Temperature Correction for VOC Degradation Rate Coefficients

The possibility of adjusting first-order degradation rates for changes in water temperature was investigated. The Arrhenius equation was used for the corrections, in the form shown in Equation 1 (1). Reference (1) uses the Arrhenius equation in the context of wastewater treatment, where the concentrations of organic material are typically several orders of magnitude higher than in the lakes treated in this paper. Its use in environmental situations is thought to be reasonable (2), but is not well attested in the literature. For that reason, and because of the large uncertainty in the choice of degradation rate coefficients, the rate coefficients used in this paper were not adjusted for water temperature variations.

To account for changes in degradation rates with lake temperature, the rates given in Rathbun (3) were assumed to apply at 20º C and were adjusted as follows:

\[ k_T = k_{20} \theta^{(T-20)} \]  

(1)

where \( k_{20} \) is the given rate coefficient, \( T \) is water temperature (ºC), and \( k_T \) is the temperature-corrected first-order coefficient. \( \theta \) is a temperature correction factor, which typically ranges from 1.02 to 1.05 (2). The new concentration in a given computational layer is computed by:

\[ C = C_0 e^{-k_T \Delta t} \]  

(2)
where $C_0$ is the concentration at the start of the time step, $C$ is the concentration at the end of the time step, and $\Delta t$ is the time step length.

The relative importance of correcting degradation coefficients for water temperature was evaluated by comparing simulations in which temperature correction was enabled (theta = 1.05) with those in which it was not (theta = 1.0). Results for Donner Lake, Calero Reservoir and Lake Perris are shown in Figs. 1 through 3, respectively. At Donner Lake, temperatures at the 4 meter depth during July and August remained slightly below 20º C. As a result, corrected rate coefficients were slightly lower than uncorrected values, resulting in slightly higher MTBE concentrations for the corrected case. With the drop in lake temperature in early September the difference between corrected and uncorrected concentrations increased, reaching a maximum of 0.13 $\mu$g·l$^{-1}$ at the end of the month. 0.13 $\mu$g·l$^{-1}$ represents a relative percent difference (RPD) of 12.9 percent.

At Calero Reservoir, MTBE concentrations for the corrected and uncorrected cases were indistinguishable for most of the year. Table 4 in the main paper shows that specific volatilization flux at Calero Reservoir was approximately 5 times the specific degradation flux, where for Donner Lake and Lake Perris, the two fluxes were very similar. Thus, the relative importance of degradation at Calero Reservoir was reduced, which in turn reduced the effect of temperature corrections.

At Lake Perris, shown in Fig. 3, epilimnetic temperatures during the summer are substantially higher than 20º C, which has the effect of increasing the degradation rate and lowering MTBE concentrations. The maximum MTBE concentration difference
between simulations using temperature corrections and those not was 2.17 µg·l⁻¹, which occurred in early September and represented an RPD of 16.7 percent.

Figure 1. Simulated MTBE levels in Donner Lake, with and without correcting degradation coefficients for varying water temperature. Values of theta of 1.05 and 1.00 refer to corrected and uncorrected coefficients, respectively. Water temperature is the simulated value at a depth of 4 meters.
Figure 2. Simulated MTBE levels in Calero Reservoir, with and without correcting degradation coefficients for varying water temperature. Values of theta of 1.05 and 1.00 refer to corrected and uncorrected coefficients, respectively. Water temperature is the simulated value at a depth of 4 meters.
Figure 3. Simulated MTBE levels in Lake Perris, with and without correcting degradation coefficients for varying water temperature. Values of theta of 1.05 and 1.00 refer to corrected and uncorrected coefficients, respectively. Water temperature is the simulated value at a depth of 4 meters.

References


(2) Young, T.M. Department of Civil and Environmental Engineering, University of California, Davis, Davis, CA. Personal communication, 2003.