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Toxic Emission Factor Determination Using Median Lethal Time Data

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Although the median lethal concentration (LC50) is a useful measure of toxicity, it provides no information about the total quantity of toxic material being produced. Thus, because of differences in flow, it is possible for an effluent with low toxicity (high LC50) to have a larger impact on the environment than an effluent with high toxicity (low LC50). The toxic emission factor (TEF) circumvents this problem.

The factor is defined by

$$TEF = (100/LC50) \times Q \quad (1)$$

For pulp mill effluents, the LC50 is usually the 96-hr median lethal concentration (%) determined for a freshwater salmonid and Q is the flow of effluent per air-dry tonne of pulp production (m^3/adt). (The term 100/LC50 is known as the number of toxic units (TU)).

The TEF is the total dilution needed for an effluent to have a toxicity of 1 TU (LC50 = 100%). For instance, an effluent produced at 20 m^3/adt with an LC50 of 10% would have a toxicity of 1 TU when diluted to 200 m^3/adt. In theory, the LC50 is directly related to the volume at which an effluent is produced. Thus, if an effluent's flow is doubled through dilution, its LC50 would also be expected to double thereby maintaining the same TEF.

In addition to enabling the toxicity of effluents produced at different rates to be compared, there are several other advantages in the use of TEFs. Firstly, TEFs increase as toxicity increases, unlike LC50 values. This makes the comprehension of results easier. Secondly, when used as the basis for regulation, TEFs encourage the conservation of water used by industry. Regulation based on LC50s can actually penalize conservation efforts. Lastly, TEFs

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are additive in the absence of interactive effects. Thus, the relative contributions of individual streams to combined effluent toxicity can be ascertained.

Determination of the LC50 for use in Eq 1 can be problematic when dealing with effluents that are produced in the laboratory from experimental trials. Usually such effluents have unknown toxicity and can only be produced in limited quantities. Thus, it can be difficult to perform the LC50 test with enough effluent concentrations to yield a result that has the accuracy needed to distinguish it from other results. A technique for determining the TEF using median lethal time (LT50) data was accordingly proposed (Farr 1991) to solve these difficulties.

If the fundamental relationship between the concentration of an effluent, C (%), and the LT50 (min) is linear, then

$$\log LT50 = m \log C + b \quad (2)$$

is valid where m and b are the slope and intercept respectively. When C is l00%, the resulting median lethal time is denoted LT50', and Eq 2 becomes

$$\log LT50' = m \log l00 + b \quad (3)$$

Likewise, when the median lethal time is equal to 5,760 min, C is the 96-hr LC50, and Eq 2 becomes

$$\log 5{,}760 = m \log LC50 + b \quad (4)$$

Rearranging and substituting Eqs 3 and 4 respectively for the 100 and LC50 terms in Eq 1 yields

$$TEF = 10^{(\log LT50' - 1og5{,}760)/m} \times Q \quad (5)$$

Thus, the TEF can be determined from the LT50 at 100% concentration and the slope of the relationship between concentration and median lethal time.

MATERIALS AND METHODS

Three chlorination stage effluents were produced from unbleached softwood kraft pulp at different levels of filtrate recycle using a continuous laboratory-scale pulp bleaching apparatus (Farr et al. 1995). Residual bleaching chemical (chlorine and chlorine dioxide) was reduced with sodium thiosulphate. The effluents were stored for less than 24 hr at 4°C in sealed polyethylene carboys prior to the commencement of toxicity tests.

The effluents were tested to determine LT50 values according to standard methodology (British Columbia Ministry of Environment 1982). Under-yearling rainbow trout (*Oncorhynchus mykiss)* obtained from the

Provincial Hatchery in Abbotsford, British Columbia, were used as the test fish. Static toxicity tests with aeration were performed using 10 fish in a total test volume of 25 L. Each effluent was tested at 100, 62, and 38% concentration (v/v). Dechlorinated tap water from the city of North Vancouver, British Columbia, was used for dilution and controls. There were no control mortalities during this study. Testing was carried out at a pH of 7.0 and a mean temperature of 13.5°C (SD = 0.9°C). The average fish had a blotted weight of 1.4 g and a fork length of 5.0 cm.

LT50 values were calculated by the method of Litchfield (1949), which is a nomographical simplification of the method of Bliss (1937). One case (run 2, 38%) that was not covered by the nomographs required the use of the original technique to account for a partially abnormal response. Volume factors were calculated by dividing the test volume by the product of the total weight of test fish and the time taken to reach 100% mortality.

RESULTS AND DISCUSSION

The LT50 data for the nine tests is given in Table 1. The slope of Eq 2 is given for each effluent in Table 2 along with the TEFs that were calculated via Eq 5.

Table 1. Median lethal time data.

Run	Concn. (X)	LT50[a] (min)		Slope[a,b]		Vol. factor ($L.g^{-1}d^{-1}$)
1	100	202	180–227	1.21	1.11–1.31	16.9
	62	391	368–416	1.10	1.04–1.16	11.0
	38	641	612–671	1.08	1.04–1.11	4.9
2	100	318	280–361	1.21	1.09–1.35	4.7
	62	729	688–773	1.10	1.05–1.15	2.9
	38	1256	1132–1394	1.12	1.02–1.22	1.3
3	100	149	138–161	1.14	1.07–1.20	11.1
	62	268	252–285	1.10	1.06–1.15	5.7
	38	482	467–497	1.05	1.03–1.08	4.1

[a]Ranges are 95% confidence intervals.
[b]Mortality (probability) versus time (logarithmic).

The LT50 data fit Eq 2 very well as evidenced by the coefficients of determination (see Table 2). Previous work by Leach and Thakore (1976) showed that chlorination effluent from kraft pulp bleaching conforms to the linear relationship described by Eq 2 even at concentrations near the 96-hr LC50. Nine chlorination effluents (four industrial and five synthetic) representing a wide range of pulps and bleaching conditions were found to have slopes between

Table 2. Toxic emission factor data.

Run	Q (m^3/adt)	m^a	r^2	TEF (TU·m^3/adt)
1	42.9	-1.193	0.992	711
2	33.9	-1.419	0.984	261
3	24.9	-1.213	>0.999	507

[a]Slope of logarithmic plot (Eq 2) of LT50 versus concn.

-1.11 and -1.71 for rainbow trout ($r^2 > 0.91$). These values are in good agreement with the slopes found here.

It should be pointed out that Eq 2 is not consistent with the concept of a threshold concentration. At sufficiently low concentrations, organisms can be expected to survive indefinitely thereby invalidating the linear assumption. In instances where linearity cannot be demonstrated for exposures of 4 d, two options are available. TEFs could be calculated for shorter exposures (e.g., 48 hr) where linearity can be established. Alternatively, 96-hr values could still be calculated as a means of comparing differences between effluent treatments. Individual results would have no relevance.

Because the LT50 technique used here involved few test concentrations (n = 3), a reasonable measure of the variability could not be obtained directly. However, cases in the literature where more measurements are available can be used indirectly. In this instance, the data of Leach and Thakore (1976) was utilized. The results from a synthetic effluent made from toxic material that was extracted from a chlorination effluent (Mill XI) were fit with Eq 2. The slope and intercept were found to be -1.278 and 4.502 respectively (n = 8, r^2= 0.985) and the residuals showed no irregularities. This regression predicted the 96-hr LC50 to be 3.8% and inverse regression analysis (Draper and Smith 1981) gave a 95% confidence interval of 2.4-5.6%. With Q at 8.7 m^3/adt, the corresponding TEF and 95% confidence interval were calculated via Eq 1 to be 229 and 155-363 TU·m^3/adt respectively. Similarities between the effluents and species tested give some validity to this approach. In cases where suitable data in the literature are unavailable, at least one representative effluent would have to be tested more extensively in order to reliably estimate variability.

The determination of TEFs with LT50 data has several advantages over traditional LC50 techniques. The

longest LT50 test performed here (run 2, 38%) took less than 30 hr to complete, whereas the LC50 method requires 96 hr. In addition, the LT50 technique used only three concentrations, whereas the LC50 technique requires at least five concentrations beyond those needed in the preliminary estimation of toxicity. Thus, the LT50 method requires less effluent and fewer test organisms.

One of the difficulties with the 96-hr LC50 test is the depletion of toxicants with time due to uptake by fish and degradation. Thus, Walden et al. (1975) developed minimum effluent volume factors for pulp mill effluents that account for fish size and exposure. For static tests, the factor was found to be 0.5 $L \cdot g^{-1} d^{-1}$. This level was adopted as the standard in the method (British Columbia Ministry of Environment 1982) used here. It is often difficult to meet the requirement because of limitations on the availability of both sufficient quantities of effluent and suitably sized fish. Although flow-through tests allow the use of lower volume factors, they require much more effluent than static tests. Alternatively, the use of smaller test organisms such as daphnids and bacteria has decreased the amount of effluent (and time) needed to determine an LC50. However, because most effluent regulations are based on freshwater salmonids and because correlations between test organisms are not absolute, the use of such data is limited.

The use of the LT50 technique substantially increases the volume factor by minimizing the time of exposure. The volume factors for the nine tests performed here (see Table 1) were all well above the minimum level of 0.5 $L \cdot g^{-1} d^{-1}$. The average value was 7.0 $L \cdot g^{-1} d^{-1}$. If these tests had been performed using the 96-hr LC50 technique, then the average factor (0.4 $L \cdot g^{-1} d^{-1}$) would not have met the guideline.

The use of volume factors less than 0.5 $L \cdot g^{-1} d^{-1}$ in static toxicity tests causes the resulting 96-hr LC50 to be higher than the true value. Because of toxicant depletion, higher concentrations of effluent are required to maintain toxic levels of constituents. Accordingly, extrapolated median lethal time data yield lower LC50 values than median lethal concentration data for which the critical level is not met. The work of Leach and Thakore (1975) supports this. The toxicities of five compounds, which cause a significant portion of the toxicity in softwood extraction effluent, were determined using both LC50 and LT50 tests. The volume factor was 0.25 $L \cdot g^{-1} d^{-1}$ for the LC50 tests and 1.0 $L \cdot g^{-1} d^{-1}$ for the LT50 tests. The 96-hr LC50s of the five compounds determined by extrapolation of LT50 data

were on average 41% lower than the values determined by standard methodology. Curvature in the relationship between concentration and lethal time might also have reinforced the differences.

The determination of TEFs (or LC50s) through extrapolation of LT50 data appears to be a useful technique. It is best applied where the assumption of linearity between concentration and lethal time data can be confirmed either from the literature or in the laboratory.

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