Natural attenuation potential of downwelling streams for perfluorochemicals and other emerging contaminants

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Abstract Stream augmentation with tertiary treated municipal wastewater—i.e., recycled water—is increasingly considered as an ecologically beneficial way to utilize recycled water, especially in semi-arid regions of the American Southwest. There is concern that emerging contaminants, i.e. unregulated but biologically active organic compounds, may be present in recycled water and will impact on the aquatic environment and the underlying groundwater. Emerging contaminants include a wide variety of chemically disparate compounds, including pharmaceuticals, endocrine disruptors, and residues of perfluorochemical surfactants (PFCs). This paper presents background data on the occurrence and transport of PFC in Upper Silver Creek (USC) and Coyote Creek, in San Jose, California. USC feeds into Coyote Creek, which discharges into San Francisco Bay. Augmenting the natural flow of Coyote Creek with highly treated recycled water is currently being considered as a means to provide more freshwater to the river ecosystem. The reach of interest is approximately 1,000 m where USC flows on alluvial fan deposits. Data indicate that some PFCs are refractory

Keywords Hyporheic zone; losing stream; natural attenuation; perfluorinated chemicals

Introduction

This study addresses the fate of organic fluorochemicals (PFCs), especially perfluorinated surfactants such as perfluorooctanoate (PFOA) and perfluorooctanosulfonate (PFOS), in a river system studied for potential augmentation with recycled water. PFCs are ubiquitous in aquatic environment (waste waters: Boulanger et al., 2005; surface waters: Hansen et al., 2002; ground waters: Moody et al., 2003; and drinking waters: Skutlarek et al., 2006). The contamination of ground water with PFCs was found at sites where fire retardants were routinely used in fire fighting drills (Moody et al., 2003). These authors reported that PFOS compounds were present in groundwater in measurable quantities years after their last use. PFCs are used as liquid repellants, surfactants and coatings, and as foams for firefighting. They are ubiquitous in a variety of other uses (carpet goods, packaging; Schultz et al., 2003). Their transport behavior in aqueous systems is poorly understood. Higgins et al. (2005) found perfluorinated chemical compounds (PFCs) in sediments of the San Franciscan Bay and in domestic sludge. These authors quantified sorption of PFOS to biosolids and demonstrated sewage sludge is a major sink of PFCs during municipal wastewater treatment. However, conventional biological wastewater treatment plants are not overall removing these PFCs consistent with their biological persistence.

In a few instances, rivers have been demonstrated to have natural attenuation capacity for pharmaceuticals and personal care products. For instance, the Santa Ana River in Southern California, which is nearly 100% tertiary-treated municipal wastewater, the concentrations of pharmaceuticals were shown to be significantly attenuated along a stretch of 11 km (Ding et al., 1999; Gross et al., 2005; Lin et al., 2005). During transport for 18 hrs, half lives...
of contaminant attenuation ranged from 9 days to 1 minute. At distances of a few tens of metres, however, compounds like sulfate and EDTA did not show any attenuation. In greater detail, it is necessary to understand the effect of sediment water interactions on a smaller scale.

Here we hypothesize that hyporheic flow (flow that infiltrates into and exfiltrates from the hyporheic zone) on relatively short time scales plays a significant role in the overall attenuation of trace contaminants. The hyporheic zone is the shallow zone immediately underlying the riverbed and is difficult to characterize without detailed tracer tests (Bencala et al., 1983). Hyporheic flow is much slower than that of the river and it may be viewed as young or hyporheic groundwater (Hoehn & Cirpka, 2006). Hyporheic groundwater is in prolonged contact with the biologically active surfaces (biofilms) of gravel and sands of the riverbed thereby creating conditions favorable for natural attenuation by biodegradation and sorption. It is planned to augment Upper Silver Creek of San Jose, CA (USC) with tertiary-cleaned waste water (“recycled water”, RW). In preparation for a study in which the impact of a release of RW into USC and Coyote Creek (CC) will be investigated, we characterized a reach of about 300 m of USC above its confluence with CC. After confluence, CC flows through San Jose and discharges into the San Francisco Bay (Figure 1). The particular issues that are addressed include temperature effects with respect to warm water fishery and the fate of trace organic compounds, including PFCs. Here we characterize the flow system and present results of PFC measurements from before the start of the augmentation of USC with RW.

Site exploration and investigation

The experimental site is located at the eastern edge of Santa Clara Valley, at the foot of the Yerba Buena hills in San Jose, CA (Figure 1). Here USC formed a small holocene alluvial fan with stream terrace deposits (USGS, 2006). The catchment of USC extends to about 48 km², in an elongated valley formed by the USC fault. It opens to the Santa Clara Valley groundwater basin (San Jose flood plain), which is extensively used. The alluvial deposits at the experimental site are filled with ground water, which probably recharges the productive ground water. From the proposed injection point of RW, USC flows for about 0.3 km in a natural riparian forest, and then in a concrete channel to the confluence with CC (Figure 2). The flow rate of USC was estimated in May 2006 to be at about 0.04 m³/s. During rain
periods in winter, flow can be higher by a factor of 100–1,000. Data from 1999 to 2005 of a
gauge station in CC shows a streamflow recession constant of about 0.005 per day, which is
effective from April to November.

Between March and July 2006, the site was instrumented with 2 “pushed” wells in the
bed of USC (PW1 and PW2 in Figure 2) that tap hyporheic ground water at depths of about
0.2 m. Three groundwater wells have been drilled into the local aquifer (GW1, GW2a, and
GW2c; distances from USC, see Figure 2). Core material from the wells GW1, GW2a and
GW2c revealed silty gravels and sands. The hydraulic conductivity of the local aquifer
material is about $2 \times 10^{-4}$ m/sec (material of well GW2a less permeable than that of the
other wells). Well GW3 near CC was drilled in the upper section of the regional gravel and
sand aquifer of the San Jose flood plain. Loggers for water temperature were placed in
USC, the pushed and the drilled wells. These loggers were analyzed for time series (Hoehn
& Cirpka, 2006). Surface water and ground water from the pushed wells revealed daily sinu-
soidal amplitudes of water temperatures. The amplitudes of PW1 were slightly dampened
and retarded with respect to those of the creek. This indicates downwelling of creek water
and evidence for hyporheic ground water. A subsurface residence time for hyporheic water
of 15–40 minutes was taken from the data. The temperature in well PW2 goes in
parallel with SW2 indicating likely short-circuiting of surface water. Flow from the creek’s
bed to local alluvial ground water could not be inferred from the temperature data in the
drilled wells.

The radioactive isotope $^{222}$Rn of the noble gas radon was used as a natural tracer for
mixed groundwater ages of up to 15 days (Hoehn & von Gunten, 1989). No Rn was
found at two dates, in the samples of USC and in well PW1 (detection limit for radon
concentration in water, about 0.5 Bq/L). There may have been short-circuiting of surface
water to well PW1. In well PW2, the Rn concentrations were slightly above the detection
limit, at both sampling dates (0.6 – 1.1 Bq/L). This points to a small fraction of hypo-
rheic ground water, with an estimated residence time in the subsurface of 5–10 hours.
This estimation contradicts the findings of the water temperature measurement in the
pushed wells. High Rn concentrations of up to 17 Bq/L, were measured in the drilled
wells. This concentration was assumed to represent steady-state conditions (i.e., mixed

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Figure 2  Satellite view of experimental USC reach and installations (http://maps.google.com/). Insets show
from top to bottom: sampling site; PFOS, PFOA, and total PFC concentrations (sites SW3, SW4, and
GW3 outside sketch)
Rn water ages of >15 days), The wells GW1 and GW2c revealed concentrations significantly below 17 Bq/L, resulting in mixed Rn water ages of <15 days.

Recycled, surface, and ground waters from pushed and from drilled wells were sampled to characterize preaugmentation background chemical conditions. Compared to CC, the water from USC has a higher concentration in DOC, and a lower Ca/Mg ratio, both by a factor of up to five. The Ca/Mg ratio decreased gradually along the flow path from USC to CC. The specific electrical conductance and the chloride concentrations in USC are higher than those of CC, by a factor of about two. Both creeks showed a geochemical composition that is different from that of RW. The ground water in the pushed wells was somewhat less concentrated in Na and more in Ca. The groundwater in the drilled wells GW1 and GW2a was less concentrated in Mg and more in Na than the surface waters. The composition of the ground water of well GW2c was similar to that of the surface waters of USC, and the composition of well GW3 was similar to that of CC. The water samples revealed a small temporal variability of the measured concentrations, at 4 sampling dates between July 2005 and May 2006.

Results and discussion

Ten PFC compounds were detected in RW, USC and CC, in October and in November, 2005. Sites SW1 – SW3 are located at USC, site SW4 at CC, near well GW3 (Figure 2). Total PFC concentrations were at 0.42 ± 0.14 μg/L for RW, 0.11 ± 0.014 μg/L for USC, and 0.018 ± 0.009 μg/L for CC (well GW3: 0.03 μg/L, single measurement). The results between the two months are consistent. Levels of individual PFCs and distributions were also consistent for both RW and surface waters. PFOS and PFOA make up the majority of the PFCs (for full names of compounds, see Boulanger et al., 2005). PFHpA and PFNA appear in the RW, but not in the surface water. USC has higher PFC concentrations than CC. Table 1 shows that on May 4, 2006, PFOS was found ubiquitously in all sampled waters. Dilution could be the explanation for the decreasing concentrations, from USC to CC, and in CC (analyses not shown). From the measured concentrations it becomes clear that PFOS and PFOA are the main contaminants in the aqueous phase. On this date, PFOA could not be detected in SW4 and in the two other surface-water sites of CC that are not shown here. High concentrations were detected in the ground water that cannot be explained. Some compounds were detected in ground water in minute concentrations. The compound PFHxS was found exclusively in ground water, suggesting that it is a degradation product in the specific physico-chemical environment of the ground water. We do not know the source of...

### Table 1

Means of two replica PFC concentrations on May 4, 2006, in ng/L

<table>
<thead>
<tr>
<th>site</th>
<th>compound</th>
<th>RW</th>
<th>SW1</th>
<th>SW2</th>
<th>SW3</th>
<th>SW4</th>
<th>PW1</th>
<th>PW2</th>
<th>GW1</th>
<th>GW2a</th>
<th>GW2c</th>
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<td></td>
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<td>PFOS</td>
<td>374</td>
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<td>44</td>
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<td>Total</td>
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<td>48</td>
<td>14</td>
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<td>54</td>
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<, detection limit (DL; method modified from Schultz et al., 2003; DL: 1.0 ng/L for PFOS, 0.4 ng/L for PFOA). 1), for names of sites, see Figure 1 and text.
these compounds and assume that they are ubiquitous. Thus it is not surprising to us to detect them in both surface and ground water.

**Figure 2** includes the PFOS, PFOA and total PFC concentrations. Mass flow of the total PFC concentrations in USC can be assessed with the estimated flow rate for May 2006, to be at $(0.04 \text{ m}^2/\text{s}) \times (50 \text{ ng/L}) = 0.2 \text{ g/d}$. For the ground water, a discharge rate through the valley outlet was estimated using Darcy's Law: $\text{width} \times \text{thickness} \times \text{hydraulic gradient} \times \text{hydraulic conductivity} = 20 \text{ m}^3/\text{d}$. Mass flow is then $(20 \text{ m}^3/\text{d}) \times (200 \text{ ng/L}) = 0.05 \text{ g/d}$. About four times as much PFCs are transported in USC than in the accompanying ground water. A total per capita mass flow of $5 \mu$g/d would result from an assumed 10,000 inhabitants living in the catchment.

The catchment of USC is a partly open and partly residential area. From the results we imply that PFOA could be a compound that is flushed from household items. Notably, the concentrations were higher in the ground water wells than in the pushed wells, and higher in the pushed wells than in the USC water. Sampling in May 2006 could show a memory effect of PFC flushing from the very wet winter and spring of 2005/2006. The concentrations in the ground water of well GW2c were higher than those in the other drilled wells. The high PFC concentrations might be a sign for an influence of this well by downwelling conditions of USC. Changes in the ratios of PFOS and PFOA relative to total concentrations of USC water to ground water could help assessing, whether downwelling was a process that could alter initial compounds into metabolites. PFOS to total PFC ratios do not change from USC water to ground water (0.7–0.9). PFOA to total PFC ratios change slightly from 0.2–0.3 in USC to 0.1–0.2 in ground water, which is deemed insignificant. The two compounds seem not to undergo significant changes during the subsurface transport of the investigated site.

The concentrations found here compare with the results of earlier studies. The maximum concentration of total PFCs in all drinking water samples taken in the Rhine-Ruhr area (Germany) after a contamination was detected to be at 598 ng/L, and the major component PFOA at 519 ng/L (Skutlarek *et al.*, 2006). This result compares with the concentrations found for the RW of our study, creek water and ground water being somewhat lower. Mass flow of PFCs in river Glatt, Switzerland, was found by Huset *et al.* (2006) to be at 25–27 g/d, which is higher than that of USC by a factor of about 100. The reason for this difference might be that the densely populated catchment of river Glatt is more industrialized, or that there might be a single industrial emitter. Per capita mass flow was found to be at 70 mg/d PFOS, which is more than 4 orders of magnitude more than in the USC catchment. Groundwater from wells around a fire-training area contained the perfluorinated surfactants, PFOS, PFOA, PFHxS and perfluorohexanesulfonate, ranging in concentration from 3 to 120 mg/L. This is up to 6 orders of magnitude more than what was found in the USC area (Moody *et al.*, 2003). A transport study of ammonium perfluorooctanoate (APFO) from a point source near a fluoropolymer manufacturing facility to water and soil revealed that APFO air emissions deposited onto the soil and migrated downward with precipitation into the underlying aquifer (Davis *et al.*, 2007). This could explain the ubiquitous occurrence of PFCs in ground water.

**Conclusions**

From our investigation, we conclude that among the PFC chemicals, PFOS and PFOA are important groundwater contaminants. They seem to be easily transported in surface and ground water, to show a low sorption rate, and to be very stable. The contamination of the USC site is less severe than was found in other cases given here. The detection of perfluorinated compounds in residential and pristine areas is critical from an environmental perspective. The reaches of USC and CC at the experimental site may not
be long enough for the detection of a possible natural attenuation of PFOA or PFOS. Contaminants should be traced along CC down to the San Francisco Bay, when the residence times become longer. The creek’s hyporheic zone may not be tapped well enough with the two pushed wells. To this end, we have now pairs of push wells (depth 0.6 and 0.9 m) at 3 sites. Probably USC water is not directly recharging the drilled wells at the experimental site. Indirect infiltration from more upstream reaches of USC seems to be more probable. An augmentation of USC with RW can result in somewhat higher concentrations in USC.

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References