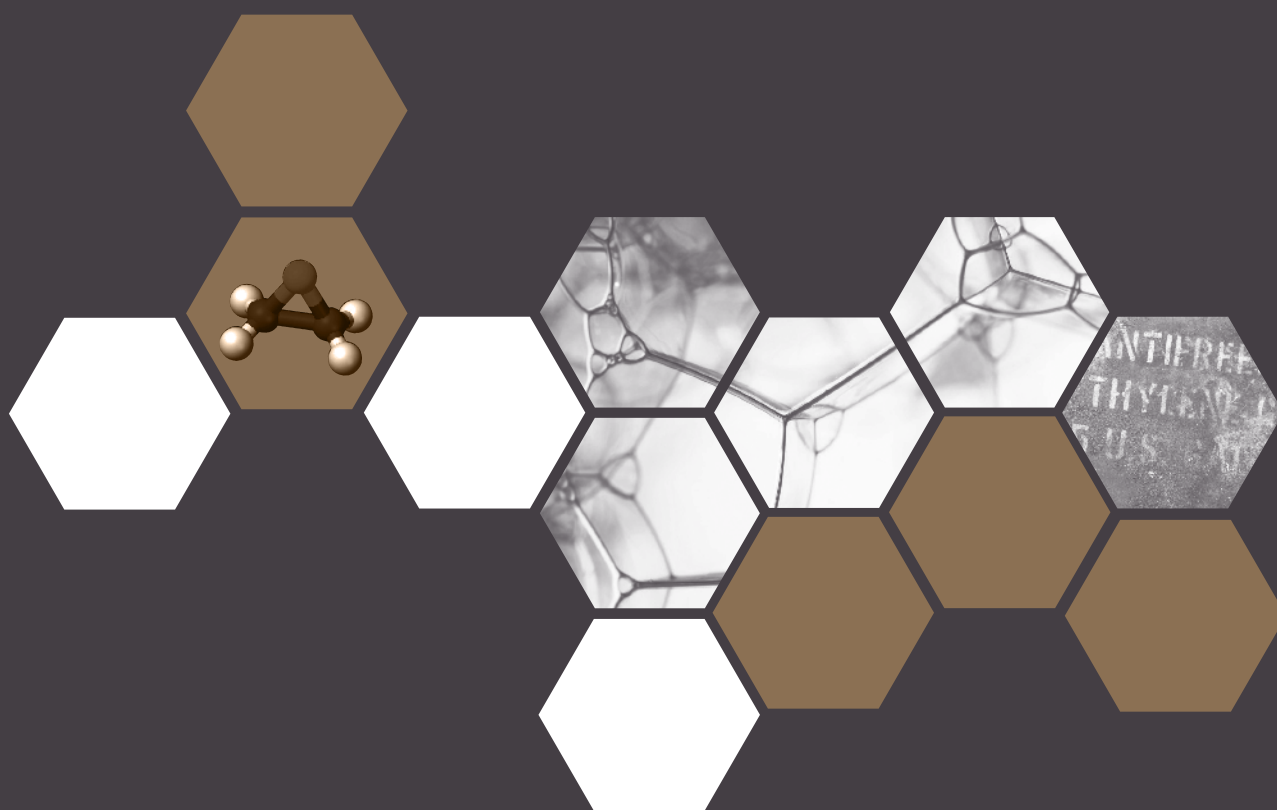


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To the Reader

Manual Preparation

As members and affiliated companies of the American Chemistry Council, we support efforts to improve the industry's responsible management of chemicals. To assist in this effort, the American Chemistry Council's Ethylene Oxide/Ethylene Glycols Panel supported the creation and publication of this manual. The Panel is comprised of the following companies:

Balchem Corporation/ARC Specialty Products

BASF Corporation

Bayer Material Science LLC

Celanese Ltd.

Champion Technologies

Croda, Inc.

The Dow Chemical Company

Eastman Chemical Company

Honeywell

Shell Chemical LP

The development of this manual was led by the Panel's Ethylene Oxide Safety Task Group (EOSTG), a group comprised of producers and users of ethylene oxide. The EOSTG functions to generate, collect, evaluate and share information to support product stewardship with regard to ethylene oxide. The EOSTG formed a manual work group, chaired by Keith Vogel of Lyondell Chemical Company, to lead the development of this document. The following work group members provided significant contributions:

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4.0 Environmental Effects of Ethylene Oxide

4.1 Introduction

This Chapter provides a brief overview of information pertaining to potential effects of EO to environmental media.

4.2 Properties in the Environment

Because it is highly reactive, EO does not persist indefinitely in the atmosphere, soil or water. EO is characterized by the following properties:

- EO is somewhat persistent in the atmosphere, but evidence indicates that it ultimately degrades by the process of photolysis;
- EO does not readily absorb into sediments or soils and does not persist in soils; if absorbed, soil organisms will over time convert EO to glycols eliminating any persistence in the soil;
- EO has low to moderate aquatic toxicity;
- EO does not persist in water due to conversion to glycol by hydrolysis or degradation of hydrolysis products, by both biotic and abiotic processes;
- EO does not bioconcentrate in environmental media.

Hydrolysis

Ethylene oxide degrades in both air and natural water via radical formation and hydrolysis, leading to the formation of glycols and halogenated alcohols (the latter forming in the presence of sodium chloride), which in turn degrade into simpler molecules such as carbon dioxide and water. Soil organisms may also convert EO to glycols [30].

Chemical hydrolysis is a major removal process for EO. At ambient temperatures and in fresh water, conversion of EO in water to glycols occurs at a slow rate requiring weeks for completion. The rate of EO hydrolysis can be increased by either changes in pH and/or temperature. Acidic conditions, in particular, can have a large positive effect on hydrolysis rates [7]. The data for EO indicates that water temperature will probably have a greater effect on half-life than expected pH differences in natural waters [1]. The hydrolysis product, ethylene glycol, is biodegraded rapidly in the aquatic environment [8].

Recently developed kinetics for EO hydrolysis with water predict similar half-lives as seen in Figure 4.1 [31].

Table 4.1 Environmentally Relevant Parameters of Ethylene Oxide

Parameter	Units	Value	Reference
Water solubility	mg/L	miscible	[2]
Vapor pressure at 20°C	mm Hg	1095	[2]
Atmospheric Boiling Point	°C	10.6	[1]
Henry's Law Constant at 20°C	atm·m ³ /mol	1.4 x 10 ⁻⁴	[1]
Octanol-water partition coefficient (log Kow)	L/kg	-0.30	[3]
Soil-sediment partition coefficient (log Koc)	L/kg	1.2	[18]
Bioconcentration factor (BCF)*	L/kg	0.35	[4][5]
Theoretical oxygen demand (ThOD)	O ₂ /g EO	1.82	[6]

* Calculated using $\log BCF = 0.76 \log Kow - 0.23$ ([4], [5])

Figure 4.1 Neutral EO/Water/Glycol Kinetics - Isothermal Case, Initially EO/Water mixture

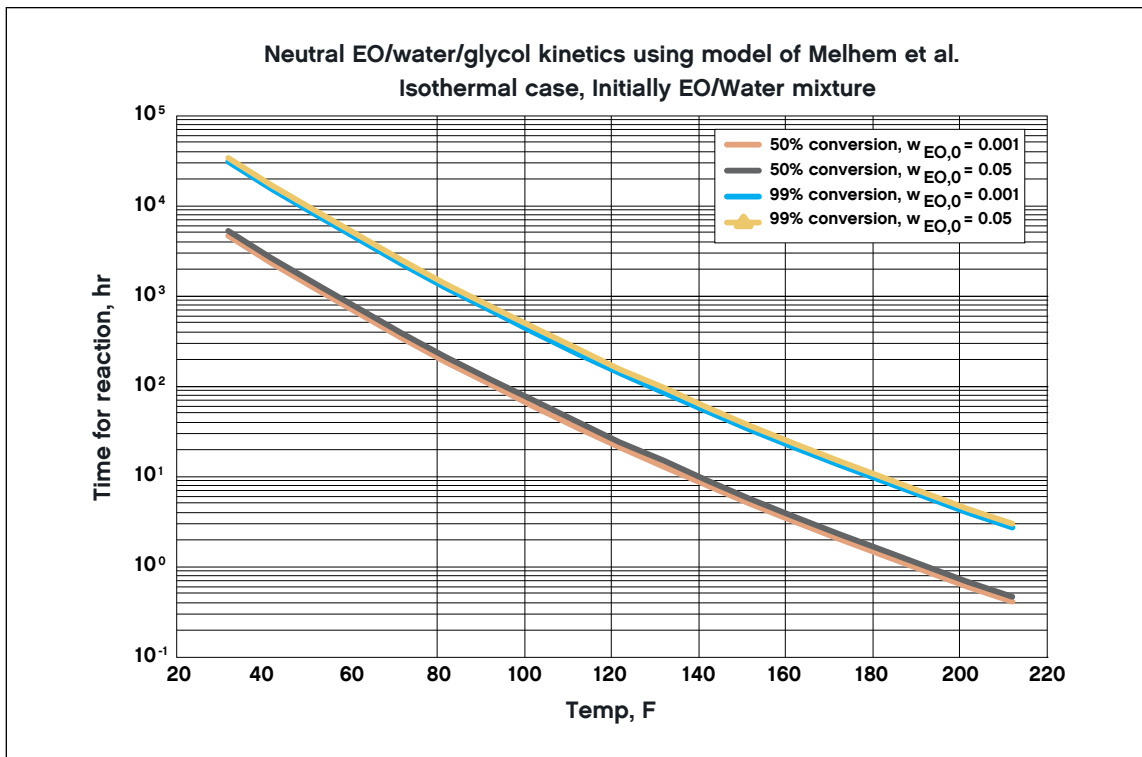
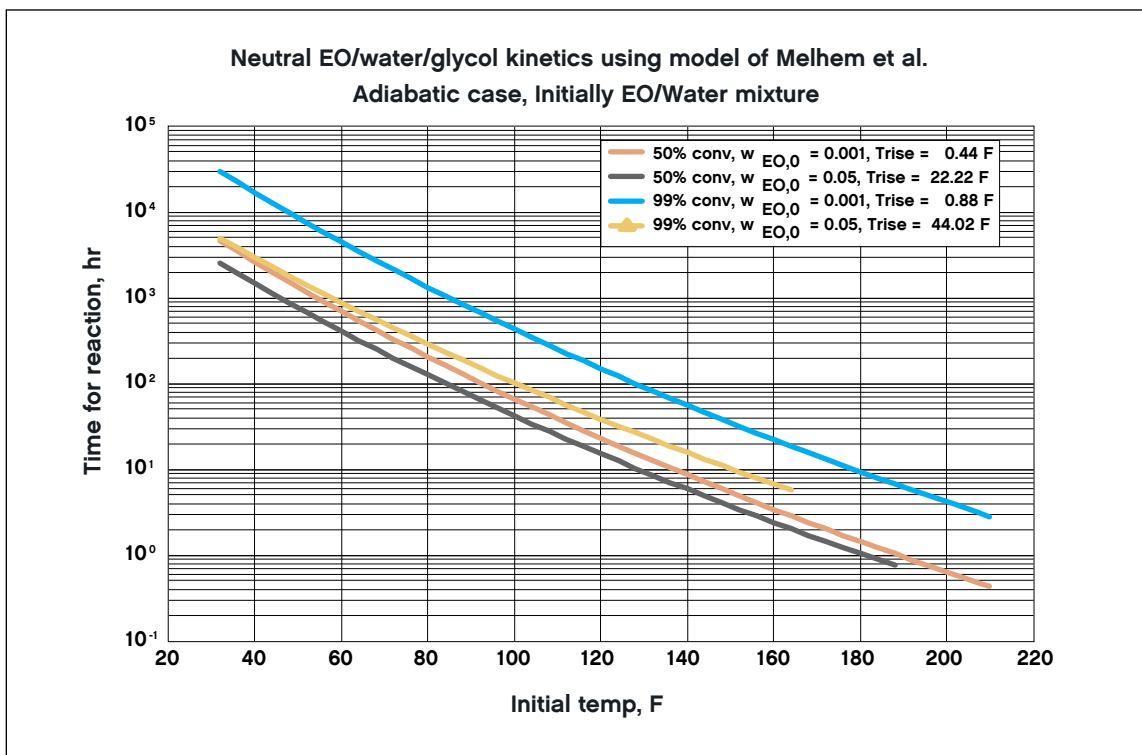


Figure 4.2 Neutral EO/Water/Glycol Kinetics - Adiabatic Case, Initially EO/Water



The half-life for 1000 ppmw in water at 77°F (25°C) is 10 days. Under isothermal conditions, 99% conversion is achieved in approximately 70 days. Figure 4.2 shows conversion data for EO in water assuming adiabatic conditions. At very low EO concentrations, there is little difference in the half-life assuming isothermal or adiabatic conditions. However, at higher EO concentrations, the results may be more significant. Adiabatic conditions may be a more reasonable assumption for spill containment tanks. Comparing adiabatic with isothermal conditions for 5% wt EO in water, the half-life is 6 versus 12 days with a 13°F (-11°C) temperature rise. The time to achieve 99% conversion is 14 versus 76 days with a 25°F (-4°C) temperature rise.

Volatilization

Because of its volatility, EO has a tendency to evaporate from water or soil to the air. The Henry's Law Constant is 1.4×10^{-4} atm-m³/mole [1]. It has been shown that the transfer rate of EO from natural waters is about 0.36 times that of oxygen under the same conditions [1]. A 4-hour aeration test resulted in 100% removal from water [9], and the volatilization half-lives for removal from a model river and model lake are 5.9 hours and 3.8 days, respectively [10].

Persistence in Air

Earlier studies suggested that EO is not persistent in air due to washout by rain [1] and degradation by chemical processes [11]. However, more recent work has indicated that EO was not readily deposited by rain [12], [13], and the dominant chemical removal process is the reaction with the hydroxyl radical. Based on the most recent determinations of the average atmospheric hydroxyl radical

concentration [14] and its reaction rate with EO, [15] the atmospheric half-life of EO is estimated to be 105 days. Under the U.S. Clean Air Act, EO is classified as a toxic air pollutant and regulated as a volatile organic compound.

Biodegradation

A series of biodegradation experiments (biological oxygen demand tests) have been conducted and results are summarized in Table 4.2. These results indicate that EO is rapidly and extensively biodegraded under aerobic conditions. More rapid biodegradation is expected in acclimated systems [16], [17]. Thus, EO will biodegrade in aerobic systems such as rivers, lakes and activated sludge units. However, high concentrations of EO may cause inhibition of bacterial respiration in activated sludge units. The IC50 (concentration that inhibited bacterial growth by 50%) in an activated sludge test (non-acclimated) was in the range of 10-100 mg/L [1].

In testing of a full-scale chemical plant activated sludge unit, EO was shown to rapidly biodegrade to non-detectable levels [17]. Measured EO biodegradation kinetics were determined in this study and were successfully used to predict the measured activated sludge unit EO concentrations [17].

Environmental Partitioning

Environmental partitioning is useful in modeling the transport of EO through environmental media. Fugacity modeling evaluates a scenario in which a chemical is continuously discharged into one of three compartments: air, water, or soil. Following entry into a single environmental compartment, chemicals are redistributed as governed by

Table 4.2 Biological Degradation Data for Ethylene Oxide

Process	Results	Comments	Reference
aerobic	5-d BOD = 20%	standard BOD test	[9]
	10-d BOD = 62%		
	20-d BOD = 70%		
aerobic	5-d BOD = 3%	standard BOD test	[19]
aerobic	20-d BOD = 52%	lightly seeded BOD test	[1]

Table 4.3 Aquatic Toxicity Data for Ethylene Oxide*

Species	Results	Comments	Reference
Fathead minnow	Maximum safe concentration (96-h) = 41 mg/L	no effect concentration	[9]
Fathead minnow	96-h LC50 = 57 mg/L	static; fresh water	[9]
Fathead minnow	24-h LC50 = 86, 90, 274 mg/L 48-h LC50 = 89 mg/L 96-h LC50 = 84 mg/L	static; fresh water	[1]
Goldfish	24-h LC50 = 90 mg/L	static; fresh water	[20]
Daphnia magna	24-h LC50 = 260, 270, >300 mg/L 48-h LC50 = 137, 200, 300 mg/L	static; fresh water	[1]
Brine shrimp	24-h LC50 = 350, 570, >500 mg/L 48-h LC50 = 490, >500, 1000 mg/L	static; salt water	[1]

* Table includes multiple results from separate tests.

compound-specific physical properties, as well as by advection and dispersion. Chemical concentrations are also simultaneously reduced in the environment by compartment-specific degradation processes. Concentrations in each environmental compartment are calculated when advection, inter-media transfers and degradation are at equilibrium.

Overall distribution of EO in the environment has been characterized in Canada using the ChemCAN Level III fugacity model [18]. The predicted overall persistence was estimated at 3 days with 77% partitioning to air, 23% to water, and less than 1% to soil and sediment. Due to its short overall persistence time, higher EO concentrations were estimated to occur closest to release points.

4.3 Ecotoxicological Effects

EO aquatic toxicity studies have been conducted using fish and crustaceans. The results indicate that EO has low to moderate aquatic toxicity (Table 4.3), with toxicity measurements (LC50 in acute tests) ranging from 57 to 274 mg/L for fish and 137 to 1,000 mg/L for crustaceans.

The effect of EO on the growth and development of plants has also been investigated. Heck and Pires [21] reported that atmospheric concentrations of 10 ppm showed no effects on plants after seven days of exposure, but tests conducted at higher EO concentrations of up to 1000 ppm in air caused

death for all of the five plant species studied. EO levels in biota have not been reported [18]. The bioaccumulation potential is expected to be low because of EO's low octanol/water partition coefficient.

4.4 Environmental Evaluation of Ethylene Oxide Spills

The Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) reportable quantity for a release of EO to the environment is 10 pounds. (40 CFR 302.4.)

Soil

EO is poorly adsorbed to soil. In a spill to soil, much of the EO will be lost to evaporation and the balance will infiltrate the ground. Environmental considerations include downward penetration of EO toward the groundwater table. Some of the EO will convert over time to ethylene glycol through hydrolysis; however, this process is relatively slow. Note that ethylene glycol would biodegrade rapidly (0.2 to 0.9 day half-life) [22].

Once the EO has infiltrated the soil, evaporation will continue but at a reduced rate. Diluting an EO release with water will increase the viscosity of the resulting mixture and will have the net effect of reducing the speed of downward movement in the soil. If the soil surface is saturated with moisture at the time of the release, as might be the case

after a rain, the EO will tend to run off or pond and eventually evaporate, hydrolyze or biodegrade.

After a spill, the generator of waste must determine if the material to be disposed of is regulated as a hazardous waste. Although EO is not a listed hazardous waste under U.S. environmental regulations, as a pure substance it exhibits the characteristic of ignitability (D001). Soils and residue from a spill therefore must be analyzed to determine if the materials being disposed meet the criteria for classification as a hazardous waste. Once this determination is made, an appropriate disposal technique can be selected in accordance with federal and state disposal requirements.

Water Systems

When spilled on water, EO will volatilize and simultaneously spread on the surface of and mix with the water. The EO may also simultaneously hydrolyze and biodegrade in bodies of water. EPA has developed models to simulate the fate and transport of chemicals within watershed areas [23]. These models are publicly available on the Internet.

EO Air Dispersion and Sampling

Chemical releases are typically evaluated using computer models. EPA developed ALOHA® software for evaluating an episodic chemical release and the downwind dispersion of the chemical cloud [24]. EPA also developed the SCREEN3 air dispersion model for evaluating chemicals that disperse as a plume from point, area, flare, and volume sources [25]. Both of these screening tools are available for free from EPA.

Other air dispersion modeling software is commercially available. Some of these models may be easier to use than EPA's models; some may offer more modeling options, such as multi-media modeling of releases to air, water, or soil.

Several methods are available to measure EO in ambient air. Real-time field measurements can be made in the 5-10 ppb range using a portable gas chromatograph with a photoionization detector using NIOSH Method 3702 [26]. Additionally, the measurement of lower concentrations (below 1 ppb) has been validated using EPA Method TO-15 and Summa™ canisters for sampling

[27]. The method is designed to be similar to Method TO-15 using evacuated canisters and gas chromatography-mass spectrometry (GC-MS). Additional information is available from commercial vendors specializing in air sampling and analysis.

4.5 Fugitive Emissions

Fugitive emissions are those that enter the atmosphere from a source other than a smoke stack, process vent or a storage vessel. Fugitive emissions include equipment leaks, evaporative losses from surface impoundments, spills, and releases from building ventilation systems. EO fugitive emissions are typically calculated rather than measured. In some cases, fugitive emissions can be a large contributor to reported emissions.

Fugitive emissions are subject to federal regulations, but in most states, the primary implementing regulations are state air quality regulations. State requirements vary; however, equipment leaks are typically regulated through leak detection and repair (LDAR) programs. Federal rules cover the frequency and protocol for monitoring valves, connectors, pump seals, compressors and other fugitive emission sources. Emissions can be estimated using field leak concentration data (screening data) in EPA-developed correlation equations [28]. Commercially available software is available to document LDAR compliance and estimate fugitive emissions based on screening data.

Secondary air emissions from wastewater systems are another type of fugitive emissions. Several computer models with varying degrees of sophistication have been developed to estimate secondary emissions. The publicly available EPA WATER9 software estimates air emissions from wastewater collection, storage, treatment and disposal facilities [29]. Proprietary software is also available from commercial vendors. Some modeling issues to consider are how well the modeled emissions agree with field measurements, ability to simulate complex configurations, the number of chemicals in the physiochemical property database and the ease of use of the software.