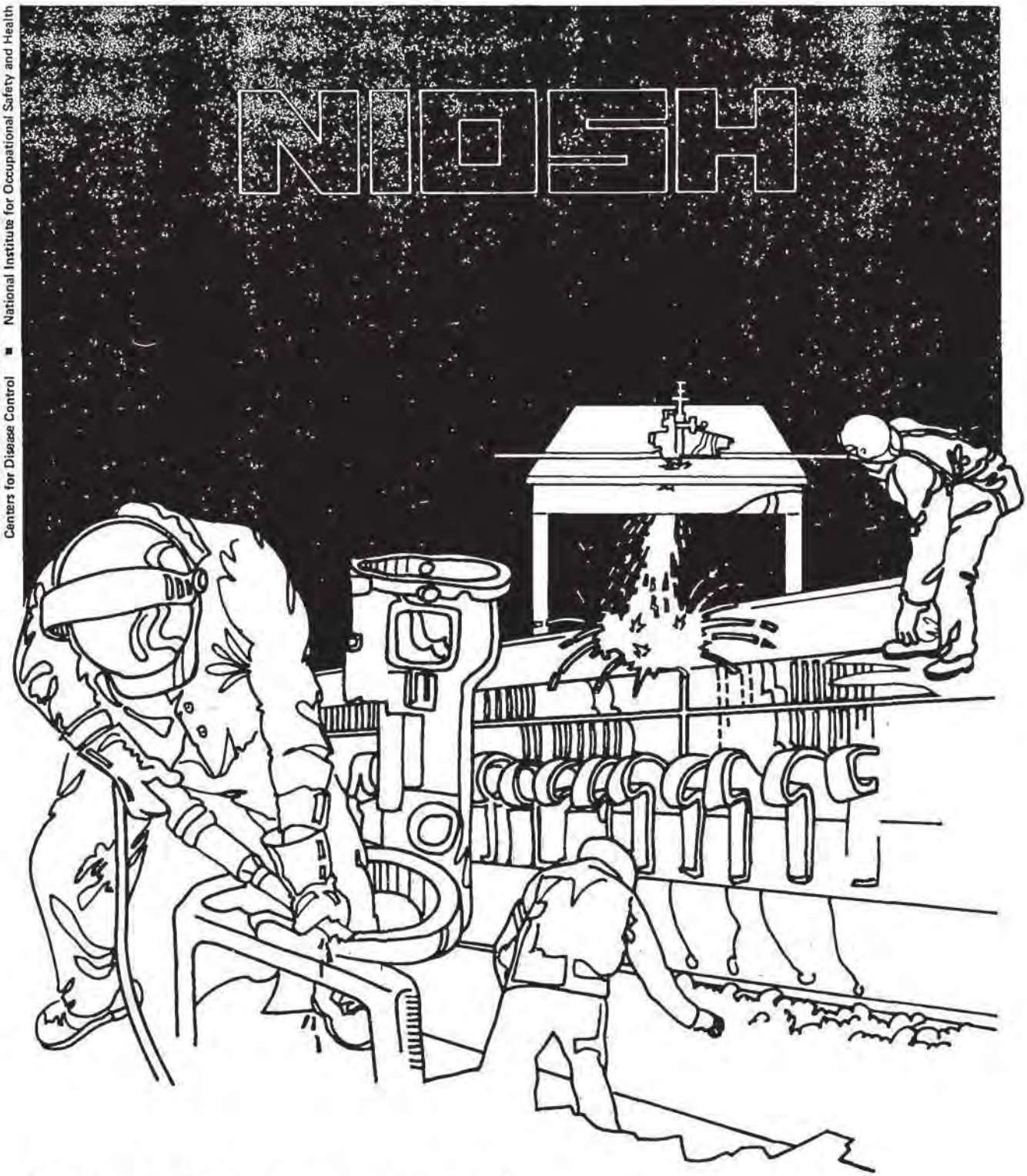
U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES ■ Public Health Service
Centers for Disease Control ■ National Institute for Occupational Safety and Health



Health Hazard Evaluation Report

HETA 81-176-968
ROCKY MOUNTAIN ARSENAL, BASIN F
COMMERCE CITY, COLORADO

PREFACE

The Hazard Evaluations and Technical Assistance Branch of NIOSH conducts field investigations of possible health hazards in the workplace. These investigations are conducted under the authority of Section 20(a)(6) of the Occupational Safety and Health Act of 1970, 29 U.S.C. 669(a)(6) which authorizes the Secretary of Health and Human Services, following a written request from any employer or authorized representative of employees, to determine whether any substance normally found in the place of employment has potentially toxic effects in such concentrations as used or found.

The Hazard Evaluations and Technical Assistance Branch also provides, upon request, medical, nursing, and industrial hygiene technical and consultative assistance (TA) to Federal, state, and local agencies; labor; industry and other groups or individuals to control occupational health hazards and to prevent related trauma and disease.

Mention of company names or products does not constitute endorsement by the National Institute for Occupational Safety and Health.

HETA 81-176-968
OCTOBER 1981
ROCKY MOUNTAIN ARSENAL, BASIN F
COMMERCE CITY, COLORADO

NIOSH INVESTIGATORS:
Theodore W. Thoburn, M.D.
Bobby J. Gunter, Ph.D., IH

I. SUMMARY

In January 1981 the National Institute for Occupational Safety and Health (NIOSH) received a request from employees of the State of Colorado, Division of Wildlife, to evaluate adequacy of precautions taken while investigating wildlife loss at Basin F, Rocky Mountain Arsenal, and to offer an opinion as to present and future health effects from this exposure.

On March 3, 1981, two of the three Wildlife Officers were interviewed in the NIOSH offices. Permission was given to obtain the results of rather extensive medical workups done on them by a local occupational physician. An analysis of the contents of the pond had been obtained from the environmental section at the Rocky Mountain Arsenal and was attached to the hazard evaluation request. Because of the amount of information already developed, it was elected to limit the NIOSH investigation to review of the data as it became available and have the report concentrate primarily on the toxicology of substances identified and suitable protective equipment.

On July 10, 1981, the NIOSH investigators visited the Rocky Mountain Arsenal, consulted with the Army Biologist, and were driven around the perimeter of Basin F.

Symptoms reported were severe headaches and throat irritation by the end of a two hour tour of the pond. The officers experienced skin irritation when picking up sick or dead ducks without gloves. Ducks which had more than brief contact with pond water died with necks outstretched. Other wildlife having contact with the pond water have also died.

The Army's analysis of the pond water showed 11.3 parts per million (ppm) di-isopropyl methyl phosphonate (DIMP), 0.368 ppm aldrin, 0.0746 ppm endrin, and 0.0744 ppm dieldrin. They identified the following volatile compounds but gave no concentrations: dicyclopentadiene, bicycloheptadiene, diethyl benzene, dimethyl disulfide, methyl acetate, methyl isobutyl ketone (MIBK), and toluene. Inorganics identified were 49500 ppm sodium, 52000 ppm chloride, 1470 ppm arsenic, 180 ppm potassium, 63 ppm fluoride, 2.4 ppm copper, and 0.27 ppm chromium.

On the basis of the environmental data, personal interviews, and review of medical records, NIOSH concluded that a health hazard exists for Wildlife Officers monitoring Basin F from exposure to dicyclopentadiene. Although the di-isopropyl methyl phosphonate is probably responsible for the wildlife loss, the protective clothing used should be effective in preventing significant human exposure. Recommendations to reduce the health hazard at this work site are included in this report.

KEYWORDS: SIC 0971 (Hunting and Trapping, and Game Propagation), dicyclopentadiene, di-isopropyl methyl phosphonate, DIMP, pesticide wastes, wildlife loss.

II. INTRODUCTION

Basin F is an asphalt-lined pond which until four years ago received liquid waste from the pesticide plant on the Rocky Mountain Arsenal grounds run by Shell Chemical Company. Currently the only liquid received is surface run-off and a little seepage from an old sewer. The liquid is gradually evaporating and the pond may be capped in 1984. The pond is within a 90 acre enclosure with about 60 acres of water remaining. Except for a little high ground within the chain-link fence, there is no plant growth within the enclosure and no shade.

Although the asphalt lining is designed to prevent seepage, the basin is surrounded by a series of bore-holes with pipes to allow for monitoring possible seepage. At intervals along the fence there are devices designed to make noise to scare away birds and also natural gas fired "cannons" for the same purpose.

This year has been unusually wet. There were a number of pools outside the enclosure. Ground cover was quite lush in natural drainage areas. Rabbits and prairie dogs were fairly common and appeared healthy. One pheasant was sighted. Ground cover did appear drier on high ground, and on the downhill side of Basin F, suggesting that Basin F did prevent the normal run-off.

The State Division of Wildlife has been investigating duck mortality at the Arsenal since 1959. Ducks which land on the pond and immediately fly away seem to do all right. However, if the ducks remain on the pond for any length of time, they become unable to fly, crawl out of the water and die with their necks stretched out in about 25 minutes. Other birds having contact with the pond and a few rabbits have also been found dead. Coyotes feeding on the carcasses do not seem to be affected.

The Wildlife Officers requesting the investigation toured the pond three times during 1980, each tour lasting about two hours. They wore rubber waders and, on occasions, shoulder length gloves and were responsible for counting and identifying the species of dead ducks. They have reported severe headaches and throat irritation by the end of a tour of duty (in May 1980 in particular), and irritation of the skin when picking up sick ducks. Skin exposure was also possible when cleaning the boots and gloves after the tour.

III. TOXICOLOGY

Tables I and II list Substances identified in Basin F by the Army on June 19 (organics) and July 23 (inorganics), 1980. Comparison concentrations are also listed. No concentrations were available for volatile compounds, but after three years with no discharges into the pond except rain water it is unlikely that most would have appreciable concentrations. Specific gravities, vapor pressures at 20°C (68°F), and solubility are listed in Table III. Drinking water standards[1], sea water[2], and dead sea water[3] were chosen for comparison of inorganics because they represent naturally occurring solutions to which many people are exposed without appreciable health problems. Air standards[4,5,6], are given for the organics for comparison purposes for lack of any more appropriate standards.

A. Organochlorine Compounds[5]

Aldrin, Dibromo chloropropane (DBCP), Dieldrin, Endrin, and Isodrin all fall into this classification. As a group these compounds are relatively resistent to degredation either environmentally or in the body and have a strong tendency to be stored in body fat. When dry there is little hazard from skin absorption. When dissolved in oil or organic solvents they can be readily absorbed through the skin. Primary damage tends to involve the liver and kidneys. Neurologic effects have included "behavioral changes, disturbances of sensory and equilibrium functions, involuntary activity of skeletal muscles, and depression of vital centers." Convulsions have been reported with heavy exposure. DBCP can cause sterility due to a reduction in the number of normal sperm produced, with longer exposures being associated with a greater effect. Aldrin, Dieldrin, and DBCP have been shown to be animal carcinogens. Endrin is felt to require further testing. (Isodrin was not mentioned.) Aldrin, Dieldrin, and Endrin have been shown to be teratogenic.

B. Organophosphorus Compounds[5]

Di-isopropyl methyl phosphonate (DIMP), although not specifically mentioned in the reference, belongs in this classification and can be expected to show similar toxicity. Toxicity is due to the compound's ability to inhibit the enzyme cholinesterase. As this inhibition is irreversible, symptoms can be produced by either a rapid inactivation of enzyme by a large dose, or a slow loss of enzyme function by repeated small doses large enough to exceed the body's ability to replace the inactivated enzyme. Acetylcholine is produced at nerve endings in the transmission of nerve impulses in the central nervous system, at ganglia of the autonomic nervous system, and to muscles and to glands and organs controlled by the parasympathetic nervous system. Symptoms occur from the accumulation of acetylcholine because the enzyme is no longer available to break it down immediately after it is formed.

Symptoms of acute intoxication include increased bronchial secretions, salivation, sweating, slowed heart rate, constricted pupils, muscular weakness, low blood pressure, anxiety, headache, slurred speech, disorientation, and possibly convulsions and death due to respiratory failure. Some organophosphorus compounds have been shown to cause degeneration of nerves on prolonged exposure and there is a suggestion that chronic depression of cholinesterase activity can lead to subtle behavioral changes.

The degree of cholinesterase inhibition is best measured in red cells.

C. Dicyclopentadine[7,8,9]

Exposed workers have reported slight eye and throat irritation. Transitory headaches have been reported for the first two months of exposure. Increased urinary frequency has also been reported. Repeat exposures in rats and dogs have caused kidney lesions.

Dicyclopentadiene is a solid at room temperature (melting point 32.9° C - 91.2° F) with an appreciable vapor pressure when heated only slightly (10 mm at 47.6° C - 117.7° F).[7]* As dicyclopentadiene is essentially insoluble in water at 20° C (68° F)[9], it is quite possible that sufficient dicyclopentadiene is present in the sludge of the pond and the dirt at the edges to create a noxious level of vapor on hot days. This compound can also be absorbed through the skin.

D. Organic Solvents

Organic solvents as a group have very similar health effects, although they vary in potency and in the degree of irritation in relation to the effects on the central nervous system. Effects of mixtures are probably additive. Locally they can be irritating to the mucous membranes of the eyes, nose, and throat and irritating to the bronchi and lungs. Systemically they cause central nervous system depression which can be manifest as fatigue, weakness, headache, dizziness, drowsiness, "drunkenness," coma, and possibly death at high enough concentrations. Nausea is also likely. They may be irritating to the skin and prolonged skin contact can cause a dermatitis by defatting the skin. One can expect some degree of absorption through the skin, although the more irritating are less likely to allow sufficiently long contact for this to be significant.

Diethyl benzene, methyl acetate, methyl isobutyl ketone (MIBK), and toluene fall in this class.[7] Of these, toluene is the least irritating so that symptoms are mostly confined to central nervous system depression.

All of these are either soluble in water or lighter than water[10] and so would be exposed to the atmosphere. As all have measurable vapor pressures at ambient temperatures,[10] they would evaporate over time.

E. Arsenic[11,12]

Arsenic is a systemic poison which inhibits sulfhydryl (=SH) containing enzymes which are necessary for a number of essential metabolic processes in the body. Arsenic occurs in measurable levels in most foods, the highest reported being in shellfish, with clams showing 80 ppm.[11] Symptoms of arsenic poisoning include a metallic taste in the mouth, with dryness of mouth and throat, an odor of garlic on the breath, stomach pains, diarrhea, muscular cramps, frontal headaches, dizziness, depression, shock, and convulsions. Skin problems include thickenings, increased pigmentation, and ulcerations. Arsenic is teratogenic and is associated with increases in the incidence of cancer of the lung and skin.

F. Fluorides[13,14,15]

The fluoride ion is a general protoplasmic poison, affecting many tissues. It is readily absorbed through the lungs and gut and readily excreted in urine and sweat. Some fluorides are found in

*Atmospheric pressure is 760 mm at sea level.

most foods, with fruits and vegetables being lower and meat and fish being higher. Tea is particularly high showing about 10 ppm.[13] Water supplies have been found to range from 0 to 33.5 ppm, mostly below 1.0 ppm.[13] Because of its efficacy in reducing dental caries, it is recommended that, if deficient, water supplies be brought up to a concentration of about 1 ppm fluoride.[16] A 2% sodium fluoride solution (9048 ppm fluoride) has been used to paint children's teeth to reduce the incidence of dental caries.[15]

Acute poisoning is unlikely unless one is exposed to hydrogen fluoride, strong fluoride solutions, or accidentally ingests a quantity of a fluoride, such as some roach powders. Symptoms may include local numbness, deep local burns, nausea, vomiting, diarrhea, abdominal burning and cramps, thick mucous discharge from nose and mouth, general collapse with pallor, weakness, decreased respiration and pulse. Death is generally within 2 to 4 hours with the chances of recovery good if the victim has survived the first 24 hours.[14]

Chronic poisoning is more likely. The more obvious effect of excessive fluoride exposure during the development of tooth enamel is mottling, a condition which can be unsightly, but does not appear to affect the strength of the enamel. Of potentially greater effect is the deposition of excess fluoride in the bone (osseous fluorosis). The spinal column and pelvis are affected more than other bones. Effects range from slightly increased density without symptoms to calcification of ligaments, fusing of joints and narrowing of the bown marrow cavities with interference with blood cell production.[13]

G. Dimethyl Disulfide (2,3-dithiabutane)[7,17]

Very little information is available. The concentration to kill 50% of rats (LC 50) exposed by inhalation is 805 ppm.[17] "Limited information, based mainly on animal experiments, suggests that this and similar [alkyl disulfides] compounds are dangerous and may cause hemolytic anemia. They may also produce allergic dermatitis."[7] As this substance is very slightly soluble in water and has a measurable vapor pressure at ambient temperatures,[10] it would gradually evaporate from the pond.

H. Bicyclo(2,2,1) heptadiene (Norbornadiene)[17]

Almost no information was available on this substance. The intravenous does to kill 50% (LD 50) of mice is 56 mg/kg. (If it takes about the same dose for man, it would be about 4 grams--just under a teaspoonful.)

IV. FINDINGS AND CONCLUSIONS

Review of the medical work-up on the two officers did not suggest any persisting medical problem arising from their acitivity at Basin F.

Considering the history as given by the officers on interview in the NIOSH office and contained in their medical evaluation, the toxicology as found in the literature, and the results of the site visit, the following conclusions are drawn:

1. The wildlife is probably dying from exposure to the Di-isopropyl methyl phosphonate (DIMP). It is the pesticide in greatest concentration and could be expected to act as quickly as the history indicated. It undoubtedly contributed to the local symptoms when handling contaminated material without gloves.

2. The Dicyclopentadiene was probably responsible, wholely or in large part, for the symptoms of throat irritation and headache. Being insoluble it is very possible that appreciable quantities are mixed in the sludge in the bottom of the pond and deposited in the soil at the pond's edge. On hot days, in particular, water temperatures likely approach the compound's melting point amd the dry soil might well exceed it. Appreciable quantities could be expected to evaporate and cause the symptoms. It also may have contributed to the local symptoms while handling contaminated materials without gloves.

3. Although not the sole cause of symptoms, a measure of excess exposure to environmental heat may have contributed to the symptoms--the headaches in particular. As there was no shade the officers were exposed to a full solar heat load the whole time there. The waders, and when worn, the gloves to the shoulders would considerably reduce the body surface available to dispose of excess body heat due to the environmental load and the officers' own heat production due to their activity and basal metabolism. The waders would have covered 35-40% of the body surface greatly hindering its ability to lose heat by radiation or conduction and essentially eliminating its ability to lose heat by evaporation of sweat. Shoulder length gloves would cover another 18% or so.

V. RECOMMENDATIONS

1. If possible, the necessity of performing this job should be eliminated. Perhaps the quackers could be made to sound more like a danger call to the ducks. Perhaps "safe" ponds could be provided nearby (as certainly happened this year due to the rain) to lure the ducks and other wildlife to less dangerous waters.

2. If the job is to be done, it should be done in the cool of the morning, preferably on days when a breeze could be anticipated.

3. Waders and gloves do seem logical protective clothing although recent penetration studies suggest protection should not be considered complete. Care should be taken when removing and cleaning them. Perhaps some clean water and detergent could be brought to the basin to be used to clean off the gear while still within the perimeter of the fence before the gear is removed.

4. Organic cartridge respirators may help the irritative symptoms and the headaches. However the discomfort from wearing them in hot weather may outweigh their advantages if used on those days.

VI. REFERENCES

1. Hardenbergh, W.A. & Rodie, E.B., Water Supply and Waste Disposal. International Textbook Co., Scranton, PA., 1963. pp. 479-480.

2. Encyclopaedia Britannica. William Benton, Chicago. 1962. Vol. 16, page 691.

3. Ibid., Vol. 19, page 897.

4. OSHA Safety and Health Standards (29 CFR 1910) - General Industry, OSHA Publication 2206, Revised July 1, 1980, U.S. Department of Labor.

5. Criteria for a Recommended Standard...Occupational Exposure during the Manufacture and Formulation of Pesticides, DHEW (NIOSH) Publication No. 78-174, 1978.

6. Threshold Limit Values for Chemical Substances in Workroom Air Adopted by ACGIH for 1981, American Conference of Governmental Industrial Hygienists, Cincinnati, 1981.

7. Sax, N.I., Dangerous Properties of Industrial Materials, 4th Ed., Van Nostrand Reinhold Co., New York, 1975.

8. "Supplements for those substances added or changed, year 1974," Documentation of the Threshold Limit Values for Substances in Workroom Air, 3rd Ed., American Conference of Governmental Industrial Hygienists, Cincinnati, 1981.

9. Patty, F.A., ed., Industrial Hygiene and Toxicology, 2nd Ed., Interscience Publishers, New York. 1963. Vol. II, pp. 1209, 1216-1217.

10. Dean, J.A. (ed.), Lange's Handbook of Chemistry (12th edition). McGraw-Hill Book Company, New York, 1979, Section 7, Table 7-4, and Section 10, Table 10-8.

11. Reeves, A.L., "The Toxicology of Arsenic - Noncarcinogenic Effects," in Carnow, B.W., ed., Health Effects of Occupational Lead and Arsenic Exposure - A Symposium. DHEW (NIOSH) Publication No. 76-134 (1976), pp. 237-246.

12. Criteria for a Recommended Standard...Occupational Exposure to Inorganic Arsenic - New Criteria 1975. DHEW (NIOSH) Publication No. 75-149 (1975).

13. Criteria for a Recommended Standard...Occupational Exposure to Inorganic Fluorides. DHEW (NIOSH) Publication No. 76-103 (1975).

14. Gleason, M.N., Gosselin, R.E., Hodge, H.C., and Smith, R.P., Clinical Toxicology of Commercial Products, Acute Poisoning, 3rd Ed., Williams and Wilkins, Baltimore, 1969, pp. 112-116.

15. Goodman, L.S. and Gilman, A., The Pharmacological Basis of Therapeutics, 2nd Ed., The MacMillan Co., New York, 1955, pp. 828-830.

16. Hardenbergh, et al, op. cit. pp. 194-295.

17. Registry of Toxic Effects of Chemical Substances, 1979 Ed., DHHS (NIOSH) Publication No. 80-111.

18. Criteria for a Recommended Standard...Occupational Exposure to Ketones. DHEW (NIOSH) Publication No. 78-173.

VII. AUTHORSHIP AND ACKNOWLEDGMENTS

Report Prepared By: Theodore W. Thoburn, M.D.
Medical Officer
NIOSH, Region VIII
Denver, Colorado

Evaluation Assistance: Bobby J. Gunter, Ph.D.
Regional Industrial Hygienist
NIOSH, Region VIII
Denver, Colorado

Originating Office: Hazard Evaluation and Technical Assistance Branch (HETAB)
Division of Surveillance, Hazard Evaluations, and Field Studies (DSHEFS)
NIOSH, Cincinnati, Ohio

Report Typed By: Marilyn K. Schulenberg
Occupational Health Technician
NIOSH, Region VIII
Denver, Colorado

VIII. DISTRIBUTION AND AVAILABILITY

Copies of this report are currently available upon request from NIOSH, Division of Technical Services, Information Resources and Dissemination Section, 4676 Columbia Parkway, Cincinnati, Ohio 45226. After 90 days the report will be available through the National Technical Information Service (NTIS), Springfield, Virginia. Information regarding its availability through NTIS can be obtained from NIOSH, Publications Office, at the Cincinnati address.

Copies of this report have been sent to:

1. Rocky Mountain Arsenal.
2. U.S. Department of Labor/OSHA - Region VIII.
3. NIOSH - Region VIII.
4. Colorado Department of Health.
5. State Designated Agency.

For the purpose of informing affected employees, a copy of this report shall be posted in a prominent place accessible to the employees for a period of 30 calendar days.

TABLE I

Organic Substances Identified in Basin F

Rocky Mountain Arsenal
Commerce City, Colorado

June 19, 1980

Substance	Concentration Found ppm*	OSHA Air Standard[4] ppm	Recommended Air Level, NIOSH ppm**	ACGIH[6] ppm**
Non-volatile Organics				
Di-isopropyl methyl phosphonate (DIMP)	11.3	--	--	--
Aldrin	0.368	0.02(S)+	--	0.02(S)
Endrin	0.0746	0.006(S)	--	0.006(S)
Dieldrin	0.0744	0.02(S)	--	0.02(S)
Isodrin	less than 0.0005	--	--	--
Dibromo Chloropropane (DBCP)	less than 0.0002	0.001	0.010[5]	--
Volatile Organics				
Bicycloheptadiene	Not Given	--	--	--
Dicyclopentadiene	Not Given	--	--	5
Diethyl benzene	Not Given	--	--	--
Dimethyl disulfide	Not Given	--	--	--
Methyl acetate	Not Given	200	--	200
Methyl isobutyl ketone (MIBK)	Not Given	100	50[18]	50
Toluene	Not Given	200(S)	100	100(S)

+(S) = skin absorption a factor
* = parts per million - solution or air
** = Any concentration expressed in mg/M^3 (milligrams per cubic meter of air) was converted to approximate ppm (parts per million parts air) for ease of comparison.

TABLE II

Inorganic, Non-volatile Substances Identified in Basin F

Rocky Mountain Arsenal
Commerce City, Colorado

July 23, 1980

Substance	Concentration Found ppm*	Drinking Water Standard[1] ppm	Average Sea Water[2] ppm	Dead Sea Water[3] ppm
Sodium (Na)	49500	--	10680	24000
Chloride (Cl)	52000	250	19215	84700
Arsenic (As)	1470	0.05	0.003	--
Potassium (K)	180	--	385	4460
Fluoride (F)	63	1.5	1.3	--
Copper (Cu)	2.4	3.0	0.003	--
Magnesium (Mg)	0.27	125	1290	24700
Chromium (Cr)	less than 0.5	0.05	0.00005	--
Iron (Fe)	less than 0.1	0.3**	0.001	--
Mercury (Hg)	less than 0.1	--	0.00003	--
Silver (Ag)	less than 0.1	--	0.00003	--
Manganese (Mn)	less than 0.01	0.3**	0.002	--
pH (measure of acidity - alkalinity)+	8.0	10.6	--	--

* = parts per million of solution
** = Iron and Manganese together are not to exceed 0.3 ppm
+ = less than 7.0 - acid; 7.0 - neutral; greater than 7.0 - alkaline

TABLE III

Specific Gravity, Vapor Pressure, and Solubility of the Volatile Organics in Basin F[10]

Rocky Mountain Arsenal
Commerce City, Colorado

Substance	Specific Gravity (at 20°C compared to water at 4°C)	Vapor Pressure mmHg at 20°C	Solubility in Water at 20°C
Diethyl benzene	0.862 - 0.881	0.69 - 0.75	insoluble
Diethyl disulfide	0.993	3.13	very slightly soluble
Methyl acetate	0.933	172.31	33 part/100 parts water
Methyl isobutyl ketone	0.801	14.41	2 parts/100 parts water
Toluene	0.866	21.83	insoluble

"END OF DOCUMENT"

DEPARTMENT OF HEALTH AND HUMAN SERVICES
PUBLIC HEALTH SERVICE
CENTERS FOR DISEASE CONTROL
NATIONAL INSTITUTE FOR OCCUPATIONAL SAFETY AND HEALTH
ROBERT A. TAFT LABORATORIES
4676 COLUMBIA PARKWAY, CINCINNATI, OHIO 45226

OFFICIAL BUSINESS
PENALTY FOR PRIVATE USE, $300

Third Class Mail

U.S. MAIL

POSTAGE AND FEES P
U.S. DEPARTMENT OF
HHS 396