

Fate and Transport of Pharmaceutically Active Compounds in Simulated Bank Filtration System

Problem and Research Objectives

Riverbank filtration (RBF) represents a natural filtration technique that has been used to provide drinking water to communities for more than a century in Europe and half a century in the United States. RBF uses the riverbed and the underlying aquifer as natural filters to remove pollutants present in the surface water (Ray et al., 2002). As the infiltrating water moves through the porous media, dissolved contaminants as well as pathogens are removed (Ray et al., 2002). RBF is also able to moderate temperature fluctuations observed in surface waters as well as concentration peaks resulting from accidental spills (Ray et al., 2002). Straining, colloidal filtration, sorption and microbial degradation contribute to the removal and attenuation of these contaminants (Ray and Shamrukh, 2011).

Appearance of pharmaceutically active compounds (PhACs) are found in surface water sources at an increasing rate and the mechanism of removal during RBF has become a concern (Hiscock, and Grischek, 2002). Several PhACs from different prescription drugs have been found at concentrations up to the $\mu\text{g/L}$ -level in sewage influent and effluent samples and also in several surface waters located downstream from municipal sewage treatment plants (Caliman and Gavrilescu, 2009).

The objectives of this study were to evaluate the potential impact of a) variable redox conditions; b) variable organic matter content of the source water; c) seasonal variability of temperature; d) presence versus absence of riverbed sediments; and e) changes in solution ionic strength coupled with increased solution velocity on the fate, transport, and removal of several PhACs during their passage in a model RBF system.

Methodology

PhACs were selected according to their pharmaceutical class, the occurrence in the environment and public interest, their toxicity, the environmental fate, the behavior under different redox conditions, and the availability of analytical standards and adequate instrumentations. The fate and transport of these selected PhACs was investigated using short columns (Figure 1) and a two-side-by-side rectangular slab-like column (Figure 2). Short columns were used to evaluate the impact of temperature, organic content, redox conditions and bacteria on the fate and transport of selected PhACs, and to reduce the possible scenarios that are simulated in the slab. On the other hand, the slab was used to evaluate the impact of clogging on the dynamic of redox conditions as well as the removal of selected PhACs.



Figure 1. Four columns used for the short-column simulations.

Four flow-through stainless steel columns (4.75-cm internal diameter and 14.50-cm height) were simultaneously used in this study to observe the transport of PhACs through the columns (Figure 2). Light-excluding stainless steel columns were selected in order to minimize the possible effect of photo-degradation of the selected PhACs as well as the potential adsorption of these compounds on the internal wall of the column. Silica sand (#16 to #30 sieve) was acclimated in the presence of the long column (Figure 3) prior to being used as packing material for the short columns. Experiments were performed under aerobic and anaerobic conditions. In order to achieve aerobic conditions, air was continuously bubbled into the reservoir, while anaerobic conditions were obtained by keeping the reservoir closed and by purging the reservoir with nitrogen. The seasonality impact was evaluated by performing the different experiments in the laboratory (20°C) and in a refrigerator room (6°C). The effect of different levels of organic carbon on the behavior of selected PhACs was evaluated using Lake Wilson (low content) and Lake Wilson with different levels of humic acid to increase the level of organics. Sterile conditions, achieved by autoclaving silica sand 3 times at 120°C for 30 min, and filtering water collected from Lake Wilson through 0.2 µm filter and autoclaving at 120°C for 30 min, were used as abiotic control.

The 140 x 60 x 10 cm slab, made of transparent plexiglas, was covered with a thick black cardboard in order to prevent the possible microbial growth due to the light penetration through the plexiglas. The top of the slab was covered in order to reduce possible evaporation and the exposure to light. The slab was dry-packed with small increments of silica sand (#14 to #16 sieve, at the bottom, and #16 to #30 sieve) and manually compacted during this process. An overflow located 4 cm above the top layer of sand was used to maintain a constant water level above the sand. Two automatic balances, connected to a CR10X Campbell Scientific datalogger (USA), were used in order to have an in-line monitoring of the outflow. The experimental slab was equipped with oxygen and redox probes for online measurements, tensiometers to monitor pressure for clogged and unclogged conditions, and sampling ports to determine the evolution of the environmental conditions in the slab and to monitor the removal of PhACs at different depths. The number of probes and sampling ports was higher in the top section of the slab to

account for the removal occurring just beneath the biological layer (*Schmutzdeche*) formed on the top surface of the sand/soil. Offline samples were analyzed in terms of TOC, DOC, PhACs, and SUVA (254). To simulate clogged and unclogged conditions, a thin layer of fine sediments collected from Manoa Stream was added above the top portion of the sand on one side of the slab. This would enhance the development of a clogged layer at the interface of the sand/sediments.



Figure 2. Slab set-up with redox probes, oxygen probes, sampling ports and tensiometers.



Figure 3. One set of two long columns adopted for the long-column re-circulated simulations.

Principal Findings and Significance

The selected PhACs investigated during this study can be divided into:

1. PhACs persistent under different environmental conditions
2. PhACs removed only in presence of specific conditions

Sterile conditions were achieved and maintained for approximately 40 days during the study.

PhACs Persistent Under Different Environmental Conditions

Carbamazepine and gemfibrozil were persistent under aerobic and anaerobic conditions as well as during summer and winter. Limited removal (<20%) was observed in the presence of the different environmental simulated conditions. Figure 4 shows the behavior of carbamazepine in the presence of sterile and non sterile conditions, summer and winter, aerobic and anaerobic.

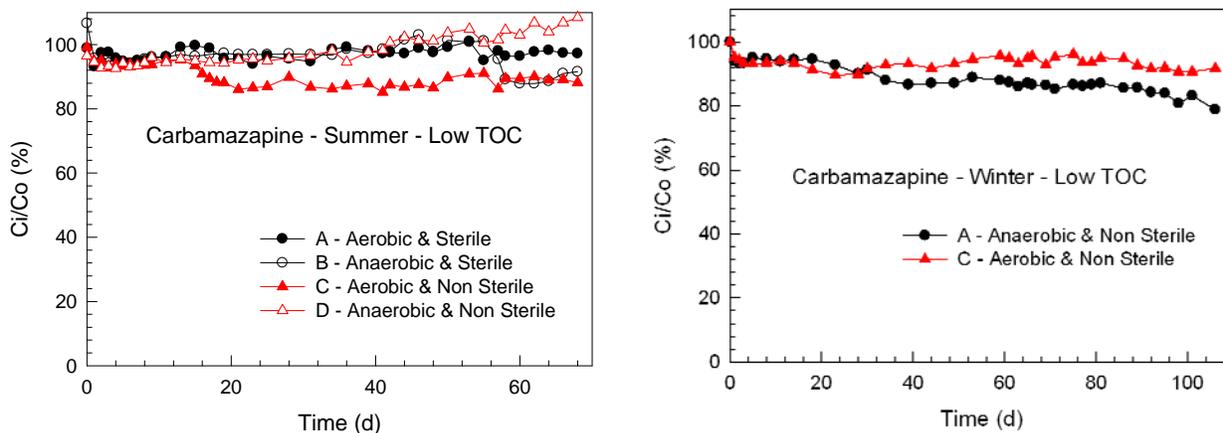


Figure 4. Impact of redox conditions and temperature on fate and transport of carbamazepine.

PhACs Impacted by Temperature and Redox Conditions

Results from this study suggest that the environmental behavior of phenazone and caffeine was highly impacted by redox conditions and seasonality at the bank filtration site. Under anaerobic conditions, both chemicals were persistent and low/limited removal (<15%) was observed (Figures 5–6). While under aerobic conditions, both chemicals were completely removed. Caffeine and phenazone were completely removed within 20 days during the summer, while only phenazone was removed during the winter. Phenazone required an acclimation period of 15 and 65 days during summer and winter, respectively. In the presence of cold temperature, the removal rate of phenazone was also slower compared to the removal rate observed during the summer.

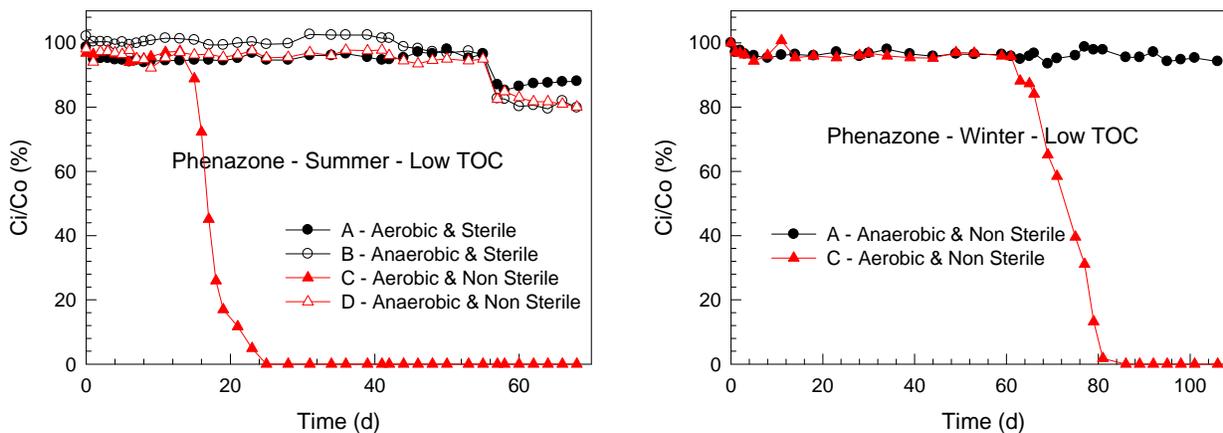


Figure 5. Impact of redox conditions and temperature on fate and transport of phenazone.

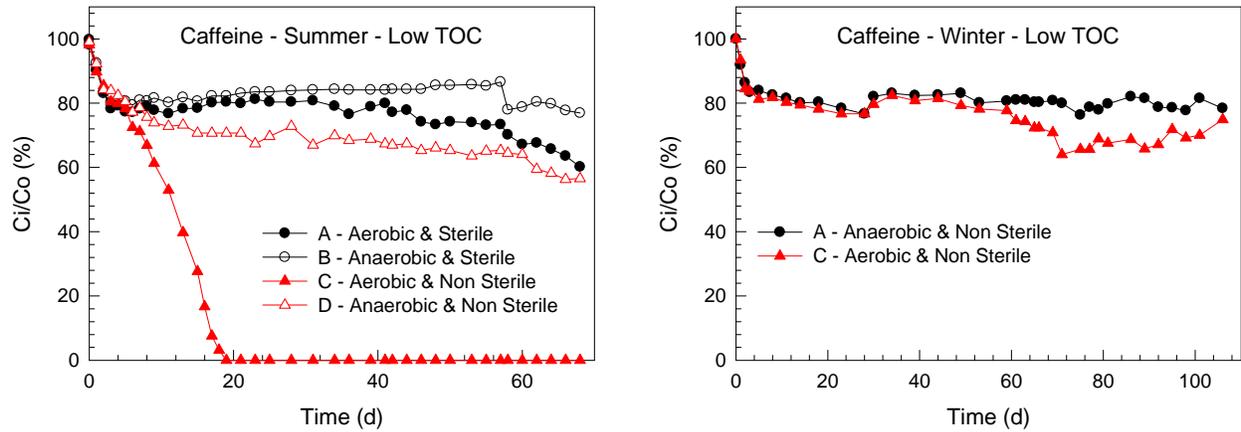


Figure 6. Impact of redox conditions and temperature on fate and transport of caffeine.

The behavior of two estrogens E1 and E2, was also impacted by temperature and redox conditions (Figures 7–8). Faster and more pronounced removal of both estrogens was observed in the presence of aerobic conditions. E1 and E2 were then completely removed within 22 days under aerobic conditions. Slower removal of E2 was observed under anaerobic conditions, while limited removal of E1 (<10%) was also observed. However, slower removal of E1 and E2 was observed under aerobic and anaerobic conditions during the winter. In the presence of sterile conditions, limited/no removal of both estrogens was observed (Figures 7–8).

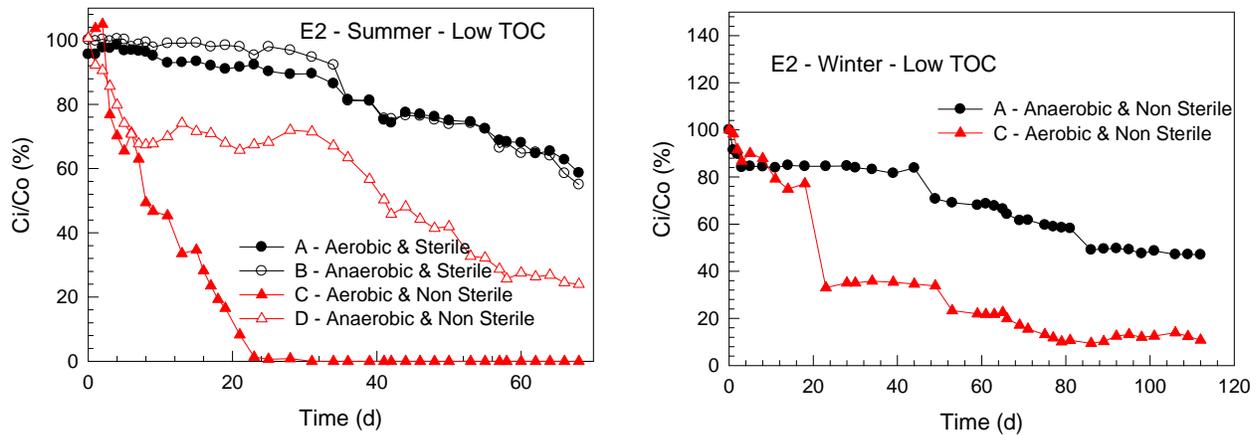


Figure 7. Impact of redox conditions and temperature on fate and transport of 17-β estradiol (E2).

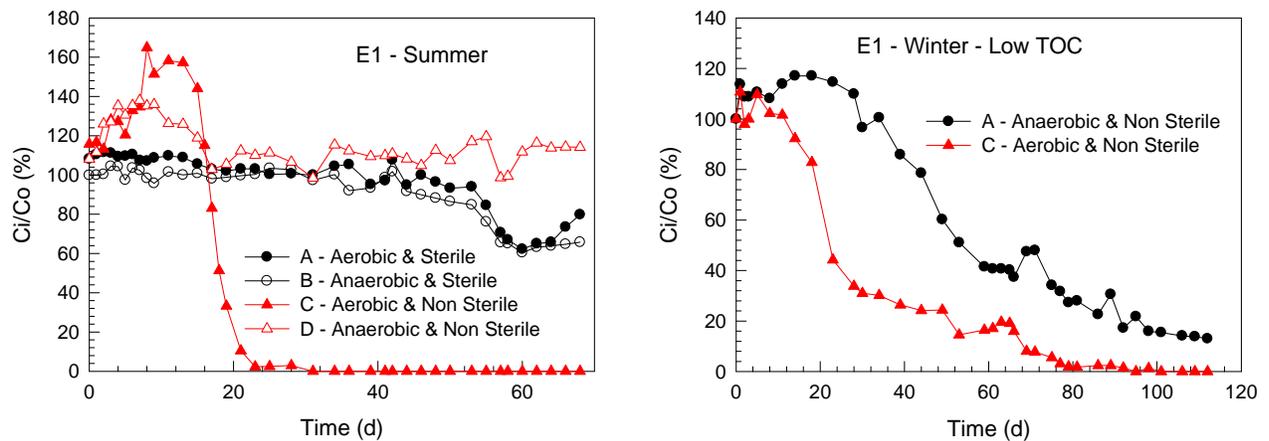


Figure 8. Impact of redox conditions and temperature on fate and transport of estrone (E1).

Publications Cited in Synopsis

- Caliman, F.A., and M. Gavrilesu, 2009, "Pharmaceuticals, personal care products and endocrine disrupting agents in the environment—A review," *Clean-Soil, Water, Air*, 37(4–5), 277–303.
- Hiscock, K.M., and T. Grischek, 2002, "Attenuation of groundwater pollution by bank filtration," *Journal of Hydrology*, 266(3–4), 139–144.
- Ray C., and M. Shamrukh, (eds.), 2011, *Riverbank Filtration for Water Security in Desert Countries*, NATO Science for Peace and Security Series C: Environmental Security, Springer, The Netherlands.
- Ray C., G. Melin, R.B. Linsky, (eds.), 2002, *Riverbank Filtration: Improving Source-Water Quality*, Kluwer Academic Publishers and National Water Research Institute, Boston.