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MEMORANDUM

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SUBJECT: PEAK-TO-MEAN AIR CONCENTRATION ESTIMATION FOR FUMIGANTS

**Background**

The Department of Pesticide Regulation (DPR) regulates fumigants as restricted materials and manages the use of these pesticides through permits or regulations restricting their use practices. The department has developed mitigation measures to minimize acute exposure of persons off-site to fumigant vapors that escape from the application site following a fumigant application. These mitigation measures are developed with the objective of avoiding the exceedance of air concentration targets set by the Medical Toxicology Branch in DPR for specific fumigants. The air concentration target exposure duration and concentration levels are set at appropriate levels for the toxicological action of a specific fumigant. For example, Methyl Bromide (MeBr) has an acute air concentration target of 2 10 parts per billion (ppb) as a 24-hour Time Weighted Average (TWA) (Nelson, 1992), while Methyl Isothiocyanate (MITC), has an acute air concentration target of 220 ppb as a 1-hour TWA (Gosselin, P. per. comm.). The differences in these targets reflects the differences in the toxicological action of these two fumigants. The air concentrations of these two targets are TWAs. To obtain a TWA air concentration the air is sampled in a continuous manner for a specific period of time and the concentration is then determined by dividing the total mass found in the final sample by the total air flow during the sampling period. The TWA air concentration is a measurement that represents a time-integral of concentration (Csanady, 1973).

**The Ensemble Mean Concept**

The concept that the TWA air concentration represents a time-integral of concentration is important to relating the measured air concentrations to air dispersion model predictions of air concentrations. DPR uses standard air dispersion modeling techniques based upon statistical representation of a pollutant plume to predict expected air concentrations of various fumigants given a specific set of application and meteorological conditions. The foundation of these



techniques dates back to G.I. Taylor's (1921) concept of diffusion by continuous motion. The underlying concept of this prediction technique is that the pollutant molecules faithfully follow the motions of the air in which they are embedded. Therefore, statistical properties of the atmospheric turbulence at the time of the pollutant release can be used to predict the statistical time history of a pollutant plume (Schnelle and Dey, 2000). Essentially, this approach is built upon the foundational assumption that atmospheric diffusion is a direct result of atmospheric turbulence (Hanna, 1982).

There is no single functional form that uniquely describes atmospheric turbulence and diffusion. However, the Gaussian function can be supported by several different arguments as an appropriate function to characterize average plume diffusion. First, the Gaussian function expresses the essentially random nature of the phenomena by analogy with the central limit theorem; namely, that the distribution of sample means from any population (with a mean,  $\mu$ , and variance  $\sigma^2$  ( $0 < \sigma^2 < \infty$ )), regardless of the underlying distribution of that population, tends towards the Gaussian distribution (Batchelor, 1949). A second basis for the assumption of a Gaussian form can also be provided by the observation that the "wanderings" of the pollutant molecules in the turbulent field of the atmosphere can be represented as a "random-walk" and therefore, the distribution of the pollutant molecules can be assumed to be approximately Gaussian in three dimensions (Csanady, 1973). Third, the Gaussian form is also a solution to both of the two basic turbulence theories: gradient transport theory and statistical theory of turbulence (Gifford, 1968). Fourth, experimental diffusion studies employing tracer releases indicate that the Gaussian functional form has wide applicability in representing atmospheric turbulence and diffusion (Hay and Pasquill, 1957). Many alternate forms of the Gaussian model are employed, but the main differences are in the exact form of the standard deviations (Singer, 1961).

The predictions obtained from using the Gaussian equation represent ensemble-mean **concentrations**. For continuous sources, the theoretical ensemble mean concentration field is a model representation of the realized time-average concentrations (Pasquill, 1962). The ensemble-mean concentration field may be interpreted as the mean (expected value or first moment) of all possible outcomes of a dispersion measurement taken under a specific set of conditions, for example a 1-hour TWA air concentration. An actual measured air concentration obtained when the measurement is made in the field is only *one realization* of that theoretical set of possible outcomes. Models have "intrinsic uncertainties" (Venkatram, 1988) and field measurements include various sources of measurement errors. This is why model predictions are not expected to exactly match measured values in space and time (Zannetti, 1990).

The measured time-weighted average concentration will most often be a result of a series of concentrations fluctuations. These fluctuations may be represented as a function composed of sinusoidal components (Pasquill, 1962), and the realized function depends on the distance from

the source and the diffusive conditions. For a ground level source, the majority of the variation of ground-level concentrations between samples of differing duration will essentially be a function of the cross-wind spread (Pasquill 1962). The TWA concentrations at a fixed position will depend upon the frequency of the corresponding wind directions during the measurement period. The Gaussian bivariate distribution describing the average pattern is made up of shorter-term periodic distributions that differ significantly from the mean (Singer, 1961). Pasquill (1962) observed that: "In reality the concentration at a fixed point is a fluctuating quantity, so that even if the average level is harmless or tolerable it does not follow that this can be assumed for the fluctuating concentration." This observation is directly related to the problem of estimating the peak concentration observed during a given longer duration averaging period.

### **Peak-to-Mean Estimation**

Gaussian dispersion models predict time-averaged concentrations at fixed points for minimum averaging times on the order of 1/4 to 1 hr. The concentrations are actually random variables with relatively small variances. However, at a fixed sampling point, as the averaging period is shortened, the plume direction fluctuations, and therefore the variance of time-weighted average air concentrations become larger. The range of observed concentrations also becomes larger. At some point some short duration maximum concentration is reached with a frequency during a longer time interval that is regarded as 'significant'. This concept is discussed and described in the literature as the 'peak-to-mean ratio.' Peak-to-mean ratios are directly related to the magnitude of concentration fluctuations at a given fixed location.

Sutton (1947) distinguished between the "instantaneous" and "time-mean" aspects of a cloud or plume. A pollutant plume section will be comparatively narrow with a high peak value on the instantaneous axis. However, if measurements are made over longer periods, (e.g. several minutes to hours) the curve of concentration across any section of the plume retains the same general shape but is broader than the instantaneous curve and has a lower peak value. The plume, in effect, swings over a wider region in response to longer period atmospheric eddies than those which affect the instantaneous measurement. The mean concentration patterns are the result of many short-term peak conditions and, therefore, a definable relationship exists between the peaks and the mean (Singer 1961). Stewart et al. (1958) found that, for measurements taken at or near the release height and sampling periods of about 3 minutes to one hour, the decrease in mean concentration with increased sampling duration followed a  $1/5$  power law.

Gifford (1959), with his fluctuating plume dispersion model, published the first major paper addressing the modeling of the peak-to-mean concept. The fluctuating plume dispersion model assumes the Gaussian form but the dispersion phenomenon is separated into a portion due to instantaneous spreading of the plume in the crosswind (y) and vertical (z) directions, and a portion due to meander of the entire plume about its mean position. Gifford (1960) observed that

short term air concentrations can be an order of magnitude greater than the time weighted average mean over a longer sampling period. Gifford (1960) also compared the theoretical results from the fluctuating plume dispersion model with actual observations of peak-to-mean concentration ratios. In general, he found good correspondence between the theoretical values and those calculated from field data. For sources and centerline receptors at or near the same height (e.g. both at ground level), peak-to-mean (Peak to Average (P/A) in Gifford (1960)) values are relatively small, about 1 to 5, even ratios of sampling times (average time/peak time) spanning from 1 to 200. It can be shown that at large downwind (large travel time) distance the peak-to-mean ratio (P/A) approaches a limit of 1 .0.

Hino (1968) found that the reduction of ground level concentrations with, increasing sampling times, for time-weighted average sampling times ranging from 10 minutes to 5 hours, follows a -1/2 power law, rather than the -1/5 power law that Stewart et al. (1958) had suggested. Hino (1968) suggests that the -1/5 power law is valid only for average sampling times less than 10 minutes. Turner (1994) recommends the Hino (1968) -1/2 power law be used as the peak-to-mean calculation method to estimate a peak short-term concentration associated with time weighted averaged samples taken over 10 minute to 5 hours. Example peak-to-mean ratios from Hino (1968), as presented in Turner (1994), are shown in Table 1. These peak-to-mean ratios are in general agreement with the peak-to-mean ratios of 1 to 5 found by Gifford (1960).

It is a common and accepted practice to apply the peak-to-mean adjustment to the longer averaging time mean air concentration prediction from Gaussian plume dispersion models in order to estimate an expected peak concentration (The, J.L. per. comm.; Pope, R.J. and P. Diosey 2000). Although Gaussian plume dispersion models can be used to predict ensemble mean air concentration over periods as short as 3 to 10 minutes, in most cases the prediction is made on a one-hour basis because that is the resolution of the weather data (e.g. National Weather Service or CIMIS weather data) (Turner 1994). The general equation to calculate the -1/2 power law peak-to-mean adjusted concentration is given below:

$$C_p = C_m \left( t_p / t_m \right)^{-1/2}$$

Where:

- $C_p$  = peak concentration over period,  $t_p$ , of interest
- $C_m$  = mean concentration over measurement period,  $t_m$
- $t_p$  = duration of peak period of interest
- $t_m$  = duration of mean measurement period

This generalized equation can be used to estimate peak concentrations of varying duration from any mean concentration of 5 hours or less. This method for estimating a peak concentration

from a mean concentration was developed by studying point source releases. A fumigant application may be a point source (e.g., commodity fumigation chamber) or an area source (e.g., agricultural field soil injection). Area source releases have not received the same level of study as point source releases. There are no literature references discussing the general applicability of the peak-to-mean estimation techniques to area sources. However, it is likely that application of the peak-to-mean adjustments derived by the equation shown above to area sources will result in conservative estimates of peak concentrations (biased high) (Johnson, B., per. comm.). Use of these peak-to-mean estimation methods is recommended for fumigant area sources as well as for fumigant point sources.

Table 1. Peak to Mean Concentration Ratios from Hino (1968) as in Turner (1994).

Sampling Period	Peak to One-Hour
One hour	1.0
30 Minutes	1.3
10 Minutes	2.3
3 Minutes	4.
1 Minute	4. to 7.
30 Seconds	4. to 10.

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