

GLYCOL ETHERS AS GROUNDWATER CONTAMINANTS

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Abstract

Ether derivatives of dihydroxy alcohols, which are formed from ethylene or propylene, comprise an important group of groundwater contaminants known as glycol ethers. Compounds in this group are used as solvents, cleaning agents, and emulsifiers in many chemical products and manufacturing operations. Glycol ethers have been associated with a variety of toxic effects, and some compounds in the group are relatively potent teratogens. The limited information available suggests that glycol ethers are common contaminants in groundwater, especially in anaerobic plumes emanating from disposal of mixed industrial and household waste. Most methods used to analyze groundwater samples cannot adequately detect $\mu\text{g/l}$ (ppb) concentrations of glycol ethers, and the existing methods perform worst for the most widely used and toxic species. A new method capable of analyzing $\mu\text{g/l}$ concentrations of glycol ethers was recently developed, and its use is recommended for groundwater samples where glycol ethers are likely to be present.

Résumé. Les éthers glycol, polluants des eaux souterraines. Les dérivés d'éther de dihydroxy-alcool, formés à partir de l'éthylène ou du propylène, constituent un important groupe de polluants des eaux souterraines connus sous le nom d'éthers glycol. Les composés de ce groupe sont utilisés comme solvants, comme agents de nettoyage et comme émulsifiants dans de nombreux produits chimiques et dans de nombreux processus de fabrication. Des effets toxiques variés ont été attribués aux éthers glycol et certains des composés sont des agents tératogènes relativement puissants. Les données disponibles, qui sont limitées, indiquent que les éthers glycol sont des polluants communs dans les eaux souterraines, particulièrement dans les panaches anaérobies émis par les décharges mixtes de déchets industriels et domestiques. La plupart des méthodes d'analyse d'échantillons d'eau souterraine ne sont pas capables de détecter convenablement des concentrations en éthers glycol de l'ordre du $\mu\text{g/l}$ (ppb); les méthodes actuelles sont médiocres pour doser les espèces toxiques les plus courantes. Une nouvelle méthode permettant de doser des concentrations en éthers glycol de l'ordre du $\mu\text{g/l}$ a été récemment mise au point; son utilisation est préconisée pour les échantillons d'eau souterraine contenant des éthers glycol.

INTRODUCTION

Glycol ethers are a widely used class of chemicals that are detected often in contaminated groundwater when library searches are made. Their high toxicity and propensity to migrate rapidly in ground water make them significant groundwater contaminants. However, these compounds are difficult to analyze, they are not

included in standard lists of target analytes, and their health effects have not been widely publicized. Consequently, the presence and behavior of glycol ethers in groundwater have not attracted the attention they deserve.

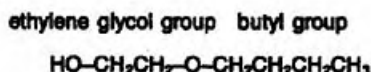
This paper reviews available information about the properties of glycol ethers, their occurrence in groundwater, analytic methods for detecting them, and

their health effects. Groundwater scientists should take account of this information when selecting analytic methods and interpreting analyses that report glycol ethers.

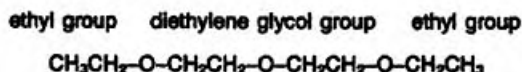
PHYSICAL AND CHEMICAL PROPERTIES

Glycol ethers are colorless liquids with a faint odor. As the name implies, they are ethers derived from glycols. The glycols are usually monomers or dimers of ethylene or propylene glycol. At least one of the two hydroxyl groups is replaced with an ether linkage to an alkyl or aryl group. Esters of glycol ethers are also generally included in the classification. The glycol ethers that are mentioned in this paper are listed in Table 1, and the structural formulas of some common glycol ethers are shown in Figure 1.

Ethylene glycol monobutyl ether:



Diethylene glycol diethyl ether:



Propylene glycol monomethyl ether:

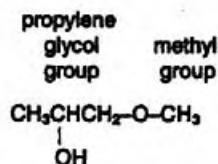


Figure 1. Structural formulas of some typical glycol ethers, showing the system of nomenclature.

Glycol ethers are referred to by a variety of names (Table 1), and analytical chemists often report glycol ethers by using IUPAC names or similar structure-based names.

Glycol ethers are hydrophilic. Partition constants between water and air and between water and olive oil for six glycol ethers, measured by Johanson and

Dynesius (1988), are summarized in Table 2. The partition constants in Table 2 were measured at 37°C using a saline solution; measurements with distilled water at a lower temperature might give substantially smaller values. Generally, the glycol ethers become more hydrophilic (that is, they have smaller oil/water partition constants) with a decreasing number of carbon atoms in either the glycol or the alkyl group. In addition, ethylene glycol monoethyl ether is more hydrophilic than its acetate ester.

USE

Glycol ethers are used in industry and in chemical products in large amounts and for a wide variety of purposes. They are often used as solvents for cellulose esters, dyes, resins, lacquers, varnishes, and stains. They are also present in varnish removers, cleaning solutions, products for treatment of leathers and textiles, and in jet fuel as a de-icing additive.

The extent of the use of glycol ethers in products can be seen from a data base of the declared contents of chemical products maintained by the Swedish Chemical Inspectorate. The results of a search of this data base for widely used glycol ethers are summarized in Figure 2. (The data base only includes ingredients considered hazardous by the manufacturer or importer. Some products containing glycol ethers, especially those of higher molecular weight, may not have been declared.)

Some idea of the extent to which glycol ethers are used in manufacturing can be obtained from the Toxics Release Inventory of the U. S. Environmental Protection Agency. This data base shows the amount of various organic and inorganic chemicals reported to have been released into air, water, or the subsurface by U. S. manufacturers. The only glycol ethers included in this inventory are the ethylene glycol monomethyl and monoethyl ethers; others need not be reported by the manufacturer.

Table 1 (Continued)

Compound	Log Oil ^a -Water ^b Partition Coefficient	Henry's Law Constant (atm-cm ³ /mol)
Ethylene glycol monomethyl ether	-1.82	7.09×10^{-7}
Ethylene glycol monomethyl ether acetate	-1.38	1.10×10^{-6}
Ethylene glycol monomethyl ether acetate	0.10	6.66×10^{-6}
Ethylene glycol monomethyl ether acetate	-0.88	2.06×10^{-6}
Ethylene glycol monomethyl ether acetate	-0.11	3.61×10^{-6}
α -Propylene glycol monomethyl ether	-1.24	2.07×10^{-6}

^aOlive oil.^b0.3 M sodium chloride solution.Source: Johnson, G., and B. Dynes, Liquid/air partition coefficients of six commonly used glycol ethers, *Br. J. Ind. Med.* 45, 561-564 (1988).

Table 2. Partition constants (at 37°C) of six glycol ethers

Chemical Name	Wiley Used Trade Name	IUPAC Name	CAS Number
Triethylene glycol monomethyl ether		2-(2-(2-ethoxyethoxy)ethoxy) ethanol	112-50-5
Triethylene glycol dimethyl ether	Triglyme	2,5,8,11-tetraoxadecane	112-49-2
Tetraethylene glycol dimethyl ether	Tetraglyme	2,5,8,11,14-pentaoxapentadecane	143-24-8
α -Propylene glycol monomethyl ether		1-methoxy-2-propanol	107-98-2
β -Propylene glycol monomethyl ether		2-methoxy-1-propanol	1589-47-5
α -Propylene glycol monomethyl ether acetate		1-methoxy-2-propyl acetate	108-65-6
Dipropylene glycol monomethyl ether		1-(2-methoxy-1-methylethoxy)-2-propanol	20324-32-7
Tripropylene glycol monomethyl ether		1-(2-(2-methoxy-1-methylethoxy)-1-methylethoxy)-2-propanol	20324-33-8

^aCommercial dipropylene glycol monomethyl ether is a mixture of isomers, with this one constituting about 85%. In the industrial hygiene literature, dipropylene glycol monomethyl ether is generally referred to by the CAS number 34590-94-8.

Table 1. Glycol ethers referred to in this study.

Chemical Name	Wiley Used Trade Name	IUPAC Name	CAS Number
Ethylene glycol monomethyl ether	Methyl cellosolve	2-methoxyethanol	109-86-4
Ethylene glycol monomethyl ether acetate	Methyl cellosolve acetate	2-methoxyethyl acetate	110-49-6
Ethylene glycol monomethyl ether	Cellosolve	2-ethoxyethanol	110-80-5
Ethylene glycol monomethyl ether acetate	Cellosolve acetate	2-ethoxyethyl acetate	111-15-9
Ethylene glycol monomethyl ether		2- α -propoxyethanol	2807-30-9
Ethylene glycol monomethyl ether	Isopropyl cellosolve	2-isopropoxyethanol	109-59-1
Ethylene glycol monobutyl ether	Butyl cellosolve	2-butoxyethanol	111-76-2
Ethylene glycol monobutyl ether acetate	Butyl cellosolve acetate	2-butoxyethyl acetate	112-07-2
Ethylene glycol dimethyl ether	Monoglyme	1,2-dimethoxyethane	110-71-4
Ethylene glycol diethyl ether	Diethyl cellosolve	1,2-diethoxyethane	629-14-1
Diethylene glycol monomethyl ether	Methyl carbitol	2-(2-methoxyethoxy) ethanol	111-77-3
Diethylene glycol monomethyl ether	Carbitol	2-(2-ethoxyethoxy) ethanol	111-90-0
Diethylene glycol monomethyl ether acetate		2-(2-ethoxyethoxy) ethyl acetate	112-15-2
Diethylene glycol monobutyl ether	Butyl carbitol	2-(2-butoxyethoxy) ethanol	112-34-5
Diethylene glycol monobutyl ether acetate	Butyl carbitol acetate	2-(2-butoxyethoxy) ethyl acetate	124-17-4
Diethylene glycol dimethyl ether	Diglyme	1,1'-oxy bis (2-methoxyethane)	111-96-6
Diethylene glycol diethyl ether	Diethyl carbitol	1,1'-oxy bis (2-ethoxyethane)	112-36-7
Triethylene glycol monomethyl ether		2-(2-(2-methoxyethoxy)ethoxy) ethanol	112-35-6

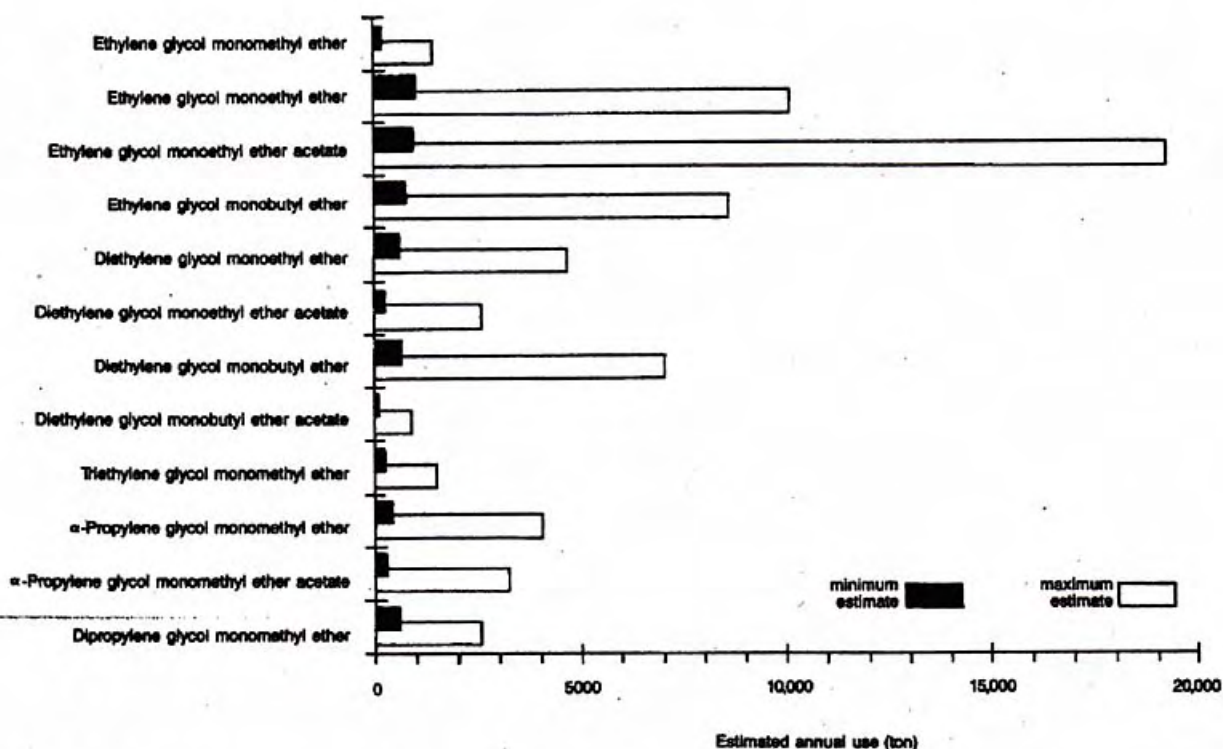


Figure 2. Estimated annual use of the most common glycol ethers in Sweden based on data from the Products Register of the Swedish Chemical Inspectorate as of March 1991 (Ulf Rick, Personal Communication).

In 1988, the most recent year for which data have been compiled, 3320 metric tons of ethylene glycol monomethyl ether and 1380 metric tons of ethylene glycol monoethyl ether were released into the environment (USEPA, 1990). Both species ranked high in amount released among the 322 chemicals and classes of chemicals for which information was collected; the monomethyl ether was 64th and the monoethyl was 89th.

ANALYTICAL METHODS

The analyses we are aware of that have detected glycol ethers in groundwater are of two types.

Where glycol ethers have been target analytes, a gas chromatograph/mass spectrometer (GC/MS) has been used with the aqueous sample injected directly into the instrument. Detection limits with this method are high, on the order of 5 mg/l.

The other detections represent tentative identifications based on "library searches," that is, comparisons of mass spectra derived from analyses with a library of standard mass spectra. The methods used

are USEPA Methods 624 and 625 (or variants), which extract contaminants from the sample into an organic solvent or purge them into a gas (USEPA, 1982).

The two USEPA methods perform poorly for glycol ethers because these compounds are very soluble in water. They tend to remain in the aqueous phase rather than pass into the gas or solvent. Analysis of glycol ethers by the two USEPA methods is discussed in Appendix A.

Because of the extraction problem, the USEPA methods have elevated detection limits for glycol ethers. Furthermore, the reported concentration represents only the amount extracted rather than the amount in the sample. This difficulty is most severe for the two most common and most toxic members of the class, ethylene glycol monomethyl and monoethyl ethers. Experiments described briefly in Appendix A show that ethylene glycol monomethyl ether cannot be detected by either of the USEPA methods at concentrations exceeding 100 mg/l.

A method for detection of glycol ethers at much lower concentrations has been developed by one of the authors (Johanson et al., 1986) and applied to the detection of ethylene glycol monobutyl ether in water

and biological samples. The method consists of three steps: (1) salting out of the glycol ether in toluene, (2) derivatization with pentafluorobenzoyl chloride, and (3) capillary gas chromatography with electron capture detection. A brief description of this method is given in Appendix B.

OCCURRENCE IN GROUNDWATER

Because they are not commonly target analytes in groundwater investigations, little is known about the occurrence of glycol ethers in groundwater. Available information suggests, however, that they are common at sites of contamination.

Glycol ethers detected more than 20 times by library searches in solvent extraction analyses at USEPA Superfund sites are presented in Table 3. Table 3 has been extracted from a data base of about 300,000 analyses of groundwater, surface water, and soil samples at Superfund sites (Eckel et al., 1989). We should emphasize that the glycol ethers were found in less than 1 in 1000 samples, not 1000 sites. Furthermore, because of the process by which library searches are reported, the samples in which they were found are only a fraction of the samples in which they were present. Note also that the total number of samples includes blanks, soil samples, surface water samples, etc.; glycol ethers are found mostly in groundwater samples. The relative frequency of detection of glycol ethers compared to other non-target analytes can be found in the column of the table headed "rank among all compounds" (Table 3). Note that the ranks shown are relatively high, especially since the ranking includes frequently detected laboratory and field contaminants as well as many compounds (especially polycyclic aromatics) that are frequently found in soil samples but rarely in water samples. All identifications are tentative.

Some widely used glycol ethers are frequently detected in groundwater. However, ethylene glycol monomethyl and monoethyl ethers and all the glycol ether acetates never seem to be detected in groundwater. Furthermore, higher molecular-weight glycol ethers seem to be more widespread in groundwater than their reported use would suggest.

The failure to detect short-chain glycol ethers at Superfund sites is easily explained by limitations of the analytical methods, as discussed in Appendix A. The reason for the absence of the acetates is uncertain, but perhaps they are unstable in groundwater. (In animals and man, glycol ether acetates are rapidly hydrolyzed by

esterases present in the blood and nasal mucosa (Stott and McKenna, 1985; Johanson and Dynesius, 1988)). The source of higher molecular-weight glycol ethers is uncertain.

Table 3. Detection of extractable glycol ethers by library search at superfund sites.

Compound	Number of Times Detected	Rank Among All Compounds	Median Retention Index ^a	Mean Retention Index ^a	Relative Standard Deviation (%)
Ethylene glycol monomethyl ether	166	87	138.2	141.2	12
Diethylene glycol monomethyl ether	63	206	144.4	144.8	1.9
Diethylene glycol monoethyl ether	70	188	161.2	161.3	0.04
Diethylene glycol dimethyl ether	37	323	202.7	202.2	1.0
1-(2-Benzyloxyethyl) ethane ^b	39	308	201.1	203.3	7.4
Diethylene glycol diethyl ether	22	482	159.9	169.8	9.4
Triethylene glycol monomethyl ether	20	517	214	197.7	17.7

^aNaphthalene-100, phenanthrene-100, and chrysene-400.

^bThis is not, strictly speaking, a glycol ether, but it is a closely related compound that has been detected rather frequently in contaminated ground water and thus is included here. Source: Unpublished data from U. S. Environmental Protection Agency Sample Management Office, compiled by W. P. Eckel.

CASE STUDIES

The following examples of sites where groundwater is contaminated by glycol ethers are drawn from the consulting experience of one of the authors (BR).

Winthrop Landfill, Winthrop, Maine, USA

The Winthrop Landfill was a municipal landfill which also received industrial waste from the plastics industry. Municipal waste disposal continued over many decades; the main episode of industrial chemical disposal was in 1975. The landfill is located in a former sand and gravel pit in a glacial moraine.

When the investigation began in 1983, ethylene glycol monomethyl ether was identified as a target analyte by interviewing former employees of a plastics plant that sent most of the industrial waste to the landfill. Samples collected since 1984 have been analyzed for this species by either direct injection into a GC/MS or the USEPA volatile purge method. Stated detection limits have been on the order of 5 mg/l. Three samples have contained ethylene glycol monomethyl ether at concentrations from 30 to 42 mg/l.

Library searches have detected several other glycol ethers. Di- and tripropylene glycol monomethyl ethers have been identified repeatedly in semivolatile analyses. Ethylene glycol diethyl ether was identified once in a volatile analysis.

Contaminated groundwater from this site is flowing into a lake. Numerous groundwater contaminants have been detected in the lake. However, the high detection limits for ethylene glycol monomethyl ether make the analytic data useless for determining whether this compound is in the lake.

Hipps Road Landfill, Jacksonville, Florida, USA

The Hipps Road Landfill was excavated into a sandy coastal plain aquifer of 20 m approximate thickness in Jacksonville, Florida. It received a mixture of household waste and wastes from naval aircraft maintenance and paint stripping from 1968 to 1970.

Residential wells in the vicinity, most of them completed in a thin limestone layer separated from the sand by a discontinuous clay, developed unusual odors and tastes in subsequent years. An initial investigation in 1983 failed to detect the presence of glycol ethers. In reconnaissance sampling in 1984, a library search on the most contaminated monitoring well reported 200 $\mu\text{g/l}$ of diethylene glycol diethyl ether, 50 $\mu\text{g/l}$ of ethylene glycol monobutyl ether, and 10 $\mu\text{g/l}$ of diethylene glycol monobutyl ether.

A detailed investigation was conducted in the subsequent year. Library searches of water samples indicated that the three monitoring wells completed within the contaminant plume in the lower part of the sand, the most contaminated depth interval, all contained 50 to 100 $\mu\text{g/l}$ of diethylene glycol diethyl ether, although, in one well, the analyst reported it as an unspecified ethylene glycol ether. Even without taking account of needed correction factors (see Appendix A), this made it one of the most abundant contaminants in the plume.

One additional round of samples was collected in 1989. Analyses of these samples did not include library searches, except for three split samples. One of these, from the limestone, contained a reported 7 $\mu\text{g/l}$ of triethylene glycol monoethyl ether and 4 $\mu\text{g/l}$ of tetraethylene glycol dimethyl ether. The present authors, by re-examination of the mass spectra and comparison of GC retention indices (see Appendix A) with measurements of known standards, have concluded that these two constituents are better identified as diethylene glycol diethyl ether and triethylene glycol dimethyl ether.

The remedy selected for groundwater at the site is extraction and treatment by air stripping. The principal objective of the operation is removal of vinyl chloride. No objective has been set for removal of glycol ethers from the water.

In 1990, a review of the previous work at this site led to recognition of the significance of glycol ethers as contaminants. Further examination of the 1985 mass spectra identified additional glycol ether contaminants. At that time, diethylene glycol diethyl ether and other high molecular-weight glycol ethers appear to have been present throughout an anaerobic plume leading northeastward from the landfill through the lower part of the sand aquifer.

Industrial Excess Landfill, Uniontown, Ohio, USA

The Industrial Excess Landfill was located in a former gravel pit excavated into complex glacial outwash and till deposits near Akron, Ohio, USA. During the 1960s, it received a mixture of municipal waste and a variety of industrial wastes, many of them from the rubber industry.

Residential wells immediately adjacent to the landfill were contaminated by vinyl chloride and other compounds. In library searches of samples from the residential wells, ethylene glycol diethyl ether was identified in the volatile organic analysis at estimated (uncorrected) concentrations from 4 to 31 $\mu\text{g/l}$. The identification of the diethyl ether was made independently by several laboratories, eventually by five. In four monitoring wells, ethylene glycol monopropyl ether was detected by extraction analysis. One sample also was reported to contain the monobutyl ether, but the retention time suggests that this identification is doubtful.

Small air strippers were installed in the basements of the residences to treat the well water. Upon installation, these units were tested by analyzing their influent and effluent. In one house, the treated water was reported to contain 2 $\mu\text{g/l}$ of ethylene glycol diethyl ether, [the correction factor in this sample (see Appendix A) could easily be 50 or more. The response factor for methyl ethyl ketone, which appears to have a somewhat larger Henry's Law constant, was 0.02] while none was detected in the influent. The air strippers were judged successful because they were removing vinyl chloride effectively, and they remained in use for more than two years until the residents were evacuated.

The complexity of the geology at this site is such that a clear synthesis of contaminant movement has not yet been developed. Furthermore, the depth of the

private wells is not certain. Monitoring data do, however, indicate that these wells draw anaerobic water that has been affected by the landfill.

Discussion of the Case Studies

These case studies, along with several other sites not discussed here, have common features of both scientific and practical interest.

When the oxidation state of groundwater in which glycol ethers were found was known, the waters were anoxic. The histories of these sites show that these chemicals can persist for more than a decade in such an environment. In no case were they detected in groundwater that appeared to be oxic, which suggests that, in aerobic subsurface environments, they may be biodegraded at least moderately rapidly.

When the glycol ethers were detected by library search, little attention was paid. Indeed, in most of these cases, there is no evidence that anyone had even translated the IUPAC names under which these chemicals are reported to common names until the issue was raised by one of the present authors.

HEALTH EFFECTS

Several reviews of the toxicity of glycol ethers are available (ECETOC, 1985; Gudbergsson, 1985; Illing and Tinkler, 1985; Johanson, 1990; NIOSH, 1990; WHO, 1990). Glycol ethers are low to moderate in acute toxicity, with single-dose oral LD₅₀ values ranging between approximately 1 and 10 g/kg body weight.

Four major types of serious adverse effects, teratogenicity, testicular toxicity, bone marrow depression, and hemolysis, have been demonstrated for some of the glycol ethers. Teratogenic and testicular effects and bone marrow depression have been shown in rats, mice, and rabbits after exposure to ethylene glycol monomethyl and monoethyl ethers and their acetate esters. Occasional case reports, as well as some investigations on occupationally exposed people, suggest that these effects may also occur in man. Teratogenic effects have also been shown in rats exposed to the monomethyl ether of diethylene glycol and the dimethyl ethers of mono-, di-, and triethylene glycol (George et al., 1987; Hardin and Eisenmann, 1987; Hardin et al., 1986; Lee et al., 1989; Price et al., 1987) and in rabbits exposed to the β isomer of propylene glycol monomethyl ether acetate.

In general, the toxicity of the glycol ethers decreases with increasing length of the alkyl group of the molecule. The exception is ethylene glycol

monobutyl ether which, due to its hemolytic activity, is the most acutely toxic glycol ether in rats. The toxicity also decreases with increasing size of the glycol group, as well as with an increasing number of glycol groups in the molecule. The acetate esters are rapidly hydrolyzed to their parent glycol ethers by esterases in the body. Hence, on an equimolar basis, the toxicity of a glycol ether acetate is approximately equivalent to that of the corresponding glycol ether.

Effects of exposure to monoethylene glycol monoalkyl ethers are attributed to metabolic activation to alkoxyacetic acids. Teratogenicity of diethylene glycol monomethyl ether and the dimethyl ethers of mono-, di-, and triethylene glycol may be explained by metabolic production of 2-methoxyethanol (ethylene glycol monomethyl ether) by cleavage at a central ether bond and subsequent activation to 2-methoxyacetic acid. The teratogenic effect of the β isomer of propylene glycol monomethyl ether is attributed to metabolic activation to methoxypropionic acid, while the nonteratogenic α isomer is a secondary alcohol and, thus, cannot be metabolized to an acid.

The USEPA developed "reference doses" for ingestion of several glycol ethers (USEPA, 1991), which are listed in Table 4. The reference dose is an estimate of the chronic exposure to the human population (including sensitive subgroups) that is likely to be without an appreciable risk of deleterious effects. These values are not regulations, but are used by USEPA staff in making decisions about contaminated soil and groundwater.

The reference dose, which is given in units of $\mu\text{g/kg/day}$, is normally converted to an acceptable concentration in drinking water by multiplying by a human body weight of 70 kg and dividing by a water consumption of 2 l/day. However, glycol ethers are readily absorbed through the skin, providing another route of exposure. In addition, the dermal absorption of glycol ether may be enhanced from aqueous solutions (Johanson and Fernstrom, 1988).

Table 4. Oral reference doses for glycol ethers set by USEPA ($\mu\text{g/kg/day}$).

Compound	Subchronic RfD	Chronic RfD
Ethylene glycol monomethyl ether	10	1
Ethylene glycol monomethyl ether acetate	20	2
Ethylene glycol monomethyl ether	500	400
Ethylene glycol monomethyl ether acetate	300	300
Diethylene glycol monomethyl ether	3000	3000
Propylene glycol monomethyl ether	7000	700
Propylene glycol monomethyl ether	7000	700

Source: Health effects assessment summary tables, Fourth quarter, FY-1990, U. S. Environmental Protection Agency Report CERCLA 9200 6-303 (30-4), 1990.

RECOMMENDATIONS AND CONCLUSIONS

Glycol ethers are widely used industrial chemicals. They appear to be relatively common in contaminated groundwater, especially in anaerobic plumes emanating from landfills containing a mixture of household and industrial waste.

The toxicity of common glycol ethers makes their presence in groundwater a matter of concern. Ethylene glycol monomethyl and monoethyl ethers and their acetates are teratogenic and cause testicular damage and bone marrow depression at relatively low doses in laboratory animals. Ethylene glycol monopropyl and monobutyl ethers and their acetates may cause hemolysis and hemolytic anemia. Propylene glycol ethers, diglycol ethers, and triglycol ethers appear generally to be considerably less toxic than the ethylene glycol ethers.

Hydrogeologists should carefully review results of library searches at toxic waste sites for evidence that glycol ethers are present. In interpreting results, the downward biases in the concentrations reported by the standard USEPA analytical methods should be taken into account. The extreme difficulty of detecting two of the most toxic and most widely used glycol ethers, ethylene glycol monomethyl and monoethyl ethers, should also be borne in mind.

A very sensitive method is now available to analyze for glycol monoalkyl ethers. At sites where library searches have detected glycol ethers of any kind, or where there is otherwise reason to believe glycol ethers are present, this method should be used to analyze groundwater samples. In particular, this method should be used routinely at locations where an unknown mixture of industrial solvents has contaminated groundwater.

APPENDIX A

ANALYSIS OF GLYCOL ETHERS BY USEPA STANDARD METHODS

Glycol ethers detected in groundwater, when they are not target analytes, are identified by library searches of mass spectra. The mass spectra are generally obtained by two standard USEPA methods (USEPA, 1982). Method 625, which is responsible for the great majority of glycol ether detections, is used for the analysis of base-neutral and acid extractable semi-volatile compounds in groundwater. This method is based on extraction into dichloromethane, followed by GC/MS analysis. Method 624 is a purge-and-trap

analysis for volatile species. For several reasons, analyses of samples containing glycol ethers by these methods will often fail to detect their presence and will tend to understate their concentrations when they are detected.

Incomplete Extraction

Because glycol ethers are hydrophilic and have low Henry's Law constants, they are poorly extracted into either the gas or the dichloromethane phase. The concentrations reported by the USEPA methods represent only the portion of the glycol ether extracted, not the total amount present in the original sample. Consequently, the true concentrations will tend systematically to exceed the reported concentrations. The size of this bias will depend on the species' interphase partition coefficients (given for some glycol ethers in Table 2) and the extraction method.

An experiment was conducted to measure the bias in the semi-volatile method due to incomplete extraction. Well water samples of 500 mL in volume from the Hipps Road Landfill plume were spiked with 100 mg/L each of ethylene glycol monomethyl and monobutyl ethers and diethylene glycol diethyl ether and extracted three times sequentially with 30 mL of dichloromethane using a separatory funnel. The dichloromethane extracts were dried by using anhydrous sodium sulfate and reduced in volume to 0.5 mL. After dilution to the appropriate volume with dichloromethane, both glycol ethers in the extracts were analyzed by using high resolution gas chromatography/mass spectrometry. This procedure closely resembles EPA Method 625. In Method 625, the sample is first extracted at pH 13 and then at pH 1; the extraction efficiency of glycol ethers is not expected to be sensitive to pH.

The measured recovery of ethylene glycol monobutyl ether was $6.7\% \pm 3.1\%$. The measured recovery of diethylene glycol diethyl ether, corrected for a small peak in the blank, was $12.9\% \pm 3.4\%$. The errors given are absolute standard deviations in three replicate experiments. Ethylene glycol monomethyl ether could not be detected because it co-eluted with dichloromethane.

Hydrogeologists should correct glycol ether concentrations measured by Method 625 to compensate for the bias caused by poor extraction. The best correction factors are measured by analyzing spiked samples on the same day with the same instrument. Often, measurements of spiked samples will not be available. In such cases, reported concentrations can be corrected by the square root of the measured recoveries

reported in this paper, if the extraction has been conducted by separatory funnel. When samples are extracted with a continuous extractor, the bias is less than with a separatory funnel.

Quantitation with the semi-volatile extraction method involves a response factor that is set to unity for species identified by library search. (The response factor is defined in such a way that, even when measured, it would not compensate for incomplete extraction.) A response factor of 0.092 was measured for tripropylene glycol monomethyl ether (USEPA, 1988) using method 1625C, which is a variant of method 625. This result suggests that the assumption of a unit response factor may introduce another downward bias in reported concentrations of glycol ethers.

In purge-and-trap analyses for volatiles, the response factors used to compute reported concentrations of target analytes do implicitly take account of the efficiency with which the analytes are purged into the gas phase. Again, the response factor is set to unity for species found by library search. Compounds with low Henry's Law constants, such as glycol ethers, will not pass into the gas phase efficiently. This will make their response factors smaller than unity, causing concentrations of non-target analytes to be underestimated.

Because of the poor purge efficiency, no ethylene glycol monomethyl ether was detectable (even below the stated detection limits) in samples spiked by two laboratories with 100 mg/l of the substance and analyzed by method 624 (H. A. McDaniel, Jr., Biospherics Inc., and R. Flynn, Compuchem Laboratories, unpublished data).

Packed Columns

The USEPA methods allow the laboratory the choice of using packed or capillary columns. Glycol ethers can adsorb to packed columns and desorb to later samples. One author (GJ) found this effect to result in poor reproducibility in analyses of ethylene glycol monobutyl ether using packed columns.

Retention Times

Identifications by library search are based only on comparison of mass spectra and do not consider retention times in the gas chromatograph. For this reason, such identifications are less reliable than identifications of target analytes. However, the reliability of such identifications can be greatly increased if the retention times are considered.

To minimize day-to-day instrument variability when comparing absolute retention times (RT) obtained from gas chromatography, the use of retention indices is recommended. A retention index (RI) is calculated from the GC according to its relative position between two retention markers (m_1 and m_2); the markers are usually represented by a series of n-alkanes or polynuclear aromatic hydrocarbons. The retention index of species a is given by:

$$RI(a) = \frac{RT(a) - RT(m_1)}{RT(m_2) - RT(m_1)} 100 + RI(m_1)$$

Retention indices have much less variability than retention times because variables which affect the retention time of the analytes will presumably affect the retention markers in a closely related fashion.

Retention indices are strictly comparable only for a specified type of GC column, GC carrier gas, and temperature program. If all of these are held constant, the standard deviation among RIs should be less than 1%. In principle, the RI should be independent of matrix variables; for peaks arriving before naphthalene, naphthalene and phenanthrene are used as markers.

Table 3 gives the median and relative standard deviation of the retention index of each glycol ether frequently identified in USEPA Superfund semivolatile library searches. The retention indices are calculated using a system devised by Lee et al. (1979) in which naphthalene, phenanthrene, and chrysene are given the values 200, 300, and 400. (Eckel et al., 1989). In cases where the retention indices of peaks identified as a particular compound have a small standard deviation, it can be concluded that the same compound was being identified each time, and the identification was probably correct. Where retention indices are more scattered, the scatter may be attributable either to misidentification or to differences among GC methods.

APPENDIX B

ANALYTICAL METHOD FOR MONOALKYL GLYCOL ETHERS

A brief description of an analytical method for monoalkyl glycol ethers is as follows. A more complete description is given by Johanson et al. (1986).

The sample, an internal standard (hexanol and/or heptanol in water), toluene, and an aqueous solution of sodium sulfate saturated at 50°C are added to a glass vial which is sealed and vigorously shaken. Following

phase separation by centrifugation, the toluene phase is transferred to a new vial, and pyridine and pentafluorobenzoyl chloride are added. The vial is sealed and shaken for one hour at 50°C. The solvent phase is evaporated, and the residues dissolved in methanol/water and thereafter extracted into hexane. The hexane phase is collected and washed once more with methanol/water prior to GC analysis. Investigations by GC/MS have confirmed that derivatization of 2-butoxyethanol yields butoxyethyl pentafluorobenzoate, as expected.

The method error expressed as relative standard deviation was 11% to 12%, and the detection limit in blood samples was approximately 0.1 $\mu\text{mol/l}$ (10 $\mu\text{g/l}$) (Johanson and Fernstrom, 1988; Johanson et al., 1986). In samples containing less organic contamination than blood, such as groundwater, the sensitivity may be greatly improved, simply by increasing the sample volume relative to the volume of toluene. In analyses of 40-m groundwater samples, detection limits were estimated as 150 $\mu\text{g/l}$ for ethylene glycol monomethyl ether, 27 $\mu\text{g/l}$ for ethylene glycol monoethyl ether, 8 $\mu\text{g/l}$ for ethylene glycol monobutyl ether, and 270 $\mu\text{g/l}$ for α -propylene glycol monomethyl ether.

In principle, the method is applicable to any organic compound containing a hydroxyl or amino group. It works well for ethylene glycol monoethyl and monoisopropyl ethers. The most polar glycol ether, ethylene glycol monomethyl ether, extracts poorly into toluene, and method refinements may be needed for this compound. With this method, the glycol ether-derived peaks can, in most cases, be identified by their retention times, because the derivatization is restricted to hydroxy and amino compounds, and the capillary GC provides high resolution.

ACKNOWLEDGEMENTS

The authors would like to thank the many scientists, more than can be named here, who contributed data and advice to this study. John Young of Hampshire Research Associates and Ulf Rick of the Swedish Chemical Inspectorate generously provided unpublished data as well as their very useful advice. David Meyer, formerly of USEPA Region 5, allowed access to otherwise unavailable analyses of samples from the Industrial Excess Landfill. John Amore and Robert O'Neill of Olfacto-Labs, Harless A. McDaniel, Jr., formerly of Biospherics, Inc., and Carl Perchonock provided helpful comments on questions of chemical analysis.

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