Appendix B

Supplementary details for laboratory soil column study

B.1 Mathematical solution for first order biodegradation rate estimates

Wilson (1997) outlined an analytical solution that describes first-order biodegradation at steady-state under the following boundary conditions:

$$C_a = C_{a,0} \; at \; z = 0$$

$$C_a = 0 \; at \; z = L$$

$$C_a = C_{a,0} \frac{\sinh\left[\sqrt{\frac{\mu_c^1}{D}}(L-z)\right]}{\sinh\left[\sqrt{\frac{\mu_c^1}{D}}L\right]}$$

C_a [g m^{-3}] is the soil air concentration at distance z [m] from the source, $C_{a,o}$ [g m^{-3}] is the concentration in the source headspace, L [m] is the length of the soil column, D [m^2 day^{-1}] is the effective diffusion coefficient of a compound in soil air, and μ^1_c [day^{-1}] is a lumped first-order rate coefficient. This lumped first-order rate coefficient (μ^1_c) depends on factors such as the maximum specific substrate utilization rate (υ_{max}), the biomass in the aqueous phase (X), the half-saturation constant in the aqueous phase (K_s), and Henry's law constant (H). The effective diffusion coefficient in soil (D):

$$D = \theta_a \, \tau_a D_a$$

is reduced by a tortuosity factor (τ_a) given by Millington and Quirk (1961) below as

$$\tau_a = \frac{\theta_a^{2.33}}{\eta_{tot}^2}$$

where θ_a (m^3 air m^{-3} total) is the volumetric soil air content, η_{tot} (m^3 voids m^{-3} total) is the total porosity, and D_a [m^2 day^{-1}] is the molecular diffusion coefficient of in air.

From Ficks first law the flux at F_a at distance z [m] from the source can be calculated as:

$$F_a = -D\frac{\partial C_a}{\partial z} = \frac{C_a\sqrt{k \cdot D}\; C_{a,0}\; \cosh[\sqrt{k/D}\;(L-z)]}{z\sinh[\sqrt{k/D}\;L]}$$

The vadose zone at the surface of the source where z=0, the rate of loss per unit area of the surface of the source is given by:

$$F_a = \frac{\sqrt{k \cdot D}\, C_{a,0}\, \cosh[\sqrt{k/D}\, L]}{\sinh[\sqrt{k/D}\, L]}$$

At the top of the unsaturated zone where z = L and $C_a = 0$, the flux rate of naphthalene to the atmosphere is:

$$F_a = \frac{\sqrt{k \cdot D}\, C_{a,0}}{\sinh[\sqrt{k/D}\, L]}$$

The biodegradation rate per unit area is given by the difference between the flux out of the source $F_{a,0}$ and the flux out of the top, $F_{a,L}$:

$$F_a = \frac{\sqrt{k \cdot D}\, C_{a,0}\, (\cosh[\sqrt{k/D}\, L] - 1)}{z \sinh[\sqrt{k/D}\, L]}$$

The biodegradation rates change slowly over time due to microbiological acclimation to naphthalene. From the Millington and Quirk (1961) equation for diffusion through soil and an initial water content of 0.11 g g^{-1} for the live columns it takes naphthalene takes 15 days to diffuse the length of the soil column. Equation 3 was fitted with our concentration profiles to obtain first-order biodegradation rate coefficients (μ^1_c) for the column experiment under the assumption that rate changes in our columns over time are slow compared the to time it takes for a diffusion profile to reach semi-steady state. The flux throughout the columns was calculated from equation 4. The effective diffusion coefficient was calculated using known column soil moisture contents and total porosity with a molecular diffusion coefficient (D_a) of 0.562 m^2 day^{-1} for naphthalene at 23°C as described by Cho et al. (1992). The volumetric soil air content (θ_a) depends on the soil moisture content and the bulk density. We chose to use a bulk density value of 1.6 g cm^{-3} and averaged soil moisture contents in each column measured at the end of the experiment. For both live columns (contaminated and uncontaminated soil), θ_a was 0.2 m^3 air m^{-3} total; for the contaminated autoclaved column, θ_a was 0.25 m^3 air m^{-3} total; and for the uncontaminated autoclaved column, θ_a was 0.31 m^3 air m^{-3} total. The flux throughout the columns was calculated based on the measured concentration profile and the solution outlined by Wilson 1997. The results are shown in chapter 3.

B.2 Changes in soil properties during autoclaving

Naphthalene soil concentrations were measured at the end of the 231-day experiment. Concentrations in the contaminated autoclaved column increased with depth and ranged between 10-120 μg g^{-1} dry soil. Concentrations in the uncontaminated autoclaved column varied greatly and ranged between 10-1200 μg g^{-1} dry soil. On the other hand, both live columns maintained an averaged soil concentration of 12 μg g^{-1} dry soil throughout their length. Measured naphthalene soil concentrations throughout the length of the column show lower naphthalene sorption to the soil in the live columns than the autoclaved columns. This corresponds to the lower concentrations of naphthalene throughout the live columns due to biodegradation. Properties of the autoclaved soil may have changed after being autoclaved. Changes in organic carbon and water storing properties could affect naphthalene sorption and transport in the autoclaved columns.

Total organic carbon samples were analyzed at various depths. Contaminated soil columns (live and autoclaved) had approximately 60% more organic carbon than the uncontaminated soil columns (live and autoclaved). This difference is attributed to an increased microbial population. The more shallow contaminated soil is expected to have more organic matter from background contamination, larger microbial population and originating from larger impact of decaying roots and plant exudates, than the deeper uncontaminated soil. In addition, the live contaminated soil column had 12% more organic carbon than the autoclaved contaminated column, and the live uncontaminated soil column had 20% more organic carbon than the autoclaved uncontaminated column. It appears that the process of autoclaving the soil bakes off some of the organic matter.

The autoclaved columns lost considerable moisture even though the moisture content in the autoclaved columns was adjusted to 0.11 g g^{-1} after autoclaving and water baths humidified the incoming air. The autoclaved contaminated soil moisture content had decreased by 33% to 0.074 g g^{-1}, and the autoclaved uncontaminated soil moisture content decreased even more by 67% to 0.036 g g^{-1}. It is believed that the apparent change in soil organic carbon content during autoclaving affect the water storing properties of the soil. The lower moisture contents do not appear to discourage bacterial activity in this study. The impact of changing moisture content on diffusion of naphthalene through the soil affects the modeled biodegradation rates.