Influence of Aroclor 1242 Concentration on Polychlorinated Biphenyl Biotransformations in Hudson River Test Tube Microcosms

KENNETH M. FISH*

Environmental Laboratory, General Electric Corporate Research and Development, Schenectady, New York 12301-0008

Received 7 February 1996/Accepted 12 May 1996

When 93.3 to 933 μmol of Aroclor 1242 per kg was added to Hudson River sediment test tube microcosms, the rates of polychlorinated biphenyl biotransformations increased with increasing Aroclor 1242 concentration after a 4- to 8-week acclimation period. In contrast, when 37.3 μmol of Aroclor 1242 per kg was added, polychlorinated biphenyl biotransformations occurred at slow constant rates.

The polychlorinated biphenyls (PCBs) are a family of compounds which were produced as mixtures containing various levels of chlorination and were sold under several trade names, including Aroclor, Clophen, Kanechlor, and Phenoclor. Combinations of homolog number and chlorine distribution about the biphenyl carbon skeleton result in 209 possible PCBs, each of which is referred to as a congener. Because of their extensive commercial application (5), PCBs have accumulated in soils, sediments, and biota. Currently, there are concerns about potential health risks due to the persistence of these compounds in the environment.

The upper Hudson River was contaminated with Aroclor 1242, a commercial PCB mixture containing 42% (wt/wt) chlorine. The objective of this study was to examine the influence of Aroclor 1242 concentration on PCB biotransformations in upper Hudson River sediment. This was accomplished by partially simulating environmental conditions in the laboratory. In this paper, I describe the influence of Aroclor 1242 concentration on PCB biotransformations in test tube microcosms that have been described previously (2). The range of Aroclor 1242 concentrations used for amendment was 10 to 250 mg/kg (37.3 to 933 $\mu\text{mol/kg}$ based on an average molecular weight of 267.9 g/mol).

As shown in Fig. 1A, at zero time the starting number of chlorines per biphenyl was influenced by the amount of Aroclor 1242 added to the sediment. This value reflects the relative proportions of reductively dechlorinated PCBs present in the contaminated sediment at the time of collection (sediment PCBs) and added Aroclor 1242.

I monitored the rates and extents of reductive dechlorination by measuring the number of chlorines per biphenyl as a function of time (Fig. 1A). Autoclaved controls were unchanged during the incubation period (data not shown). The data obtained from experimental samples indicate that as the amount of added Aroclor 1242 increased, more complete dechlorination was achieved during the 16-week incubation period. With the exception of the lowest concentration tested (37.3 μmol of Aroclor 1242 per kg), the lags in activity (4 to 6 weeks) were relatively unaffected by the Aroclor 1242 concentration.

A slow constant rate of subsurface sediment dechlorination occurred when the sediment was amended with 37.3 μmol of

Aroclor 1242 per kg. Thus, in the presence of 37.3 μmol of Aroclor 1242 per kg, biotransformations took place without a lag, but this concentration was insufficient to accelerate dechlorination. From this result I hypothesize that during prolonged exposure to sediment PCBs in the Hudson River slow PCB dechlorination activity occurs.

Figure 1A shows that the maximum rates at which the number of chlorines per biphenyl decreased were similar. I also

FIG. 1. (A) Number of chlorines per biphenyl in subsurface sediments as a function of time. The values were dramatically influenced by PCBs present prior to amendment only when 37.3 or 93.3 μmol of Aroclor 1242 per kg was added. (B) Absolute amount of chlorines removed from PCBs as a function of concentration. Symbols: ●, data from this study; ○, data from reference 1; ▽, data from reference 6.

* Mailing address: P.O. Box 8, Schenectady, NY 12301-0008. Phone: (518) 387-5990. Fax: (518) 387-7611. Electronic mail address: fishkm@crd.ge.com.

FIG. 2. (A) Relative decrease in PCB concentration versus time. The relative decrease in concentration was calculated by using the following relationship: $(\text{PCBs})_t/(\text{PCBs})_0$, where $(\text{PCBs})_0$ is the concentration of PCBs at the beginning of the experiment and $(\text{PCBs})_t$ is the concentration of PCBs at time t . (B) Absolute decrease in PCBs concentration versus initial PCB concentration.

calculated the maximum rates of total chlorine removal as a function of time (Fig. 1B), which increased by 0.025 μg -atom of chlorines removed per week per μmol of Aroclor 1242 per kg added. Even though their experimental conditions were significantly different and the PCB concentrations used were much higher, both Abramowicz et al. (1) and Rhee et al. (6) obtained comparable rates (0.039 and 0.056 μg -atom of chlorines removed $\cdot [\mu\text{mol of PCBs added per kg} \cdot \text{week}]^{-1}$, respectively). For comparison, I plotted the data of these workers with my data (Fig. 1B, inset). The results indicate that for a given set of experimental conditions, the rates of anaerobic PCB dechlorination by upper Hudson River sediments (downstream of contamination) are proportional to the PCB concentration and are relatively unaffected by experimental design.

As described previously (2), the congener distributions in my experimental samples are consistent with process C biotransformations (data not shown). Briefly, this process consists of extensive *meta* plus *para* dechlorination.

Principe and I previously demonstrated that oxygen penetrated into test tube microcosm surface sediments (0 to 2 mm below the water-sediment interface) and that, as a result, aerobic biodegradation of PCBs took place (2). In addition, we found evidence that reductive dechlorination occurred in these surface sediments. Since reductive dechlorination decreases the number of chlorines per biphenyl and lightly chlorinated

FIG. 3. Concentrations of chlorobenzoates as a function of time. (A) 2-CBA. (B) 4-CBA.

congeners are most susceptible to oxidative attack by aerobic biodegrading microorganisms, there was the potential for dramatic reductions in the PCB contents of surface sediments.

Biological PCB transformations in surface sediments were monitored by comparing the total PCB concentrations as a function of time (Fig. 2). During the incubation period, the levels of PCBs decreased at all of the concentrations included in the study. Since autoclaved controls were unchanged (data not shown), I concluded that decreases in PCB concentrations indicated that biodegradation occurred. In addition, PCB biotransformation activity was a function of Aroclor 1242 concentration. When 37.3 or 93.3 μmol of Aroclor 1242 per kg was added, slight decreases in the total PCB concentration were observed throughout the 16-week incubation period (Fig. 2). When 187 to 933 μmol of Aroclor 1242 per kg was added, larger decreases occurred. The increased rate of degradation with concentration was most likely due to increased populations of PCB-biodegrading microorganisms. Increased dechlorination as a function of concentration would also increase the concentration of readily biodegradable congeners.

As described previously (2), the congener distributions in the surface layers of the experimental samples used are consistent with process Y biotransformations. Briefly, this process can be partially separated into two distinct biotransformations, namely, process M (extensive *meta* dechlorination) and aerobic biodegradation of lightly chlorinated congeners.

I compared the extents of Aroclor 1242 biodegradation in test tube microcosms with in situ aerobic biodegradation of 70% mono- and dichlorinated PCBs in the Hudson River (4). In 73 days with agitation and added nutrients, 40 to 60% of Hudson River sediment PCBs was aerobically biodegraded.

The extents of test tube microcosm biodegradations were comparable without nutrients or agitation, even though the congeners in Aroclor 1242 have a higher chlorine content (3.3 chlorines per biphenyl) and thus are less susceptible to degradation. Biodegradation in test tube microcosms should have continued with additional incubation time. In contrast, biodegradation was enhanced only temporarily by nutrients and agitation in the in situ experiment. This suggests that long-term natural restoration of Aroclor 1242-contaminated sediments may result in more extensive remediation than short-term (in situ) stimulation with nutrients.

In order to test the hypothesis that aerobic biodegradation occurs in Hudson River test tube microcosm surface sediments, I measured the concentrations of two PCB biodegradation products, 2-chlorobenzoic acid (2-CBA) and 4-CBA, as a function of time. I interpret the transient appearance of these products (Fig. 3) as evidence that aerobic oxidation occurs. The maximum amounts of 2-CBA (4 nmol/kg) and 4-CBA (0.12 nmol/kg) are comparable to the amounts found in some Hudson River sediments containing high concentrations of mono- and dichlorinated biphenyls (3).

I concluded that in the test tube microcosms studied reductive dechlorination and aerobic biodegradation of PCBs occurred when as little as 37.3 μ mol of Aroclor 1242 per kg was

added to upper Hudson River sediments. At greater concentrations biotransformations were accelerated after a lag time of 4 to 8 weeks. Furthermore, natural restoration processes in aerobic surface sediments may be more effective at decreasing PCB concentrations in Aroclor 1242-containing sediments than short-term anthropogenic stimulation.

REFERENCES

1. Abramowicz, D. A., M. J. Brennan, H. M. Van Dort, and E. L. Gallagher. 1993. Factors influencing the rate of polychlorinated biphenyls dechlorination in Hudson River sediments. *Environ. Sci. Technol.* **27**:1125–1131.
2. Fish, K. M., and J. M. Principe. 1994. Biotransformations of Aroclor 1242 in Hudson River test tube microcosms. *Appl. Environ. Microbiol.* **60**:4289–4296.
3. Flanagan, W. P., and R. J. May. 1993. Metabolite detection as evidence for naturally occurring aerobic PCB biodegradation in Hudson River sediments. *Environ. Sci. Technol.* **27**:2207–2212.
4. Harkness, M. R., J. B. McDermott, D. A. Abramowicz, J. J. Salvo, W. P. Flanagan, M. L. Stephens, F. J. Mondello, R. J. May, J. H. Lobos, et al. 1993. In situ stimulation of aerobic PCB biodegradation in Hudson River sediments. *Science (Washington, D.C.)* **259**:503–507.
5. Hutzinger, O., S. Safe, and V. Zitko. 1974. The chemistry of PCBs. CRC Press, Cleveland.
6. Rhee, G.-Y., B. Bush, C. M. Bethoney, A. DeNucci, H.-M. Oh, and R. C. Sokol. 1995. Reductive dechlorination of Aroclor 1242 in anaerobic sediments: pattern, rate and concentration dependence. *Environ. Toxicol. Chem.* **12**:1025–1032.