CASUALITIES FROM TOXIC CHEMICAL RELEASES

A military responder asked AristaTek what concentrations of a toxic chemical can be considered safe and what concentrations will result in causalities. He had in mind a display of chemical concentrations and resulting causalities overlaid on a map for a situation where a chemical warfare agent had been released, and wanted something more than numbers showing peak concentration as a function of distance downwind. This problem is not limited to chemical warfare agents but applies also to toxic chemicals in general including common materials used by industry such as chlorine and ammonia and hydrogen sulfide encountered in oil and gas production. Sometimes these toxic chemicals encountered in industry are referred to as TICs and TIMs (toxic industrial chemicals; toxic industrial materials).

In order to relate chemical concentrations in the air to causalities, we need to understand the concept of dose. As we will see, the relationship between concentration and causalities is not straightforward and is chemical dependent.

Dose

The dose is the total amount of chemical or toxicant taken up by the person (or organism). Example: 1 gram dose of potassium cyanide. The dosage is the amount of chemical or toxicant taken up per unit of body weight. Example: 10 milligrams of potassium cyanide per kilogram of body weight.

> Example: A 70 kg person drinks 2 liters of water per day which contains 100 ppb of lead. What is his dose and dosage each day?
>
> Answer: First convert ppb in water to mg/liter. The weight of one liter of water is 1000 grams (approximately) or 1,000,000 milligrams (mg). One part per million (1 ppm) in water is 1 mg/liter, and 1 ppb is 0.001 mg/liter. 100 ppb = 100 parts per billion = 0.1 mg/liter. Dose = 0.1 x 2 = 0.2 mg per day. Dosage = 0.2/70 = 0.0028 mg lead per kg of body weight per day.

In this discussion, we will consider absorption of the toxic chemical; through the skin (including eyes) and by inhalation and not consider injection or ingestion. The skin surface is roughly 18,000 cm^2 (1.8 m^2) for an 180 lb person. The surface area of the lungs is about 50 to 100 m^2. The skin is relatively impermeable to most salt ions including aqueous solutions of salts but is permeable to many toxicants (including mercury, pesticides, chemical warfare agents). Eyes and the scrotum are the most sensitive areas for absorption, and the bottom of the foot the least sensitive area. The nasopharyngeal (nose and throat) region does a good job of filtering out particulates greater than 5 µm; particles between 2 and 5 µm are mostly cleared out by mucus and cilia in the tracheobronchiolar region of the lungs. However the lungs readily absorb many toxic chemicals.

When estimating the dose by inhalation the situation gets complicated. For example, a person is in a room for 10 minutes where the air contains 300 ppm hydrogen sulfide. What is his/her dose? We might assume a breathing rate of 20 liters per minute for a person at rest and calculate a dose:

300 ppm x 34.1/24.45 = 418 mg/m^3 concentration of hydrogen sulfide in air.

418 x 20 liters/min x 10 minutes/1000 liters per m^3 = 83.6 mg dose.

But wait, things are not that simple. Not all of the hydrogen sulfide is absorbed in the lungs (some is exhaled). Also supposing the person engaged in heavy labor and his breathing rate is much higher, say 60 or 80 liters/minute.

We need to account for how much chemical is absorbed by the body during breathing and what dose is considered toxic. This is where animal studies come into effect.

Animal Studies

The favorite test animal for most toxicity studies is the laboratory rat. Sometimes mice or rabbits or rarely dogs are used. The use of primates for toxicity studies is very expensive even though monkeys and apes are considered closer to human beings. Rabbits are sometimes favored for skin absorption studies using a dermal patch containing a known amount of toxic chemical (rats and mice are too small to effectively use a patch). Dogs might be used for long-term exposure tests at sub lethal levels, and metabolic activity studied. Sometimes the animal is sacrificed after the tests and organs (liver, kidneys, bone, fat, etc.) analyzed.

When human volunteers are used, the dose is usually too small to result in any permanent damage. Blood and urine samples are withdrawn to determine the metabolic fate of the toxicant in the body. This has not always been the case. Information regarding the lethal dose of chlorine by inhalation came from use of chlorine as a poison gas on humans during World War I.

A common test is to determine the lethal dosage or lethal concentration in the air resulting in death of 50% of the test animals, referred to as LD50 or LC50. Long term effects such as increased sensitivity or cancer are not considered. The LD50 is expressed in terms of amount of chemical per kg body weight resulting in the death of 50% of the test animals, usually laboratory rats. Also specified is the route of entry (dermal patch, injection, ingestion, eyes) as the LD50 could be different depending upon the route of entry. LC50 tests are done by exposing the animals to air borne toxics for a specified period of time, usually 1 or 4 hours. The assumption is made that the LD50 and LC50 numbers from animal studies are scalable to humans.

The results of toxicity tests are made part of Material Safety Data Sheets (MSDS) made available to workers and others using toxic industrial chemicals. For the sake of brevity, not all test information may be listed but enough should be given to warn workers of the chemical hazards.

The United States National Library of Medicine under the TOXNET website maintains a Hazardous Substance Data Base for about 5000 different chemicals. The toxicity data is very complete giving animal test results and the effect of exposure of the chemical to humans including cancer studies. The website is located at http://toxnet.nlm.nih.gov/cgi-bin/sis/htmlgen?HSDB. The user may enter the name of the chemical, CAS number, or the physiological effect as part of the search routine.

Definitions

Various governmental and other organizations have taken toxicity information and developed airborne concentration estimates which will result in detrimental or even lethal effects if a person is exposed for a specified period of time. The process by which these concentrations are estimated is not straightforward and often subject to revision. Often a committee will meet and propose concentrations and the methodology by which numbers are derived from animal and other studies. There may be a review and commentary period. Some of the numbers may be labeled "draft", "temporary", "proposed", or "interim" before they are finalized.

First, some definitions.

ERPG is an acronym for Emergency Response Planning Guideline. ERPG numbers are developed by the Emergency Response Planning Committee of the American Industrial Hygiene Association (AIHA). These numbers are peer reviewed. About 7 chemicals are added every year (about 110 chemicals as of 2005). One-hour rat exposure tests are used as a starting point if available. Three levels of concern are recognized which are defined as follows:

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

ERPG-2: The maximum airborne concentration below which it is believed that nearly all individuals could be exposed for up to one hour without experiencing or developing irreversible or other serious health effects or symptoms which could impair an individual's ability to take protective action.

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

TEEL is an acronym for Temporary Emergency Exposure Limit. TEEL numbers are developed by the Subcommittee on Consequence Assessment and Protective Actions (SCAPA), under the U.S. Department of Energy (DOE). One-hour ERPG or AEGL levels are used by SCAPA if available, but for many chemicals ERPG and AEGL numbers have not been developed. TEELs have been published for roughly 2500 chemicals. Three levels of concern are defined as follows (a 1-hour exposure is implied):

TEEL-1: The maximum airborne concentration below which it is believed that nearly all individuals could be exposed without experiencing other than mild transient adverse health effects or perceiving a clearly defined, objectionable odor.

TEEL-2: The maximum airborne concentration below which it is believed that nearly all individuals could be exposed without experiencing or developing irreversible or other serious health effects or symptoms which could impair an individual's ability to take protective action.

TEEL-3: The maximum airborne concentration below which it is believed that nearly all individuals could be exposed without experiencing or developing life-threatening health effects.

There is also a TEEL-0 category for minimal consequences

AEGL is an acronym for Acute Exposure Guideline Level. By acute is meant a single, non-repetitive exposure for not more than 8 hours; it is intended to describe the risk to humans from rare or once-in-a-lifetime exposure to chemicals. The numbers are developed by the Federal Advisory Committee and stakeholder members and are peer reviewed by the National Academy of Sciences, and public participation is invited through Federal Register notices (see http://www.epa.gov/opt/aegl/pubs/process.htm for details). The numbers are favored by the U.S. Environmental Protection Agency. Four review levels are recognized (draft, proposed, interim, and final). The numbers are developed for different exposure periods (10 min, 30 min, 1 hour, 4 hours, and 8 hours). Three levels of concern are defined as follows:

AEGL-1: The airborne concentration of a substance above which it is predicted that the general population, including susceptible individuals, could experience notable discomfort, irritation, or certain asymptomatic nonsensory effects.

AEGL-2: The airborne concentration of a substance above which it is predicted that the general population, including susceptible individuals, could experience irreversible or other serious, long-lasting adverse health effects or an impaired ability to escape.

AEGL-3: The airborne concentration of a substance above which it is predicted that the general population, including susceptible individuals, could experience life-threatening health effects or death.

It is recognized that certain individuals (people with asthma, infants, the elderly, etc.., could experience these effects at concentrations below the corresponding AEGL.

MEG is an acronym for Military Exposure Guidelines. The MEGs are structured somewhat like the AEGLs except they are intended for deployed military personnel, e.g. healthy, young adults and not for infants, children, elderly, overweight, or people whose health is already impaired, or sensitive individuals. The ability of deployed military personnel to do their assigned duties is also considered. The concentrations were developed by the U.S. Army Center for Health Promotion and Preventive Medicine (USACHPPM) and are published in a document called "TG 230 Chemical Exposure Guidelines for Deployed Military Personnel", Jan. 2002 and updates. Guidelines are listed for different times of exposure including 24-hour, 14 day, and 1 year continuous exposure. The longer exposure times take into account the potential for cancer or other permanent disease. Examples of definitions for a shorter time period are as follows:

1-hour duration, minimal: The airborne concentration above which continuous exposure for 1 hour could begin to produce mild, non-disabling, transient, reversible effects, if any. Such effects should not impair performance. Increasing concentrations and/or duration of exposure could result in performance degradation, especially for tasks requiring specific mental/visual acuity or physical dexterity/strength.

1-hour duration, significant: The airborne concentration above which continuous exposure for 1 hour could begin to produce irreversible, permanent, or serious health effects that may result in performance degradation or incapacitate a small portion of individuals. Increasing concentrations and/or duration of exposure will increase incidence and severity of effects.

1-hour duration, severe: The airborne concentration above which continuous exposure for 1 hour could begin to produce life-threatening or lethal effects in a small portion of individuals. Increasing concentrations and/or duration of exposure will increase incidence of lethality and severity of non-lethal severe effects.

The categories of "minimal", "significant", and "severe" are not used for 8 hour, 24 hour, 14 day, and 1 year exposure. For example, the 1 year category reads as follows:

1-year: The airborne concentration for continuous exposure (356 days, 24 hours/day) that is considered protective against health effects including chronic disease and increased risk of cancer (i.e., cancer risk greater than 1×10^{-4}). No performance degradation or long-term health consequences are expected with exposure at or below this level. Increasing concentrations and/or duration could result in performance degradation or increase the potential for delayed/permanent disease (e.g. kidney disease or cancer).

NIOSH and OSHA (National Institute for Occupational Safety and Health; Occupational Safety and Health Administration) have also published concentrations intended for use by workers, employers, and occupational health professionals. The concentration numbers are listed in the NIOSH Pocket Guide to Chemical Hazards and some are codified into regulations (29 CFR part 1910.1000)

IDLH: Immediately Dangerous to Life and Health. The intent by NIOSH is to list a maximum airborne concentration to which a worker could be exposed for a period of 30 minutes in the event of failure of respiratory protection equipment without loss of life or irreversible health effects or severe eye or respiratory irritation or other deleterious effects that would prevent his/her escape.

How Do The Concentrations Compare?

Table 1 compares the various airborne concentrations discussed in the above definitions for a one hour exposure time using example chemicals. If an ERPG has been published, this is listed (otherwise the TEEL value is listed as in the case of GB and VX at all levels, and TEEL-1 for arsine, phosgene, and hydrogen cyanide).

Table 1: Levels of Concern for One Hour Exposure Time.

Chemical	ERPG-1 or TEEL-1	ERPG-2 or TEEL-2	ERPG-3 or TEEL-3	AEGL-1	AEGL-2	AEGL-3	MEG-minimal	MEG-significant	MEG-severe	LC50
Ammonia, ppm	25	150	750	30	160	1100	25	110	230	7338
Agent GB (sarin), ppm	0.0005	0.006	0.022	0.00048	0.006	0.022	0.00048	0.006	0.022	0.16
Agent VX, ppm	0.000016	0.00027	0.00091	0.000016	0.00027	0.00091	0.000016	0.00027	0.00091	Very low
Arsine, ppm	0.5	0.5	1.5	Not recommended	0.17	0.5	Not recommended	0.167	0.5	30
Boron trifluoride, mg/m^3	2	30	100	2.7	37	110	0.6	16	39	828
Carbon monoxide, ppm	200	350	500	Not recommended	83	330	Not recommended	116	400	4590
Chlorine, ppm	1	3	20	0.5	2	20	0.5	2	20	293
Fluorine, ppm	0.5	5	20	1.7	5	13	1.4	5	11	185
Hydrogen cyanide, ppm	2	10	25	2	7.1	15	2	7	15	71
Hydrogen sulfide, ppm	0.1	30	100	0.51	27	50	0.5	27	50	712
Phosgene, ppm	0.1	0.2	1	Not recommended	2	3.6	0.1	0.3	0.75	5
Sulfur dioxide, ppm	0.3	3	15	0.2	0.75	27	Not determined	3	15	2520

Comment: LC50 from Table B1 of 2004 ERG Development Document, Argonne National Laboratories, except GB and VX. From TOXNET, the LC50 value for Sarin for humans is estimated to be 1 ppm for a 10 minute period. Since GB dose is accumulative, this calculates out to be 0.16 ppm for a 1 hour period. The LD50 value for VX (rabbit, subcutaneous) is 0.0153 mg/kg.

When table 1 is examined, no particular pattern can be discerned. Sometimes AEGLs or ERPG are greater than the MEGs and sometimes they are lower and sometimes the same numbers are used. Nor can any pattern can be discovered between the concentrations for various levels (1, 2, 3, or minimal, significant, or severe, or the ratio of any level to LC50. The numbers published are judgment calls as established by the various governmental groups using available toxicity test results considering the definitions for ERPG, AEGL, and MEG.

Sometimes the MEGs are even lower than the corresponding AEGLs. Part of the reason may be subjective analysis by different people who establish the rules, but MEGs consider the ability of deployed military personnel to do their assigned tasks. The original military responder asked about causalities, but if the person cannot do his duty he/she is causality.

One issue that needs to be addressed is the number of significant figures in the listed airborne concentrations. The original toxicity studies may be accurate to only one significant figure, e,g. LC50 = 5.2 + or – 1.8 ppm for 4 hour exposure using a rat as a test animal. There may be additional tests at lower concentration levels. Sometimes the tests performed by different organizations are even inconsistent. Subjective decisions are required in estimating results. The final number after going through various calculations may be uncertain by a factor of two and even that is affected by subjective issues. But sometimes the number might be displayed to several significant figures and not rounded giving the impression that the number is known to great accuracy. One common example where the number of significant figures is apparently increased is in the conversion between ppm and mg/m^3 . We might convert ERPG-1 for hydrogen cyanide from 2 ppm to 1.82 mg/m^3 but 1.82 mg/m^3 is not any more accurate.

The process of by which toxicity data is used to estimate levels of concern are best answered by contacting the agencies which develop the numbers. The American Industrial Hygiene Association publishes documentation for each chemical for which an ERPG is developed.

If there is no other toxicity information available other than TC50 data, sometimes 0.01 times the LC50 value might be used by regulatory agencies in setting a level 2 category if an official number does not exist, e.g. a "tentative" ERPG-2 for use in setting a Protective Action Distance in the 2004 Emergency Response Guidebook by the Department of Transportation set equal to 0.01 times LC50. Also, 0.1 times the TC50 value sometimes is used as an approximation to IDLH subject to the constraint that IDLH also must be less than 0.1 times the Lower Explosive Limit in air.

Exposure Duration

In the simplest analysis, the inhaled chemical accumulates in the body and is not excreted or exhaled. Assuming a constant breathing rate, the dose then equals the concentration times time times the breathing rate:

$$\text{Dose} = k\,C\,t$$

Where k = breathing rate
C = airborne concentration
t = time of exposure

In reality, many chemicals are excreted (exhaled) and only a proportion accumulates. Also accumulation may not occur until a threshold concentration is reached.

$$\text{Dose} = k\,(C - a)\,t^n$$

Where a = threshold concentration and n is derived from experimental data. Typically n is roughly equal to -0.5, but this varies with the chemical.

Let's see how this works. Table 2 presents AEGL-3 levels for different times of exposure.

Table 2. AEGL-3 Levels of Concern for Different Times of Exposure

Chemical	**10 Minute**	**30 Minute**	**60 Minute**	**4 Hours**	**8 Hours**
Ammonia, ppm	2700	1600	1100	550	390
Agent GB, ppm	0.11	0.057	0.039	0.021	0.025
Carbon monoxide, ppm	1700	600	330	150	130
Chlorine, ppm	50	28	20	10	7.1
Hydrogen cyanide, ppm	27	21	15	8.6	6.6
Hydrogen sulfide, ppm	76	59	50	37	31
Phosgene, ppm	3.6	1.5	0.75	0.2	0.09

As expected, the concentration representing level 3 is lower for the longer exposure time. But the response is chemical dependent. Chlorine, ammonia, and agent GB (Sarin) fit the equation [Dose = $k\,(C - a)\,t^n$] with n = -0.5 and a << C. For carbon dioxide and ammonia, n is closer to -1 and "a" for carbon monoxide is about 95 ppm. For hydrogen sulfide, n is roughly -0.23. For hydrogen cyanide, n is closer to -0.4.

At the level 1 (AEGL-1), the concentrations tend to be more flat for different times of exposure for many chemicals. For a few chemicals, the AEGL-1 concentration is the same regardless of the time of exposure at least up to and including 8 hours. An example is ammonia, where AEGL-1 = 30 ppm for all times of exposure between 10 minutes and 8 hours.

For exposure times greater than 8 hours, or repeated exposure at different times (e.g. another incidents on different days), other effects start to manifest itself such as possible increased risk for cancer and/or motor impairment, and the dose equation and the AEGL numbers do not apply. Again, the degree to which this happens depends upon the chemical.

Toxic Vapor Cloud Modeling

The PEAC tool allows for modeling two extremes: (1) very short term release as in an explosion or (2) long term, continuous release. Models are available in the public domain which consider a release for a specified time (e.g. 2 minutes) and then examines concentrations as a function of distance downwind.

The owners of AristaTek, Inc., under a combination government and private contract, set up a series of tests at the Nevada HazMat Test Facility (near Mercury, Nevada) in the mid 1990's where a dense gas was released for varying periods of time under different conditions. Almost 100 different tests were performed under different meteorological conditions and with different structures in the path of the toxic cloud. For each test, almost 100 sensors were placed downwind of the release to measure real-time concentrations at various locations and heights. When the information gathered was compared with model predictions, we noted:

- Generally, for flat surfaces and for moderate wind speeds (what modelers refer to as the "D" or neutral stability conditions) the various models agreed with measured concentrations within a factor of two.
- Buildings (the tests used plywood flaps) tended to break up the toxic cloud movement, and the cloud height was higher than predicted by models. This was also seen in small-scale wind tunnel simulations.
- Buildings also affected local concentrations and the time required to scour out residuals after the "cloud" passed.
- Under stable, low wind conditions, clear skies (what modelers refer to as the F stability or even the intermediate E stability) it takes a much longer time for the toxic airborne chemical to "scour out" than predicted by the models. The degree of cloud spreading is greater in the downwind direction than in the crosswind direction, and greater as the cloud recedes compared to an approaching cloud. Buildings enhance this effect. Changing meteorology (e.g. if the air becomes more stable with time, as in the case of a release near sunset) may enhance this effect.

The bottom line is that if there are buildings especially under stable air conditions, it takes longer for toxic residuals to clear out than what would be expected by running most models. This means that the exposure time would be greater.

The effect of buildings and other issues which affect modeling is discussed in the November 2003 issue of the First Responder newsletter, "Common Sense Corrections to Air Dispersion Models for Toxic Chemical Releases", available at http://www.aristatek.com/Newsletter/03%2011%20November/Technical%20Dialogue.htm .

Another issue which must be considered is that the source rarely releases a constant rate. For example, there may be an initial explosion releasing a large quantity of a toxic material to the air. Perhaps much of the chemical will spill on the ground and evaporate. This might mean that the model will need to be run as an "explosive puff" and again as an evaporating liquid pool to estimate a total dose. This can get complicated.

It is very important that responders when using models note the time of day, date, location, estimate a wind speed and direction (at least categorize it as calm, slight wind, moderate wind, or strong wind, and sky cover, and general terrain situation when using models.

Summary

A responder wishing to consider causalities overlaid on a map showing downwind concentrations must consider (1) levels of concern, (2) duration and concentrations of the toxic cloud at various locations, and (3) nature of the source. Levels of concern specifying both concentrations and duration of exposure for many chemicals are publicly available. Less certain may be concentrations and duration of the chemical cloud, as conditions can change with time or affected by buildings and typography, but ballpark estimates can often be made.