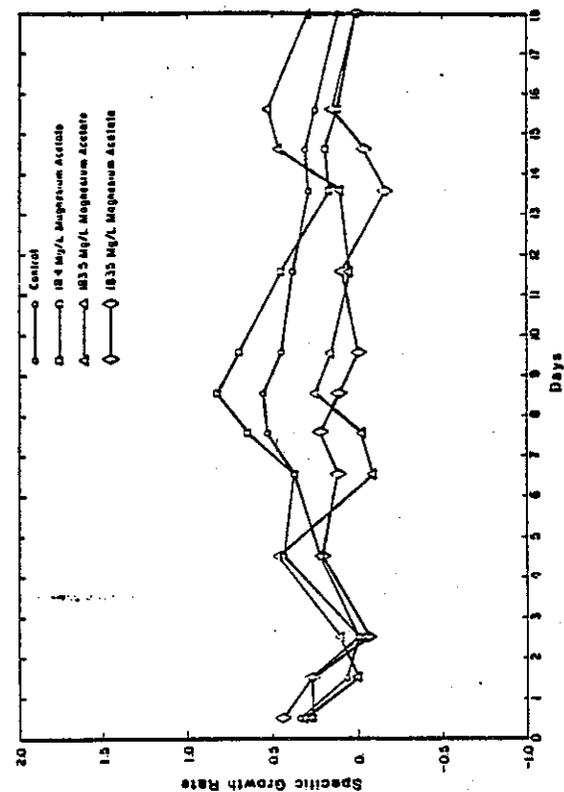
THE SPECIFIC GROWTH RATE (Two Day Moving Average) OF ANABAENA FLOS-AQUAE GROWN IN CALCIUM MAGNESIUM ACETATE COMPARED TO A CONTROL. (1/18/83-2/7/83)



THE SPECIFIC GROWTH RATE (Two Day Moving Average) OF ANABAENA FLOS-AQUAE GROWN IN CALCIUM ACETATE COMPARED TO A CONTROL. (1/18/83-2/7/83)



THE SPECIFIC GROWTH RATE (Two Day Moving Average) OF ANABAENA FLOS-AQUAE GROWN IN SODIUM CHLORIDE COMPARED TO A CONTROL. (1/18/83-2/7/83)



THE SPECIFIC GROWTH RATE (Two Day Moving Average) OF ANABAENA FLOS-AQUAE GROWN IN MAGNESIUM ACETATE COMPARED TO A CONTROL. (1/18/83-2/7/83)

Figure 18. The specific growth rate (two-day moving average) of Anabaena flos-aquae grown in various concentrations of NaCl, CMA, calcium acetate and magnesium acetate (1/18/83 - 2/7/83).

The calcium acetate and magnesium acetate treatments exhibited a reduced standing crop in the higher treatment levels compared to the controls. The maximum standing crop in the control and in the 15.1 mg/liter treatment of calcium acetate developed significantly larger standing crops than either the 150.7 mg/liter and 1507 mg/liter concentrations of calcium acetate. There was no significant difference between the control and the 15.1 mg/liter treatment. For magnesium acetate all treatment levels exhibited a depressed maximum standing crop.

Natural Water Bioassay (12/14/82 - 12/24/82) - The maximum standing crops of the combined S. capricornutum and indigenous algae in various concentrations of NaCl, CMA, calcium acetate and magnesium acetate are shown in Figure 19. The specific growth rates (two day moving average) are shown in Figure 20 for the different treatments. The results of this bioassay are somewhat different from the unialgal S. capricornutum bioassays.

During the experiment all of the NaCl treatment showed similar maximum standing crops. The highest concentration of CMA (1671 mg/liter) treatment showed significantly less growth than the controls.

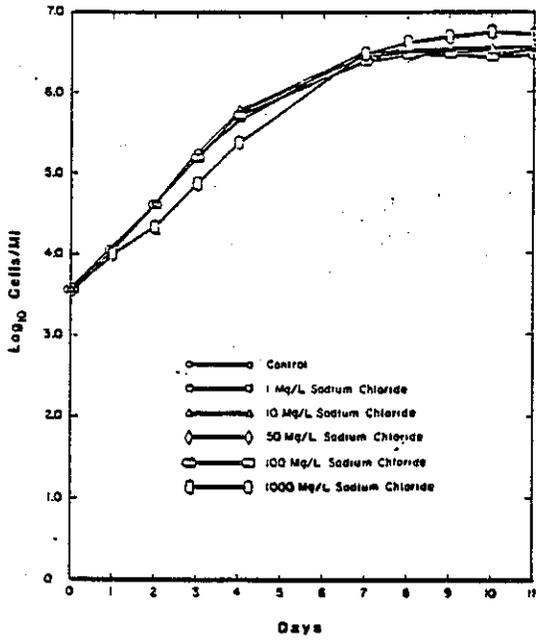
The highest concentration of CMA (1671 mg/liter) treatment showed significantly greater growth than lower level sodium chloride treatments, but was not significantly different from the controls.

For magnesium acetate, there was no significant difference among any of the treatments or the control by the end of the experiment. There was a large variance among the replicates which made the analysis difficult.

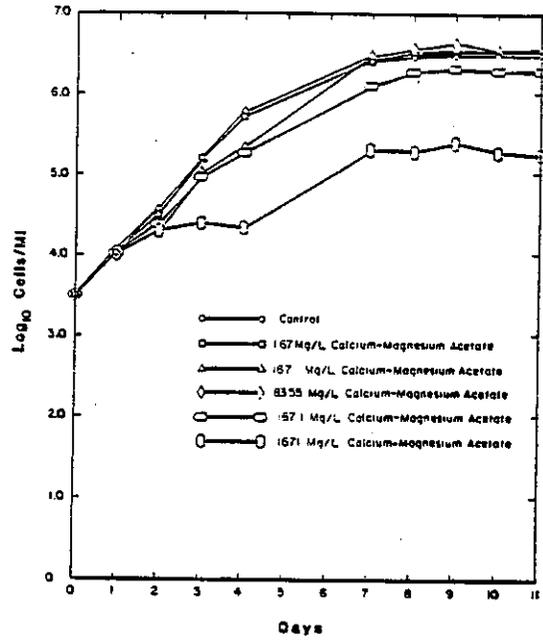
For calcium acetate, the 15.1 mg/liter treatment's maximum standing crop was indistinguishable from the control. The other treatments had distinctly lower maximum standing crop than the controls.

Except for the highest NaCl level, there is little difference in maximum specific growth rate among the NaCl treatments and the control. CMA treatments exhibit a maximum specific growth rate depression at the highest concentration. Both calcium acetate and the magnesium acetate show specific growth rate depressions at the higher treatment levels, however, the magnesium acetate seem to recover towards the end of the experiment.

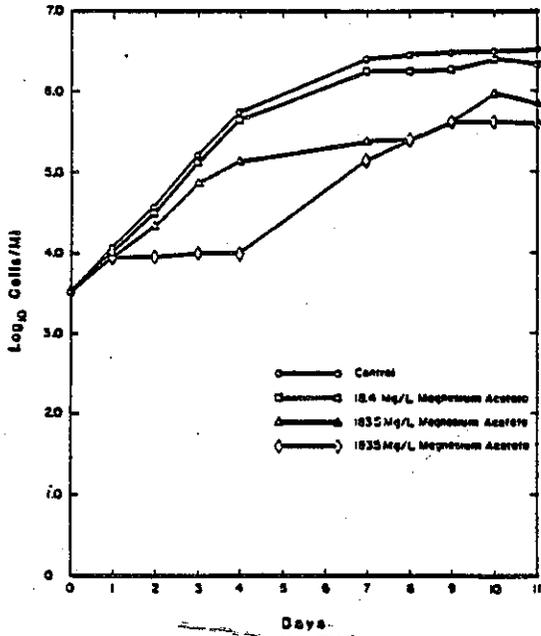
Natural Water Bioassay (12/28/82 - 1/6/83) - The maximum standing crops attained in various treatments of NaCl, CMA, calcium acetate, and magnesium acetate



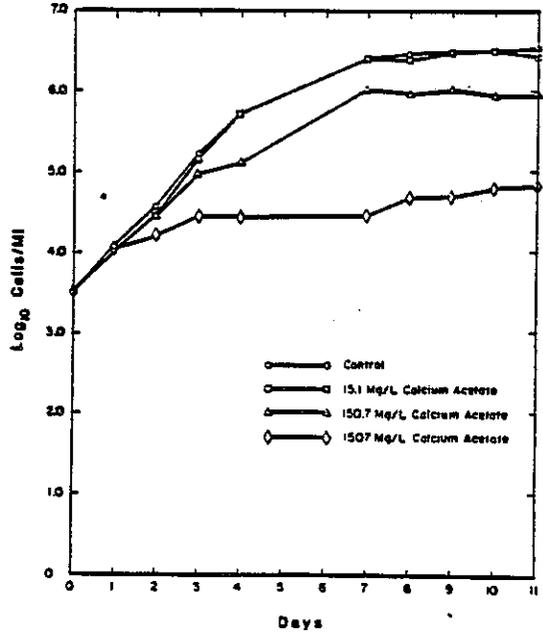
RESPONSE OF SELENASTRUM CAPRICORNUTUM AND INDIGENOUS ALGAE TO NaCl (12/14/82-12/24/82)



RESPONSE OF SELENASTRUM CAPRICORNUTUM AND INDIGENOUS ALGAE TO CALCIUM-MAGNESIUM ACETATE (12/14/82-12/24/82)



RESPONSE OF SELENASTRUM CAPRICORNUTUM AND INDIGENOUS ALGAE TO MAGNESIUM ACETATE (12/14/82-12/24/82)



RESPONSE OF SELENASTRUM CAPRICORNUTUM AND INDIGENOUS ALGAE TO CALCIUM ACETATE (12/14/82-12/24/82)

Figure 19. The growth of the combined *Selenastrum capricornutum* and indigenous algae (American River) in various concentrations of NaCl, CMA, calcium acetate and magnesium acetate (12/14/82 - 12/24/82).

is shown in Figure 21. The specific growth rates (two day moving average) is shown in Figure 22 for different treatments.

The results of this bioassay for NaCl were similar to the first natural water bioassay. From the 4th day to the next to the last day there were no differences among standing crops of the various NaCl treatments or the control. On the last day of the experiment, the lowest treatment level (1 mg/liter) exhibited a significantly lower standing crop than the other treatments.

For CMA the control and the lower level CMA treatments had significantly greater standing crops at the end of the experiment than did the 1671 mg/liter treatment, but there was no statistical difference among them.

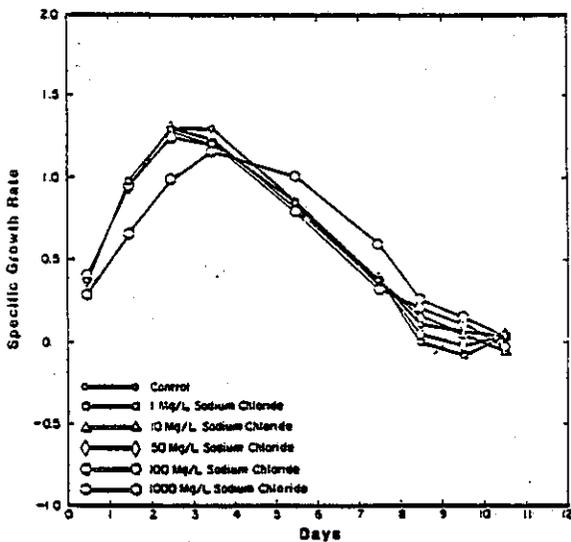
For calcium acetate, the control and the lowest level treatment were significantly different from the two highest treatment levels from the third day of the test to the last day of the test. On the last day of the test, the highest treatment had a significantly lower biomass than the other treatments and control which were not significantly different among themselves.

Magnesium acetate showed a significantly depressed standing crop for the highest treatment for the last day of the test. There was no significant difference among the other treatments and controls.

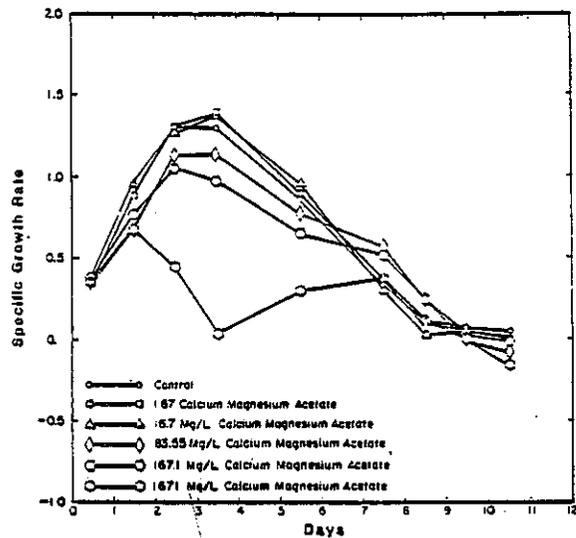
The specific growth rates (two day moving average) show results similar to those of the first natural water bioassay. The NaCl treatments did not show any significant differences, except for an initial specific growth rate depression for the 1000 mg/liter treatment, and a specific growth rate depression in the 1 mg/liter treatment. The CMA, calcium acetate and magnesium acetate specific growth rates all show an initial growth rate depression for the two highest levels followed by an increase in the specific growth rate in the last days of the experiment for the next to highest treatment level.

d. Conclusions.

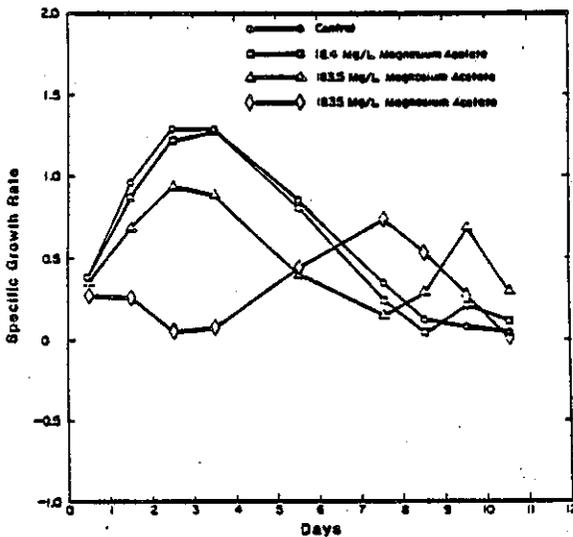
The *S. capricornutum* unialgal bioassays indicated that NaCl, up to 1000 mg/liter had no apparent statistically significant effect on maximum standing crop or specific growth rate. The *A. flos-aquae* 1000 mg/liter, NaCl treatment showed a statistically significant growth difference. Initially, the treatment exhibited increased growth, but by the end of the experiment this treatment exhibited decreased



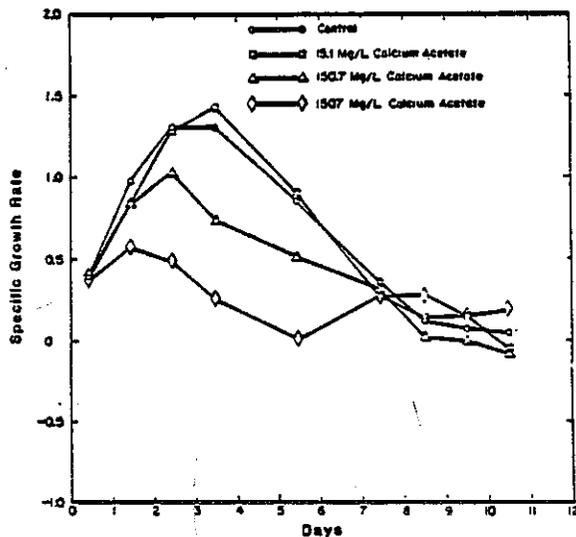
SPECIFIC GROWTH RATE (Two Day Moving Average) OF SELENASTRUM CAPRICORNUTUM AND INDIGENOUS ALGAE GROWN IN SODIUM CHLORIDE COMPARED TO A CONTROL. (12/14/82-12/24/82)



SPECIFIC GROWTH RATE (Two Day Moving Average) OF SELENASTRUM CAPRICORNUTUM AND INDIGENOUS ALGAE GROWN IN CALCIUM MAGNESIUM ACETATE COMPARED TO A CONTROL. (12/14/82-12/24/82)

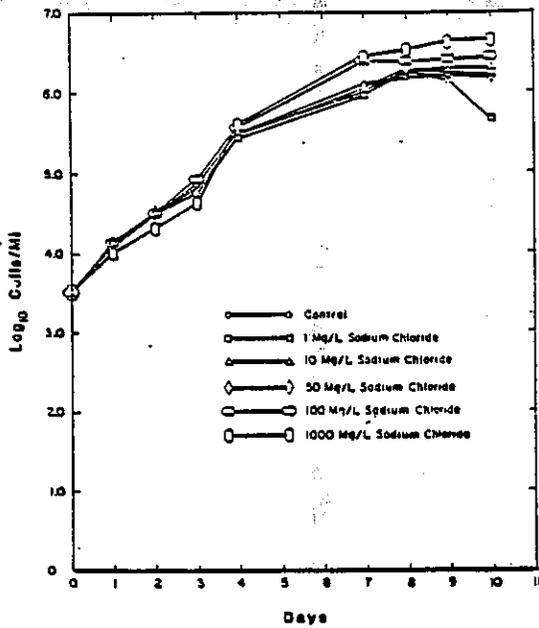


SPECIFIC GROWTH RATE (Two Day Moving Average) OF SELENASTRUM CAPRICORNUTUM AND INDIGENOUS ALGAE GROWN IN MAGNESIUM ACETATE COMPARED TO A CONTROL. (12/14/82-12/24/82)

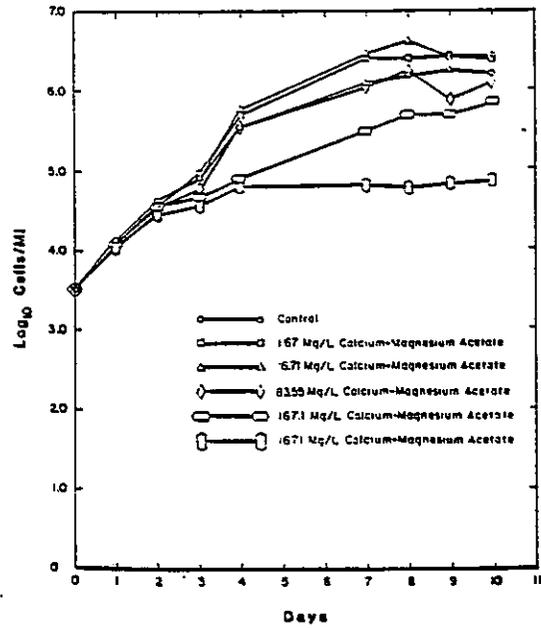


SPECIFIC GROWTH RATE (Two Day Moving Average) OF SELENASTRUM CAPRICORNUTUM AND INDIGENOUS ALGAE GROWN IN CALCIUM ACETATE COMPARED TO A CONTROL. (12/14/82-12/24/82)

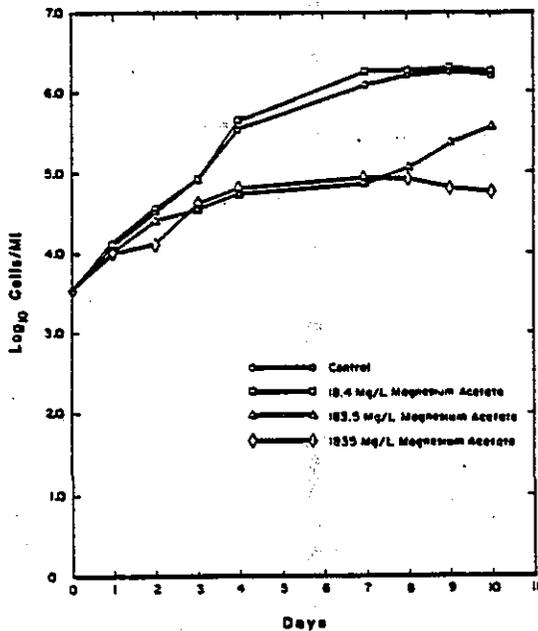
Figure 20. The specific growth rate (two-day moving average) of the combined Selenastrum capricornutum and indigenous algae (American River) grown in various concentrations of NaCl, CMA, calcium acetate and magnesium acetate (12/14/82 - 12/24/82).



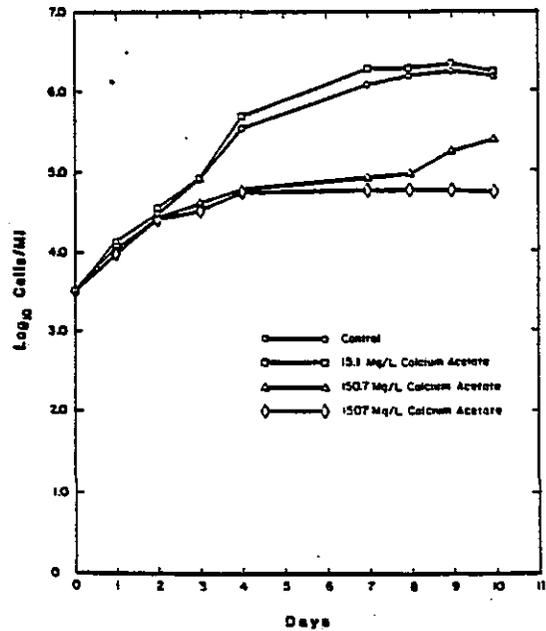
RESPONSE OF SELENASTRUM CAPRICORNUTUM
AND INDIGENOUS ALGAE TO NaCl
(12/28/82-01/06/83)



RESPONSE OF SELENASTRUM CAPRICORNUTUM
AND INDIGENOUS ALGAE TO CMA
(12/28/82-01/06/83)



RESPONSE OF SELENASTRUM CAPRICORNUTUM
AND INDIGENOUS ALGAE TO MAGNESIUM ACETATE
(12/28/82-01/06/83)



RESPONSE OF SELENASTRUM CAPRICORNUTUM
AND INDIGENOUS ALGAE TO CALCIUM ACETATE
(12/28/82-01/06/83)

Figure 21. The growth of the combined Selenastrum capricornutum and indigenous algae (Bear River) in various concentrations of NaCl, CMA, calcium acetate and magnesium acetate (12/28/82 - 01/06/83).

at Davis (13).

b. Materials and Methods

During this study, it was assumed that some of the CMA applied to control ice and snow would leave the roadway as runoff, or as traffic generated aerosols. To test for the impacts of CMA leaving the roadway as runoff, plants were irrigated with CMA solutions. To test for the impacts of CMA leaving the roadway as aerosols, other test plants had their tops sprayed with CMA solutions. NaCl was also applied to test plants as irrigation solutions or as aerosols. Additionally, one plant of each species was used as a control.

The concentrations of CMA and NaCl used in the irrigation water were selected to bracket the CMA concentrations expected to occur, or the NaCl concentrations known to occur, within 25 feet of the highway. The aerosol concentrations approximated the concentrations expected or found in snowmelt on highway surfaces.

The plants that were used in testing were obtained either as bare root stock or in one and two gallon containers in various soil mixtures. Plants received as bare root stock were inspected, soaked in a water bath, and root pruned to remove damaged or diseased roots. Bare root plants were planted in appropriate sized containers in a potting mix of sand, redwood bark and peat moss. Plants from the Western U.S. were received in 1 and 2 gallon plastic containers containing a potting mix of Douglas Fir bark and sawdust.

All plants were maintained in the nursery can yard of the Environmental Horticultural Department of U.C. Davis. Test solutions were made by dissolving appropriate amounts of CMA in tap water.

Soil irrigation test solutions contained 5, 10, 50, or 100 milliequivalents (meq) of CMA or NaCl; the control consisted of tap water. Sufficient solution was applied at each application to allow about 25% of the solution to leach through the soil. Throughout testing we endeavored to provide the plant's soil an ionic concentration equal to the test solution applied. Three plants of each species were treated with each concentration of CMA or NaCl. One plant of each species was used as a control.

Between February and June of 1982 a total of five applications were made. The application dates were determined by monitoring the amount of salts

remaining in the soil.

The test solutions for spray applications were made by dissolving the appropriate amounts of CMA or NaCl in tap water. The concentrations used were 0.1, 0.5, 1.0, and 2.0 N. Between February and May 1982 four spray applications were made.

The early 1982 results suggested that CMA was less damaging than NaCl in 14 of the species tested, while four showed about the same degree of damage as NaCl. However, various technical problems prevented a good quantitative examination.

A second season of treatment was conducted to improve the quantitative nature of the data. Rabbit Brush (Chrysothamnus nauseosus) was not tested in the second season.

The type, extent and progression of injury was determined by visual observation. The treatment damage was analyzed by comparing replicates for each treatment level with the control plants used as a standard.

c. Results

Tables 12 and 13 show numerical comparisons of the damage caused by NaCl and CMA. Table 12 rates the treatment caused damage on a scale from 1 to 5. One indicates no treatment damage, while 5 indicates severely damaged plants. Table 13 groups the 4 separate treatment levels together so that for both soil and spray treatment application modes, the treatment related damage for NaCl and CMA may be directly compared. In Table 13 a low number corresponds to minimal damage, while a high number indicates maximum damage. Nine species were more severely damaged by NaCl, one species was more severely damaged by CMA, and in eight species the degree of damage was too low to allow a comparison. In general, the spray treatments produced greater damage than the irrigation treatments.

Plants which were of poor quality masked the treatment related damage. Additionally, the organic potting mix for seven plant species strongly absorbed the applied ions, interfering with the plant's ability to absorb the ions. The soil absorption of salt ions buffered the treatment related injury.

As with other laboratory studies, this study has its limitations. Different species react to the stress of NaCl and CMA differently. Also, different soil types will influence the impacts of NaCl and CMA.

(TABLE 12 Cont)

SPECIES		SOIL				SPRAY			
		5meq	10meq	50meq	100meq	0.1N	0.5N	1.0N	2.0N
<u>Thuja occidentalis</u> Arborvitae	NaCl	1	1	2	4	1	2	2	5
	CMA	1	1	1	1	1	1	1	1
<u>Viburnum lantana</u> Wayfaring Tree	NaCl	2	3	4	5 ^a	2	3	5	5 ^a
	CMA	1	2	1	2	1	1	2	2

LEGEND

<u>Damage %</u>	<u>Numerical Ranking</u>
0	1
0-25	2
25-50	3
50-75	4
75-100	5

FOOTNOTES

- a. Treatment series includes dead replicate(s).
- b. Treatment series includes replicate(s) which died of causes other than being totally treatment related. Environmental stresses other than test treatment suspected as cause of death.
- c. Drought/heat stress damage; replicate(s) observed to have been severely wilted.
- d. Plants of poor original quality.
- e. Includes plants with regrowth foliage; all previous 1982 foliage was destroyed by the treatments.
- f. Treatment series includes replicate(s) partially removed by California state pathologists to test for oak wilt (Ceratocystis fagacearum).
- g. Treatment series includes replicate(s) totally removed by California state pathologists to test for oak wilt (Ceratocystis fagacearum).
- h. Not used in second season.

TABLE 13

NaCl, CMA DAMAGE RATE COMPARISONS

SPECIES	SOIL		SPRAY	
	NaCl	CMA	NaCl	CMA
Abies	2	1	8	1
Acer	6	1	5	1
Amelanchier	5	1	6	1
Arctostaphylos	4	1	13	7
Betula	7	1	7	1
Calocedrus	3	3	7	2
Chrysothamnus	2	1	2	1
Cornus	5	1	6	2
Elaeagnus	1	4	5	0
Fraxinus	2	0	5	3
Malus	4	1	8	1
Pinus jeffreyi	2	1	6	1
P. lambertiana	6	1	8	1
Quercus alba	3	3	5	2
Q. borealis	6	7	9	2
Salix	1	0	9	2
Thuja	4	0	6	0
Viburnum	10	2	11	1

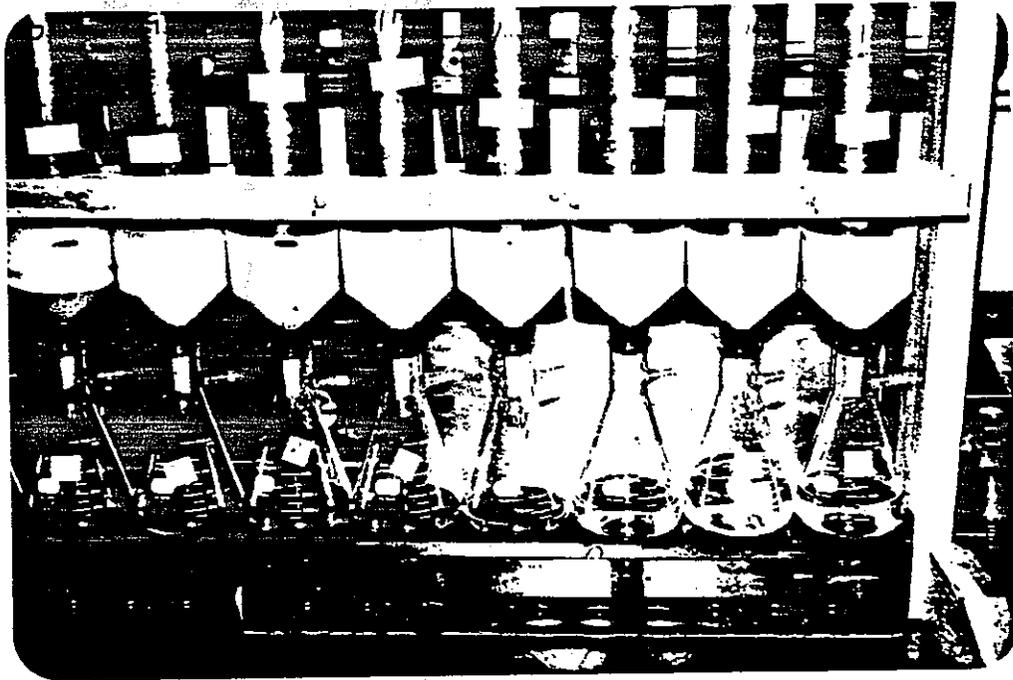


Figure 23. Holding rack with Lysimeter tubes and flask.

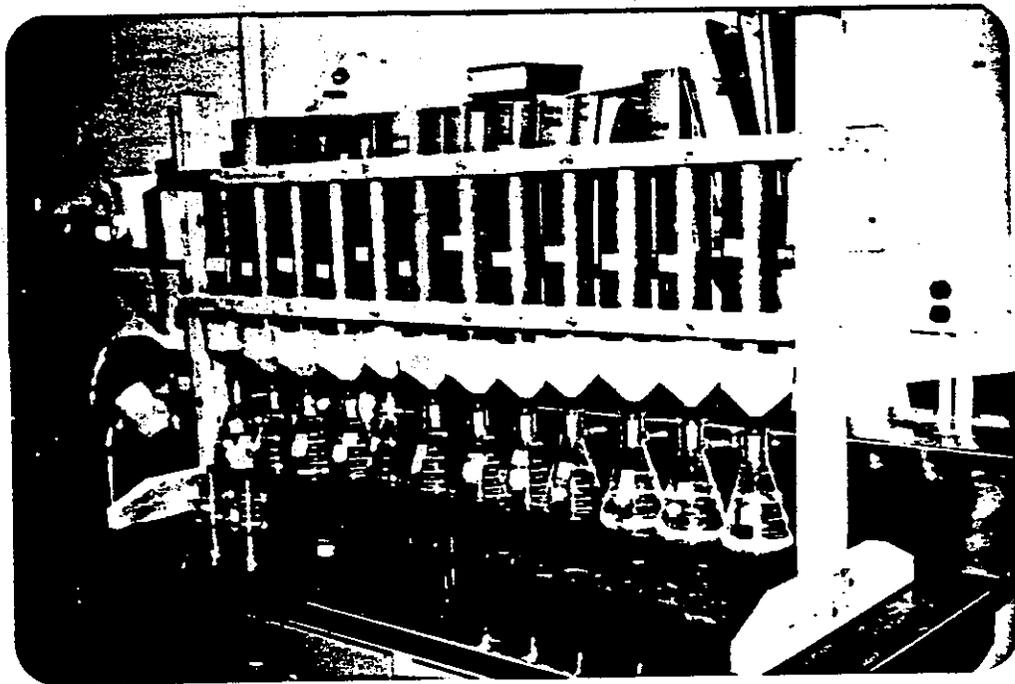


Figure 24. General Laboratory setup for soil Lysimeter testing.

2. Soil Evaluation

In response to FHWA requests, the State transportation agencies of Minnesota, West Virginia and Maryland sent soil samples and information about the samples to the TransLab for evaluation. Additionally, two soil types from the Lake Tahoe Basin were sampled by TransLab personnel. Of the 11 soils sampled, 7 were selected for testing.

Soils were received in thin-walled tubes, approximately 12-18 inches in depth and were relatively compacted and undisturbed. The compactness, in addition to the high clay contents of some samples, necessitated treating the samples as disturbed soils rather than undisturbed as originally planned. Most of the samples were compacted to the point no test solution would be able to percolate through the soil during testing procedures.

Soils tested included one Maryland soil from Anne Arundel County, three soils from West Virginia, two soils from Minnesota and a soil from California's Lake Tahoe Basin. Description of the soils sampled are:

Maryland —

Monmouth Collington Association. This soil is an ultisol that developed from unconsolidated marine sediments of various sizes that were deposited in the Atlantic Coastal Plain. The soil is sandy to loamy. The soil sample represents the horizons just below the topsoil.

Minnesota

Clontarf fine sandy loam. The sample was taken in Chippewa County. This is sandy loam found in stream deltas and outwash plains, in areas of gently sloping topography. This soil is moderately well drained.

Marysland loam is a nearly level, poorly drained, calcareous soil found in channels, on stream deltas and outwash plains. This sample was from Chippewa County. The permeability of this soil is moderate in the surface layers and rapid in the lower sandy levels. Surface runoff is slow while available water capacity is moderate. Organic content is high and the surface layer is mildly to moderately alkaline.

West Virginia

The West Virginia samples were soils from the DeKalb Series in Fayette County. The DeKalb series consists of moderately deep, well drained soils on ridge tops, hillsides, and mountainsides. These soils are formed in acid material weathered from sandstone. Slopes range from 3 to 70 percent, but are generally more than 40 percent.

DeKalb soils have a low to moderate available moisture capacity and rapid permeability. Natural fertility is generally low. In gently sloping areas, non-stony DeKalb soils are suited to crops, hay and pasture. Permanent pasture does poorly on these somewhat droughty soils. Trees grow fair to well and most of the acreage is wooded.

The entire soil profile is strongly acid to very strongly acid.

Sample #1 has a coarser texture containing fewer sandstone fragments and is more droughty than previously described. It is described as DeKalb fine sandy loam from 1 to 10 percent slopes. This soil is suited to all crops commonly grown in the two counties. Short-rooted pasture plants do poorly and the hazard of erosion is severe in unprotected areas. This sample apparently had not been contaminated with deicing salts.

Samples #2 and #3 are classified as DeKalb channery loam from 30 to 40 percent slopes and are representative of this series with the exception of the surface being free of stones. Sample #3 may have been affected by some deicing salts during past winters.

Lake Tahoe

The Lake Tahoe sample was taken along highway 89 approximately 2.5 miles northwest of the Highway 50/89 separation. Triplicate samples were taken 40 feet from the edge of the pavement.

The samples were from Elmira-Gefo soil association found from the Tahoe Valley to the California-Nevada state line. The soils of this association are formed in granitic materials on glacial outwash fans and moraines. The Elmira series are somewhat excessively drained soils underlain by sandy granitic alluvium. Within the Elmira series, slopes are 0-30 percent which is between the elevations of 6200-6500 feet and normally 20-35 inches precipitation per annum. Characteristically, vegetation is an open stand of sagebrush with coniferous forest and perennial grasses.

Methods

Lysimeters (soil containers) were used to contain the soil samples for the percolation testing. The lysimeters were constructed from 20 gage seamless brass tubing, 3 inches inside diameter and 12 inches long. Supports within the lysimeter for holding the filter paper and soil samples consisted of circles of coarse brass screen cut to fit and silver soldered in place 1-1/2 inches from the tube bottom. During the test, lysimeters were held vertical with a wooden rack (Figures 23 and 24). Test filtrate which had passed through the soil column was collected in a 500 ml Erylemeyer flask.

Samples selected for testing were removed from the shipping tubes. Only the upper 12 inches of each sample was used for testing. Each sample was made up of three replicates. Some soil from each replicate of the sample was combined to make a test sample. Each test sample was air-dried, using fans for air circulation and ground by a power mortar and pestle to pass a 2mm screen. Most soils had one or more distinct layers within the top foot of soil. This method breaks down the normal stratification of the upper 12 inches of soil structure producing a uniformly disturbed sample that is representative of the upper

one foot of the soil horizon.

From each prepared soil sample, three 500 gram subsamples were taken for the testing procedure. Each 500 gram replicate subsample was placed into separate lysimeters fitted with a layer of #40 whatman filter paper placed on top of the retaining screen. Three lysimeters with identical replicate subsamples were used for each soil type. The 500 gram samples were added in one motion to minimize particle size segregation. The lysimeters containing filter and soil on top of the filter were dropped 20 times through a distance of 2.5 cm onto a flat wooden block on a bench surface. The uniform "tapping" of the lysimeters and subsample was intended to achieve relatively uniform compaction. Once the samples had been "tapped", another close fitting whatman filter was placed on top of the sample. This filter was used to ensure minimal soil disturbance when the cylinders were loaded with liquids to be tested.

Preliminary testing indicated that approximately 750 ml of test solution should be charged in the lysimeter to ensure 500 ml of filtrate for chemical determinations on selected parameters.

Because project funding limited testing to only one concentration of calcium-magnesium acetate and distilled water, a 1 N reagent grade concentration was selected. The 1 N CMA concentration, while stronger than could be expected in a field situation (except in very unusual cases) would allow an evaluation of the chemical's potential for extracting nutrients and/or metals from the soil environment.

The soil loaded lysimeters were charged with 750 ml of 1 N CMA or the distilled water control and allowed to percolate until they stopped dripping filtrate or adequate sample for chemical determinations was secured. Filtrate was iced and immediately taken to the California Department of Water Resources Chemistry Laboratory for analysis. Parameters analyzed for were: pH, specific conductance, hydrolyzable orthophosphate, nitrate, potassium, and chemical oxygen demand.

Results

Tables 13 and 14 summarize the results of the chemical analysis. The results note a range for the three replicates and a mean in parenthesis. Distilled water and 1 N CMA chemical analysis are noted at the bottom of the table. The 1 N CMA used for the testing had a pH of 8.1. The results only compare the amount of metals or nutrients removed by either 1 N CMA or a distilled water control. The relationship between the amount of metal/nutrient removal and the total available in a particular soil was not determined. A general soil chemistry analysis for each soil was not conducted.

The results indicate that iron was removed by 1 N CMA at a significant level when compared to the control in five of the seven soils tested. Likewise, the effect of CMA on aluminum

removal is significant in five of the seven soils tested. Three of the seven soil results showed no aluminum in either the control or CMA treatment. It is not known if this reflects absence of aluminum in these soils or that it did not move in response to treatments.

Sodium movement from the soil was noted in some of the soils, however, it was significant in only two cases, one of which (West Virginia #1) was known to have been contaminated by deicing salt. Significant removal of orthophosphate was noted in only one soil but five of the seven soils showed significant removal of hydrolyzable orthophosphate resulting from the leaching of CMA. Nitrate removal was not significant in most of the soils. However, five of the seven soils did exhibit a significant loss of potassium when compared to the controls.

Based on the results noted in Tables 13 and 14, it appears 1 N calcium-magnesium acetate has the potential to remove significant amounts of iron, aluminum, sodium, hydrolyzable orthophosphate and potassium from the soil.

This soil analysis was very limited. The results indicate that a 1 N CMA solution can remove some ions from a lysimeter. However, the laboratory conditions used in testing are not the same as the conditions which will be encountered in actual use. Further studies should be performed both in the laboratory and in the field.

Table 14 - Leachate Volume Specific Conductance and COD Summary from the Soil Study.

	<u>Leachate Volume ml</u>	<u>Specific Conductance μmhos/cm</u>	<u>COD mg/Liter</u>
MD2			
CMA	567	30,730	63,400
DH ₂ O	582	115	233
MN1			
CMA	584	31,300	61,800
DH ₂ O	568	130	67.6
MN ³			
CMA	587	31,160	66,000
DH ₂ O	580	247	54.0
WV1			
CMA	547	30,930	61,100
DH ₂ O	548	193	122.3
WV2			
CMA	564	30,600	62,100
DH ₂ O	565	214	121.0
WV3			
CMA	543	31,230	65,700
DH ₂ O	553	352	48.0
CAT			
CMA	577	31,000	66,500
DH ₂ O	587	82	78.8
IN CMA		25,500	66,800
Distilled H ₂ O		12.9	0

Table 15 - Nutrient and Metal Summary From Soil Study (mg/Liter)

	<u>Iron</u>	<u>Aluminum</u>	<u>Calcium</u>	<u>Magnesium</u>	<u>Sodium</u>	<u>Orthophosphate</u>	<u>Hydrolyzable Orthophosphate</u>	<u>Nitrate</u>	<u>Potassium</u>
Md2									
CMA	4.0	40.0	9593.0	5900.0	1600.0	0.09	0.1	0.97	23.0
DH ₂ O	0.3	0.0	2.3	2.0	4.0	0.00	0.1	0.65	4.7
MN1									
CMA	0.2	0	9900.0	5783.0	14.3	0.07	0.07	3.2	29.3
DH ₂ O	0.17	0	9.3	2.7	1.0	0.14	0.11*	2.8	3.4
MN3									
CMA	0.2	0	10,433	5267	14.0	0.07	0.05	3.0	17.3
DH ₂ O	0	0	38.7	7.0	2.0	0.007	0.1	2.4	2.3
WV1									
CMA	3.7	12.7	9650.0	5283.0	45.7	0.07	0.007*	1.0	4.83
DH ₂ O	0.9	2.3	5.3	1.0	29.0	0.02	0.02	0.65	2.1
WV2									
CMA	0.6	26.7	9450.0	5783.0	2.0	0	0.06	11.0	2.4
DH ₂ O	0	0	14.0	2.0	5.3	0.02	0.03	10.7	5.2
WV3									
CMA	0.2	0	9933.0	5617.0	16.7	0.03	0.03	15.3	21.3
DH ₂ O	0	0	44.3	4.7	4.7	0.02	0.04	19.3	6.3
CA1									
CMA	0.4	1.0	9867.0	5400.0	22.7	0.05	0.06	1.03	5.1
DH ₂ O	0.1	2.7	4.3	1.3	7.0	0.04	0.13	0.23	6.6
INCMA									
CMA	0.2	0	10,200.0	5500.0	13.0	0.08	0.02	0.25	7.5

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STATE OF CALIFORNIA
DEPARTMENT OF TRANSPORTATION
DIVISION OF FACILITIES CONSTRUCTION
OFFICE OF TRANSPORTATION LABORATORY

PRELIMINARY EVALUATION OF CALCIUM MAGNESIUM ACETATE
FOR USE AS A HIGHWAY DEICER IN CALIFORNIA

SEPTEMBER 1986

Under the Supervision of

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Study Supervised by

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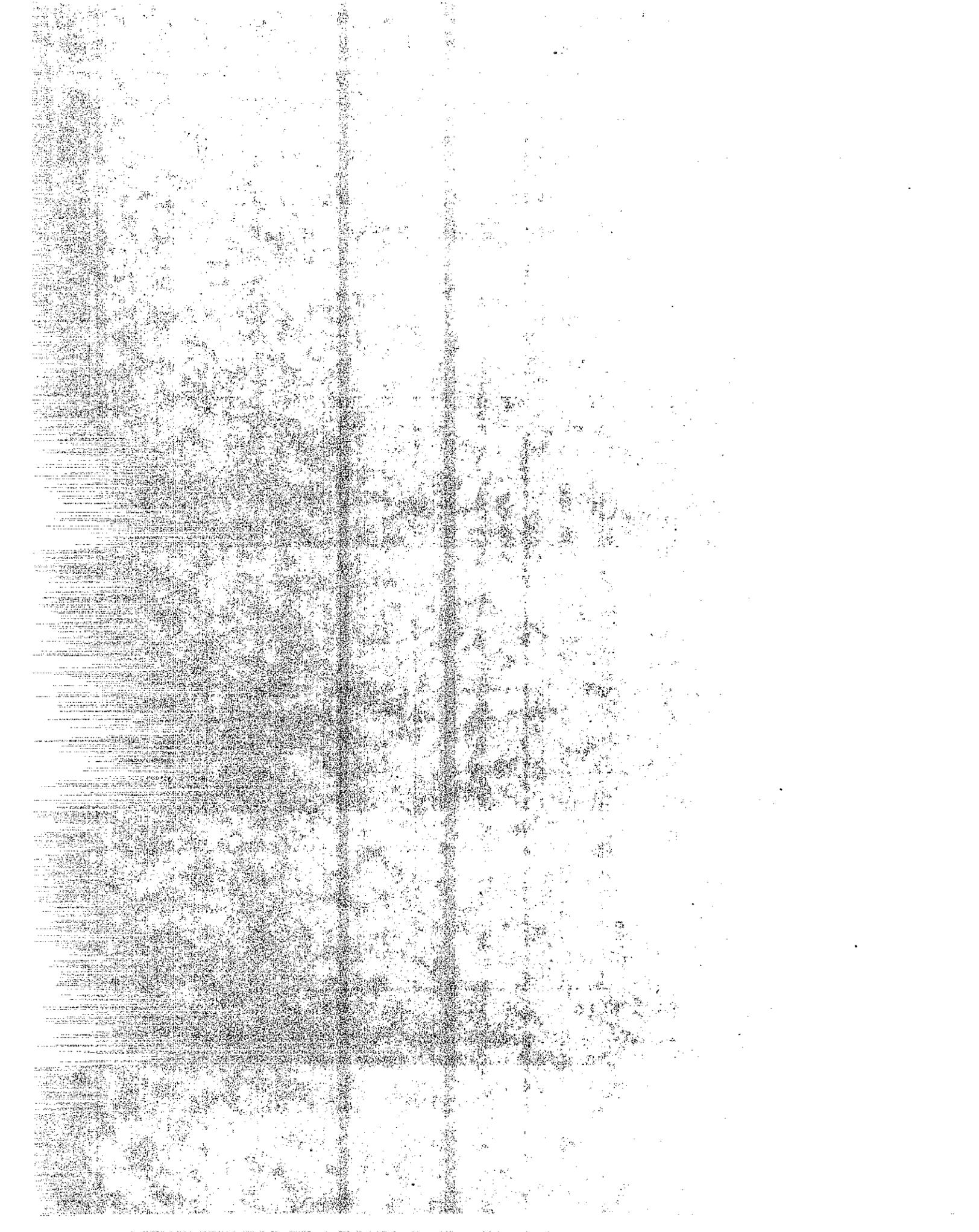
Principal Investigator and
Report Preparation

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Chief, Office of Transportation Laboratory



PROJECT IDENTIFICATION NUMBER: E86TL63

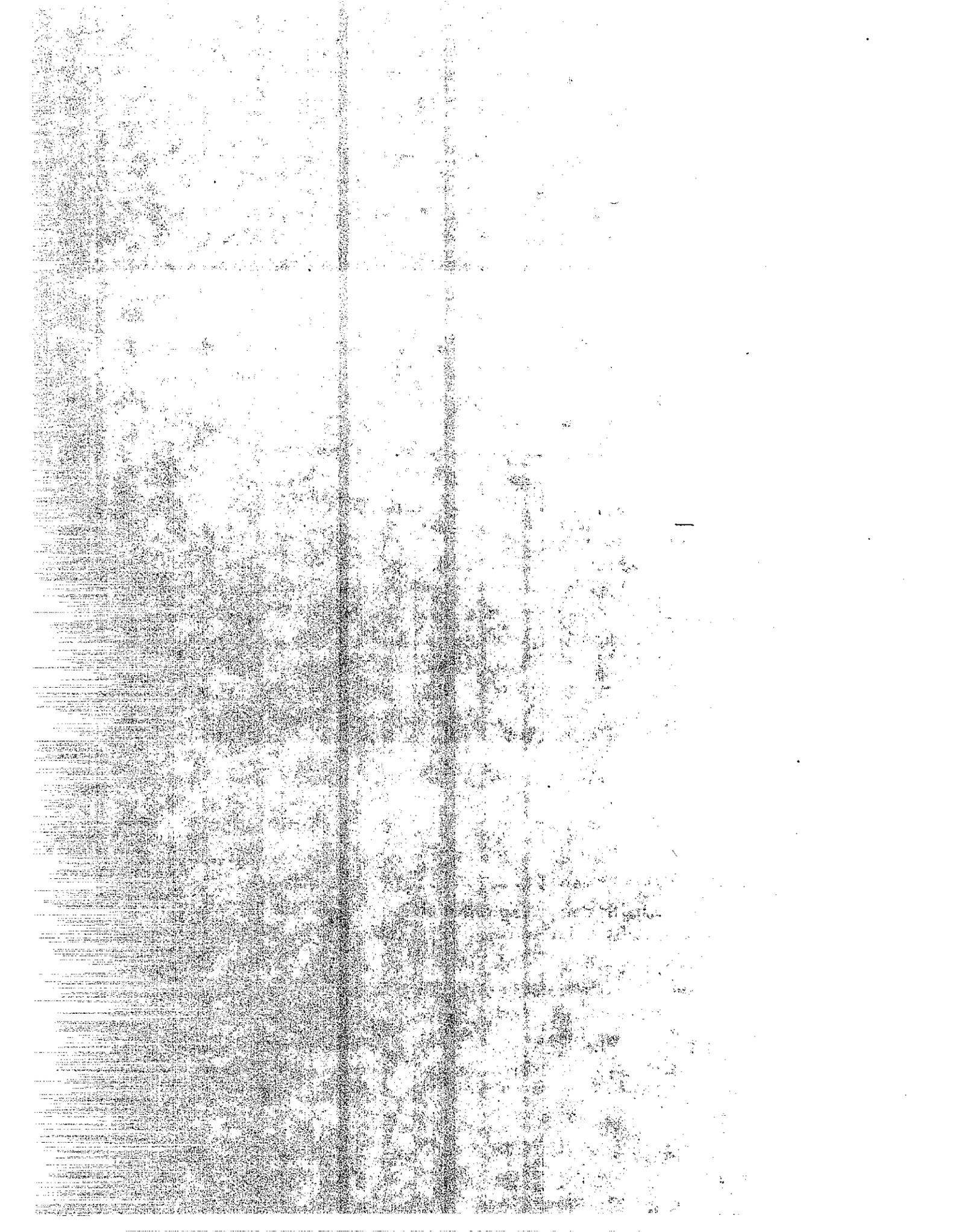
RESEARCH EXPENDITURE AUTHORIZATION: 647333

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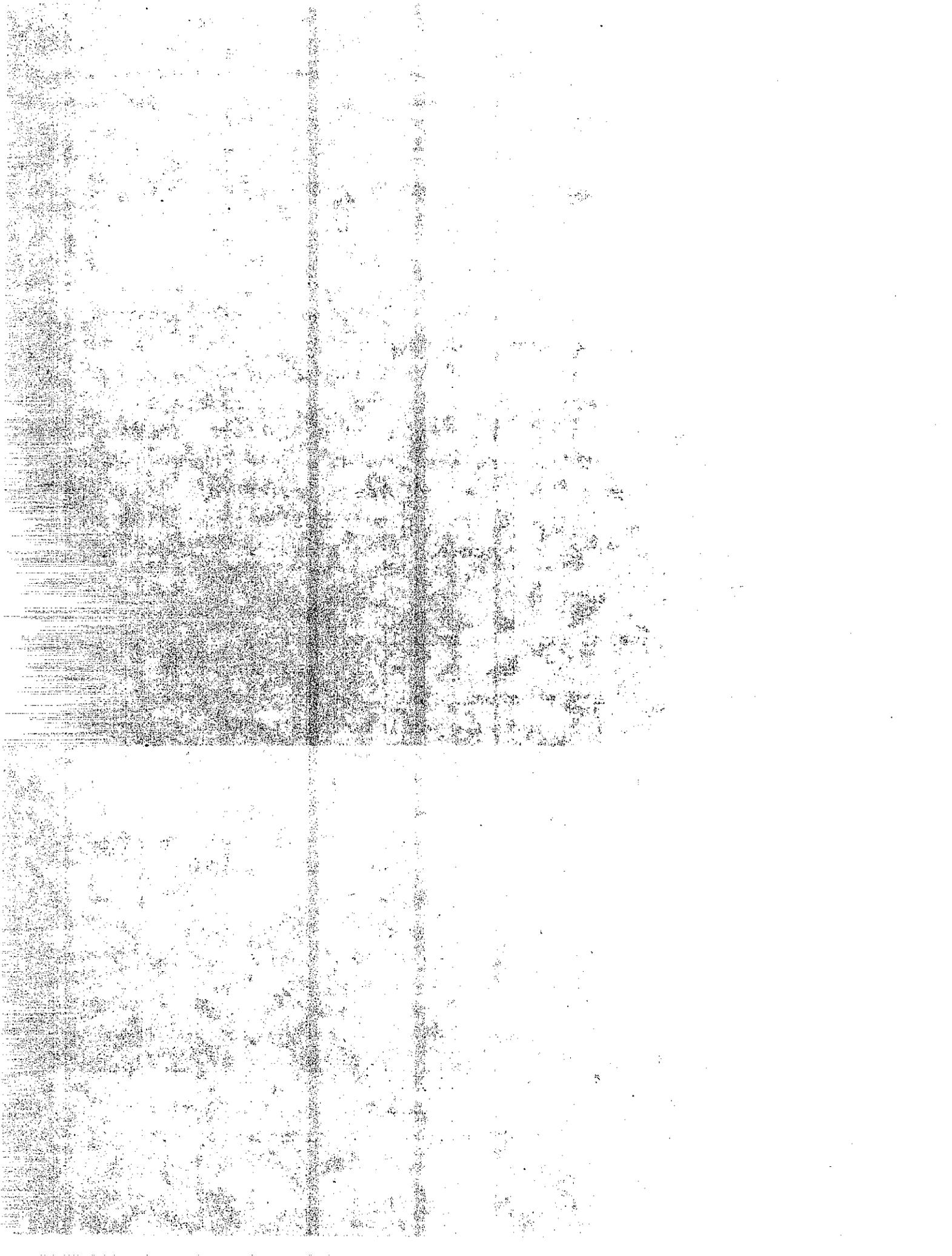


INTRODUCTION:

In California, a bare pavement policy for major highways means significant amounts of rock salt (sodium chloride) and to a lesser extent, calcium chloride, are used each year to clear highways of snow and ice-pack as rapidly as possible. Salt use on highways in California, corresponding to the snow fall pattern, is primarily confined to mountainous and north state areas. Over the last ten years we have used an average of 12,000 tons of salt per year, most on the three transsierra routes Interstate 80, Highway 50 and Highway 88 for highway deicing. Unfortunately salt has known, demonstrated, deleterious effects on highways and highway structures as well as the vehicles using the highway. The US EPA estimated, in a 1976 report, that annual costs to snow belt states for damage to structures and vehicles was in excess of two billion dollars (1).

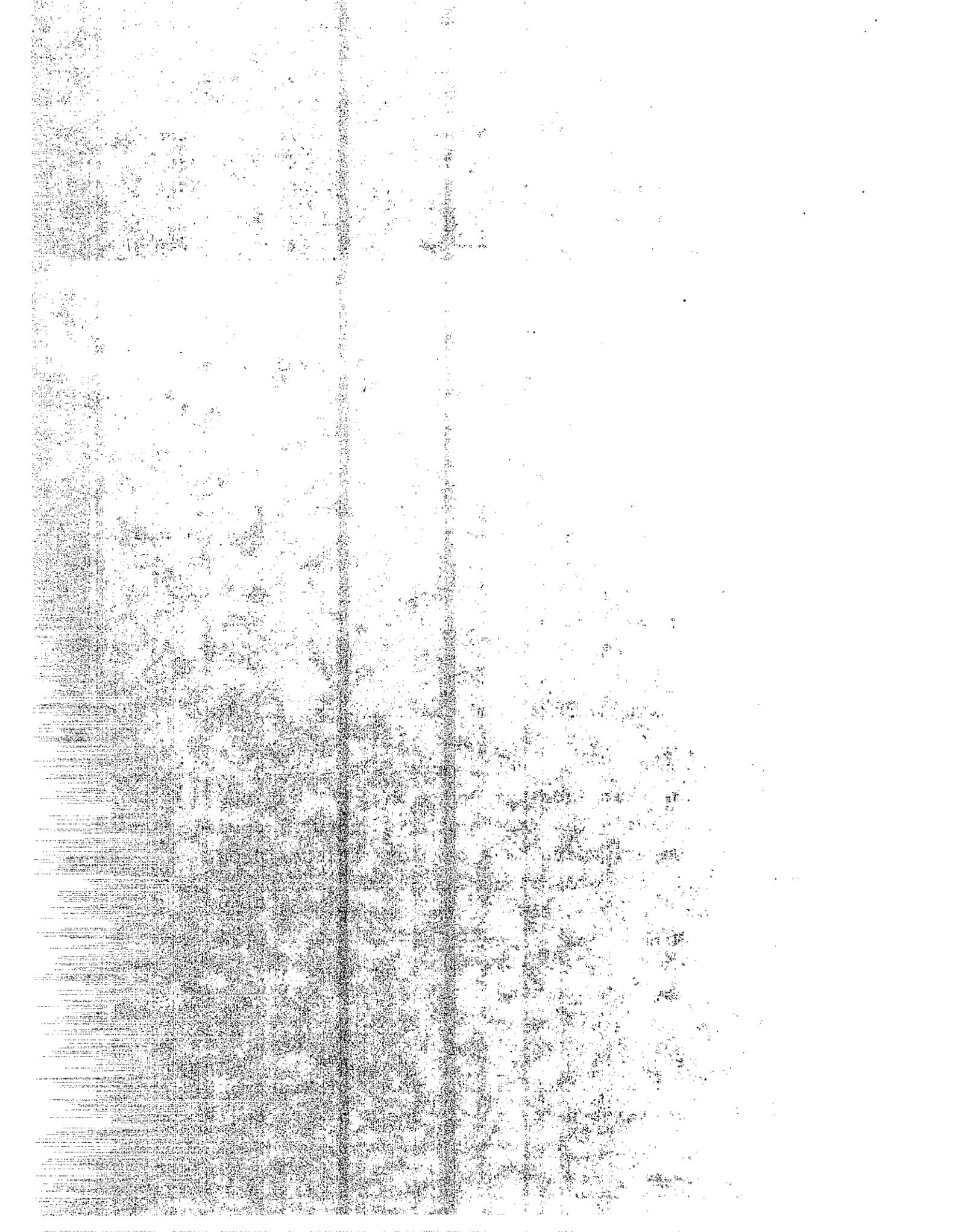
The environment is also affected by salt use. Trees, weakened by salt and susceptible to disease and pest infestation, that besides looking bad, may eventually be blown down across highways during storms or require removal by maintenance personnel. Additionally, salt-laden runoff can cause chemical change in lakes and streams along highways. Input of this runoff can cause contamination of drinking water sources and to other water bodies (2). As an example, although, it does not happen often in California, at Putts Lake along Interstate 80, a saltwater layer develops each year killing the organisms that inhabit the lake bottom. In other instances such as Lake Tahoe, Caltrans has demonstrated that salt treated with yellow prussiate of soda (YPS) adds limiting micronutrients to the lake and increases algae growth (3).

Because of the deleterious effects of rock salt, the California Department of Transportation has, since the early 1970's, been actively involved in developing alternative methods for highway



deicing. Initial research determining the effects of rock salt led to more effective salt use in environmentally sensitive areas, such as Lake Tahoe, and the use of kiln dried salt instead of YPS dried salt. Continued research has included cathodic protection of structures and structure rehabilitation. The methods developed to control salt effects have amounted to controlling the amount of rock salt used or protecting the most susceptible structures. To solve the deicing salt problem an alternative to rock salt was needed. In an effort to address the problems of rock salt and still provide effective snow and ice control, a national effort has been made since 1979. From this research, one chemical, calcium magnesium acetate (CMA), has shown the most promise as a replacement for rock salt for use as a highway deicer.

CMA works as a deicing chemical in a manner similar to rock salt and was originally proposed for use as a deicing chemical by the Bjorksten Laboratory in research sponsored by the Federal Highways Administration (4). The California Department of Transportation, as part of the FHWA and NCHRP sponsored research program, has been involved in CMA research since 1981, when the Transportation Laboratory began a project to determine the environmental effects of CMA. This research demonstrated that, in most cases, CMA is not deleterious to common plants found along the highway and is not toxic to fish and other aquatic organisms with the exception of algae (5). Other research has shown that CMA can be an effective deicer which limits the deleterious structural consequences of rock salt. However, there have been operational problems with CMA including dust, clogged spinners and other equipment used to spread CMA, higher than desired melting temperatures and storage problems (6,7). Since these original tests, there have been improvements which may have solved these problems (8). As product improvements have occurred over the last few years, the possibility that CMA could be a viable alternative to rock salt for use as a highway deicer has become evident. Therefore, during the winter of 1985-86, the California Department of Transportation, Division of Highway Maintenance in conjunction with the Transpor-



tation Laboratory and Highway District 10 undertook a test evaluation of CMA as a replacement for rock salt. This report outlines the test program and results obtained using CMA during the 1985-86 winter.

OBJECTIVE:

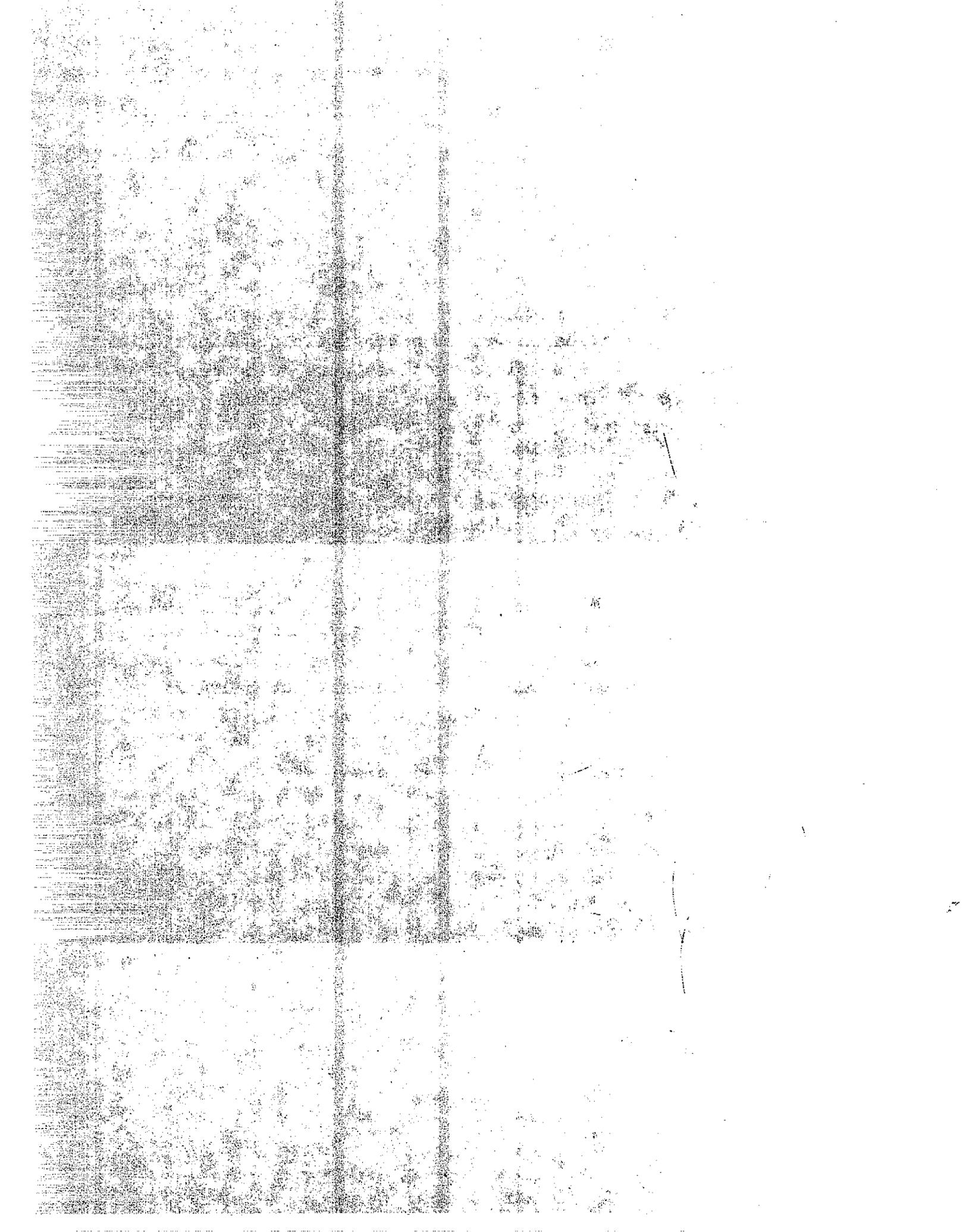
The objective of this research was to begin a field evaluation of CMA use in California. Specific objectives were to compare CMA with rock salt for deicing effectiveness and to evaluate the operational requirements of effective CMA use.

CONCLUSIONS:

1. The CMA tested was as effective a deicer as rock salt and in the case of sheltered areas, was more effective than rock salt.
2. CMA worked well when combined with cinders, but had mixing and application problems when combined with moist sand.
3. Overall, results were mixed, but encouraging.

RECOMMENDATION:

Further research using pelletized CMA on an increased scale is warranted.



CMA:

The CMA used in the test was imported from Verdugt, Inc., Holland since no company was available to produce CMA except in prohibitively large amounts in the United States. For the test 35 tons of CMA were purchased in 50 kg plastic lined, paper bags, which cost after all fees were paid about \$48,000 or \$1370 per ton. The price is much more than rock salt which can be purchased in 50 kg bags for about \$80 per ton. The CMA was an agglomerate which is about the consistency of laundry detergent and so had a high fines content. The CMA purchased also had a 3 to 7 calcium to magnesium ratio which had been demonstrated by others in an earlier test to possibly be the most effective ratio giving the lowest eutectic temperature (9).

The bag size was requested by District 10 Maintenance, since they do not have bulk storage capability at Caples Lake and must hand-load salt and CMA. During loading operations, individual bags were emptied into the bucket of a front-end loader and then the total CMA load required was moved in bulk. As a safety precaution, workers were required to use goggles, dust mask, rubber gloves, and paper coveralls when handling CMA. Even though there are no evident health hazards associated with CMA, use of safety equipment was stressed especially to avoid inhaling dust.

METHOD:

To determine the potential for CMA use in California, three sites in District 10 were chosen to use CMA instead of rock salt during the winter of 1985-86 (Figure 1). The sites were: Highway 88 between the Carson spur and Caples Lake, Highway 4 at Big Trees State Park and Highway 120 at Groveland. Because of weather conditions, only two sites, Caples Lake and Highway 120 at Groveland

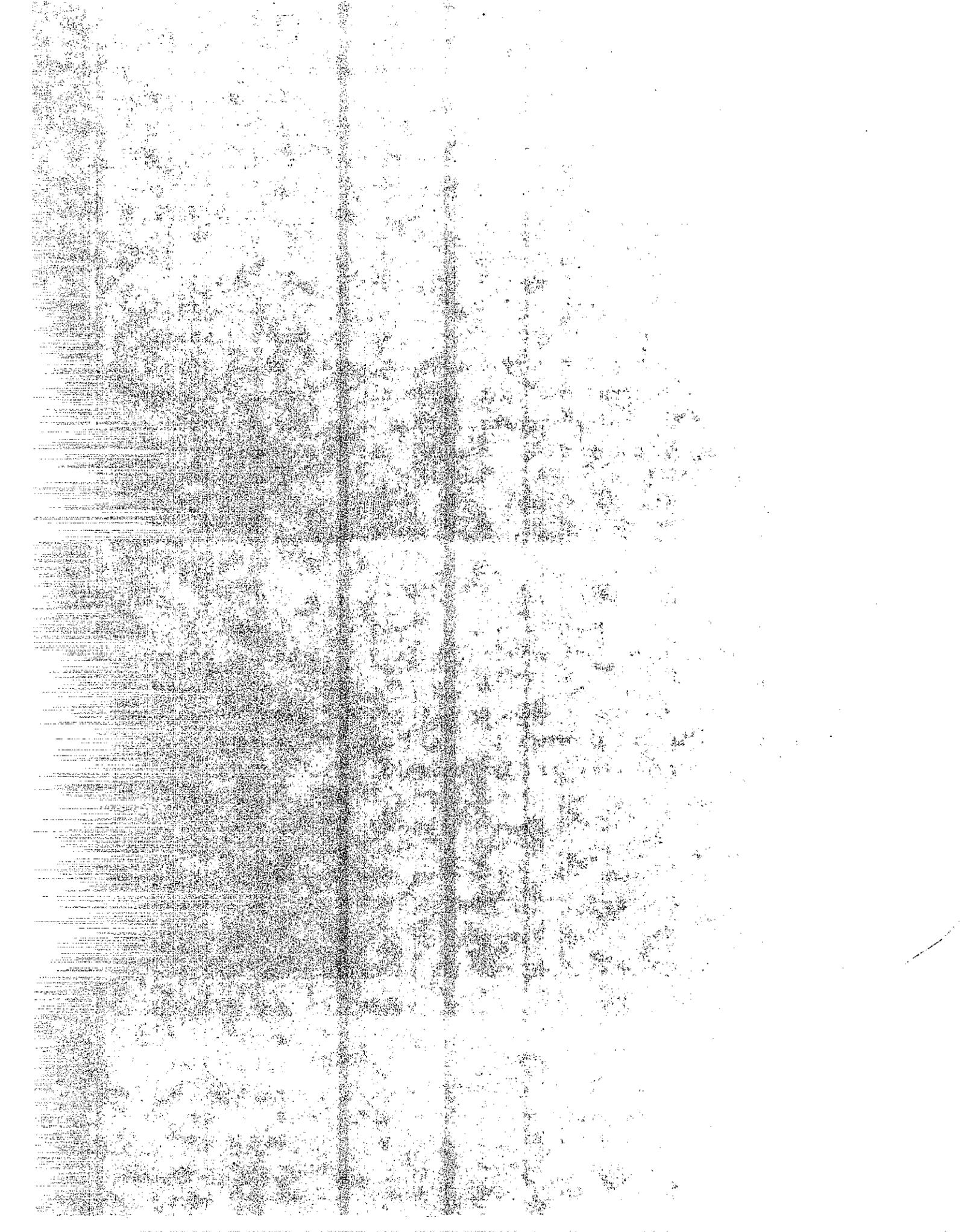
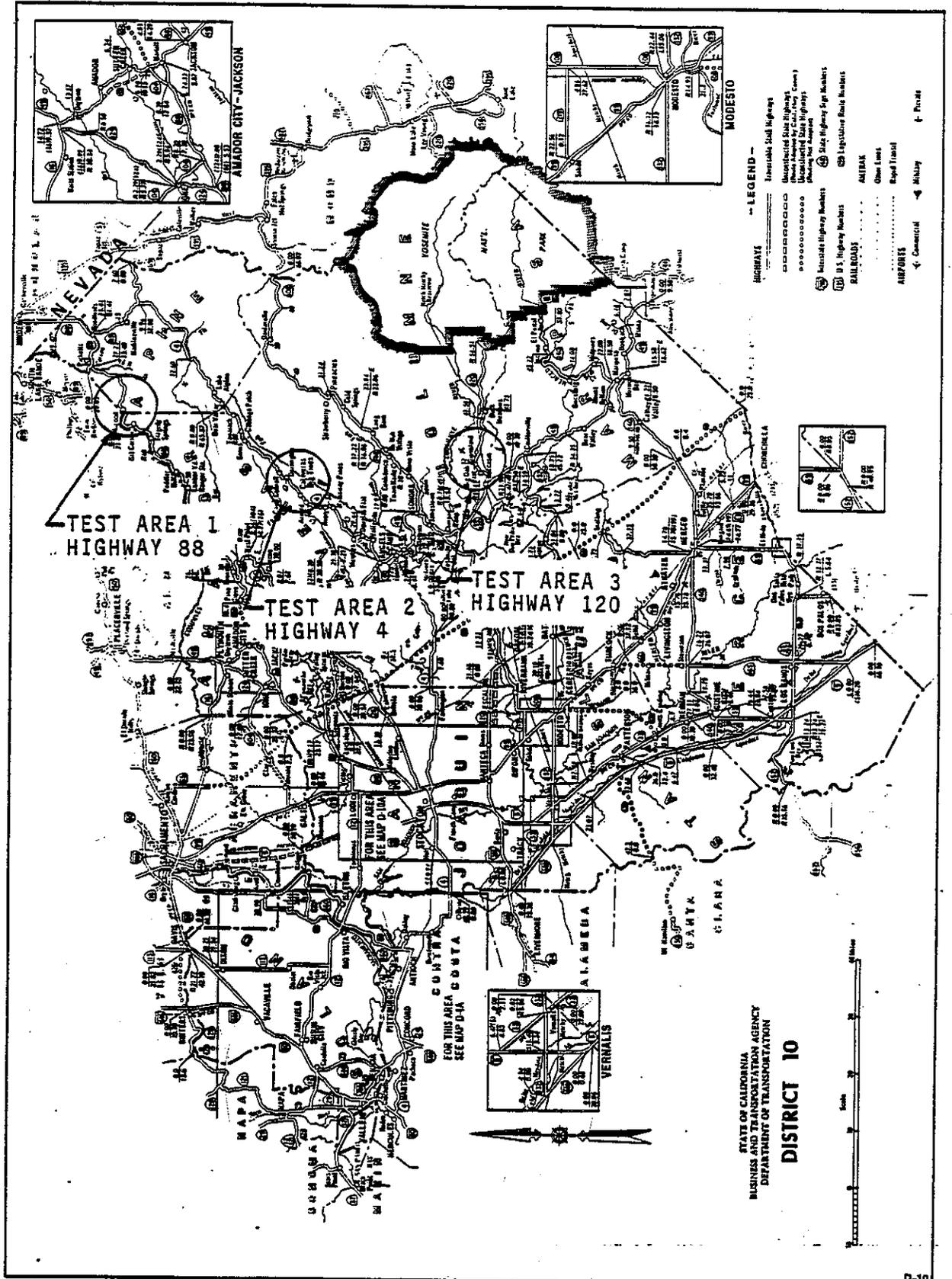
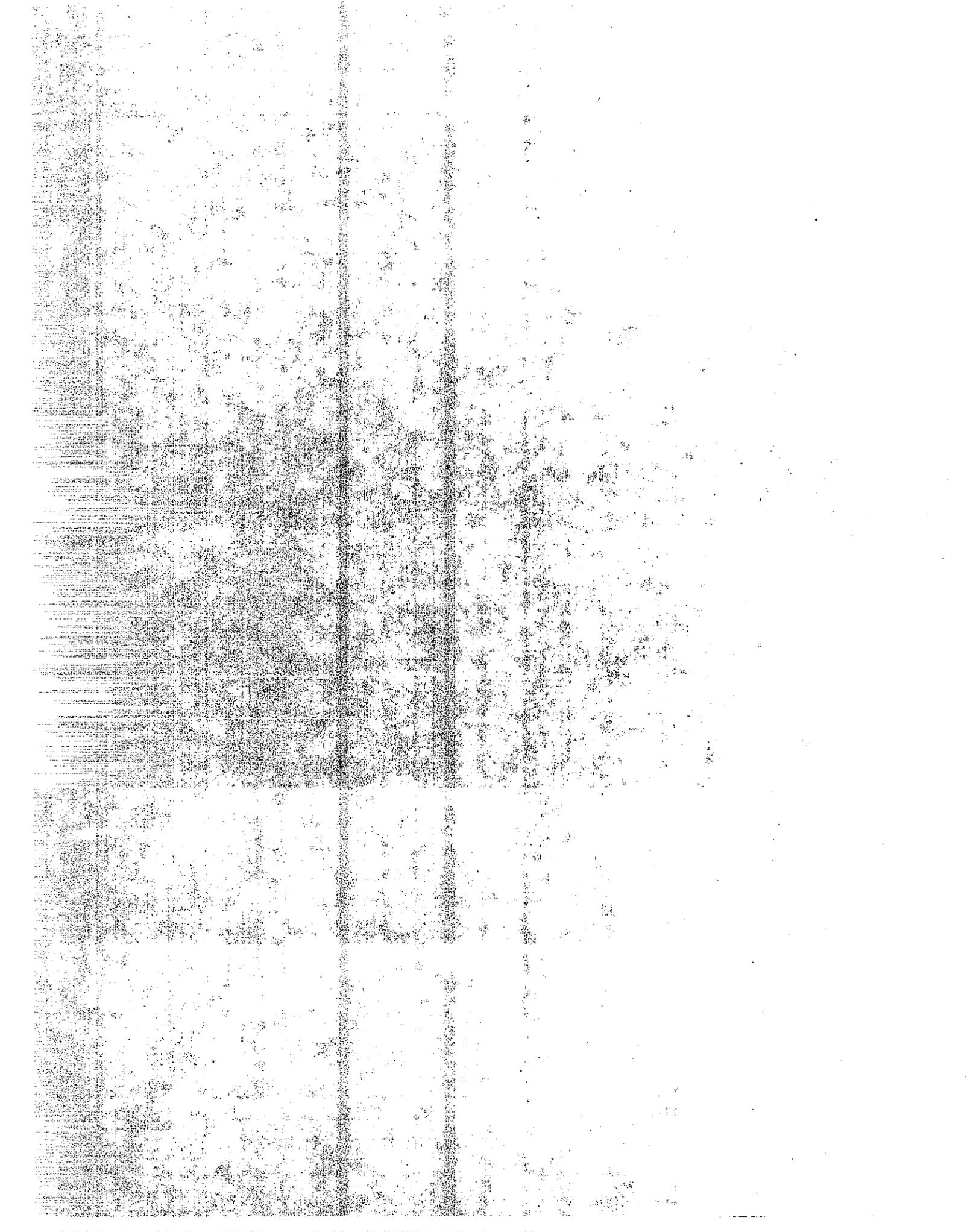


Figure 1 - CMA TEST AREAS



Unless adding errors or omissions on this map, please contact and forward to Headquarters, Office Engineer, P. O. Box 1492, Sacramento 2200

0-10
HIGHWAY DATA REVISED AS OF 12-75

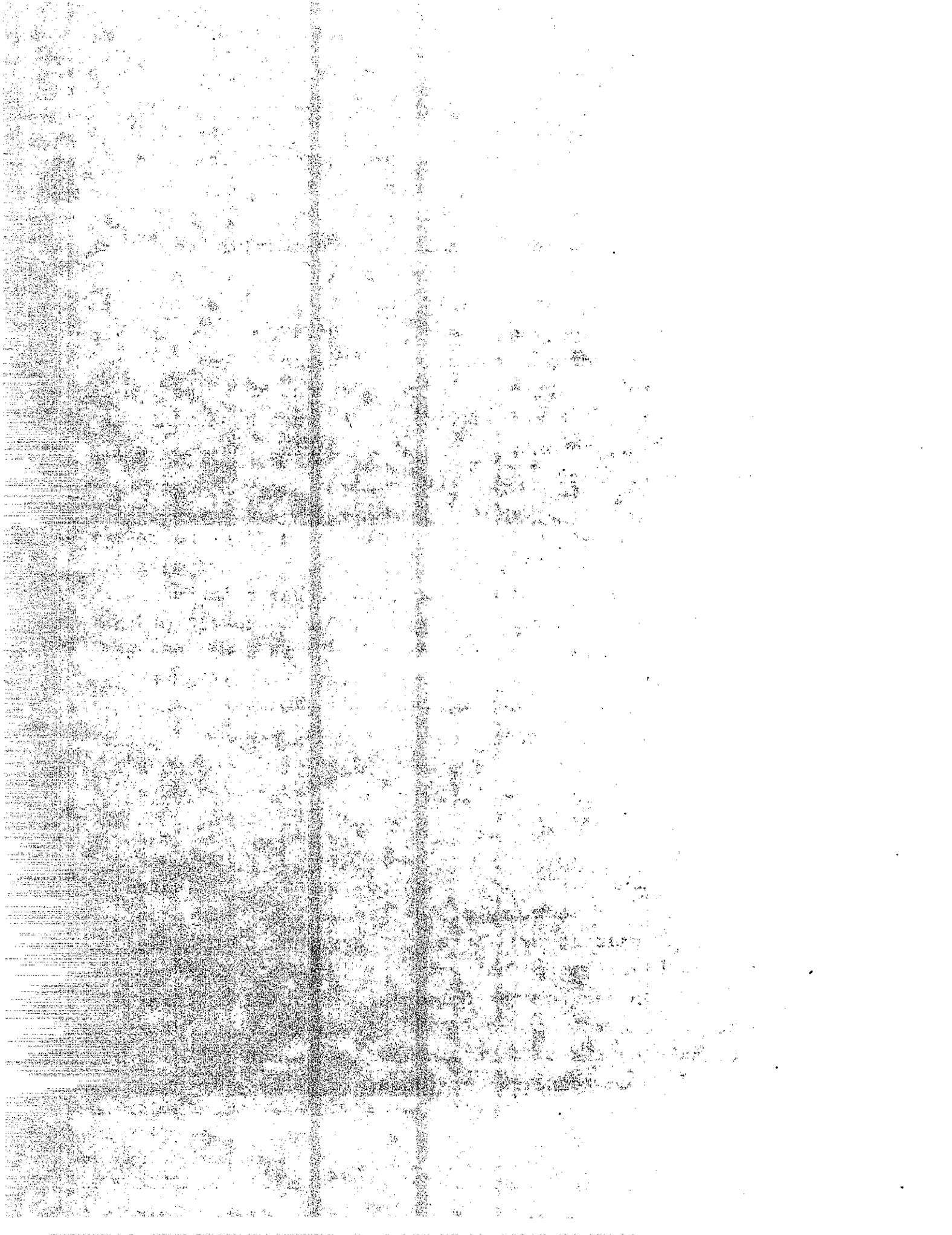


used CMA during the tests. However, only the site on Highway 88 between the Carson Spur and Caples Lake had sufficient snowfall to effectively test CMA for use during storms. The use of CMA at Groveland was restricted to frost and ice protection on cold nights. These sites are described below.

Highway 88-This is a two lane asphalt, all-weather highway which has some of the worst winter conditions of any highway in the California system. The test area is at an elevation of 7,500 to 8,000 feet. Temperatures range below 0°F to 40°F during the winter, but temperatures during storms normally range from 20°F to 28°F. During storms the wind can be very strong and rime-ice can collect on equipment. An average storm will have a snowfall in excess of three feet and snow accumulation during the year will range from 12 to 15 feet.

The test area is serviced out of the Caples Lake Maintenance Station. Normal procedures call for cinders to be mixed with varying amounts of rock salt at the discretion of the maintenance supervisor. Deicing chemicals can account for up to 25% of the load but are normally less. The aggregate mix is used when the snow starts to stick, but can be discontinued if chain controls are established. Chemicals are then used to remove pack after the storm. Salt and cinders are spread using a hopper-type truck with a hydraulically driven, stainless steel spinner using a chain type conveyor. The feeder can be calibrated and spread width can be controlled by the operator from 8 to 40 feet.

For the test on Highway 88, both CMA/cinders and salt/cinders were used on different sections of the Caples Lake maintenance area using normal deicing procedures. The amount of CMA used in each load was equivalent to the amount of rock salt that would have been used. Because of the molecular weight of CMA, an equivalent weight of CMA to salt is 1.67 to 1; therefore, approximately twice as much CMA as salt was used by weight for each comparable load. The CMA/cinders were used exclusively in the designated test areas, which consisted of the Carson Spur and the

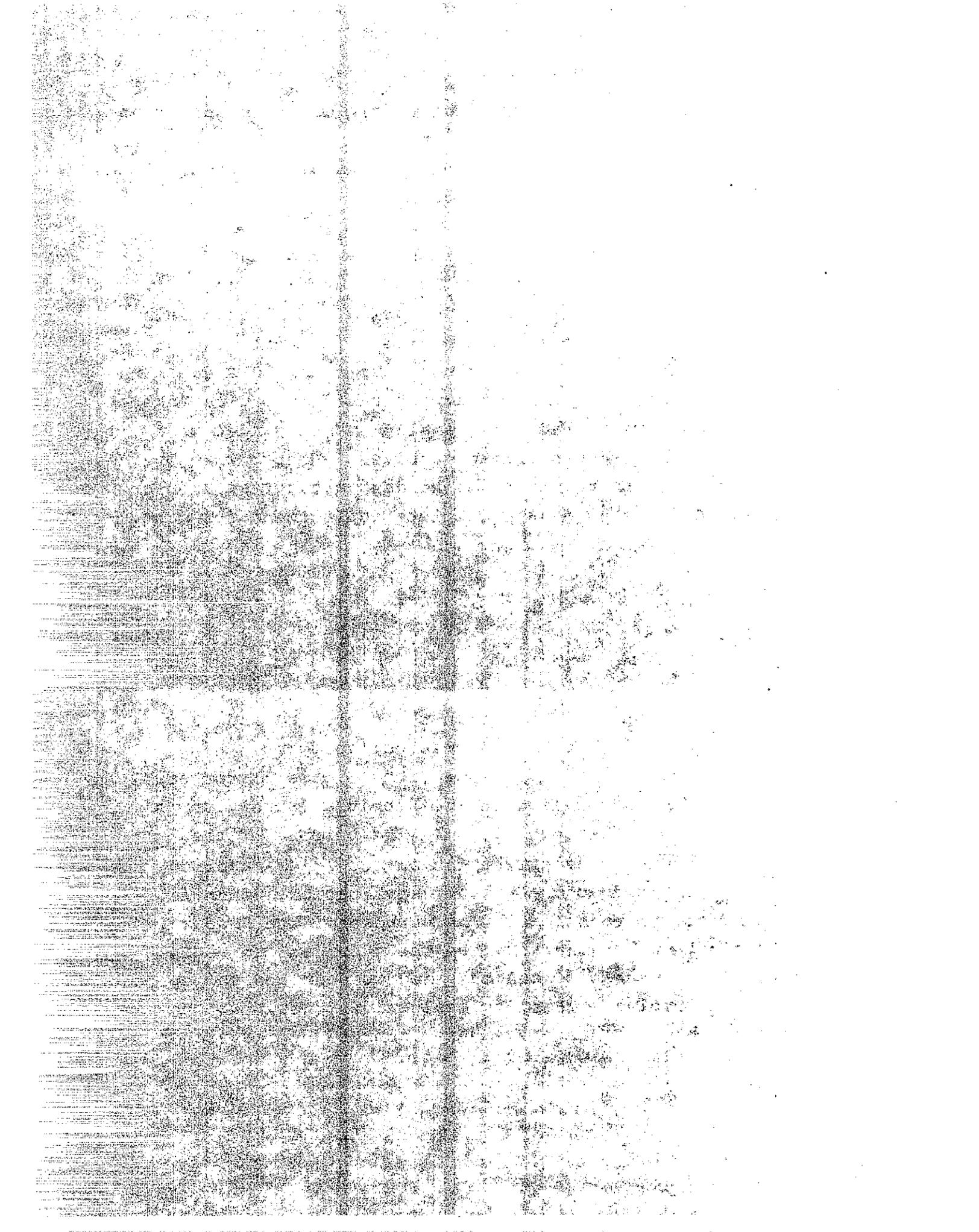


spillway area near Caples Lake (Figure 2). Both of these sections have northern exposures and have consistently caused significant problems for maintenance crews during pack removal. Other areas within the Caples Lake station area of responsibility received salt/cinders and served as the control.

Highway 120-This is a two lane asphalt highway around Groveland at an elevation of about 2500 feet. Temperatures are normally above freezing during the day but drop during the night causing icy spots on curves and exposed structures. The test area was serviced out of the Groveland Maintenance Station. CMA was mixed with sand in a manner similar to that described at Caples Lake. CMA/sand mixtures were spread using a slip-in box sander on a dump truck. The mixture was spread at sites as determined by the maintenance supervisor and there was no designated test area or control area. CMA was used as a complete replacement for salt.

EVALUATION METHOD:

In all cases where CMA was used, both the operators and their supervisors were required to submit evaluation forms. Each operator was to submit a "Driver's Report" (Figure 3) for each load of CMA and each supervisor was to submit a "Supervisor's Evaluation" (Figure 4) for each storm. The purpose of the "Driver's Report" was to determine the amount of CMA applied, the conditions that existed at the time of application and an estimate of the effect of each load. The purpose of the "Supervisor's Evaluation" was to characterize the storm and to estimate the overall effectiveness of CMA compared to salt and the operational problems involved. Besides evaluation forms, two CMA deicing operations at Caples Lake were observed by research personnel from Translab and Headquarters Maintenance.



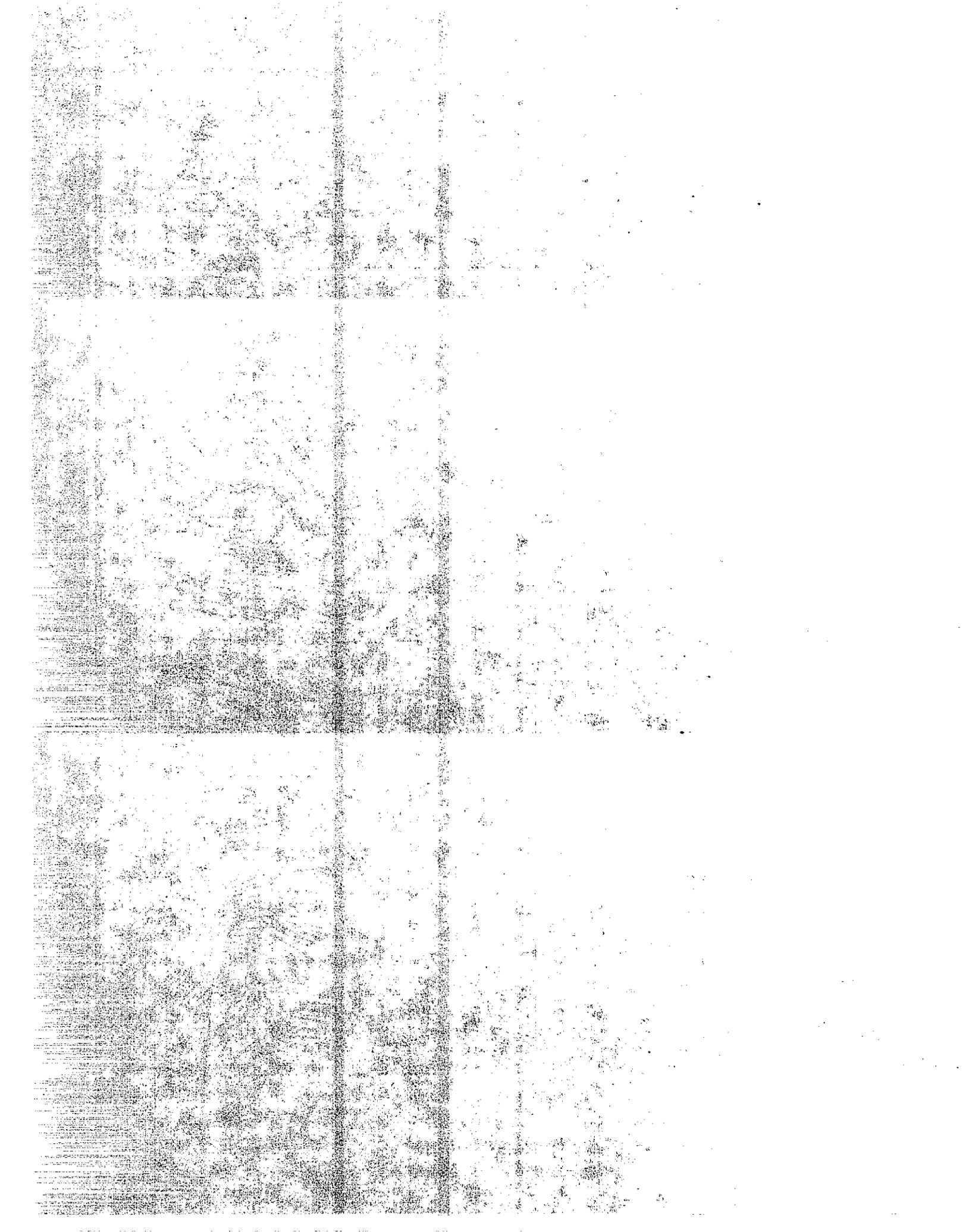


Figure 3 - Driver's Report

CALIFORNIA DEPARTMENT OF TRANSPORTATION

CMA EVALUATION

Driver's Report
Load and Spreading Data

Driver: _____

Co/Rte/PM: _____

Maint Station: _____

Time: _____

Date: _____

A. LOAD: _____ lbs CMA/T sand

B. WEATHER:

Temp: _____ °C Wind: _____ mph

Precipitation Description: WET, DRY, BLOWING SNOW, CLEAR
(Circle appropriate Description) FREEZING RAIN, SLEET, MIXED SNOW/RAIN

Time Precipitation Began: _____

C. SPREAD DATA:

Time Spreading Began _____

Lane miles spread _____

Spreader Type _____

Width of Pattern _____

D. RESULTS:

Overall opinion of CMA _____ FAVORABLE _____ UNFAVORABLE

Handling Difficulty (compared to salt) _____ MORE _____ LESS _____ NO DIFFERENCE

Spreading Problems with Equipment _____ SIGNIFICANT _____ NOT SIGNIFICANT

Time to Obtain Pack Free Surface _____ MORE _____ LESS _____ SAME
(compared to other methods)

E. COMMENTS:



Figure 4 - Supervisor's Evaluation
CALIFORNIA DEPARTMENT OF TRANSPORTATION
CMA EVALUATION

Supervisor's Evaluation

Supervisor: _____

Co/Rte/PM: _____

Maint. Station: _____

Time: _____

Date: _____

A. STORM DATA:

Total snow fall _____ inches Max rate of snow fall _____ in/hr

Duration of storm _____ hours

Temp. range _____ °C

Wind _____ mph

B. LOAD: For storm - Total lbs CMA used _____

Total tons sand used _____

C. SPREAD DATA:

Approx time after storm began chemical spreading began _____ min.

Approx rate of spread _____ lbs/mi CMA

Total number of applications during storm _____

Average time between applications _____

D. RESULTS:

Spread Pattern: ___ GOOD ___ POOR ___ BLOWN OFF ROAD SURFACE

Melting Action: ___ Evidence of chemical penetration to pavement

___ Evidence of partial melting

___ Chemical not effective

E. OPINION:

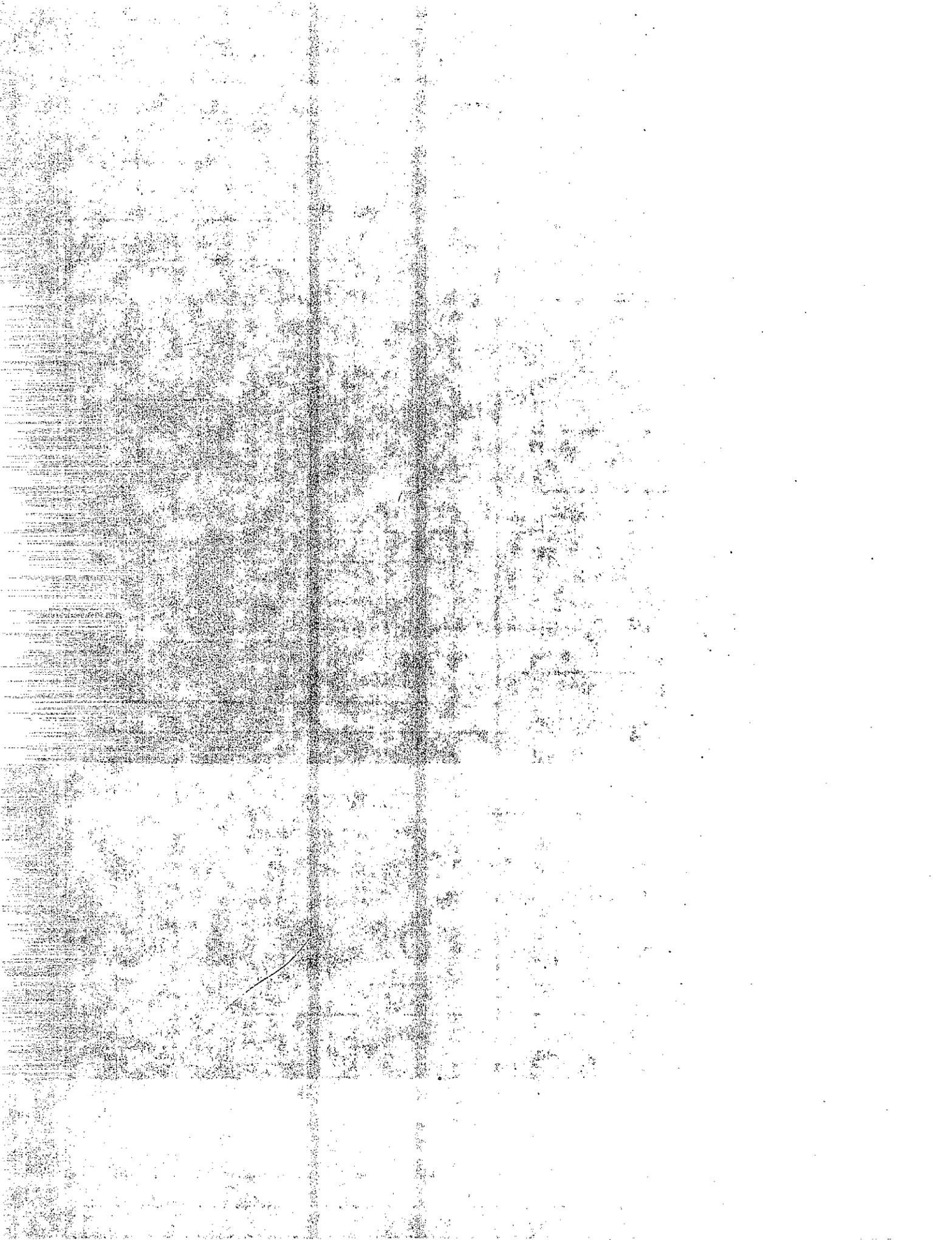
Overall opinion of CMA: _____ FAVORABLE _____ UNFAVORABLE

Handling Difficulty _____ MORE _____ LESS _____ SOME
(compared to salt)

Spreading Problems with Equipment _____ SIGNIFICANT _____ NOT SIGNIFICANT

Time to Obtain Pack Free Surface _____ MORE _____ LESS _____ SAME
(compared to other methods)

F. COMMENTS ON ABOVE: Explain negative/positive aspects.



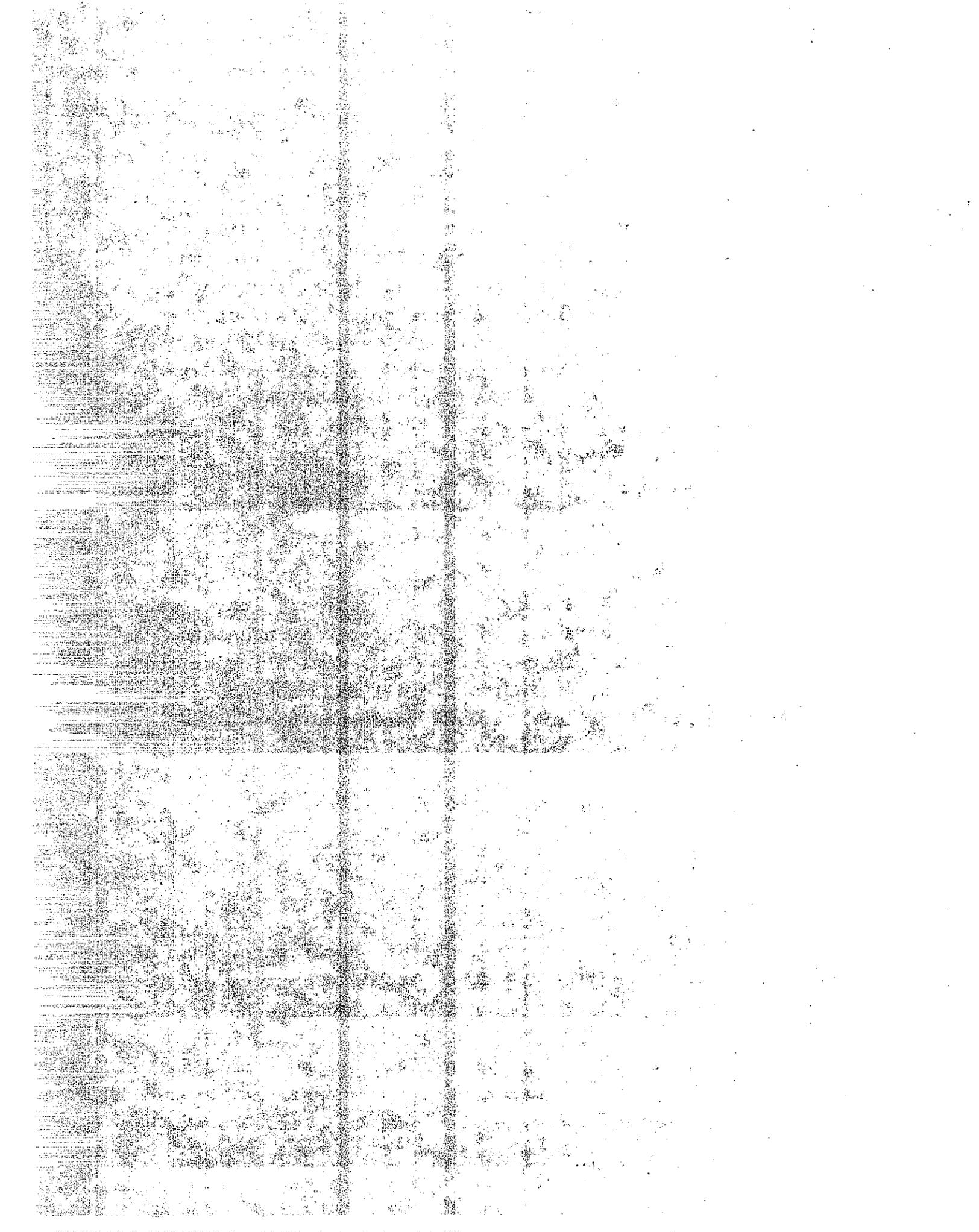
RESULTS AND DISCUSSION:

CMA was used for deicing on the Highway 88 test area at Caples Lake and the Highway 120 test area at Groveland. On Highway 88, there were five snow storms for which CMA was used, while on Highway 120, CMA was used for ice control only. Evaluation forms were submitted from Caples Lake and Groveland Maintenance stations, however, at Caples Lake operators only filled out the "Driver's Report" once for each storm and at Groveland, the maintenance supervisor filled out a "Driver's Report" weekly and submitted it instead of the "Supervisor's Evaluation". Nonetheless, sufficient information was available included in the evaluation forms submitted by maintenance personnel and from onsite evaluations by research personnel to meet the objectives of the study.

At Caples Lake, evaluations of CMA submitted by the supervisor were mixed. Of the five "Supervisor's Evaluations", three were favorable and two were unfavorable of CMA for use in deicing operations. The unfavorable responses were, however, submitted at the beginning of the test period, while all favorable responses were submitted after considerable experience had been gained in CMA use.

The "Driver's Reports" were less favorable toward CMA use. Of the five reports submitted, only one was favorable. However, these reports were submitted by two operators. One of the operators had a definite negative feeling about CMA and all three of his reports were negative: The second operator initially submitted an unfavorable report, but later after gaining experience, submitted a favorable report primarily due to a perceived improved performance over salt.

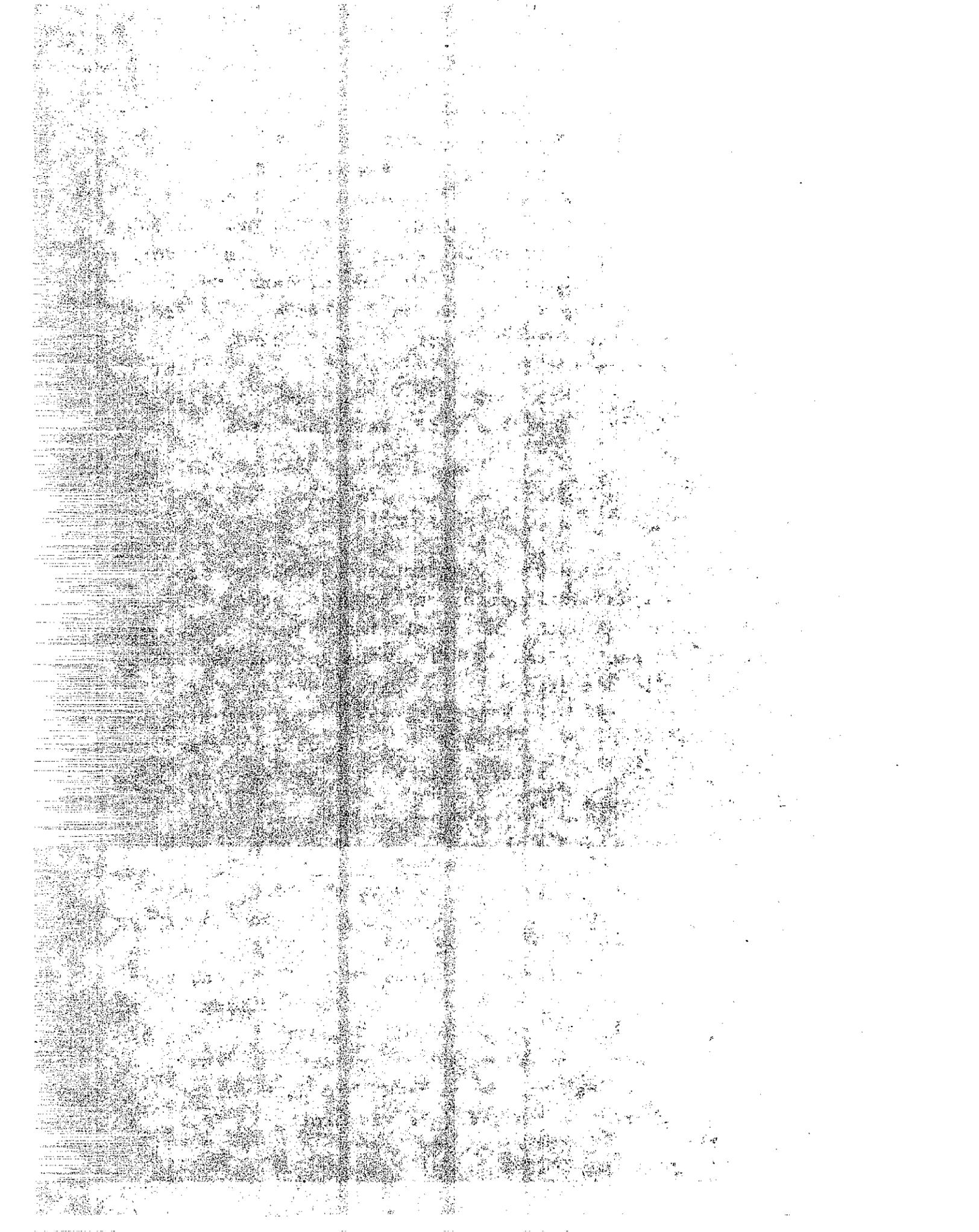
A significant problem initially was product caking resulting in material sticking to the truck bed wall and substantial amounts of dust produced during deicing operations when large chunks of



CMA were thrown from the spinner. This problem was attributable to the loading method used. Originally, the CMA was placed in the truck hopper alternating layers with cinders as was common practice with salt and cinder mixes. However, this practice caused the CMA to clump, to stick to the hopper sides and to be thrown by the spinner in large chunks. The loading procedures were modified by the crew so that CMA was premixed with cinders and then loaded in the truck. To mix CMA and cinders, the amount of CMA required to be mixed was loaded in the bucket of a front-end loader and then placed with a partial load of cinders. Additional cinders were then added to make up a full load. Final mixing of the CMA and cinders occurred as the mix was loaded into the hopper of the truck. The result of premixing was a relatively uniform mix which fed into the spinner well. There were no further problems from CMA forming clumps and all CMA was dispensed from the truck hopper along with the cinders.

After the loading methods were revised other associated problems were reduced. There was still some dusting associated with the CMA; however, mixing CMA with cinders eliminated much of the dust problem reported in earlier tests. Also, the spinner as well as hopper and feeder did not clog or even collect deposits of CMA during deicing operations. In all cases the CMA/cinder mix worked as well as the salt/cinder mix and both operators and supervisors felt that the CMA/cinder mixes worked better than salt/cinder mixes in some cases.

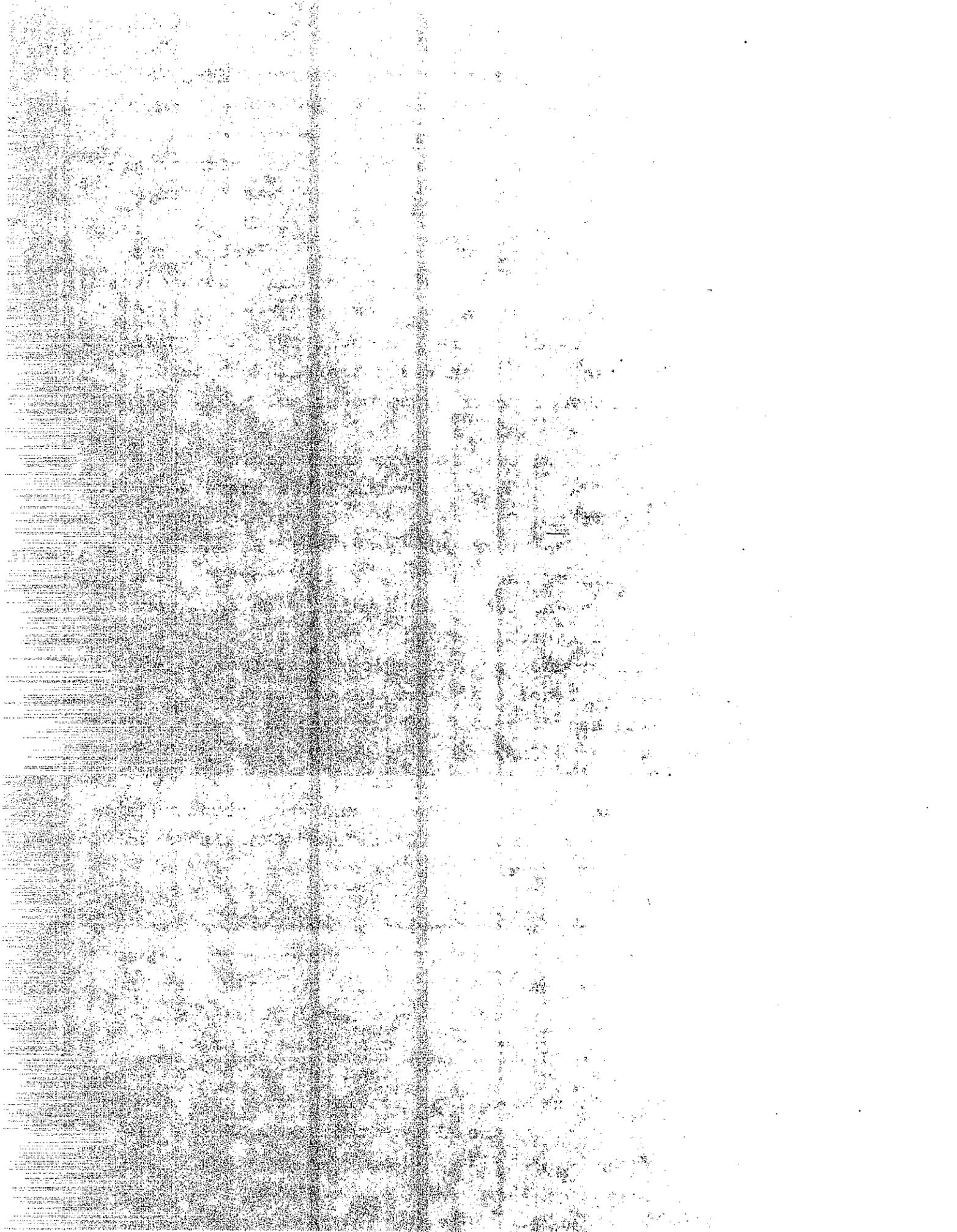
During one observation period by research personnel, when the outside air temperature was 26°F, there were some significant differences observed between deicing operations conducted using salt/cinder mixes as opposed to CMA/cinder mixes. Two different exposures were observed, a direct exposure to sunlight and a protected exposure. The highway surface exposed to sunlight melted rapidly after either salt or CMA was applied and at the time of observation the surface temperature of the roadbed was 40°F. There was a difference observed between CMA and salt which occurred in areas where the road surface was protected from



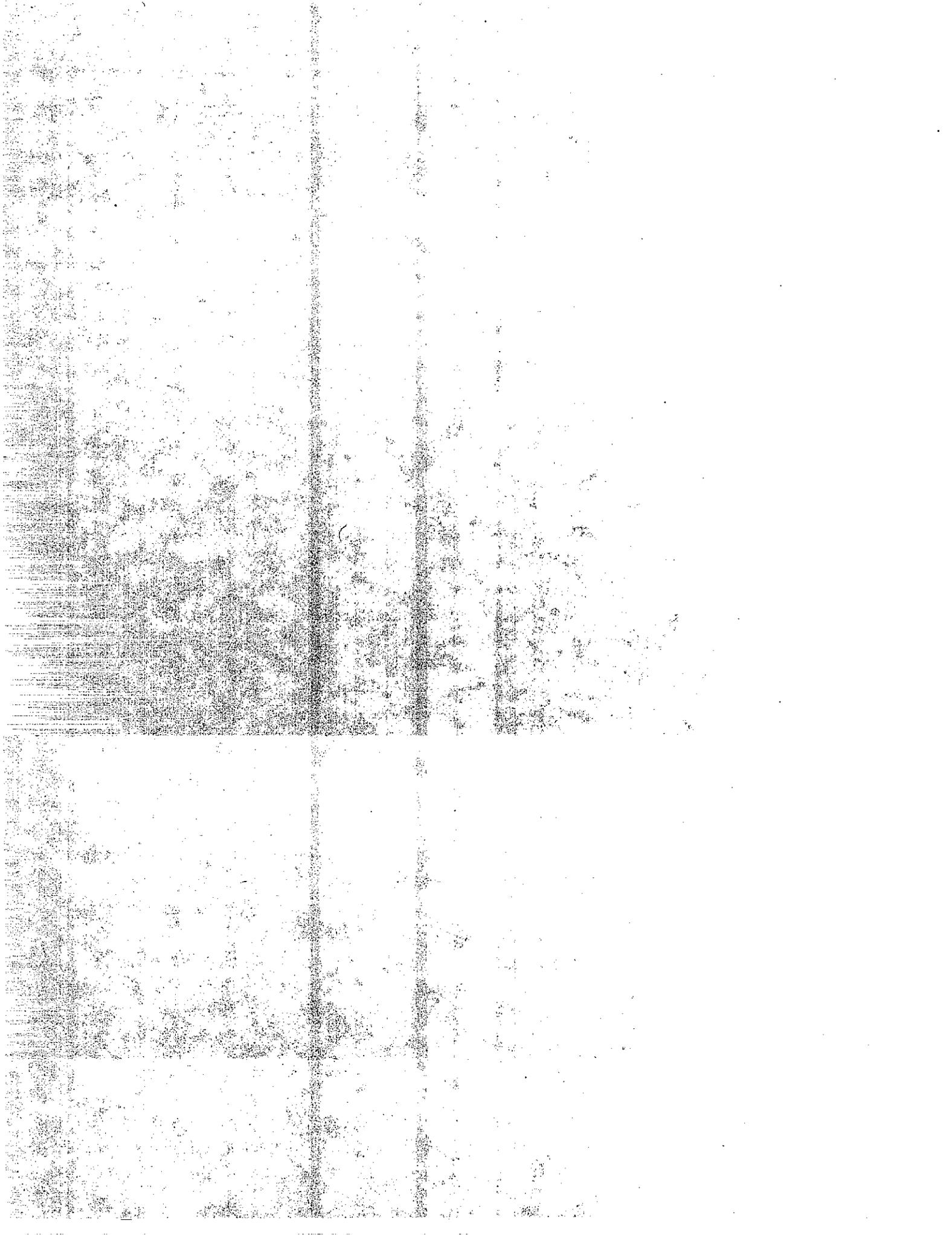
direct sunlight. In this case, the road surface temperature was the ambient temperature, 26°F. Neither CMA nor salt melted the pack as in the previous situation, however, the CMA caused the pack to become tacky and the cinders mixed with the pack apparently increasing traction. Using salt, the pack was not so affected and cinders had a tendency to bounce off the roadway. On the road, the spread pattern for CMA was good. Operators commented that the cinders spread were staying on the road and that pack removal using plows was easier when CMA had been applied than when salt had been used. There was, however, no significant difference noted between the CMA and salt when ambient temperature dropped to a point where refreezing occurred.

At Groveland, evaluations of CMA use were unfavorable. There were no "Supervisor's Evaluations" submitted, but there were five "Driver's Reports" detailing CMA use. The "Driver's Reports" submitted were, in fact, weekly summaries of deicing activity at the test area. The primary use for CMA was ice/frost prevention in curves and cold areas and the CMA was mixed with sand normally in a 1 to 3 CMA to sand ratio. Personnel using the CMA/sand mix did not feel that the product prevented ice/frost from forming any better than rock salt and that more CMA was required to produce the same results as rock salt. There were also significant handling problems with the CMA/sand mix. Most of the problems were apparently caused by mixing the agglomerate CMA with wet sand. The CMA absorbed moisture, clumped and then produced significant dust when it was applied. The clumped CMA also stuck to equipment making cleanup a problem.

Even considering the problems at Groveland, overall, we consider our first, limited experience with CMA to be encouraging. As such, we are intending to use CMA again this coming winter in larger-scale tests on Interstate 80 and other routes as well as again at Caples Lake on Highway 88. During the winter of 1986-87, we plan to use the newly developed pelletized CMA, which should limit dust problems as well as provide for a bulk storage capability. We will also try the CMA coated sand. While the



initial cost of CMA is high, commercial prices quoted for this coming year have dropped to about 1/3 the cost of the CMA we purchased last year and CMA will be available from U.S. producers. Even this cost is much higher than rock salt, but considering the cost of replacing bridge decks it may turn out that CMA will ultimately be more economical. Only time and additional testing can discover the answer.



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