XAD-4 mediated desorption of pentachlorobenzene from laboratory-spiked sediment

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Introduction: Sorption-desorption is a major process determining the fate and bioavailability of hydrophobic organic compounds (HOCs) in sediments and soils [1]. The current approach to exposure assessment commonly relies on the total concentration, but the level that is biologically available might not be related to this. In addition, the level that is biologically available may decline over time as the chemical becomes sequestered in the soil/sediment by ageing. Desorption kinetics as well as the distribution over the rapid, slow and very slow fractions are of importance for modeling the uptake and degradation by organisms as well as contaminant transport. Desorption with sorbents, such as Tenax or XAD, has been shown to be an effective approach for estimating desorption kinetics of HOCs from soils and sediments [2]. However, studies have been primarily focused on PAHs and relatively little information is available to assess the relationship between desorption and bioavailability for hydrophobic organochlorines. The objective of this laboratory study is to investigate the desorption kinetics of pentachlorobenzene (QCB) as a model compound of hydrophobic organochlorine using XAD-4-mediated desorption.

Methods: A sediment sample was collected in Lake Ludas, one of the protected areas in the northern province of Serbia, Vojvodina. Experiments were performed on whole sediment samples and fraction < 125 µm to investigate particle size dependence using two equilibration times (2 weeks and 3 months). Sediment samples were spiked with methanol stock solution to achieve initial concentration of QCB of 800 µg/kg. Synthetic sorbent XAD-4 (Supelco, USA) was used as a sink to trap QCB desorbed from sediment. Abiotic slurry containing 2 g (dry wt) of spiked sediment and 100 ml aqueous solution of 0.01 M $CaCl_2$ and 300 mg/l $HgCl_2$ was added into desorption flask (100-ml glass Erlenmayer). XAD-4 (2 g) was added and desorption mixtures were tumbled at room temperature over 144 h. At each sampling point (2, 4, 6, 8, 12, 24, 48, 96 and 144 h) the desorption mixtures were centrifuged at 3000g for 15 min and the XAD-4, floating on top of the supernatant, was transferred into a 50 ml separation funnel and extracted three times with 20 ml of ethylether. The residual concentration of QCB in sediment was determined after sediment extraction with hexane/acetone mixture for 24 h. QCB concentration was analysed using gas chromatography-electron capture detection (GC/ECD; Agilent Technologies 6890 with ^{63}Ni ECD) on a DB-608 column (J&W Scientific) and quantified according to external standard calibration. The desorption kinetics were fitted to the biphasic model which includes the fast and slow compartments [2,3] using least squares method.

Results and discussion: The XAD-4-mediated desorption of QCB from the laboratory-spiked sediment used in the study exhibited biphasic kinetics. k_{slow} is observed to decrease with increasing equilibration time (by a factor 1.4 and 1.6 between 2 weeks and 3 months for whole sediment and fraction < 125 µm, respectively), while F_{slow} slightly increases (by a factor 2.4 and 1.3 between 2 weeks and 3 months for whole sediment and fraction < 125 µm, respectively). The combination of an increase in F_{slow} and a decrease in k_{slow} between 2 weeks and 3 months can be explained by proceeding diffusion into the slowly exchanging sediment part (higher F_{slow}) and by the presence of the solute at more remote locations from which desorption is slower (lower k_{slow}). The increase in F_{slow} is only slight, whereas the incubation difference between the 2 weeks and 3 months equilibration times is 6-fold. Possible explanation for the only slight increase in F_{slow} is that the partitioning into the slow part approaches equilibrium after 3 months and therefore F_{slow} does not increase linearly in time between 2 weeks and 3 months.

References: [1] Pignatello and Xing (1996) *Environ Sci Technol* **30**:1-11; [2] Cornelissen et al., (1997) *Chemospere* **35**:2405-2416; [3] Cornelissen et al., (2001) *Environ Toxicol Chem* **20**: 706-711.