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Long Term Sorption Studies of Benzene and Toluene onto Soils

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Although the basic mass transfer of dissolved substances in water to a solid phase is often considered as a simple, partitioning process, in reality, several processes may indeed be taking place. Weber (1972) describes three consecutive steps in the adsorption of materials from solution by porous adsorbents. These include film diffusion, pore diffusion, and adsorption on the interior surface of the pore. A simple partitioning model does not account for these rate limiting processes: it is essentially an instantaneous transfer occurring upon the molecular contact with the solid. Hence, an equilibrium expression is used to describe this process.

The simple partitioning model often breaks down when the question of desorption is raised. The equilibrium expression defining a partition coefficient or a distribution coefficient is predicated upon the assumption that the adsorption and desorption processes are essentially forward and reverse or completely reversible reactions. Many investigators including DiToro and Horzempa 1982) have shown this to not be the case. Debate as to whether adsorption/desorption is hysteretic or irreversible has occurred. It has even been suggested that the processes are indeed reversible but the experiments are flawed. What remains constant is that the elementary, reversible partitioning model is limited. Some investigators (Wang, et al. 1993) have proposed that sorption is a combination of two processes, adsorption and partitioning.

The study described in this paper focuses on an aspect of the two process sorption mechanism model, namely experimentation to dilineate the two processes. It is hypothesized that the primary, or partitioning, process is very fast, described as an essentially equilibrium process. The secondary, or adsorption, process is slower and, thus, rate limiting. Long term batch adsorption experiments should show as rapid uptake by

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the solids, defining a first, psuedo equilibrium, followed by a slower uptake until a final equilibrium is reached. The experiments show that biological uptake can mask the secondary phase. Our experiments describe how the effects of biological uptake can be minimized in long term experiments.

MATERIALS AND METHODS

The adsorbents used in this study are natural soils extracted from five different locations in New Jersey. Soils were prepared for experimentation by first air-drying for one week. Each soil was then blended using the homogenizing technique of coning and quartering (Carver 1971). Finally, debris was eliminated by passes through 0.25-inch and 2-mm sieves. Soil properties are listed in Table 1. Organic matter content was determined by the Rutgers Soil Testing Laboratory using the Walkley and Black modification of the rapid dichromate oxidation technique (Nelson and Somers 1982) with organic carbon content defined as 59% of the organic matter content.

Table 1. Soil properties.

	Sand %	Silt %	Clay %	Texture	pH s.u.	Organic Matter %
Adelphia	72	14	14	Sandy	5.2	1.4
Pequest	44	44	12	Sandy loam	5.2	2.1
Quakertown	20	60	20	Silt loam	6.8	3.9
Towacco	92	6	2	Loamy sand	8.4	0.2
Cohansey	90	8	2	Sandy	4.2	4.4

We attempted to minimize anticipated biological activity in our experiments by sterilizing the soil by gamma irradiation. Other methods, such as autoclaving, were rejected as they might seriously alter the nature of the organic matter. A series of 150-ml glass bottles were filled with soil, capped, and sealed with teflon tape. These were then sent to the Nuclear Reactor Facility at the University of Virginia who performed the irradiation. All water used in our experiments was treated by distillation and reverse osmosis.

Three methods were performed for the batch adsorption studies. These were performed in 100-ml closed crimp vials with teflon lined stoppers. For Method 1, all glassware was heated in a 70 °C oven for 24 hours prior to use. The glassware was then cooled to room temperature. Stock solutions of benzene and toluene in water were made in head space free teflon bags. Calcium chloride was added for ionic balance to a 0.02 M solution. Four grams of soil was introduced into the vials. Several vials were kept soil free for use as controls. Then 26 ml of either the benzene or toluene stock solution was added. The vials were immediately crimped with the teflon lined stoppers. The vials were then stored in a 4°C room until 24 hours prior to analysis at which time they were placed in a 22°C temperature bath. Bottles were selected for analysis at predetermined times and analyzed in triplicate. Sampling for either benzene or toluene was performed by piercing the teflon cap with a gas sampling syringe and drawing a volume of head space gas from the vial. The sample gas was then injected into a Hewlett Packard 5840 gas chromatograph (GC) equipped with a flame ionisation detector. The aqueous phase concentrations were then calculated from Henry's Law.

Method 2 was identical to Method 1 except that all glassware used to make the stock solutions, pipettes vials, teflon liners and caps were autoclaved at 121°C for 20 minutes before use and the vials containing just soil were exposed to ultraviolet light for 15 min. Only benzene was examined by this method.

Method 3 attempted to create anoxic conditions in the vials by purging with nitrogen gas. By doing this we attempted to minimize the possibility of aerobic activity in the vials. As in Method 2, all glassware was autoclaved prior to use. In addition, all water was boiled. A 15 g mass of soil was added to each vial and then filled with 40 ml volume of water. The vials were then purged with nitrogen gas. The purging system was comprised of a tank of Matheson Ultra-pure nitrogen to which a regulator was attacted. The regulator delivered the gas to a series of four teflon tubes which fed the experimental vials. A hypodermic needle was fastened to the end of each tube to sparge the gas into the soil/water matrix. Gas was delivered at 1 L/min to both the water (7 min.) and the head space (7 min.) after which each vial was sealed and crimped. Sampling for either the benzene or toluene was performed by piercing the teflon cap with syringe and drawing a liquid sample from the experimental vial. The sample was then injected into a Tekmar Model ALS 2016 Purge and Trap instrument and then analyzed by GC.

RESULTS AND DISCUSSION

Results for Method 1 for the benzene systems are displayed in Fig. 1. All the data presented in this paper are normalized to the control vial (no soil)

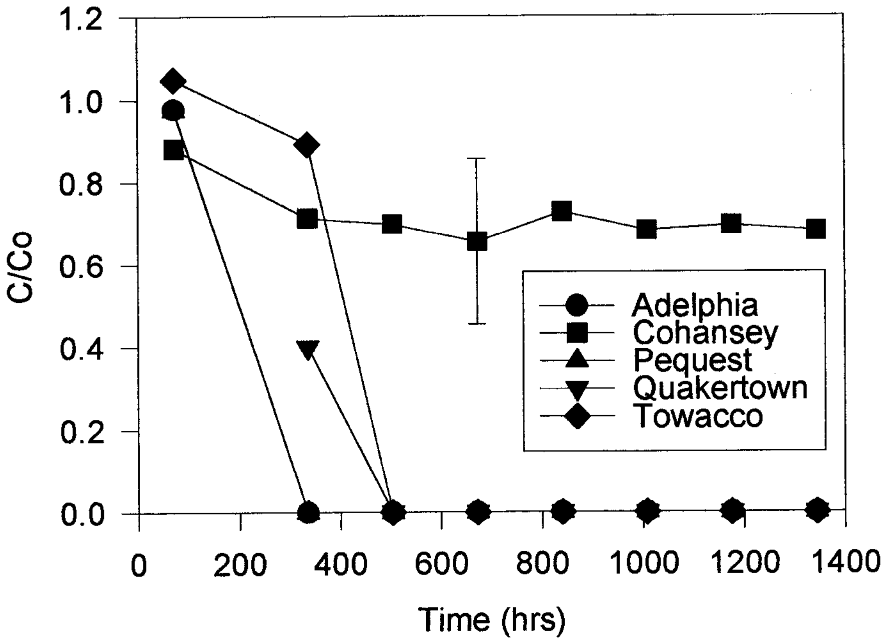

Figure 1. Benzene rate studies - Method 1.

systems. Thus, any losses will be factored out. In fact all controls were within ±8% throughout the study, which we considered excellent for this type of work. The data display a sudden drop-off between 300 and 500 hrs. for all the soil systems except the Cohansey, which begins to drop-off after 1700 hrs. It should be noted that many short term adsorption exquilibrium studies are performed assumming an equilibrium less than 96 hrs. These results show that the rapid drop-off occurs later.

Method 1 toluene results are displayed in Fig. 2. The same type of rapid drop-off is also noted here, but occurs at different times for each of the soil systems, but in all cases, after 200 hrs. At this point, we hypothesized that biochemical activity was taking place in the vials. To test this hypothesis, we employed Method 2 for the benzene systems and Method 3 for both benzene and toluene systems.

Method 2 shows the effect of autoclaving the systems. Only benzene was employed to evaluate this method. The benzene systems are displayed in Fig. 3. In comparing these results with those from Method 1 (Fig. l), one can see that Method 2 delayed the drop-off but did not eliminate it. This suggested that biochemical activity was taking place.

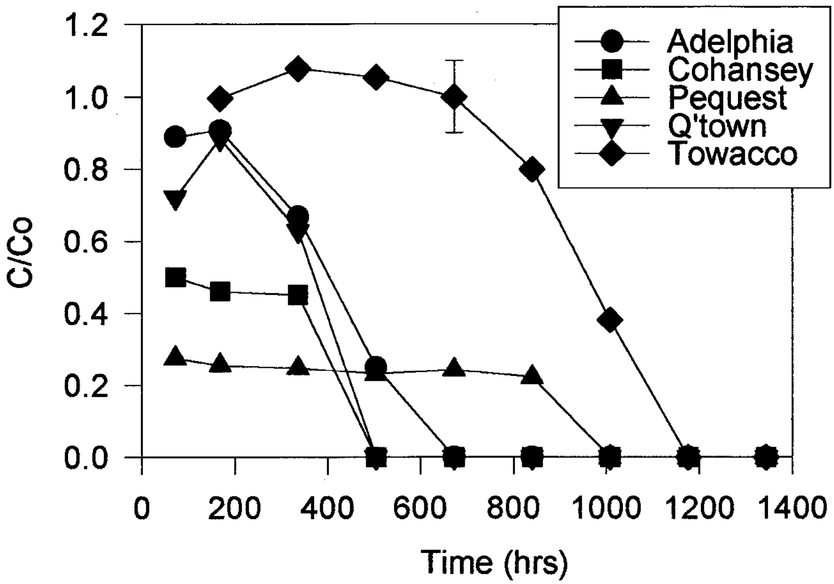

Figure 2. Toluene rate studies - Method 1.

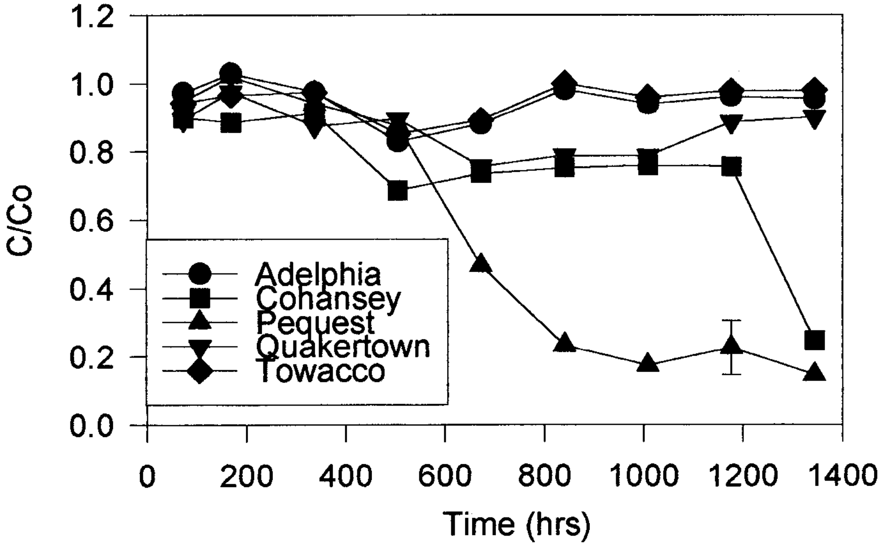

Figure 3. Benzene rate studies - Method 2.

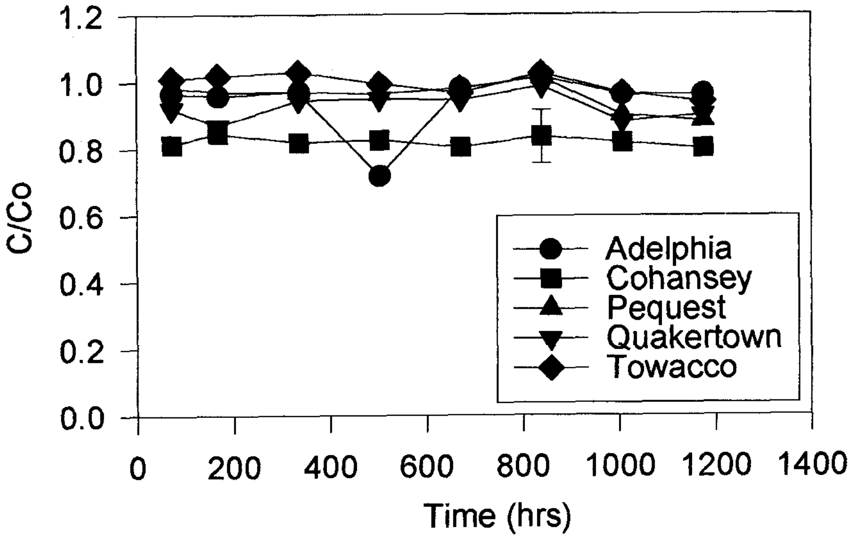

Figure 4. Benzene rate studies - Method 3.

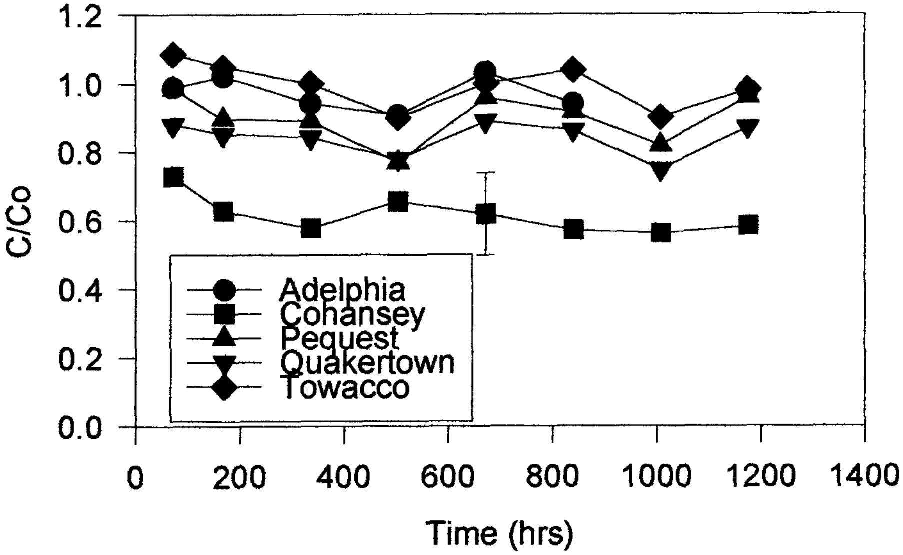

Figure 5. Toluene rate studies - Method 3.

Although it has been well established that benzene and toluene can be degraded under aerobic conditions, some investigators have demonstrated that benzene (Edwards and Grbic-Galic 1992) and toluene (Schocher et al 1991) can be degraded under anaerobic conditions. Those investigators appeared to have designed their experiments to enhance anaerobic degradation. In designing Method 3: we hypothesized that the drop-off we were observing in our experiments was due to aerobic activity.

Fig. 4 shows the results employing Method 3 for the benzene systems. The drop-off obseved in Methods 1 and 2 has been eliminated. What is also apparent is that a virtual steady-state is reached for all systems; there is no discernable long-term decay which would be suggestive of a slow second phase sorption for benzene on these soil systems. The differences in the obtained steady-state concentration is a function of organic matter present in each soil. As expected, the soils with the higher organic matter contents adsorb more of the benzene and thus display lower liquid phase concentrations. The same observations can be made for the toluene systems displayed in Fig. 5. In addition and as expected, the toluene exhibits a greater sorptive affinity for the solids (Ahlert and Uchrin 1990).

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