Technical Dialogue

WHAT CHEMICAL CONCENTRATION IS SAFE?

The Problem:

A chemical spill has occurred or can potentially occur and a public evacuation is ordered. The evacuation is ordered because the chemical is toxic and is or may become airborne. Even if the chemical is a liquid and spills on the ground, the liquid will likely evaporate dispersing the chemical in the air. Explosions can occur releasing large quantities of the chemical at once. Anyone downwind of the release can inhale the chemical. A decision must be made on the evacuation distance, or whether in some situations people may remain inside buildings with windows closed until the danger has passed. There are practical limits of how many people can be evacuated and the evacuation distance. Obviously some people will or can potentially be exposed to the chemical in the air. What concentration in the air might be considered safe?

This is not an easy question to answer. Some chemicals are dangerous because when inhaled they interfere with the body metabolism. Some irritate the eyes and airway making it difficult to breath. Some such as benzene and carbon tetrachloride are known or suspected carcinogens. Some gases such as methane are not toxic in itself but are dangerous if air concentrations are high enough that an explosion or fire can occur, or if the gas displaces oxygen.
Also, individuals vary. A healthy adult might safely be exposed to a chemical for a specified period of time without any serious short-term or long-term effects (other than perhaps an unpleasant odor or minor irritation). But the same situation might have serious long-term effects for sensitive individuals, including infants, the elderly, people whose breathing is impaired or on some medications. Synergistic effects can occur because of long-term exposure to other chemicals such as from breathing tobacco smoke.

Inhalation is not the only route of exposure. The chemical may be absorbed through the skin or ingested or get into the water supply. This is particularly true if the chemical is a particulate or an aerosol and settles on the ground or is mixed with precipitation. Clothing may become contaminated. Some chemicals are converted to harmless materials over time or become too dilute to be of concern but others such as lead and mercury are persistent and can accumulate in the body.

Dose

The total amount of chemical taken in by the person is the dose. For example, if a person drinks 2 liters of water during a day and that water is contaminated with 0.001 milligrams of mercury per liter (one part per billion), his or her uptake of mercury for that day is 0.002 milligrams. Over time, some of that mercury will be eliminated from the body but some will stay in the body and accumulate. Mercury, especially methyl mercury, has an affinity for brain tissue and may result in muscle tremors and personality changes. Kidney damage may occur.

In another example, a person inhales air containing an average of 300 parts per million (ppm) of hydrogen sulfide for 10 minutes. Assuming an average adult breathing rate of 20 liters/minute his or her total dose is $20 x 10 x 300 x 10^{-6} = 0.06$ liters. Hydrogen sulfide is one of those chemicals in which a very low concentration inhaled for a long time (e.g. 1 ppm for 25 hours) should be relatively harmless, but life-threatening if inhaled at 300 ppm for 10 minutes even though the total dose is the same. Exposure to very high concentrations can result in paralysis of the respiratory center of the brain, apnea (respiration ceases), sudden collapse, and death.

2000 Emergency Response Guidebook

The PEAC Tool includes the Initial Isolation and Protective Action Distances listed in the Department of Transportation's Emergency Response Guidebook. The Emergency Response Guidebook (published in year 2000) distances are based on gas dispersion modeling for chemicals toxic by inhalation. The distances listed are tied into a Level of Concern for the chemical of interest, expressed in concentration units (e.g. parts per million or milligrams per cubic meter) in the atmosphere.

Documentation for the modeling and Levels of Concern is presented in the following publication:

Brown, D.F., A.J. Policastro, W.E. Dunn, R.A. Carhart, M.A. Lazaro, W.A. Freeman, and M. Krumpolc. October 2000 (made available in 2001). Development of the Table of Initial Isolation and Protective Action Distances for the *2000 Emergency Response Guidebook*. ANL/DIS-00-1. Decision and Information Sciences Division, Argon National Laboratory, Argonne, Illinois.

When developing the numbers, a set of between 40,000 and 100,000 hypothetical transportation accidents for each chemical was modeled. The results for each chemical were arranged in four broad categories:

- Small Spills (5 to 55 gallons), daytime
- Small Spills (5 to 55 gallons), nighttime
- Large Spills (over 55 gallons), daytime
- Large spills (over 55 gallons), nighttime

A 90-percentile safe distance value was selected for each group, meaning that for 90% of the accidents modeled, the Protective Action Distance was equal to or less than the distance predicted. Certain chemicals have several more categories under the general headings "when spilled on land" or "when spilled in water". Chemical warfare agents and certain dangerous industrial chemicals have headings "when used as a weapon" or "as a spill". For the "when spilled in water" category, the modeling and Level of Concern is based on the reaction products have with water and not on the chemical itself. For example, bromine trifluoride reacts violently with water producing hydrogen fluoride and perhaps bromine. The "when used as a weapon" category assumes that all of the chemical is released at once as in a terrorist explosion. The PEAC user can mimic this by selecting the BLEVE or sudden pressure release mode.

The 2000 Emergency Response Guidebook Level of Concern is based on the American Industrial Hygiene Association's numbers. Every year, the American Industrial Hygiene Association of Akron, Ohio publishes Emergency Response Planning Guidelines (ERPG) for about 7 to 10 chemicals at levels 1, 2, and 3 (called ERPG-1, ERPG-2, and EPRG-3). Levels for about 100 chemicals have been published to date. The "Initial Isolation Zone" is based on the ERPG-3 level together with a 5-minute exposure time (even though the ERPG-3 concentration as developed by the American Industrial Hygiene Association is based on an one-hour exposure). The Protective Action Distance is based on the ERPG-2 level.

The 2000 Emergency Response Guidebook lists many more chemicals than the 100 or so chemicals for which ERPG-2 and ERPG-3 levels have been established. Therefore the 2000 Emergency Response Guidebook used surrogate numbers to represent ERPG-2 and ERPG-3. The numbers used are listed in reference cited above and are also cited in the PEAC tool. For many chemicals, the Guidebook used a surrogate value of 0.01 LC_{50} for ERPG-2 and 0.1 LC_{50} for ERPG-3. Here, LC_{50} is the 1-hour lethal concentration for 50% of the exposed population of a laboratory test animal (data for rats preferred over other animals).

American Industrial Hygiene Association's ERPG-2 and ERPG-3

The three Levels of Concern have been incorporated into the PEAC tool. All levels assume a 1-hour exposure to the chemical. New chemicals are added to the list annually, and occasionally an old listing is updated. The three levels are defined as follows:

ERPG-1: The maximum airborne concentration below which most individuals could be exposed for up to one hour without experiencing anything other than mild transient adverse health effects or perceiving a clearly defined objectionable odor.

ERPG-2: The maximum airborne concentration below which most individuals could be exposed for up to one hour without experiencing or developing irreversible or other serious health effects, or symptoms that could impair their ability to take protective action.

ERPG-3: The maximum airborne concentration below which most individuals could be exposed for up to one hour without experiencing or developing life-threatening health effects.

DOE's Temporary Emergency Exposure Limits

The U.S. Department of Energy Subcommittee on Consequence Assessment and Protective Actions (SCAPA) has developed Temporary Emergency Exposure Limits (TEEL-1, TEEL-2, and TEEL-3) for about 2000 chemicals as approximations to ERPG-1, ERPG-2, and ERPG-3 values to be used as temporary guidance by DOE and its contractors until the peer-reviewed ERPG values developed by AIHA are published. Most of the DOE numbers are in the PEAC™ tool. The list is updated at least annually. The TEEL-1, TEEL-2, and TEEL-3 values can be obtained from the SCAPA website (http://www.bnl.gov/scapa/).

Worker Exposure to Chemicals

The United States Occupational Safety and Health (OSHA) regulations (under 40 CFR Part 1910.1000; CFR = Code of Federal Regulations) specify time-weighted average concentrations (OSHA-TWA) in the workplace for an eight hour per day, 40 hours per week exposure. OSHA may list eight-hour per day limits in regulations as permissible exposure level (PEL), which is the maximum amount of chemical that a person can be exposed to, and usually is the same as the TWA The PEL values may be transitional numbers before a final TWA number is published. Usually PEL numbers are listed on Material Safety Data Sheets. For some chemicals, OSHA further specifies ceiling values for some specified time period (usually 15 minutes) meaning that the worker should not be exposed to concentrations above the ceiling value even though the TWA exposure is in compliance. OSHA also has specified Short Term Exposure Limits (STEL) for chemicals, which is the maximum amount of substance that a worker can be exposed to in 15 minutes, four times a day, with a minimum of one-hour between exposures. Usually (but not always) the 15 minute ceiling limit and the STEL are the same numbers.

The National Institute for Occupational Safety and Health (NIOSH) also specifies time-weighted average concentrations for an eight hour day, 40 hours per week exposure which are sometimes different from the OSHA regulations. In addition, NIOSH also specifies Immediately Dangerous to Life and Health (IDLH) concentrations which represent the maximum concentration from which a worker could escape in 30 minutes without experiencing any escape-impairing (e.g., severe eye or respiratory irritation) or irreversible health effects. The IDHL concentrations do not consider long term adverse effects such as cancer. The definition of IDHL was originally based on the U.S. Mine Safety and Health Administration stipulation (30 CFR Part 11.3(t)) to ensure the ability of a worker to escape in 30 minutes in case respiratory protective equipment fails. NIOSH reviewed and revised the IDHL values, adding to it a criteria that the IDHL value must not exceed 10% of the Lower Explosive Limit (LEL) in air even though relevant toxicological data indicated irreversible health effects or impairment of escape existed at higher concentrations.

The American Conference of Governmental Industrial Hygienists (ACGIH) also has established advisory exposure guidelines that represent the amount of substance that most people can be exposed to day after day without harmful effects, which are listed as Threshold Limit Values (TLV). These may be listed as Time Weighted Averages, Short Term Exposure Limits, or Ceiling Values.

The toxic endpoint used in U.S. EPA Risk Management Plans under 40 CFR Part 68 is either based on ERPG-2 values or is 0.1 times the IDHL value or (for a few chemicals) is estimated at some fraction of LC_{50} values for some animal.

What Concentration is Safe?

The PEAC tool does not answer this question, but instead lists concentrations as developed by various organizations. These concentrations are candidates for various Levels of Concern and include:

2000 Emergency Response Guidebook Level of Concern for PAD
ERPG-1 (or (TEEL-1)
ERPG-2 (or TEEL-2)
ERPG-3 (or TEEL-3)
IDHL
STEL
TWA (8-hour exposure, or other exposure), with flag if it is a ceiling limit.

There is another flag if NIOSH Pocket Guide to Chemical Hazards indicates a potential occupational carcinogen

In the TWA case, the most conservative (lowest concentration) of the numbers generated by either OSHA, NIOSH, or ACGIH as published in the NIOSH Pocket Guide to Chemical Hazards is displayed in the PEAC® tool.

Some comparisons of toxic inhalation endpoints which may be used as levels of concern are listed in table 1.

Table 1. Example Toxic Inhalation Concentration Limits

Concentrations in ppm unless otherwise specified

Chemical	ERPG-1	ERPG-2	ERPG-3	OSHA TWA	NIOSH TWA	IDLH
acetaldehyde	10	200	1000	200	Ca	2000
acrolein	0.1	0.5	3	0.1	0.1	2
ammonia	25	150	750	ST 50	25	300
benzene	25	150	1000	0.1	0.1 Ca	500
bromine	0.2	1	5	0.1	0.1	3
1,3-Butadiene	10	200	5000	1000	Ca	2000
carbon disulfide	1	50	500	20	1	500
carbon monoxide	200	350	500	50	35	1200
carbon tetrachloride	20	100	750	ST 10	2 Ca	200
chlorine	1	3	20	1	0.5	10
chlorotrifluoroethylene	20	100	300	no data	no data	
dimethyldichlorosilane	0.8	5	25	5 (HCl)	5 (HCl)	
dimethylamine	1	100	500	10	10	500
ethylene oxide	na	50	500	1	Ca	800
formaldehyde	1	10	25	0.75	Ca	30
hydrogen chloride	3	20	100	5	5	50
hydrogen cyanide	na	10	25	10	ST 4.7	50
hydrogen fluoride	2	30	50	3	3	30

hydrogen sulfide	0.1	30	100	20	10	100
isobutryronitrile	10	50	200	n.l.	8	30
methanol	200	1000	5000	200	200	6000
methyl isocyanate	0.025	0.5	5	0.02	0.02	3
methylene chloride	200	750	4000	500	Ca	
methyltrichlorosilane	0.5	3	15	see HCl	see HCl	
monomethylamine	10	100	500	10	10	100
phenol	10	50	200	5	5	250
phosgene	na	0.2	1	0.1	0.1	2
phosphine	na	0.5	5	0.3	0.3	50
propylene oxide	50	250	750	100	Ca	400
styrene	50	250	1000	100	50	700
sulfur dioxide	0.3	3	15	5	2	100
sulfuric acid	2 mg/m^3	10 mg/m^3	30 mg/m^3	1 mg/m^3	1 mg/m^3	
toluene	50	300	1000	200	100	500
trimethylamine	0.1	100	500	n.l. (5)	10	
vinyl acetate	5	75	500	n.l. (10)	4	

Notes: na = not appropriate
n.l. = not listed (number in brackets is PEL)
ST = short term or ceiling value during a normal work day
Ca = NIOSH potential occupational carcinogen (if no value listed, NIOSH recommends occupational exposure to the lowest feasible concentration)
HCl means that for the chemicals listed react with air moisture producing HCl and the numbers listed are for HCl