

Acute Toxicity of Thallium to *Daphnia magna* and *Ceriodaphnia dubia*

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Thallium in the environment has been attracting some attention recently because intoxication from thallium is very common and occurs worldwide (Li and Aldis 1997; Malbrain et al 1997; Manzo and Sabbioni 1988; Zhou and Liu 1985), and there is an increased demand for its compounds by high-tech industries (Smith and Carson 1977). Tl is used as a catalyst in certain alloys, optical lens, jewelry, low temperature thermometers, semiconductors, dyes and pigments and scintillation counters (Smith and Carson 1977). The mammalian toxicity of thallium is comparable to that of mercury, but greater than those of cadmium, copper, lead, and zinc (Manzo and Sabbioni 1988; Wallwork et al. 1985; Zhou and Liu 1985; Zitko 1975; Zitko et al. 1975). Due to its toxicity, Tl is listed as a priority pollutant along with Pb, Cd and Hg by the US Environmental Protection Agency (Keith and Telliard 1979). The concentrations of Tl in freshwaters range from 1 to 1350 ng/L (Axner et al. 1993; Cheam et al. 1995; Lukaszewski et al. 1996; Miyazaki and Tao 1991). Tl is also more abundant in the Great Lakes waters than Cd and Hg (Cheam et al. 1995; Lin and Nriagu 1999). Thus, its aquatic toxicity should be carefully evaluated in order to appropriately assess its potential impact on the aquatic environment. According to sparse reports on aquatic toxicity of this metal species, Tl is more toxic than Ni, Cu, or Zn but less toxic than Cd or Hg to *Hyalella azteca* on a water-concentration basis (Borgmann et al. 1998). Unlike bivalent metal toxicants, the primary ionic form of Tl in oxygenated water is monovalent, and its principal analogue is K. Therefore Tl toxicity and uptake was known to be affected by K concentrations in water. Daphnids are very sensitive to a broad spectrum of toxicants and are distributed widely in the Northern Hemisphere, and therefore have been attractive test organisms also due to their short generation cycle and ease of culture and maintenance (Benfield and Buikema 1980). In this study, the acute toxicity of this metal was evaluated with two *Daphnia* species.

MATERIALS AND METHODS

The stock solution of thallium nitrate was prepared by diluting the 1000 ppm thallium nitrate standard solution (Perkin-Elmer) with moderately hard water, and the pH was adjusted to approximately 8 with 0.1 N NaOH solution. Then test solutions of a series of concentrations were generated. Moderately hard water was

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prepared in accordance with the U.S. EPA guidelines (1993, 1994). It was used for culture and the maintenance of test organisms as well as for dilution in preparation of exposure concentrations.

Daphnia magna and *Ceriodaphnia dubia*, cultured in the laboratory at the University of Michigan, were used for the acute toxicity assays. *D. magna* and *C. dubia* were maintained and fed daily in an incubator room at $20 \pm 1^\circ\text{C}$ and at $25 \pm 1^\circ\text{C}$, respectively. Newly hatched babies < 24 hour old were harvested and used for testing. All other aspects of the culture and maintenance of test species were carried out following U.S. EPA guidelines (1993, 1994). For acute toxicity testing, detailed procedures delineated by U.S. EPA were followed. Water quality parameters such as pH, temperature, dissolved oxygen and specific conductivity of the test solutions and the control were measured and logged. Acute reference toxicity tests with the same species were performed to assure similar sensitivities of each organism over this study. The concentration ranges for definitive toxicity tests were obtained by conducting preliminary 24-hr toxicity testing.

Each test employed five different concentrations plus a control and each of concentrations had four replicates with five organisms. After 48 hours, the number of survivors was counted. The ToxStat (version 3.5) with the Probit procedure was used to estimate EC50 value.

RESULTS AND DISCUSSION

Table 1 shows the results of three acute toxicity tests with *D. magna*. On average, an EC50 value of 1.66 mg/L was obtained from these assays. AD-1 was conducted in broader concentration ranges so that it resulted in slightly lower estimates. However all three EC50 estimates appeared to correspond well with one another.

Table 1. Acute toxicity of thallium nitrate to *Daphnia magna*.

Test Number	EC50 (48 hr, mg/L)	95% Confidence Interval
AD-1	1.45	1.08-1.77
AD-2	1.86	1.68-2.18
AD-3	1.66	1.46-1.92

Table 2 summarizes toxicities of several metals to *D. magna*. According to the EC50 estimate we obtained from this study, thallium displayed greater toxicity than manganese, cobalt, nickel, arsenic, cadmium, tin, barium, and lead; however, thallium was less toxic to *D. magna* than chromium, copper, zinc, silver, mercury or lanthanum.

Two tests were conducted with *C. dubia*, and the results are shown in Table 3. *C. dubia* indicated greater susceptibility to thallium than *D. magna* by the factor of 2.5. The probability unit of mortality versus Tl concentration on the logarithmic scale and their predicted regression lines for *D. magna* and *C. dubia* are described

in Figure 1. In addition, the observed mortality of *D. magna* and *C. dubia* after 48-hour exposure to Tl(I) are shown in Figure 2.

Table 2. Acute toxicity of heavy metals to *Daphnia magna*.

	EC50 (mg/L)		Reference
	24 hr.	48 hr.	
HgCl ₂	0.0081	0.0052	Khangorot and Ray 1989
AgNO ₃	0.023	0.01	Khangorot and Ray 1989
CuSO ₄ •5H ₂ O	0.536	0.093	Khangorot and Ray 1989
ZnSO ₄ •7H ₂ O	1.00	0.56	Khangorot and Ray 1989
CdCl ₂ •H ₂ O	4.66	1.88	Khangorot and Ray 1989
CoCl ₂ •6H ₂ O	2.61	1.49	Khangorot and Ray 1989
NiCl ₂ •6H ₂ O	10.90	7.59	Khangorot and Ray 1989
MnCl ₂	10.00	8.28	Khangorot and Ray 1989
SnCl ₂ •2H ₂ O	38.00	21.56	Khangorot and Ray 1989
BaCl ₂	52.82	32.00	Khangorot and Ray 1989
As ⁵⁺	51.88	44.46	Fargasova 1993
Pb ²⁺	8.317	3.73	Fargasova 1993
Cr ⁶⁺	1	0.364	Fargasova 1993
Hg ²⁺	0.054	0.0186	Fargasova 1993
CuSO ₄		0.073	Aramabasic et al. 1995
Pb(NO ₃) ₂		55.6	Aramabasic et al. 1995
ZnSO ₄		0.075	Aramabasic et al. 1995
La	0.485	0.0432	Barry and Meehan 2000

Table 3. Acute toxicity of thallium nitrate to *Ceriodaphnia dubia*.

Test Number	EC50 (48 hr, mg/L)	95% (Confidence Interval)
AC-1	0.649	0.593-0.832
AC-2	0.672	0.618-0.711

The estimated average EC50s for *D. magna* and *C. dubia* are 1.66 and 0.66 mg/L, respectively, which indicate that thallium(I) is very toxic to *Daphnia* species (Lundgren 1992; Nishiuchi 1974). The EC01s are also obtained with the probit model; they are 0.81 and 0.41 mg/L for *D. magna* and *C. dubia*, respectively. The ratios of EC01 to EC50 (EC01/EC50) for *Daphnia magna* and *Ceriodaphnia dubia* are 0.5 and 0.6, respectively, which indicate the safety margin of Tl(I) is modest and should therefore be handled carefully.

The disparity between these two species demonstrates that the surface area-to-volume may be a critical factor influencing the toxicity of Tl(I) to

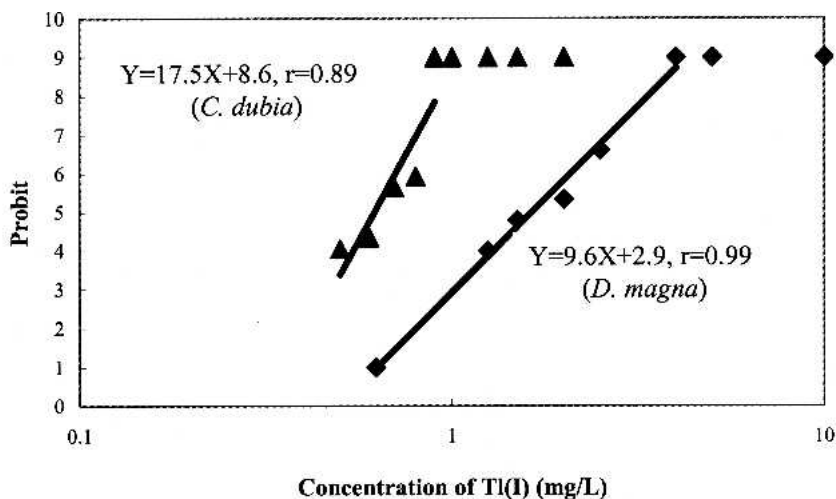


Figure 1. Probit versus Tl concentration on a logarithmic Scale for *D. magna* and *C. dubia*.

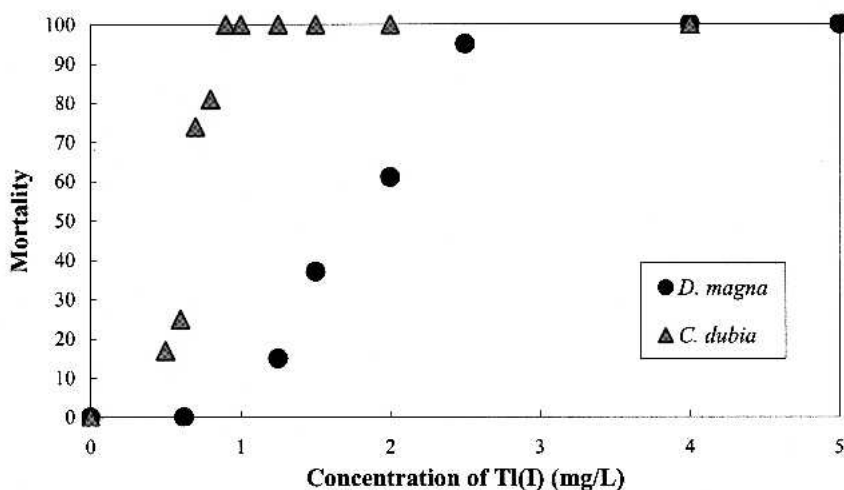


Figure 2. Mortality of Daphnia after 48 hour exposure to Tl(I).

Daphnia species, since *D. magna* (2.6 ~ 6 mm for female adult) is much larger than *C. dubia* (0.3 ~ 0.6 mm for female adult). Because of its ionic radius (1.6 Å) and the electronegativity constant (1.62), Tl(I) should behave like potassium, and to a lesser extent rubidium and silver, in aquatic ecosystems (Bodek et al 1988; Flegal et al 1989). Like the alkali metal analogues, TlOH and Tl₂O are readily soluble in water and Tl⁺ forms relatively few strong complexes. However, the

bioavailability of Tl(I) may be depressed when Tl(I) forms complexes and the observed toxicity could be less than expected in natural systems. Because the level of major ions in fresh waters is approximately 1×10^{-4} M, 10% of Tl(I) (assuming $[Tl] < 1 \times 10^{-5}$ M) can be expected in its complex forms if the stability constant is greater than 1×10^3 ; for instance, $TIPO_4^{2-}$ ($\log K=3.14$), $TIHCO_3$ ($\log K=3.42$). On the other hand, monovalent thallium resembles silver in forming a very insoluble sulfide (solubility product for Tl_2S is $10^{-21.2}$) and sparingly soluble halide complexes that are light sensitive (Lin and Nriagu 1998). The pH of the aquatic environment also affects the chemical species of metals and thus their bioavailability. The proportion of $Tl(OH)$ is only significant if the pH is greater than 9.5 (Lin and Nriagu 1998), and this does not usually happen in natural systems. Hardness is another important factor influencing the observed toxicity of metals, for example, copper (Borgmann et al 1998). However, hardness might only significantly affect the toxicity of bivalent cations; therefore, may not influence on the toxicity of Tl(I). This study clearly indicates that Tl(I) is very toxic to daphnids and the toxicity may not be abated by the hardness; thus may have potential to cause crucial deterioration of aquatic ecosystems.

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