Environmental Health Perspectives
Vol. 57, pp. 91-95, 1984

Measuring Exposures to Glycol Ethers

by David E. Clapp,* Dennis D. Zaebst* and Robert F. Herrick*

In 1981, NIOSH began investigating the potential reproductive health effects resulting from exposures to a class of organic solvents known generically as glycol ethers (GE). This research was begun as a result of the NIOSH criteria document development program which revealed little data available on the health effects of glycol ether exposure. Toxicologic research was begun by NIOSH and other researchers which suggested substantial reproductive effects in animals. These animal data motivated a study of human exposures in the occupational setting. In 1981 and 1982 NIOSH conducted several walk-through surveys which included preliminary measurements of exposures in a variety of industries including painting trades, coal mining, production blending and distribution facilities, aircraft fueling, and communications equipment repair facilities. The human exposure data from these surveys is summarized in this paper with most results well below 1 parts per million (ppm) and only a few values approaching 10 ppm. Blood samples were collected at one site resulting in GE concentrations below the limit of detection.

Exposures to airborne glycol ethers, in the industries investigated during the collection of this data, revealed several problems in reliably sampling GE at low concentrations. It became apparent, from the data and observations of work practices, that air monitoring alone provided an inadequate index of GE exposure. Further field studies of exposure to GE are anticipated, pending location of additional groups of exposed workers and development of more reliable methods for characterizing exposure, especially biological monitoring.

Introduction

The Industrywide Studies Branch (IWSB), of NIOSH's Division of Surveillance, Health Hazard Evaluations and Field Studies (DSHEFS), is specifically charged under the OSHA Act of 1970 to perform epidemiological and industrial hygiene studies of broad groups of workers in industries with potentially hazardous exposures. This branch has completed a number of important investigations under this mandate including studies of exposures to benzene, asbestos, ionizing radiation, vinyl chloride, and carbon disulfide, to name a few. Most of these earlier studies were devoted to suspected carcinogens and sometimes included a search for a relationship between air sampling data and measures of carcinogenic potential such as the Ames Mutagenicity Assay (in urine samples).

More recently, NIOSH has directed research studies toward potential reproductive toxins. Currently, IWSB is studying exposures to ethylene dibromide and radiofrequency radiation both of which are suspected of producing adverse reproductive effects. The study of the reproductive effects of glycol ethers arose as a result of the NIOSH criteria document development program. In reviewing chemicals for study, few data were available on the health effects of glycol ethers. Toxicological research was begun by the NIOSH Division of Biomedical and Behavioral Science (DBBS). At about the same time, an IWSB search was begun for an exposed cohort of workers with sufficient exposures to the glycol ethers for a possible reproductive epidemiological study.

The objectives of this search included the identification of an adequate number of workers for a study which could lead to a conclusion regarding the relationship between exposure and reproductive impairment. This objective was complex, since human effects were basically unknown, and an element of the research was the prospective identification of effects which might befall a population with sufficient exposure. Implicit in this problem is the question "What exposure concentration is sufficient to produce effects in humans"? Since the answer to this question was unknown, the field research was primarily structured as an extent of exposure survey in various industries where glycol ethers were known to be present. Based upon the results of those investigations, the feasibility of a broader reproductive epidemiology survey would be considered.

This paper describes the effort to quantify human exposures to glycol ethers in a variety of industries. Some of the surveys were conducted only to collect glycol ether exposure data. In other cases, glycol ether exposure data were collected as a part of surveys directed toward studying other chemical or physical hazards. This paper describes the difficulties encoun-

*Industrial Hygiene Section, Industrywide Studies Branch, Division of Surveillance, Hazard Evaluations and Field Studies, National Institute for Occupational Safety and Health, Cincinnati, OH 45226.

tered in assessing exposures to glycol ethers in several industrial settings. In several cases, field data were collected; however, the low volatility of the glycol ethers clearly limits the effectiveness of air sampling as an assessment of personal exposure. Also, the absence of a biological monitoring method for assessing exposure to glycol ethers further reduces chances for characterizing human exposure by collecting and analyzing urine or blood samples.

Physical Properties of Glycol Ethers

The physical properties of glycol ethers are reviewed here as they relate to difficulties in industrial hygiene measurements. The most frequently produced glycol ethers (monoethyl, monobutyl and monomethyl) are colorless liquids at room temperature. Furthermore, all have relatively low vapor pressures of 4, 0.6 and 6 mm of mercury at 20°C, respectively. These low vapor pressures, as compared to other solvents such as benzene (75 mm of mercury), indicate that the glycol ethers are not readily vaporized into the breathing zone of workers who handle the chemicals at or near room temperature. In addition, airborne exposures alone were not expected to accurately reflect total exposure. Since the most widely used glycol ethers are liquids at room temperature, absorption of these chemicals through the skin was recognized as a major route of entry into the body. The skin absorption hazard of glycol ethers is evidenced by the OSHA standards and ACGIH threshold limit values which include a "skin" notation, indicating that the glycol ethers are readily absorbed through the cutaneous route.

Exposure Standards

Permissible exposure limits (PEL) for glycol ethers have been promulgated by the Occupational Safety and Health Administration (OSHA). The American Conference of Governmental Industrial Hygienists (ACGIH) recommends (*1*) Threshold Limit Values (TLV) which are based on recent toxicologial and epidemiological data and are therefore frequently lower than the OSHA PEL. Furthermore, ACGIH has published intentions to reduce the TLV for the more toxic glycol ethers. The OSHA PEL and ACGIH TLV values are summarized in Table 1 for the glycol ethers for which values are published. The data in Table 1 provide a relative scale of toxicity for the members of the glycol ether family. These exposure standards provide a basis for interpreting the measured airborne exposure levels discussed in this paper.

Results of Field Sampling Surveys

In presenting the results of field sampling, the surveys will be discussed in chronological order beginning with those surveys specifically devoted to sampling for glycol ethers. These results are summarized from reports which are on file in IWSB. Complete reports may be obtained using the citation data included in the reference section of this paper. Following a discussion of these specific glycol ether surveys, results of glycol ether levels from surveys intended for other purposes will be summarized.

The first survey of glycol ether exposures in February 1981 investigated the use of 2-butoxyethanol as a component of Wen-Don Corporation's Dustallay, a wetting agent (*2*). Wetting agents function as a surfactant which act as caking agents to reduce or eliminate dust suspended in the air. This survey was conducted by the NIOSH Division of Respiratory Disease Studies (DRDS) in Morgantown, WV. The survey was motivated by complaints of rash and skin irritation (face, foot, hands, buttocks) among workers potentially exposed to Dustallay. These signs subsided approximately 1 week after onset and have not recurred. The samples collected during the NIOSH survey of Dustallay exposures revealed no detectable levels of exposure to 2-butoxyethanol. Upon subsequent investigation it was discovered that the Wen-Don Corporation had substituted diethylene glycol monobutyl ether for 2–butoxyethanol in Dustallay shortly prior to the NIOSH survey. Since the manufacturer made this substitution without notification, the NIOSH field team could not have anticipated the change. Subsequent re-analysis of samples for diethylene glycol monobutyl ether revealed no detectable amounts of this substitute glycol ether.

The next NIOSH survey of glycol ethers was conducted by IWSB industrial hygienists in June of 1981 (*3*). This study was directed toward potential exposures in a manufacturing setting where large volumes of glycol ethers are handled. The facility

Table 1. Current exposure standards for glycol ethers.

Chemical	Exposure standards, ppm		
	OSHA PEL	ACGIH TLV	ACGIH intended change
2-Butoxyethanol	50	25	—
2-Ethoxyethanol	200	50	5
2-Ethoxyethyl acetate	100	50	5
2-Methoxyethanol	25	25	5
2-Methoxyethyl acetate	25	25	5
Isopropoxyethanol[a]	—	25	—

[a]Not widely used in industry.

studied is a large chemical complex in the Kanawa Valley near Charleston, WV. The plant is primarily engaged in the production, chemical mixing, and redistribution of specialty chemicals. Large volumes of glycol ethers were on hand and were in various uses in the plant. These uses included transesterification, refining (to produce brake fluids), bulk terminal facility, the mixing and loading area, and the drum filling facility. The transesterification and refining operations were expected to be unlikely locations for exposure since both processes were well contained, continuous flow operations with few employees present during routine operations. The bulk terminal was judged to be a location of potential exposure (25 employees in the area); however, glycol ethers were infrequently handled and when handled, exposures were of short duration. The mixing and loading area was an operation with an exposure potential similar to the bulk terminal facility. Employees in this operation largely opened and closed valves to deliver materials to mixing tanks and tank trucks. Visual inspection suggested possible high exposures at switchbanks where connections were made between pipelines, tanks, and loading racks. As with the bulk terminal, operations at the switchbanks were infrequent and involved few personnel.

In the plant as a whole, the most likely site of exposure to glycol ethers was expected in the drum filling operations. In this area, bulk materials are packaged into containers ranging in size from 8–oz glass bottles to 55–gal steel drums. In filling the drums, the quantity of chemicals and the design of the filling equipment occasionally led to minor spills on surfaces of drums or floors. Local exhaust ventilation was in place to minimize exposure to vapors resulting from these accidental spills.

Due to laboratory difficulties, the NIOSH samples collected on this survey were not analyzed. The plant industrial hygienist who accompanied NIOSH on this survey collected duplicate samples, and those results were included in the NIOSH report and are shown in Table 2.

A second IWSB survey was conducted at Randolph Air Force Base, TX, in December 1981 (*4*). This survey focused on 2-methoxyethanol which is blended into military jet fuel as an anti-icing additive. The potential for exposure in this process is extremely low due to the low concentration of 2-methoxyethanol in jet fuel. An analysis of a bulk fuel sample collected on this survey revealed a concentration of 0.63 mg/g of 2-methoxyethanol in the aircraft fuel. This level of concentration is consistent with the manufacturer's specifications. Personal samples were collected at several points in the refueling operation reflecting exposures well below 1 ppm. A single high result, 4.7 ppm, occurred when a bypass valve was opened during a refueling operation. These results confirm an expected low level of exposure to glycol ethers in aircraft refueling operations.

A third and final IWSB survey was conducted in May 1982 at a communications equipment service center in Georgia (*5*). In this facility, approximately half of the 300 workers occasionally used 2-ethoxyethanol to clean small parts. The glycol ether was supplied at the workstations in small metal cans ranging in size from 4 oz to 14 oz. The solvent was used by dampening a tissue or shop rag with solvent then wiping the surface to be cleaned. No local ventilation or personal protective equipment was routinely used, although general dilution ventilation was in use throughout the plant. Rubber gloves were available for worker use. However, no workers were observed using the gloves during the survey. Workers typically used from 4 to 16 oz per month of 2-ethoxyethanol, depending on the type of operation and the work practices of the individual worker.

Since air sampling in previous surveys revealed extremely low breathing zone concentrations, biological sampling was attempted in this survey. Research by Nakaaki (*6*) has suggested that glycol ethers can be detected in blood after exposure of the liquid on the skin. While the reported research investigated skin absorption of 2-methoxyethanol, NIOSH scientists felt similar analysis was applicable for 2-ethoxyethanol. For this survey, blood samples were drawn late in the day in order to reflect exposure from a total shift. The results of analysis of the blood samples indicated all values below the limit of detection (less than 5 μg of 2-ethoxyethanol/mL of blood).

The personal breathing zone samples revealed concentrations of 2-ethoxyethanol ranging from 0.18 to 0.58 ppm. These values, as with all IWSB breathing zone results for glycol ethers, were well below OSHA's PEL and ACGIH TLV (existing or intended changes). These results, coupled with the biological sampling results, suggested that this work environment was not a likely site for study of human effects of exposure to glycol ethers. This conclusion was disappointing, since a large population of workers performs similar operations throughout the United States at the company's other facilities.

As noted earlier, other IWSB studies included limited

Table 2. Glycol ether exposure data for manufacturing plant.

	Glycol ether exposure, ppm			
	Personal		Area	
	Low	High	Low	High
2-Butoxyethanol	ND	0.1	ND	1.7
2-Ethoxyethanol	ND	0.6	0.5	1.5
2-Ethoxyethyl acetate	ND	1.2	0.4	1.1
2-Methoxyethanol	0.1	2.8	—	—

Table 3. Glycol ether exposure data: highest values by area of the manufacturing plant.

	Glycol ether exposure, ppm			
	MICC (personal)	Switchbank (area)	Lab sink (area)	Drumming (personal)
2-Butoxyethanol	0.1	0.1	0.9	—
2-Ethoxyethanol	0.6	1.1	1.5	—
2-Ethoxyethyl acetate	1.2	1.1	0.8	—
2-Methoxyethanol	—	—	—	2.8

sampling for glycol ethers. In these surveys, the glycol ethers were typically solvents or carriers in paints or inks. A series of surveys for exposures in the spray painting industries included sampling for monomethyl, monobutyl and monoethyl glycol ethers. The results of these surveys revealed typical concentrations of 2.3, 0.75 and 0.37 ppm for each of these glycol ethers, respectively. Another setting for exposures to glycol ethers was in a screen printing operation which was investigated in a study of radiofrequency heat sealers (*7*). The principal intent of these studies was the investigation of potential human reproductive effects due to exposure to RF radiation. Since glycol ethers manifest reproductive effects in humans, a quantitation of these chemicals was deemed prudent in order to rule out potential confounding effects of exposure to chemical teratogens. The principal glycol ethers used in this operation were 2-butoxyethanol and 2-butoxyethyl acetate. The highest exposures to these chemicals were 1.4 ppm and 0.75 ppm, respectively. These results are in a similar magnitude of exposures measured in other settings and did not indicate a sufficiently high level to confound potential effects due to exposure to nonionizing radiation.

NIOSH has conducted health hazard evaluations (HHE) of industries where exposure to glycol ethers were investigated. These studies were typically in response to worker complaints and did not involve large numbers of samples nor an assessment of the appropriateness of the exposed group of workers for a follow-up reproductive epidemiology study. Some of the exposures in these surveys, however, ranged up to 10 ppm. Interested readers may request copies of reports of these studies from NIOSH's Hazard Evaluation and Technical Assistance Branch (HETAB) within DSHEFS.

Conclusions

These field studies corroborate that glycol ethers are widely used in U.S. industries. Typically, the concentration of glycol ether in the finished product is very low, and, because of this and the low volatility of these chemicals, breathing zone measurements are extremely low.

Breathing zone monitoring of airborne glycol ether exposures, by itself, is an unsatisfactory method for estimating worker exposure. Since the glycol ethers are relatively nonvolatile, the likelihood of inhalation as a major route of entry into the body is small. Skin absorption is a recognized route of entry, but no satisfactory methods for estimating body burden have been established.

The search for a biological monitoring method for glycol ethers is continuing. It is evident that these chemicals will be present in the blood of workers who are exposed. However, the low exposures result in similarly low blood levels which are below the limit of detection of currently available instrumentation. Metabolites of glycol ethers in urine are still elusive. There is some promise that such metabolites will be identified, but other chemicals (e.g., certain pharmaceuticals) which may result in similar metabolites must be ruled out before urine monitoring will be feasible. The most promising industrial setting for a study of glycol ether exposures appears to be the telephone repair industry. In this industry, glycol ethers are used as pure compounds with relatively little control (e.g., ventilation, gloves) of possible exposure. In the absence of a biological monitoring method which is effective at these low exposure levels, a quantification of worker exposure appears infeasible at this time.

The NIOSH Industrywide Study Branch is remaining alert to possible additional sites for surveys or for promising biological monitoring methods. If either sites or methods look promising, additional field studies will be undertaken. It is hoped that these studies will identify sufficient exposure to undertake a reproductive health study. The results of such a survey may ultimately provide an answer to the question of reproductive health impact due to exposure to glycol ethers.

REFERENCES

1. ACGIH. Threshold Limit Values for Chemical Substances and Physical Agents in the work Environment with Intended Changes for 1982. American Conference of Governmental Industrial Hygienists, Cincinnati, 1982.
2. NIOSH. Potential miner exposure to 2–butoxyethanol while controlling dust with spray containing wetting agents at carbon fuel #31 mine. Mining Environmental Target Surveillance Investigation, Chesapeake, WV, Division of Respiratory Disease Studies, Environmental Investigations Branch, NIOSH, Morgantown, WV, March 1982.
3. NIOSH. Walk-through survey report of glycol ether processing and distribution facilities, Union Carbide Corporation, South Charleston Plant, South Charleston, WV. Industrial Hygiene Section, Industrywide Studies Branch, Division of Surveillance, Hazard Evaluations and Field Studies, NIOSH, Cincinnati, January 1982.
4. NIOSH. Draft walk-through survey report of aircraft refueling,

Randolph Air Force Base, TX. Industrial Hygiene Section, Industrywide Studies Branch, Division of Surveillance, Hazard Evaluations and Field Studies, NIOSH, Cincinnati, July 1983.
5. NIOSH. Walk-through survey report, Western Electric Company, Atlanta Service Center, Atlanta, Ga. Industrial Hygiene Section, Industrywide Studies Branch, Division of Surveillance, Hazard Evaluations, and Field Studies, NIOSH, Cincinnati, January 1983.
6. Nakaaki, K., Fukabori, S., and Toda, O. An experimental study on percutaneous absorption of some organic solvents. J. Sci. Labour 56(No. 122): 1–9 (1980).
7. NIOSH. Industrial hygiene survey report in support of epidemiologic study of RF heat sealer operations. Industrial Hygiene Section, Industrywide Studies Branch, Division of Surveillance, Hazard Evaluations and Field Studies, NIOSH, Cincinnati, February 1981.