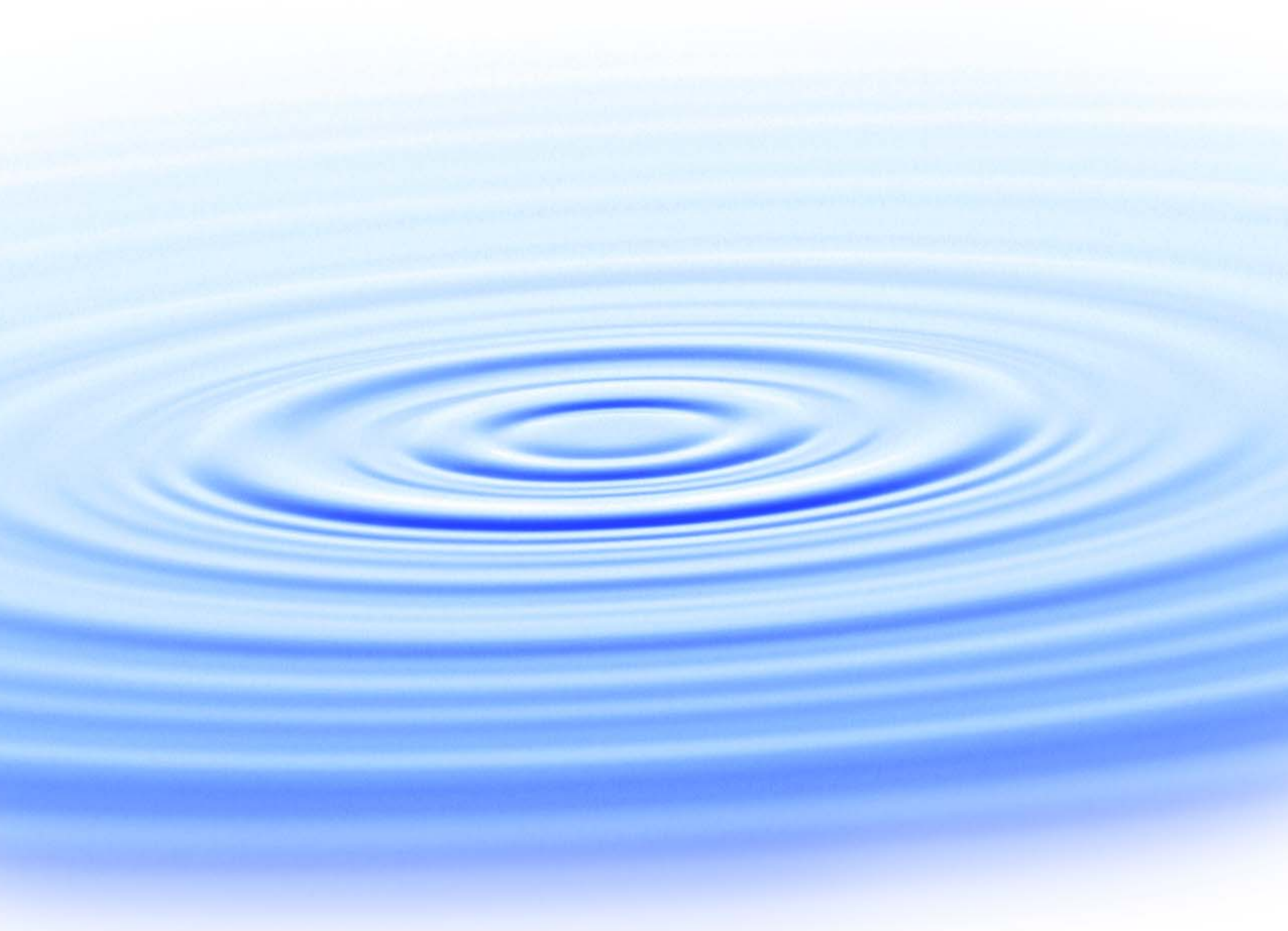
Attenuation of Emerging Contaminants in Streams Augmented with Recycled Water



WateReuse Research Foundation

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About the WateReuse Research Foundation

The mission of the WateReuse Research Foundation is to conduct and promote applied research on the reclamation, recycling, reuse, and desalination of water. The Foundation's research advances the science of water reuse and supports communities across the United States and abroad in their efforts to create new sources of high quality water through reclamation, recycling, reuse, and desalination while protecting public health and the environment.

The Foundation sponsors research on all aspects of water reuse, including emerging chemical contaminants, microbiological agents, treatment technologies, salinity management and desalination, public perception and acceptance, economics, and marketing. The Foundation's research informs the public of the safety of reclaimed water and provides water professionals with the tools and knowledge to meet their commitment of increasing reliability and quality.

The Foundation's funding partners include the Bureau of Reclamation, the California State Water Resources Control Board, the California Energy Commission, and the California Department of Water Resources. Funding is also provided by the Foundation's subscribers, water and wastewater agencies, and other interested organizations.

Attenuation of Emerging Contaminants in Streams Augmented with Recycled Water

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Acronyms

APEMs	alkylphenol polyethoxylate metabolites
APECs	alkylphenol polyethoxycarboxylates
APEOs	alkylphenol polyethoxylates
APs	alkylphenols
CA DHS	California Department of Health Services
CAPECs	carboxylated alkylphenol polyethoxycarboxylates
CEQA	California Environmental Quality Act
DOC	dissolved organic carbon
EPA	Environmental Protection Agency
FOSA	perfluorooctane sulfonamide
HAAs	haloacetic acids
LOEC	lowest observed effect concentration
MF	microfiltration
NBBS	*N*-butylbenzene sulfonamide
NDMA	*N*-nitrosodimethylamine
N-EtFOSA	*N*-ethyl perfluorooctane sulfonamide
N-EtFOSAA	*N*-ethyl perfluorooctane sulfonamido acetate
N-EtFOSE	*N*-ethyl perfluorooctane sulfonamidoethanol
PFDA	perfluorodecanoate
PFDS	perfluorodecanesulfonate
PFHpA	perfluoroheptanoate
PFHxS	perfluorohexanesulfonate
PFOA	perfluorooctanoate
PFOS	perfluorooctane sulfonate
RO	reverse osmosis
RWQCB	Regional Water Quality Control Board
SCVWD	Santa Clara Valley Water District
SJ/SC WPCP	San Jose/Santa Clara Water Pollution Control Plant
SMARTS	Simple Model for the Atmospheric Radiative Transfer of Sunshine
TCPPs	tris-propylphosphates
THMs	trihalomethanes
UCMR	Unregulated Contaminant Monitoring Rule
VOCs	volatile organic compounds
WT	water tracer

Foreword

The WateReuse Research Foundation, a nonprofit corporation, sponsors research that advances the science of water reclamation, recycling, reuse, and desalination. The Foundation funds projects that meet the water reuse and desalination research needs of water and wastewater agencies and the public. The goal of the Foundation's research is to ensure that water reuse and desalination projects provide high quality water, protect public health, and improve the environment.

An Operating Plan guides the Foundation's research program. Under the plan, a research agenda of high-priority topics is maintained. The agenda is developed in cooperation with the water reuse and desalination communities including water professionals, academics, and Foundation subscribers. The Foundation's research focuses on a broad range of water reuse research topics including:

- Defining and addressing emerging contaminants
- Public perceptions of the benefits and risks of water reuse
- Management practices related to indirect potable reuse
- Groundwater recharge and aquifer storage and recovery
- Evaluation and methods for managing salinity and desalination
- Economics and marketing of water reuse

The Operating Plan outlines the role of the Foundation's Research Advisory Committee (RAC), Project Advisory Committees (PACs), and Foundation staff. The RAC sets priorities, recommends projects for funding, and provides advice and recommendations on the Foundation's research agenda and other related efforts. PACs are convened for each project and provide technical review and oversight. The Foundation's RAC and PACs consist of experts in their fields and provide the Foundation with an independent review, which ensures the credibility of the Foundation's research results. The Foundation's Project Managers facilitate the efforts of the RAC and PACs and provide overall management of projects.

The Foundation's primary funding partners include the Bureau of Reclamation, California State Water Resources Control Board, the California Energy Commission, Foundation subscribers, water and wastewater agencies, and other interested organizations. The Foundation leverages its financial and intellectual capital through these partnerships and other funding relationships.

This research study was designed to supplement a planned water recycling pilot project initiated by the Santa Clara Valley Water District. The goal of the pilot project was to augment Coyote Creek in San Jose, CA, via release of local recycled water to the tributary Upper Silver Creek. The supplemental research effort evaluated the hypothesis that potential impacts of wastewater-derived organic contaminants may be mitigated by significant natural attenuation of those compounds at the site.

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We also gratefully acknowledge the efforts of the PAC:

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Executive Summary

Water agencies in the United States and elsewhere are expanding wastewater reclamation (or water reuse) as part of their water supply portfolio to meet the needs of growing populations. Recycling water via stream flow augmentation is an example of an environmental application of reclaimed wastewater. The reused water must be protective of both stream ecology and groundwater and comply with local and regional regulations. Currently there are limited data available to assess such water augmentation schemes *a priori*, and detailed, site-specific evaluations are needed. Water recycling for environmental applications requires consideration of a complex set of benefits and risks. For example, wastewater may contain trace levels of organic contaminants, some of which may be carcinogens, toxins, or endocrine disruptors. The presence of these microconstituents in the receiving water body may have ecotoxicological consequences, as well as pose potential human health risks. Although water reuse is generally regarded as a sustainable approach to water supply management, the presence of trace organic contaminants raises concerns about the use of this water in applications including environmental enhancement.

The present research study was designed to supplement a planned water recycling pilot project initiated by the Santa Clara Valley Water District. The goal of the pilot project was to augment Coyote Creek in San Jose, CA, via release of local recycled water to the tributary Upper Silver Creek. The supplemental research effort evaluated the hypothesis that potential impacts of wastewater-derived organic contaminants may be mitigated by significant natural attenuation of those compounds at the site. Objectives of the present research study included developing insight into attenuation mechanisms of emerging contaminants that have been discovered only relatively recently, including *N*-nitrosodimethylamine (NDMA) and perfluorochemicals. Other planned objectives included investigating the usefulness of rhodamine WT (water tracer) for predicting the attenuation of wastewater-derived organic contaminants with river transport. The objective involving the tracer was not completed because of cancellation of stream flow augmentation, and therefore research conducted on the environmental photolysis of NDMA and perfluorochemicals is presented as a substitute task.

The overall project approach was divided into two components—the field site assessment and laboratory investigations of contaminant fate. Field site assessment included the selection of water quality constituents, their analytical method development, and sampling campaigns for the targeted analytes in the recycled water, surface water, and groundwater. Additional site characterization included assessment of stream and groundwater hydrology via well installation and planned stream gauging and tracer tests. The laboratory investigation of environmental fate included biodegradation, sorption, and photolysis of particular organic contaminants.

The assessment of the microconstituent risk associated with augmenting a semiurban stream with recycled water is complicated because different constituents may be present in different concentrations in both the augmentation and background site water. In this project, the recycled water quality was better than the site water with respect to metals and microbes. However, the recycled water contained some constituents that were not present in the creek, such as NDMA and alkylphenol (AP) polyethoxylate metabolites (APEMs). Some constituents were present in both, such as perfluorochemicals, organophosphates, and *N*-butylbenzene sulfonamide (NBBS).

Although there was no known wastewater discharge into Upper Silver and Coyote creeks, baseline site characterization revealed the presence of perfluorochemicals in the surface water and underlying groundwater at concentrations that were similar to the wastewater considered for augmentation, highlighting the importance of baseline system characterization for decision making and risk evaluation in water reuse for environmental enhancement. As expected from their known occurrence in wastewater and persistence during wastewater treatment, perfluorochemicals were also detected in the recycled water from the San Jose/Santa Clara Water Pollution Control Plant intended for the stream augmentation. Concentrations of total perfluorochemicals ranged from 350 to 587 ng/L. Concentrations of perfluorooctanoate (PFOA) and perfluorooctane sulfonate (PFOS) ranged from 83 to 180 and 190 to 374 ng/L, respectively. While many perfluorochemical monitoring studies focus on PFOA and PFOS, the results of the present study showed that inclusion of other perfluorochemicals in the monitoring program may identify several additional perfluorochemicals, resulting in a much greater total perfluorochemical concentration.

With respect to ecotoxicological effects, perfluorochemical release via recycled water into sensitive ecosystems requires evaluation, both for planned and unplanned (incidental) water recycling operations. Perfluorochemicals bioaccumulate in aquatic and terrestrial organisms, and the resulting tissue concentrations constitute an internal dose that may be more ecotoxicologically relevant than the aquatic perfluorochemical concentration. The recycled water and two of the six creek monitoring sites exceeded a nonregulatory threshold concentration of 50 ng of PFOS/L that is viewed as protective of upper trophic level avian species that consume organisms in equilibrium with the water. Ultimately, the augmentation of the creek was cancelled because of concerns about the presence of perfluorochemicals in the recycled water.

The laboratory investigation of NDMA biodegradation showed that NDMA is poorly degradable biologically, a finding that was consistent with literature reports. Significant biotransformation of NDMA would therefore not be expected during river and groundwater transport in the Upper Silver Creek and Coyote Creek systems. However, NDMA and six other *N*-nitrosamines were found to undergo direct photolysis when exposed to simulated sunlight. Irradiations of 765 W/m^2, representing Southern California midsummer, midday sun, resulted in half-lives of 16 min for NDMA and 12 to 15 min for the other nitrosamines. The quantum yield for NDMA was determined to be $\Phi = 0.41$ and $\Phi = 0.43–0.61$ for the other nitrosamines. Products of NDMA photolysis included methylamine, dimethylamine, nitrite, nitrate, and formate, with nitrogen and carbon balances exceeding 98 and 79%, respectively. Because biodegradation is relatively slow and sorption to sediment is negligible, aquatic photolysis of NDMA is generally expected to be the most significant natural attenuation process in surface water, even at relatively low levels of solar irradiation ($t_{1/2} = 8–38$ h at 244– 855 W/m^2, 51° N latitude, 1-m depth).

In contrast to the *N*-nitrosamines, perfluorochemicals (selected perfluorooctane-sulfonamides) were found to undergo *in*direct photolysis when irradiated in a solar simulator in aqueous hydrogen peroxide solutions. Indirect photolysis (mediated by hydroxyl radical) was observed for *N*-ethyl perfluorooctane sulfonamidoethanol (*N*-EtFOSE), *N*-ethyl perfluorooctane sulfonamide (*N*-EtFOSA), *N*-ethyl perfluorooctane sulfonamido acetate (*N*-EtFOSAA), and perfluorooctane sulfonamide (FOSAA; see Figure 3.2 for structures). Final degradation products of hydroxyl radical-mediated indirect photolysis of perfluorooctanesulfonamides were PFOA and perfluorooctane sulfonamide (FOSA), as they did not undergo additional degradation. A proposed reaction pathway for degradation of the parent perfluorochemical, *N*-EtFOSE, to the other perfluoroalkanesulfonamides, FOSA, and

PFOA was developed and includes oxidation and *N*-dealkylation steps. Given the low rates expected for biodegradation and limited sorption, indirect photolysis of perfluorochemicals may be important in the determination of their environmental fate in sunlit surface water systems. However, the rates of indirect photolysis observed were quite low, and thus significant rates of transformation would not be expected over the creek study reach. Some transformation may be possible during additional travel time to San Francisco Bay, depending upon the sunlight irradiation and reactive intermediates available to facilitate indirect photolysis of perfluorochemicals.

Biotransformation of APEMs was also assessed. Based on this study, significant biotransformation of APEMs could be expected at the creek site upon infiltration of water containing APEMs into the hyporheic and subsurface zones, particularly considering the long travel times of groundwater. However, literature research suggests that under aerobic conditions, relatively stable AP polyethoxycarboxylates (APECs) may be formed. Under anaerobic conditions, biodegradation may continue to form APs. Further degradation of APs under anaerobic conditions is typically not observed, but some biotransformation under aerobic conditions may occur. For all microconstituents present in the recycled water, water quality monitoring of the surface water and groundwater following stream flow augmentation would be required to fully assess whether microconstituent concentrations, if detected, were significant following the expected attenuation and dilution with site water.

The final section of the current report presents the lessons learned from the collaborative work to implement a stream flow augmentation pilot project. The results of the environmental impact review of the project, conducted pursuant to the California Environmental Quality Act, are included in this report, as is a discussion of the technical and programmatic challenges faced by the project team. The augmentation was ultimately cancelled because the investigation detected compounds that posed potential legal vulnerability. Unknown compounds and compounds with undefined regulatory limits make the environmental impact review process difficult and implementation of water recycling unpredictable. Research demonstrations are needed to advance the science of water reuse and the regulatory process. It is, therefore, necessary that recycled water providers continue to search for ways to successfully implement experiments of limited duration and scale.

CHAPTER 1
PROBLEM DESCRIPTION AND OBJECTIVES

1.1 A CASE STUDY

This report presents the motivation and technical results of a combined field and laboratory study that was designed to assess attenuation of microconstituents in a creek augmented with recycled water. This research study was designed to supplement a planned stream augmentation pilot project in which the flow of Coyote Creek, a small, semiurban creek in San Jose, CA, was to be augmented with local recycled water via release to the tributary Upper Silver Creek. This report also provides a discussion of the rationale that led to project termination when results indicated the presence of potentially harmful contaminants in the recycled water.

Preparation for the release included site assessment and supporting laboratory studies, as well as the attainment of required permits and planning for necessary equipment and site construction, hydrological tracer tests, and postrelease impact assessment. Although the project team acknowledged the importance of potential biological impacts associated with wastewater discharge, the scope of our work was limited to assessment of chemical constituents in the recycled water and at the site, partly because recycled water release was intended to occur over a very limited duration (fewer than 6 months), and therefore minimal observable biological impacts were expected. Thus, field monitoring and supporting laboratory studies focused on the presence and fate of selected wastewater-derived chemical constituents. Together with the results of the field and laboratory investigations, this report presents a case study for the use of recycled water for environmental enhancement via augmentation of stream flow. The augmentation is termed an “environmental enhancement” rather than a “restoration” because the latter implies a specific historical understanding of the environmental system at the site and suggests that the modifications will return the site to these “natural” conditions. Such a transformation was not intended in the present project, which instead was designed to be a research demonstration and chemical impact assessment.

The motivations of the Santa Clara Valley Water District (the District), the organization that initiated and managed the augmentation project, were to study the impacts of using recycled water for augmenting stream flow of a semiurban creek (Coyote Creek, San Jose, CA) and to identify potential barriers to further stream flow augmentation in the region. A long-term motivation was to be able to maintain instream flow of the recycled water, thereby making more of the high-quality reservoir water, currently feeding the creek, available for domestic supply. More and more, water agencies in the United States and elsewhere are recognizing that the addition of wastewater reclamation (or water reuse) to their water supply portfolio will be necessary to meet the needs of growing populations and to face future uncertainties. These uncertainties include the threat of droughts, changing water regulations, and the potential effects of global climate change on water supply. While the traditional solution to increase water supplies has been to import water from distant sources, this option has been vanishing with population growth spreading across the southwestern United States and elsewhere.

Increased amounts of water are needed not only to meet basic water needs for human activities (industrial, agricultural, landscaping, etc.) but also to support ecosystems. In cases where human uses have diminished the water source that an ecosystem depends on, one option is to treat impaired sources—including tertiary wastewater effluents—such that the treated water can replenish the water source and thus enhance the local environment. Therefore in this case, recycling water via stream flow augmentation is an example of an environmental application of reclaimed wastewater. In the case of a stream with impaired water quality, a common situation in developed areas (Walsh et al., 2005), augmenting the stream with recycled water can enhance the stream environment by continuously flushing base stream flow for water quality improvement and by providing increased flow for fish. Furthermore, augmented streams with adequate flow will have increased aesthetic value and provide enhanced noncontact recreation. However, the reused water must be protective of both stream ecology and groundwater and comply with local and regional regulations. Currently there are limited data and regulatory experience available to assess such water augmentation schemes a priori, and detailed, site-specific evaluations are needed. Although this project was designed to address only technical issues, regulatory constraints had to be observed.

Though the release of treated wastewater to surface water has historically been commonplace given the lack of alternatives, deliberate augmentation of streams with reclaimed wastewater poses a number of regulatory, technical and scientific challenges that may impede widespread implementation. These issues were certainly encountered in this case, ranging from the design of delivery of the wastewater to the stream, the attainment of necessary permits, and public perception. Because wastewater may contain trace levels of organic contaminants, an additional issue was the seemingly infinite list of potentially risky chemicals, the presence of which conceivably could be monitored analytically. Some of these chemicals may be carcinogens, toxins, or endocrine disruptors. The identification of these compounds in wastewater or the receiving water body depends on (a) the application of analytical methods to specifically target the desired compound and (b) the detection limits of the analytical method. The presence of these microconstituents in the receiving water body may have ecotoxicological consequences, as well as pose potential human health risks. Although the concentration of chemical contaminants may be naturally attenuated in the stream system, thereby reducing known or suspected chemical risks, evaluating contaminant attenuation in rivers requires an adequate understanding of the interaction among the contaminants, stream flow, and the underlying groundwater. Clearly, the use of water recycling for environmental enhancement requires consideration of a complex set of benefits and risks, given that a natural source (rain, groundwater, or rivers) is replaced or augmented with tertiary effluent.

1.2 BRIEF PROJECT BACKGROUND

A brief summary of the project background is presented here; a more detailed project history is offered in the final section of this report, Section 5.0.

The source of Coyote Creek is located in the upper reaches of the Santa Clara Valley and flows over 20 miles through suburban and urban areas to its mouth in South San Francisco Bay. The City of San Jose (the City) previously proposed to augment stream flow in Coyote Creek by up to 400% with recycled water from the San Jose/Santa Clara Water Pollution Control Plant (SJ/SC WPCP). Several relevant supporting studies were conducted for the City. Chief among these studies was the Revised Initial Study (2000), which evaluated the ecological and groundwater impacts of the augmentation. A primary objective of the San Jose scheme was to improve cold-water habitat in Coyote Creek; thus, in addition to dechlorination, the recycled water was to be chilled significantly prior to release into the creek. The project site overlies the Santa Clara groundwater basin, containing a shallow unconfined aquifer with poor water quality and a deeper confined drinking water aquifer. A regional aquitard separates the two aquifers in many areas, including the studied reach of Coyote Creek (SCVWD, 2007). Given the location of the City's proposed outfall at Singleton Landfill, recycled water in Coyote Creek would flow only over the regional aquitard and infiltration to the potable deep aquifer would be unlikely. The report noted that there is a low probability of infiltration to the shallow aquifer because of the claylike composition of the creek bottom; nevertheless, monitoring of shallow aquifer water quality was recommended to confirm that no recharge with recycled water was taking place.

Another concern that arose during the City planning was the degradation of water quality by trace organics and endocrine disruptors. The concern stemmed from the appearance of these compounds in the aquatic environment, because some of them are biologically active and are viewed as potentially harmful to wildlife and human health.

In late October 2000, the City obtained a permit from the California Regional Water Quality Control Board (RWQCB) to implement a demonstration stream flow augmentation project in Coyote Creek. However, the City decided not to proceed with the project and the RWQCB permit expired in June 2003. The District then undertook the project. Stanford University was later brought on as a project partner to investigate the impact and fate of selected emerging contaminants. However, the District cancelled the augmentation in the spring of 2008 because of concerns over the presence of perfluorochemicals that were detected in the recycled water intended for the augmentation.

1.3 RATIONALE

The stated rationale for the District's pilot project to augment stream flow with recycled water is that it increases the use of recycled water by the District in Santa Clara County, which is consistent with the desires and policies of the District Board of Directors (the Board). It also has the potential to provide augmented creek flows for environment benefit as part of the environmental stewardship mission of the Board.

The rationale for the supplemental research project described in the present study was that it allowed for assessment of potential impacts. As described in the project work plan (SCVWD, 2004), it was proposed that Stanford University (a project partner) would use the augmentation to test the central hypothesis that natural biological, physical, and chemical action during stream flow can improve the stream's water quality via natural attenuation of wastewater-derived, trace organic constituents. Likewise, natural action during the infiltration of surface water into groundwater can further improve the water quality of the infiltrating water. The natural attenuation of any microconstituents present in the recycled water would thus mitigate impact of these constituents on the environment and reduce any potential impact on drinking water supplies. As described later in this report, a number of laboratory studies were performed to assess potential attenuation mechanisms and rates expected for the study site (for example, biodegradation, sorption, and photolysis) for selected contaminants detected in the recycled water intended for the augmentation.

The hypothesis that natural attenuation will occur during stream flow was based upon prior studies conducted by Stanford University researchers, among others. With support from the Orange County Water District, Reinhard et al. conducted a study of water quality changes in the Santa Ana River in Southern California (Reinhard et al., 1999; Reinhard and Ding, 2001; Gross et al., 2004). The Santa Ana River carries nearly 100% tertiary treated water during the summer months. It was found that trace organic contaminants such as pharmaceuticals and alkylphenol (AP) polyethoxylate (APEO) metabolites (APEMs; biological degradation products of nonionic detergents) are significantly attenuated during river transport, suggesting that the river itself acts as an efficient treatment system. The subsequent infiltration of river water into the ground led to significant additional water quality improvement in terms of total organic carbon (dissolved and particulate) and trace organics.

In a supporting laboratory study, Lin and Reinhard (2005) demonstrated that some pharmaceuticals (ketoprofen, propanolol, and naproxen) and hormones (estriol, estrone, 17β-estradiol, and 17α-ethinylestradiol) can be expected to photodegrade in river water exposed to sunlight, whereas other pharmaceuticals (ibuprofen and gemfibrozil) will degrade by microbes. A subsequent field investigation on the Santa Ana River confirmed that photodegradation processes are likely to contribute significantly to the removal of light-sensitive contaminants during river flow and that the majority of the removals for the photoresistant chemicals were a combination of sorption and biotransformation (Lin et al., 2006). Together, these processes carry out the observed natural attenuation of contaminants during river flow. Our current understanding is insufficient, however, for applying the findings of Santa Ana River studies to Coyote Creek conditions.

1.4 OBJECTIVES AND TASKS

The objectives of the pilot project initiated by the District are described in Section 5.0 and involved the assessment of water quality impacts associated with using tertiary treated wastewater to augment stream flow. The tertiary treated water, or recycled water, was to be released into the stream approximately 15 mi upstream from the San Francisco Bay. The study originally proposed to add from 2 to 6 cubic ft of recycled water per s to Coyote Creek, corresponding to two to three times base summer flow. When the possibility of engineered chilling was eliminated because of expense, the augmentation plan was amended to involve temperature monitoring and flow adjustment because of concerns about temperature impacts on the stream, resulting in an estimate that the recycled water addition would be equal to or less than the base summer flow.

As stated in the project work plan (SCVWD, 2004),

> The overall goal of the stream augmentation project is *to assess the potential impact of large-scale augmentation of the Coyote Creek flow with tertiary treated water on the water quality of the river and the underlying groundwater. If results indicate adverse effects, appropriate treatment methods will be evaluated. These treatment methods may include reverse osmosis treatment, soil treatment, or blending with higher quality water.*

As noted earlier, the present research study was designed to supplement the pilot project. The original monitoring plan was limited to a group of constituents including pharmaceuticals, APEMs, and other compounds. With support from the WateReuse Research Foundation, the project scope was expanded. Specifically, the set of monitored compounds was modified to include trace contaminants identified at analytically significant concentrations in the wastewater to be used for augmentation, and supporting studies of attenuation processes for these compounds were designed. In addition, it was recognized that a hydrological tracer test would be necessary to fully describe the physical stream system. Because methods for investigating contaminant fate in flowing surface water are poorly developed, rhodamine water tracer (WT) was selected as a nonconservative tracer to assess its usefulness in predicting attenuation of other nonconservative compounds (namely, wastewater-derived, trace organic contaminants). This tracer was intended to coincide with a traditional conservative tracer and temperature monitoring to elucidate the stream hydrology and to quantify residence times of infiltration of stream water into the ground. The objectives associated with the expanded scope are the focus of this report. Specifically, the major objectives were to

- Develop insight into attenuating mechanisms,
- Extend the range of contaminants to include *N*-nitrosodimethylamine (NDMA) and perfluorochemicals, and
- Investigate the usefulness of rhodamine WT for predicting the attenuation of wastewater-derived organic contaminants with river transport.

To support these objectives, the following analogous tasks were defined:

Task 1—Supporting laboratory studies of contaminant degradation by river sediment,
Task 2—Monitoring of an expanded set of trace organic contaminants, and
Task 3—Rhodamine WT tracer test, heat propagation, and attenuation study.

However, the District cancelled the augmentation in the spring of 2008 because of concerns over the presence of perfluorochemicals in the recycled water intended for the augmentation. Additional details are available in a later section of this report, Section 5.0.

Although the other objectives were met using laboratory and field work, the final objective involving the tracer was not completed because of cancellation of stream flow augmentation. Research conducted on the environmental photolysis of NDMA and perfluorochemicals is instead presented as a substitute task. As part of the monitoring work (Task 2), analytical methods for nitrosamines and perfluorochemicals were developed or adapted from the literature.

1.5 EMERGING CONTAMINANTS STUDIED

Of particular concern were organic contaminants, which typically occur in wastewater or wastewater-impacted water at trace concentrations, commonly referred to as “trace organics” or “microconstituents”. These may include “emerging contaminants,” microconstituents for which toxicological information is sparse and official water quality criteria (for drinking or wastewater) may not be established.

Trace organics surveyed (Table 1.1) in the wastewater and at the stream site by Stanford University included pharmaceuticals (such as gemfibrozil, ibuprofen, naproxen, ketoprofen, and carbamazepine), hormones (estrone, 17α-ethinylestradiol, 17β-estradiol, estriol), APEMs, *N*-butyl benzenesulfonamide (NBBS), bisphenol A (BPA) chlorinated tris-propylphosphates (TCPPs), nitrosamines (including NDMA), and several perfluorochemicals. The APEMs include APs, short-chain APEOs, AP polyethoxycarboxylates (APECs), and carboxylated APECs (CAPECs). Analytical methods for these constituents are described in the literature and project work plan (Gross et al., 2004; SCVWD, 2004; Lin et al., 2006), with the exception of nitrosamines and perfluorochemicals, which are described in Section 1.5.3.

Nitrosamines (including NDMA) and perfluorochemicals were added to the list of target compounds because the pharmaceuticals and hormones either were not detected or were only intermittently detected in the wastewater and because nitrosamines and perfluorochemicals themselves are of particular concern. More details on the environmental occurrence and toxicology of NDMA and perfluorochemicals are given in the next sections.

Table 1.1 Water Quality Parameters Surveyed in Recycled Water, Stream, and Groundwater

Parameter		No. of Parameters
Fire Retardants		2
Tris (3-chloropropyl) phosphate		
Tris (2,3-dichloropropyl) phosphate		
Plasticizers		2
Bisphenol A (BPA)		
N-butyl benzenesulfonamide (NBBS)		
Alkylphenol polyethoxylate metabolites (APEMs; non-ionic surfactants)		4 groups
Halogenated/Chlorinated APEMs	Alkylphenols (nonyl-, octyl-)	
APEOs	APECs, CAPECs	
Pharmaceuticals		11
Acetaminophen	Iminostilbene	
Caffeine	Ketoprofen	
Carbamazepine	Naproxen	
Carisoprodol	Primidone	
Gemfibrozil	Propanolol	
Ibuprofen		
Hormones		4
Estradiol		
Estriol		
Estrone		
Ethynylestradiol		
Other Organic Compounds		
Herbicides and Pesticides		9
Trihalomethanes (disinfection byproducts)		5
Haloacetic Acids (disinfection byproducts)		7
NDMA (disinfection byproduct)		1
Perfluorochemicals		10
Metals		19
Microbes		3 groups
General Water Quality		10
On-site Parameters		4
Temperature	Conductivity	
pH	Dissolved Oxygen	

1.5.1 *N*-Nitrosamines

NDMA is one of several *N*-nitrosamines classified as probable human carcinogens by the U.S. Environmental Protection Agency (EPA; U.S. EPA, 1993). It received much attention as a potential drinking water contaminant after its 1998 detection in California drinking water wells (up to 3 μg/L) that was due to contamination from unsymmetrical dimethylhydrazine-based rocket fuel. Subsequent monitoring led to the discovery that NDMA was also a disinfection byproduct arising from the chlorination or chloramination of drinking water and wastewater (CA DHS, 2006). More potent than the trihalomethanes (THMs), NDMA concentrations of 20 to 100 ng/L typically result from the chlorination of wastewater effluent (Mitch et al., 2003). In 2002, the California Department of Health Services (CA DHS) established a 10-ng/L notification level (action level) in drinking water (CA DHS, 2006). While the potential for ecotoxicological impact has not been thoroughly investigated at environmentally relevant concentrations, *in vitro* bacterial and mammalian cell studies have shown NDMA to be a mutagen and *in vivo* studies have also shown genetic effects (Liteplo et al., 2002). In addition to NDMA, the EPA has listed five other nitrosamines within the Unregulated Contaminant Monitoring Rule 2 (UCMR 2) to be monitored from 2008 to 2010 (U.S. EPA, 2006). Some of these nitrosamines have been detected in effluent-impacted rivers (Schreiber and Mitch, 2006) and in a drinking water distribution system (Zhao et al., 2006). Structures and occurrence information for these compounds are given in Table A1 of the Appendix.

Nitrosamines resist acidic and basic hydrolysis (Saunders and Mosier, 1980; Ho et al., 1996), and field and microcosm studies of NDMA have shown that it does not readily sorb to sediments and is slow to biodegrade in soils, sediments, and surface water (Tate and Alexander, 1976; Mallik and Tesfai, 1981; Kaplan and Kaplan, 1985; Gunnison et al., 2000; Yang et al., 2005). Nitrosamines are photosensitive, however, and currently UV irradiation is the most commonly applied treatment method for NDMA removal in wastewater and drinking water (Mitch et al., 2003). Some removal may also be offered by reverse osmosis (Steinle-Darling et al., 2007; Plumlee et al., 2008b).

1.5.2 Perfluorochemicals

Perfluorochemicals are another family of emerging contaminants found in wastewater and wastewater-impacted aquatic environments. They are used in a variety of materials such as food packaging, paints, and lubricants (Kissa, 1994). In addition to detection in wastewater (Alzaga and Bayona, 2004; Boulanger et al., 2005; Schultz et al., 2006; Sinclair and Kannan, 2006; Loganathan et al., 2007), they have been found in surface water (Hansen et al., 2002; Moody et al., 2002; Boulanger et al., 2004; Boulanger et al., 2005; Simcik and Dorweiler, 2005; Rostkowski et al., 2006; Sinclair et al., 2006; Skutlarek et al., 2006; McLachlan et al., 2007; So et al., 2007), groundwater (Moody et al., 2003; Schultz et al., 2004), drinking water (Harada et al., 2003; Skutlarek et al., 2006; Paustenbach et al., 2007), and rain (Loewen et al., 2005; Scott et al., 2006). Table A2 of the Appendix summarizes the aquatic occurrence of two commonly detected perfluorochemicals, perfluorooctanoate (PFOA) and perfluorooctane sulfonate (PFOS).

Laboratory studies demonstrate that mammals readily absorb PFOA and PFOS during oral and inhalation exposures. They tend to distribute to the blood serum and the liver and can cross the blood-brain and placental barriers (Lange et al., 2006). Although research shows that PFOA, perfluorononoate (PFNA), and PFOS are not estrogenic (Maras et al., 2006), high doses of PFOA and PFOS lead to mortality, while lower doses result in hepatotoxic, immunotoxic, neurotoxic, and behavioral effects (Lange et al., 2006). When present in a mixture, PFOS may enhance the toxicity of other compounds by increasing cell membrane permeability (Hu et al., 2003; Jernbro et al., 2007).

Perfluorochemicals bioaccumulate and have been detected in biota around the world, including fish, seals, minks, albatross, bald eagles, polar bears, and humans (Giesy and Kannan, 2002; Schultz et al., 2003). Typical concentrations of PFOA and PFOS in the serum of nonoccupationally exposed humans are 3 to 35 and 7 to 82 µg/L, respectively (Hansen et al., 2001; Kannan et al., 2004). These levels merit concern, given that adverse effects have been observed in rats at levels (370-µg/L PFOA) that differ from those in humans by less than a safety factor of 100 (Butenhoff et al., 2004; Lange et al., 2006). Wildlife monitoring studies for high trophic levels report PFOS concentrations of 8 to 242 µg/L in serum in ringed seals (Kannan et al., 2001a), 3 to 34 µg/L in blood in albatross (Kannan et al., 2001b), and 0.88 to 74 µg/L in serum in red panda (Dai et al., 2006). Morikawa et al. (2006) report the concentrations of PFOS in both serum and water for turtles collected in a Japanese river, 28 to 486 µg/L in the serum and 3 to 37 ng/L in the water.

Results presented in Section 3.5 demonstrate the occurrence and persistence of a variety of perfluorochemicals, not limited to PFOA and PFOS, in recycled water. A list and structures of perfluorochemicals monitored in the wastewater and at the stream site for the present study is presented in Figure 3.2. In additon, a brief evaluation of the toxicological relevance of the measured concentrations for aquatic environments is provided in Section 3.6, given that these compounds both occur in the water and result in an internal dose following bioaccumulation and biomagnification.

1.5.3 Analytical Methods for NDMA and Perfluorochemicals

An analytical method for NDMA in wastewater and surface water was developed for the present study. For field samples of recycled water, surface water, and groundwater, 3 or 4 L was collected in 1-L amber glass bottles (rinsed three times with sample water) and was packed on ice in coolers. Sodium thiosulfate was added to recycled water samples to quench chlorine. Following return to the laboratory the same day of collection, samples were stored at 4 °C. For analysis, samples obtained from the same site were mixed to promote homogeneity and were passed through 0.2- or 0.45-µm-pore-size nylon filters. A blank of Milli-Q purified water was also prepared.

NDMA was extracted from 500 mL or 1 L of sample water (each site analyzed in replicate) by solid-phase extraction (SPE) with a 16-port vacuum extraction manifold using reservoirs packed with activated charcoal. Prior to SPE, activated charcoal was washed with Milli-Q water at the same pH as the sample and was dried overnight at 110 ºC, and 1.0 g was packed into empty 8-mL SPE reservoirs fitted with a frit and filter at the base. The charcoal was wetted with Milli-Q water before the water sample was loaded under vacuum at a flow rate less than 5 mL/min. After loading of the water sample, the bottles were rinsed three times with Milli-Q, which served to wash the charcoal. The cartridges were drained except for 1 to 2 mL of water left behind. This water was eluted into 15-mL glass collection vials. NDMA was eluted from the charcoal using 2 mL of acetonitrile (two times), 2 mL of methanol (two times), and 2 mL of acetone (two times). The extract was evaporated on a sand bath at 37 ºC, leaving 1 to 2 mL of solvent-free water. For instrumental analysis, the concentrated extracts were returned to a pH ranging from 5 to 9 by adding a small amount of concentrated NaOH. NDMA-d6 was added as an internal standard (0.3 mL of a 110-ppb solution) to 1.0 mL of extract and was stored at 4 ºC until analysis.

NDMA was quantified by liquid chromatography–tandem mass spectrometry (LC-MS/MS) by injecting 50 µl at a flow rate of 0.15 mL/min onto a liquid chromatograph from a Shimadzu LC-10AD *VP* with a Shimadzu SIL-10AD *VP* autosampler connected to a triple quadrupole mass spectrometer from Applied Biosystems (API3000). The instrument detection limit was typically 1 ppb, and the instrument reporting limit was 2 ppb of NDMA, from which the method detection limit is 4 ng/L for 500 mL of loaded water sample. For analysis of samples from laboratory studies (biodegradation, Section 2.1; photolysis, Section 2.2), samples were directly injected into the LC-MS/MS without need for prior concentration via SPE because of the low instrumental detection limits. Additional details of the analytical procedures have been reported elsewhere by Plumlee et al. (2008b).

An analytical method for perfluorochemicals in wastewater and surface water was adapted for the present study from an available sediment method (Higgins et al., 2005) and is also available in a publication by Plumlee et al. (2008a). For field sampling, water samples of recycled water, surface water, and groundwater were collected (6 to 250 mL) in polypropylene bottles (pre-rinsed with methanol and water). After rinsing of bottles three times with the sample water, samples were packed on ice in coolers and were returned to the laboratory for analysis.

Each water sample was prepared for replicate analysis. Sample preparation involved the addition of a sample aliquot to a methanol-containing microcentrifuge tube, centrifugation, and transfer of the mixture to a vial containing a 70:30 (v/v) mixture of methanol and 0.01% aqueous ammonium hydroxide. An internal standard solution containing ^{13}C-labelled perfluorochemicals was added for quantitation. No sample preconcentration via SPE was necessary because of the low instrumental detection limits.

Perfluorochemicals were quantified by the LC-MS/MS above by large-volume injection of 490 µl. Calibration standards containing each of the perfluorochemicals analyzed in the study were carefully matched in solution makeup to the sample preparation method in order to minimize matrix effects and to achieve a linear calibration curve. The same method was used for samples from laboratory studies (photolysis, Section 2.4). Additional details of method recovery and matrix effect assessment are available in Plumlee et al. (2008a).

1.6 PROJECT APPROACH

The technical project approach was divided into two components—the field site assessment and laboratory investigation of contaminant fate. Field site assessment involved the selection of water quality constituents, including emerging contaminants, their analytical method development if necessary, and the sampling campaigns for the targeted analytes in the recycled water, surface water, and groundwater. Additional site characterization included assessment of stream and groundwater hydrology via well installation and planned stream gauging and tracer tests. The laboratory investigation of contaminant fate included biodegradation, sorption, and photolysis of particular organic contaminants.

CHAPTER 2

LABORATORY STUDIES OF CONTAMINANT TRANSFORMATION

Of particular interest in this project was the detection of NDMA and perfluorochemicals in the recycled water to be used for the stream flow augmentation of Upper Silver and Coyote creeks. It was noteworthy, too, that perfluorochemicals were detected in the baseline surface water and groundwater at the site (as characterized during the baseline studies executed). Following a review of the pertinent literature, laboratory investigations of particular attenuation mechanisms for these compounds were carried out.

Specifically, rates of biodegradation of NDMA and APEMs were assessed with sediment and water collected from the site. Extensive testing of the photosensitivity of NDMA and perfluorochemicals to natural sunlight was also carried out. In adequately sunlit surface water systems, photochemical degradation may act in combination with biodegradation and sorption (and also with volatilization and dilution) to naturally attenuate the concentrations of organic contaminants. Photolysis (via direct or indirect mechanisms) plays a particularly important role in the overall environmental fate of a trace organic compound when biodegradation and sorption are slow or negligible. Direct photolysis is the result of light absorption by the compound of interest, whereas indirect photolysis involves absorption of light by a "sensitizer" that produces species that react with the compound of interest.

In some cases, environmental transformations may provide a reduction in the potential risk associated with the starting compound when the products of the reaction are harmless; in other cases, the starting compound may be transformed to a chemical or chemicals of concern. It is important to determine the identities of these products for a more complete evaluation of environmental fate and toxicity. Thus, product characterization was included in the present fate studies.

2.1 BIODEGRADATION OF NDMA

Because NDMA was detected in the wastewater intended for the augmentation (as described in Section 3.3), a laboratory study was conducted to assess whether NDMA biodegradation could be expected, and at what rates, in surface water and sediment collected from Upper Silver Creek.

Previous studies have demonstrated that NDMA biodegradation may occur in various soils and sediments and that sorption to soils or sediments does not occur significantly. Reported biodegradation half-lives range from 4 to 6 days in groundcover and turfgrass soils (Yang et al., 2005) and 11 to 39 days in soil slurries (Gunnison et al., 2000) to persistence in some soils and bog sediments (Tate and Alexander, 1976; Mallik and Tesfai, 1981). Bacteria with monooxygenase enzymes have been shown to degrade NDMA (Sharp et al., 2005). Further, the biodegradation is likely to be cometabolic, that is, fortuitous biotransformation in the presence of a primary (growth) substrate (Sharp et al., 2005; Yang et al., 2005).

2.1.1 Experimental Approach

For the present study, triplicate microcosms were prepared aerobically using two different treatments: either creek water alone or 10:1 creek water and sediment. The sediment was characterized as having a fraction organic carbon (f_{oc}) of 0.30% and was sieved to remove particle sizes above 1.168 mm. Microcosms were prepared in 100 mL glass serum bottles and sealed with rubber septa. Oxygen was added periodically to maintain aerobic conditions, and microcosms were stored at room temperature in the dark on a shaker at 150 rpm. Resazurin was used as an oxygen indicator. For both treatments, one set of microcosms (abiotic) was sterilized with sodium azide. Constant NDMA concentrations in these sterile microcosms confirmed that NDMA was not lost via an unexpected pathway (for example, volatilization or sorption to glass or septa) or via sorption to sediment, as expected from literature reports. A duplicate set of Milli-Q water microcosms served as a control. Microcosms were spiked with 100 µg/L NDMA (1.3 µM) and were respiked after a significant fraction or all of the NDMA had degraded, except for a blank microcosm that was not spiked. To monitor the disappearance of NDMA, small volumes (120 µL) were taken from the overlying water by using a sterilized syringe. Sample aliquots were centrifuged, and 100 µL was taken for analysis using the LC-MS/MS method described previously (Section 1.5.3).

2.1.2 Results and Discussion

Biodegradation of NDMA was observed in the microcosms containing either surface water alone or in combination with sediment. Disappearance of NDMA (>80%) occurred slightly more rapidly for the microcosms with sediment (requiring 91 to 127 days) than for surface water (requiring 127 to 140 days). As further evidence for biodegradation, the disappearance rate increased following the respike of the same microcosms, suggesting the adaptation and growth of the microbial community. The responsible microorganisms were not isolated. Additional details of this laboratory investigation are available in the research publication by Plumlee and Reinhard (2007).

If first-order kinetics are assumed, average half-lives for NDMA biodegradation in microcosms with sediment and surface water were $t_{1/2} = 31 \pm 19$ (SD) days and decreased to 8 ± 5 days following the respike. These rates are within the range of half-lives reported in the literature (Tate and Alexander, 1976; Mallik and Tesfai, 1981; Gunnison et al., 2000; Yang et al., 2005). Because of the relatively low rates of biodegradation observed, results indicate that biodegradation of NDMA is not likely to be a significant process for streams or rivers having fairly short residence times, such as in the case of Upper Silver and Coyote creeks (hours to days).

2.2 DIRECT PHOTOLYSIS OF NDMA

In adequately sunlit surface water systems, photochemical degradation may act in combination with biodegradation and sorption (and also with volatilization and dilution) to naturally attenuate the concentrations of organic contaminants.

Photolysis studies employing UV irradiation (Ho et al., 1996; Stefan et al., 2002; Stefan and Bolton, 2002; Sharpless and Linden, 2003; Lee et al., 2005a; Lee et al., 2005b) have shown that NDMA absorbs light and photodegrades under these conditions. However, information regarding kinetics, quantum yields, and products for NDMA photolysis under environmental conditions is lacking. Sunlight absorption by NDMA in the environment occurs at a weaker absorption band than for UV light (Chow et al., 1972; Stefan and Bolton, 2002), and the photochemistry of the transition states may differ (Turro, 1991).

#

The objectives of the present investigation were to determine rates of direct and indirect photolysis and quantum yields for seven nitrosamines under conditions of simulated natural sunlight. Nitrosamines included NDMA, *N*-nitrosomethylethylamine (NMEA), *N*-nitrosodiethylamine (NDEA), *N*-nitrosodi-*n*-propylamine (NDPA), *N*-nitrosodi-*n*-butylamine (NDBA), *N*-nitrosopiperidine (NPip), and *N*-nitrosopyrrolidine (NPyr). Structures and occurrence information for the selected nitrosamines are given in Table A1 of the Appendix. NDMA was selected for additional study, and photodegradation products were identified. An additional objective was to assess the importance of NDMA photodegradation in the environment, such as for the case of Upper Silver and Coyote creeks. From the measured quantum yield, expected aquatic photolysis rates for NDMA were calculated for a range of representative environmental conditions.

2.2.1 Experimental Approach

To assess the occurrence and rates of photolyis under environmental conditions, solutions of nitrosamines were irradiated by using an Atlas Suntest CPS+ photosimulator equipped with a 1.1-kW xenon arc lamp according to a method described elsewhere (Lin and Reinhard, 2005). Sample solutions were kept in capped quartz tubes and placed horizontally in a constant temperature (20.0 ± 1.7 °C) water bath 25 cm directly below the photosimulator lamp, and an additional tube covered in aluminum foil was placed in the photosimulator to serve as a control. Direct photolysis tests in Milli-Q water (pH 6, unadjusted) were performed at 765 W/m^2, which is equivalent to midday, midsummer sun in California (Lin and Reinhard, 2005) and were used alongside actinometry to determine nitrosamine quantum yields. To assess the potential for indirect photolysis, nitrosamines were irradiated in filtered (0.45-μm pore size) creek surface water and were compared to irradiation of nitrosamines in Milli-Q water. NDMA and the other nitrosamines were analyzed by LC-MS/MS.

To model the aquatic photolysis rate of NDMA in the environment using the compound-specific quantum yield measured in the laboratory study, global horizontal irradiance at the earth's surface over the wavelength range of 280 to 2279 nm was calculated by using SMARTS (Simple Model for the Atmospheric Radiative Transfer of Sunshine, v. 2.9.5) (Gueymard, 2006) for midlatitude and tropical locations. Inputs to SMARTS included geographical position, season, date, and time and specific parameters such as ozone abundance, atmospheric gases, and aerosol model. For the purposes of this nonspecific irradiance prediction, representative or average inputs recommended by SMARTS developers were assumed and water (non-Lambertian) was selected as the surface.

For additional details on the experimental approach and model, please refer to the research publication resulting from this work by Plumlee and Reinhard (2007).

2.2.2 Results and Discussion

Direct photolysis at irradiations of 765 W/m^2, representing Southern California midsummer, midday sun, resulted in half-lives of 16 min for NDMA and 12 to 15 min for the other nitrosamines. The quantum yield for NDMA was determined to be $\Phi = 0.41$ and $\Phi = 0.43$–0.61 for the other nitrosamines. Quantified products of NDMA photolysis included methylamine, dimethylamine, nitrite, nitrate, and formate, with nitrogen and carbon balances exceeding 98 and 79%, respectively. Indirect photolysis of nitrosamines in surface water was not observed; in fact, increasing dissolved organic carbon (DOC) reduced the NDMA photolysis rate because of light screening.

Aquatic photolysis rates in real environmental systems may be different from laboratory measurements depending upon actual solar irradiance, the light screening by the water body of interest, and the water depth. But, if the quantum yield and molar absorptivity of the chemical are known, photolysis rates in the field can be estimated for the conditions of a particular site (Schwarzenbach et al., 2003; Zepp and Cline, 1977). This exercise was performed for NDMA for a range of general environmental conditions to achieve broad applicability. Figure 2.1 shows the average photodecay rate constant estimated for NDMA in a nonspecific surface water with a depth of 1 m and intermediate light screening by the water (spectral slope = 0.02 and $\lambda_{280} = 0.3$). Midday solar irradiance was modeled by using SMARTS for three locations representing a range of latitudes from January to December. The predicted rates shown in Figure 2.1 correspond to half-lives over the year of 8–38 h in London (51° N latitude), 7–14 h in Irvine (33° N latitude, the location of the Orange County Water District site), and 6–7 h in Ecuador (2° S latitude). If the depth of the water body is reduced to 10 cm, the half-lives (corresponding to an average rate over the depth) are reduced by a factor of approximately 10. Additional results may be found in the research publication of this work (Plumlee and Reinhard, 2007).

These findings suggest that for a typical river, depending upon the depth, solar irradiation, and light screening of the water, reaching an NDMA concentration attenuated by one half-life will require (sunlit) travel times of hours to a few days. This finding is consistent with a report (Pehlivanoglu-Mantas and Sedlak, 2006) for the effluent-dominated Santa Ana River in California, in which a decrease in NDMA corresponding to approximately one half-life from the upstream wastewater treatment plant effluent (24 ng/L) to <10 ng/L downstream was observed after a 10-h residence time. Gross et al. (2004) report the increased attenuation of trace organic contaminants for the same river compared to the nearby Prado Wetlands; given the reduced NDMA photolysis rate expected with increasing DOC via light screening (Plumlee and Reinhard, 2007) and the greater DOC typically found in wetlands than in rivers, shallow rivers also may be expected to outperform wetlands with regard to NDMA attenuation.

Because biodegradation is relatively slow, aquatic photolysis of NDMA is generally expected to be more significant even at relatively low levels of solar irradiation ($t_{1/2}$ = 8–38 h at 244–855 W/m^2, 51° N latitude, 1-m depth). Based on the NDMA photodecay rates predicted in this study for a typical river, significant removal of NDMA by natural sunlight may be expected in Coyote Creek before it reaches San Francisco Bay, if recycled wastewater were to be added to this stream. However, over the short study area at Upper Silver and Coyote creeks (Figure 3.1), the amount of NDMA attenuation observed may not be significant and would depend on light intensity and other site-specific conditions.

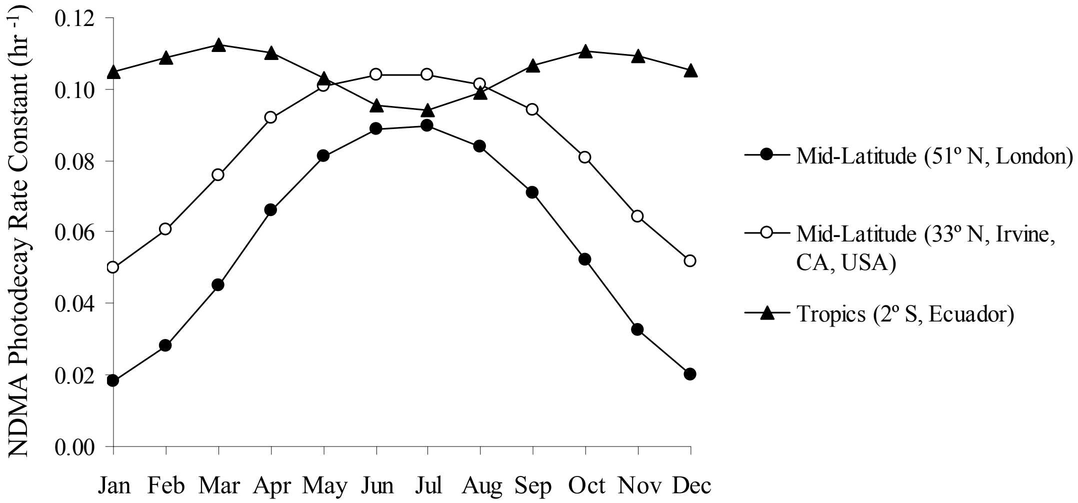

Figure 2.1 Average NDMA photodecay rate constants predicted for midday solar irradiance in mid-latitude and tropical zones in surface water with intermediate light screening and a depth of 1 m. Reprinted with permission from Plumlee and Reinhard, 2007. Copyright 2007 American Chemical Society.

2.3 BIODEGRADATION OF APEMs

APEM compounds were also detected in the recycled water intended for stream flow augmentation. To explore the potential for degradation of these types of compounds by microorganisms in sediment from the site, a laboratory study of the biological degradation of nonylphenol ethoxyacetic acid (NP_1EC) in sediment collected from Coyote Creek was performed (Montgomery-Brown et al., 2008).

In this study, NP_1EC was spiked into oxic microcosms containing sediment from Coyote Creek and was monitored to evaluate the ability of this river to degrade NP_1EC. No degradation was observed under anaerobic conditions. The biological transformation pathway was elucidated by observing the appearance of products including dicarboxylated AP ethoxyacetic acids (CA_nP_1EC; where n = the number of aliphatic carbon atoms). Novel metabolites were observed that appeared to be specific to *ortho*-isomers (versus *para*-isomers) of NP_1EC. Results also suggested that dissolved oxygen availability was important in determining the dominant biodegradation pathway. Overall, CA_8P_1ECs were the dominant metabolites of NP_1EC biodegradation initially, but CA_6P_1ECs became the dominant metabolites as biodegradation progressed.

Based on this study, significant biotransformation of APEMs may be expected at the Coyote Creek site upon infiltration of water containing APEMs into the hyporheic and subsurface zones, particularly considering the long travel times of groundwater. Research available in the literature (Jonkers et al., 2001; Montgomery-Brown and Reinhard, 2003; Montgomery-Brown et al., 2008) shows that under aerobic conditions, relatively stable APECs (with one to three ethoxy units, i.e. AP_nECs where n = 1 to 3) may be formed. Under anaerobic conditions, biodegradation may continue to form APs. Further degradation of APs under anaerobic conditions is typically not observed, but some biotransformation under aerobic conditions may occur. #

2.4 INDIRECT PHOTOLYSIS OF PERFLUOROCHEMICALS

Following the detection of perfluorochemicals in both the recycled water to be used for the augmentation and the creek system, a laboratory investigation of perfluorochemical photodegradation potential was carried out. As noted earlier in this report (Section 1.5.2), biotransformation and sorption to sediment occur to a quite limited extent for these compounds, and although these processes are important in the global accounting of perfluorochemical mass, they may be unlikely to contribute significantly to attenuation during stream transport in cases like Upper Silver and Coyote creeks. Therefore, attenuation by photolytic means was selected as the focus of the laboratory study (Plumlee et al., 2009). Although research has suggested that perfluorochemicals are not susceptible to direct photolysis (transformation upon direct absorption of light) and this finding was confirmed in the present study, no research had been conducted on the potential for indirect photolysis. In the case of indirect photolysis, target compounds react with photochemically produced reactive intermediates (such as hydroxyl radicals).

2.4.1 Experimental Approach

Perfluoroalkanesulfonamides were irradiated in aqueous hydrogen peroxide solutions using artificial sunlight to simulate aquatic environmental conditions and to study hydroxyl radical-induced transformations. These perfluorochemicals (5- to 15-µg/L initial concentration of *N*-ethyl perfluorooctane sulfonamidoethanol [*N*-EtFOSE], *N*-ethyl perfluorooctane sulfonamido acetate [*N*-EtFOSAA], *N*-methyl perfluorooctane sulfonamido acetate [*N*-MeFOSAA], *N*-ethyl perfluorooctane sulfonamide [*N*-EtFOSA], perfluorooctane sulfonamide acetate [FOSAA], perfluorooctane sulfonamide [FOSA], and PFOA) were irradiated individually in solutions of 10 mM H_2O_2 in identical capped 20-mL quartz test tubes for intervals ranging from 1 to 6 days. Additional tubes containing the target perfluorochemical and H_2O_2 were covered with aluminum foil and were irradiated simultaneously to serve as dark controls. To simulate the photochemical production of hydroxyl radical that occurs naturally in sunlit aquatic systems, H_2O_2 was used to generate hydroxyl radicals according to the reaction:

$$H_2O_2 \xrightarrow{h\nu} 2\,{}^{\bullet}OH$$

Irradiations were performed by using an Atlas Suntest CPS+ photosimulator equipped with a 1.1-kW xenon arc lamp at an intensity of 765 W/m^2. Samples were analyzed by LC-MS/MS.

Where analytical standards were available, products formed were monitored and each product was irradiated individually to elucidate the reaction pathway. Products monitored included the initial compounds (perfluoroalkanesulfonamides), perfluorocarboxylates (C_8 to C_6), perfluorinated sulfonates (C_8 to C_6), and perfluorooctane sulfinate (PFOSI) (Rhoads et al., 2008), with instrumental detection limits typically between 0.002 and 0.05 µg/L. An upper limit for the bimolecular reaction rate constant for the reaction of $\cdot OH$ and *N*-EtFOSAA was determined by using a variation of a method described by Boreen et al. (2004).

2.4.2 Results and Discussion

Indirect photolysis mediated by hydroxyl radical was observed for *N*-EtFOSE, *N*-EtFOSAA, *N*-EtFOSA, and FOSAA. A proposed reaction pathway for degradation of the parent perfluorochemical, *N*-EtFOSE, to the other perfluoroalkanesulfonamides, FOSA, and PFOA was developed (Figure 2.2) and includes oxidation and *N*-dealkylation steps. As they did not undergo additional degradation, FOSA and PFOA were the final degradation products of hydroxyl radical-mediated indirect photolysis. UV-visible absorption spectra for the perfluorochemicals, showing absorbance in the UV region below the range of natural sunlight, were also measured (Figure 2.3). Additional discussion of results may be found in the research publication (Plumlee et al., 2009).

Given the low rates expected for biodegradation and limited sorption of perfluorochemicals, indirect photolysis of perfluorochemicals may be important in the determination of their environmental fate. However, the rates of indirect photolysis observed were quite low, and thus significant rates of transformation would not be expected over the Upper Silver and Coyote creeks' study reach. Some transformation may be possible during the additional travel time to San Francisco Bay, depending on the sunlight intensity and availability of reactive intermediates (photochemically produced radicals) to facilitate indirect photolysis of perfluorochemicals. The laboratory study demonstrates that perfluorochemical (indirect) photolysis leads to formation of other perfluorochemicals via a transformation process and therefore does not constitute attenuation of perfluorochemicals in general.

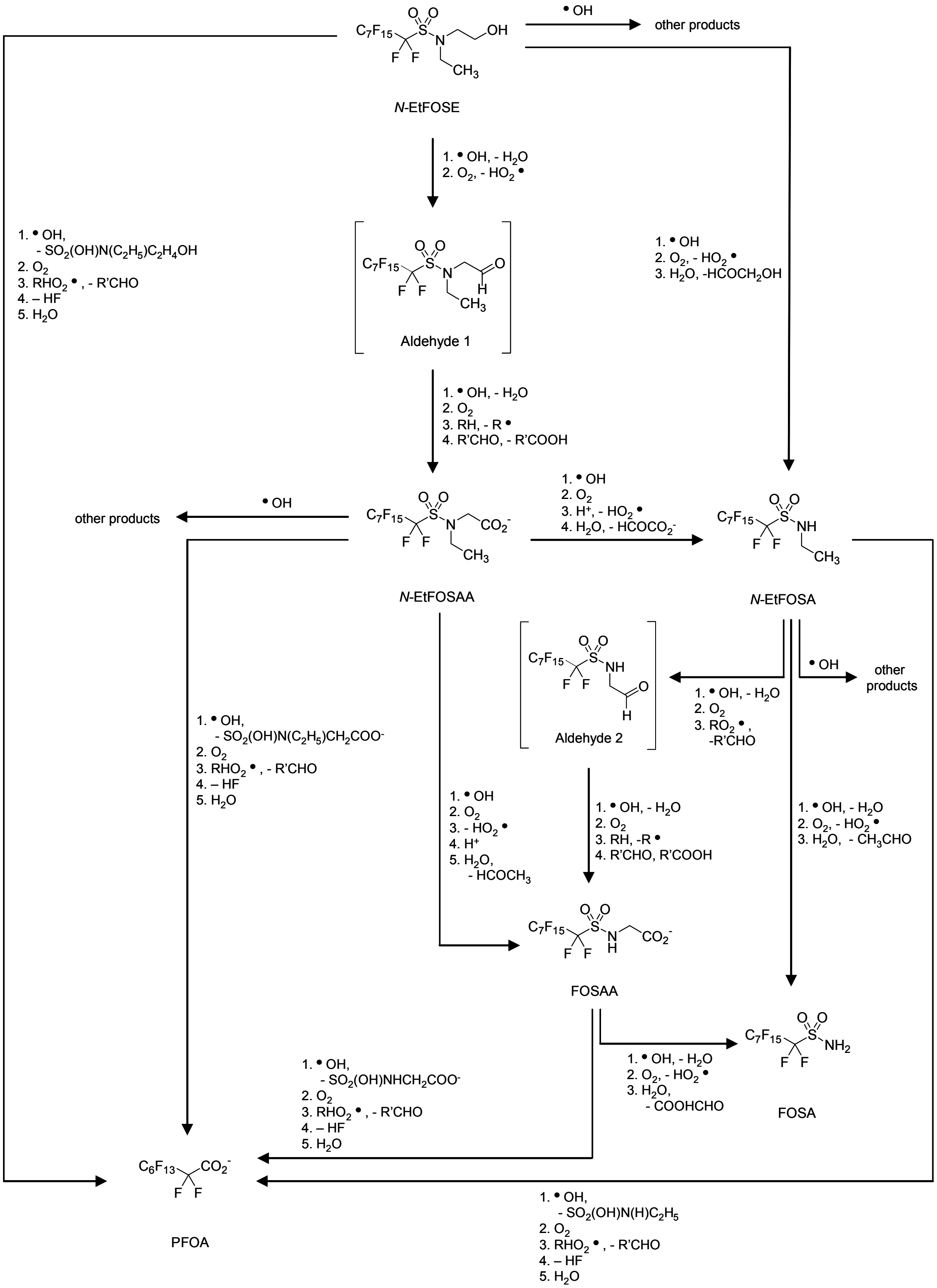

Figure 2.2. Proposed pathway for the aqueous indirect photolysis of perfluoroalkanesulfonamides via reaction with $^{\bullet}$OH. All compounds shown were observed, with the exception of the aldehydes depicted in brackets. Formation of "other products" (unknown) indicates that an incomplete fluorine mass balance was measured. Reprinted with permission from Plumlee et al., 2009. Copyright 2009 American Chemical Society.

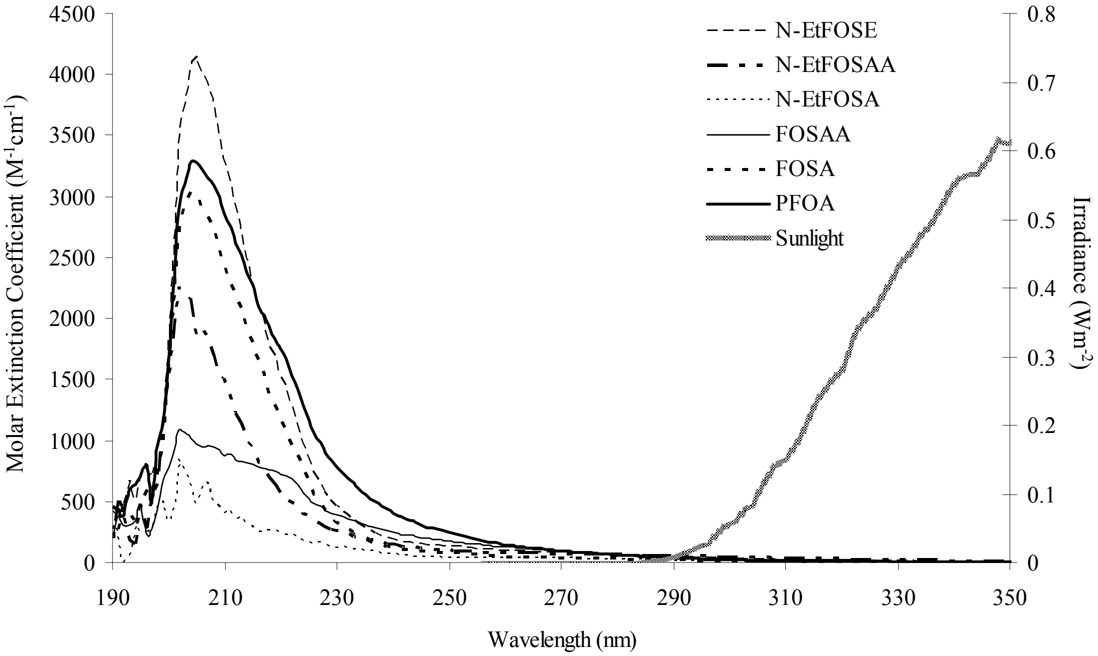

Figure 2.3. Absorbance spectra for selected perfluorochemicals in methanol. Irradiance of the photosimulator is shown on the secondary *y* axis. Reprinted with permission from Plumlee et al., 2009. Copyright 2009 American Chemical Society.

CHAPTER 3

OCCURRENCE OF EMERGING CONTAMINANTS IN RECYCLED WATER AND AT PROJECT SITE

In this section, water quality results (field site and recycled water sampling for intended stream flow augmentation, Section 3.1) are presented alongside related data from a separate study (Section 3.4) in which perfluorochemical occurrence was assessed in additional recycled waters and at a water reuse site.

3.1 SITE SELECTION AND HYDROLOGY

3.1.1 Surface Water Sampling Sites and Hydrology

The original creek location and surface water sampling sites were along Coyote Creek in San Jose, CA. Later, Upper Silver Creek (a tributary of Coyote Creek) was selected for discharge of the recycled water because of the creek's proximity to recycled water pipelines at the Yerba Buena pump station. Thus, the surface water sampling sites were modified to include both creeks. The objective was to choose sampling locations that permitted the monitoring of water quality changes in the creeks as the water flowed from the augmentation outfall point. Sampling points were selected such that, ideally, there were no additions or diversions that changed the quality or quantity of water. In addition, a control site upstream of the augmentation outfall was selected.

The final selected sampling sites are shown in Figure 3.1. Grab samples of surface water were collected from these sites along Upper Silver Creek and Coyote Creek over a reach of approximately 5 km. Samples were obtained from these sites and from the nearby Yerba Buena pump station (recycled water) in San Jose, CA, at intervals of approximately once per month for spring and summer months during 2004–2007 to establish baseline water quality conditions. This "baseline" monitoring (to establish initial conditions prior to planned augmentation with recycled water) occurred over 4 years simply because summer augmentation was often postponed until the following summer by construction or regulatory delays. The target analytes and particular field sites included each year varied slightly as the project focus and available analytical methods were refined.

As described earlier, a tracer test using rhodamine WT and bromide as well as installation of stream gauges were planned to characterize stream hydrology, but were not executed following augmentation cancellation.

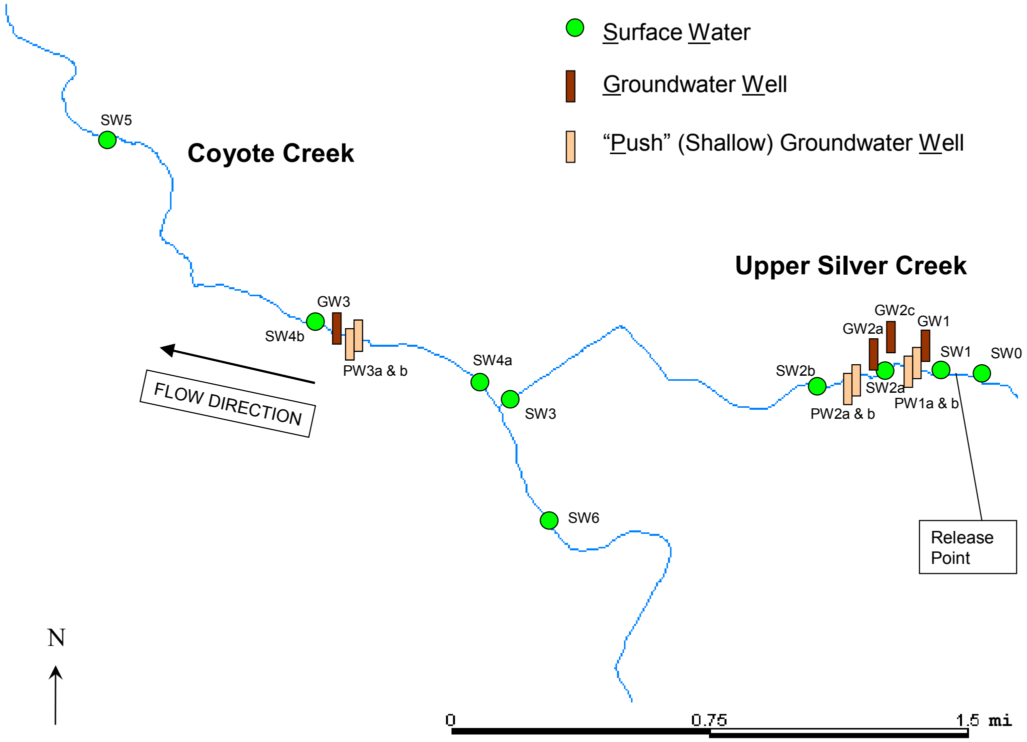

Figure 3.1. Final selection of surface water, groundwater, and hyporheic groundwater monitoring sites along Upper Silver and Coyote creeks. Adapted from Plumlee et al. (2008a), with permission from Elsevier.

3.1.2 Installation of Groundwater Wells

In addition to surface water sampling along Upper Silver and Coyote creeks, groundwater wells were installed adjacent to the creek and sampled during the baseline phase to establish initial conditions, with the intention to monitor the wells every month for 1 year during augmentation to determine whether target compounds in the recycled water impacted groundwater quality. Groundwater samples were obtained from four monitoring wells (Figure 3.1; GW1, -2a, -2c, and -3) installed to depths of 5–10 m. Depth to water ranged from 2 to 5 m for the four wells. Additional plans for augmentation that were not carried out because of the cancellation were to monitor water quality in the infiltration flow path so that contaminant attenuation could be assessed as a function of distance and residence time.

In order to use temperature as a tracer for hydraulic residence time (Anderson, 2005), temperature monitors were installed at selected surface water sites and in push wells.

3.1.3 Hyporheic Zone

In addition to the installation of traditional groundwater wells, very shallow groundwater wells were installed in the creek bed at a depth of just 0.6 to 0.9 m to capture young groundwater in the hyporheic zone, a region in which surface water and groundwater exchange and flow velocity, relative to the surface, is reduced by orders of magnitude (Hoehn and Cirpka, 2006). These "push wells" (PW1, -2, and -3) were installed in or adjacent to the creek.

3.2 MONITORING CAMPAIGNS

Presented in the next sections are the detections observed for NDMA, the perfluorochemicals, and the other microcontaminants in the recycled water and at the creek site. The 2005 baseline monitoring campaign included pharmaceuticals, hormones, organophosphates, plasticizers, and APEMs and was expanded to include NDMA and perfluorochemicals. A limited baseline water quality analysis was performed in May 2006 for the same 2005 sites plus additional push wells and groundwater wells. Prior to the final cancellation of the augmentation using recycled water, samples of the surface water, groundwater, and recycled water were also collected in June of 2007. NDMA and perfluorochemical data analysis was completed, and the results are presented here. Data analysis was not completed for the other trace organics upon cancellation of the augmentation.

Additional water quality analyses were performed in 2005–2007 by the District for the following constituents: herbicides and pesticides, THMs, volatile organic compounds (VOCs), metals, haloacetic acids (HAAs), microbes, and general water quality.

3.3 CHARACTERIZATION OF WATER QUALITY—NDMA AND PERFLUOROCHEMICALS

3.3.1 NDMA

NDMA is a disinfection byproduct formed during chlorination and chloramination and is considered a probable human carcinogen. As shown in Table 3.1, NDMA was found in the recycled water (nearly all sampling events) and was not found in the creek surface waters during the 2005–2007 baseline monitoring campaigns. In addition, NDMA was not detected in the groundwater. NDMA was not expected to occur in the site surface water and groundwater because it is a wastewater disinfection byproduct and because the site did not receive any known wastewater discharge.

Table 3.1. Concentrations of NDMA in Baseline 2005–2007 Studies (Detection Limit, 4 ng/L)

	NDMA (ng/l) in Recycled Water	Upper Silver Creek			Coyote Creek		
		SW 1	SW 2	SW 3	SW 4	SW 5	SW 6
Jun-05	51	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Aug-05	46	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Oct-05	61	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Nov-05	111	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
May-06	26	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Jun-07	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

In contrast to the 2005 and 2006 data, NDMA was not detected in the recycled wastewater collected in 2007. It is possible that the concentration of NDMA found in wastewater varies throughout the day and that at the time of the June 2007 sampling event, the concentration was simply below the method detection limit.

3.3.2 Perfluorochemicals

Perfluorochemicals have structures or substructures (carbon skeletons) that are fully fluorinated. They are used for many purposes such as textile and paper coatings, firefighting foams, and fluoropolymer manufacturing and can be found in products from the commonly used brands/products Teflon®, Scotchgard™, GORE-TEX®, and Stainmaster® (Plumlee et al., 2008a). There are many persistent degradation products of which 10 were chosen for this project because of their frequent occurrence in wastewaters and/or relevance to other research.

Perfluorochemicals were detected in Upper Silver and Coyote creeks as well as in the underlying groundwater; Table 3.2 presents the baseline concentrations determined in the springs of 2006 and 2007. The detection limits are shown with the data and vary slightly by compound and sample batch. Perfluorochemicals were also found at similar concentrations in samples from a subset of these same sites collected in 2005 (data not shown). Table 3.3 presents the concentrations of perfluorochemicals detected in the recycled water intended for the stream flow augmentation over 2005–2007. The total perfluorochemical concentrations ranged from 350 to 587 ng/L and were typically three to four times higher than in the site water.

Upper Silver Creek sites (2007) showed a range of 126 to 145 ng of total perfluorochemicals/L. If flow augmentation with reclaimed wastewater (Table 3.3 and WWTP 2 in Table 3.6) had occurred, the stream concentration was estimated to increase to approximately 300 ng/L, given a flow regime of equal parts wastewater and surface flow.

The concentrations found downstream of the confluence of Upper Silver and Coyote creeks are a result of mixing of the upstream contributions of the background perfluorochemicals found in each creek: downstream PFOS and PFOA levels are within 10 to 30% of those predicted by using flow measurements (data not shown). The source of perfluorochemicals to these two creeks is unknown but is likely to be a combination of atmospheric deposition of volatile precursors (Ellis et al., 2004; Simcik and Dorweiler, 2005; Martin et al., 2006) and surface runoff. There is currently no known upstream wastewater discharge into either creek. Results are consistent with the urban surface water sites characterized by Simcik and Dorweiler (2005), which ranged from 2 to 47 ng of PFOS/L and 0.5 to 20 ng of PFOA/L (compared to remote sites with no data to 1.2 ng of PFOS/L and no data to 0.7 ng of PFOA/L).

The concentrations detected in the hyporheic zone were typically consistent with the nearby creek water (Table 3.2), indicating that the hyporheic zone was supplied by the overlying creek and that negligible perfluorochemical attenuation occurred in the hyporheic zone. Analysis of temperature data for select sites indicated a hyporheic residence time of 15 to 60 min (Hoehn et al., 2007). No significant attenuation was expected in the hyporheic zone or with distance downstream, as the perfluorochemicals monitored resist biodegradation and as sorption is limited (Giesy and Kannan, 2002; Prevedouros et al., 2006).

Groundwater wells near the creeks showed perfluorochemical detections in all samples and generally on the order of the creek concentrations. PFOS ranged from 19 to 192 ng/L and PFOA from no data to 22 ng/L in the four groundwater wells monitored in 2006 and 2007. The source of perfluorochemicals in the groundwater is not entirely clear. Although head measurements indicate that the stream is a losing stream, the groundwater sampled is not necessarily recharged from the creek alone. For instance, urban rain (Table A2 of the

Appendix) may be a source of perfluorochemicals to the aquifer, or potentially septic systems located upstream may be the source. In addition, a nearby golf course uses reclaimed wastewater for landscaping. Nevertheless, it is likely that the creek water is a significant supplier to the nearby groundwater given that the distribution and concentrations of the perfluorochemicals are consistent between surface water and groundwater at the site. For example, perfluorohexanesulfonate (PFHxS), PFOS, perfluorodecanesulfonate (PFDS), PFOA, and perfluorodecanoate (PFDA) were always or nearly always detected in the surface water, hyporheic zone, and groundwater (2007), whereas perfluoroheptanoate (PFHpA), FOSA, and *N*-EtFOSAA were detected only intermittently and 6:2 fluorotelomer sulfonate (6:2 FtS) and PFNA were not detected.

Table 3.2. Perfluorochemicals[a] (ng/L) in Upper Silver and Coyote Creeks Monitored during Dry Months of 2006 and 2007.

	PFHxS		PFOS		PFDS		PFHpA		PFOA		PFDA		FOSA		EtFOSAA	
	May-06	Jun-07	May-06	Jun-07	May-06	Jun-07	May-06	Jun-07	May-06	Jun-07	May-06	Jun-07	May-06	Jun-07	May-06	Jun-07
Detection Limit	4	2	10	2	21	2	4	2	4	4	21	2	21	2	21	4
Creek water																
Site 1	n.d.	8.5 (1.0)	32 (11)	41 (8.3)	n.d.	36 (61)	n.d.	8.7 (1.5)	15 (0.8)	27 (10)	n.d.	11 (2)	n.d.	3.5 (0.6)	n.d.	10 (2.6)
Site 2a	n.m.	12 (1.1)	n.m.	45 (1.8)	n.m.	3.1 (0.1)	n.m.	10 (5.7)	n.m.	36 (0.7)	n.m.	12 (0.7)	n.m.	2.9 (0.3)	n.m.	5.7 (0.8)
Site 2b	n.d.	8.3 (0.5)	27 (5.7)	56 (30)	n.d.	11 (16)	n.d.	7.7 (0.8)	10 (0.4)	29 (2.3)	n.d.	19 (10)	n.d.	3.1 (0.6)	n.d.	n.d.
Site 3	n.d.	12 (2.0)	38 (4.8)	56 (4.4)	n.d.	6.3 (1.8)	n.d.	12 (1.2)	11 (0.5)	31 (6.2)	n.d.	19 (2.9)	n.d.	2.3 (0.3)	n.d.	6.1 (0.07)
Site 4	n.d.	3.8 (1.6)	14 (2.0)	25 (9.5)	n.d.	18 (15)	n.d.	4.7 (1.3)	n.d.	13 (5.2)	n.d.	13 (9.0)	n.d.	n.d.	n.d.	23.5 (24)
Site 5	n.d.	3.0 (1.2)	20 (0.8)	11 (7.3)	44 (0.0)	9.1 (6.4)	n.d.	3.2 (1.9)	n.d.	10 (6.0)	n.d.	6.0 (7.3)	n.d.	2.4 (0.2)	31 (2.1)	5.0 (0.6)
Site 6	n.d.	2.3 (0.4)	9.3 (0.6)	4.8 (0.7)	n.d.	3.4 (1.2)	n.d.	n.d.	n.d.	8.0 (4.1)	n.d.	7.7 (2.1)	n.d.	n.d.	n.d.	n.d.
Hyporheic zone																
Push well 1	n.d.	n.m.	58 (3.7)	n.m.	n.d.	n.m.	n.d.	n.m.	23 (0.3)	n.m.	n.d.	n.m.	n.d.	n.m.	n.d.	n.m.
Push well 2	n.d.	10 (1.9)	44 (12)	48 (7.5)	n.d.	15 (0.7)	n.d.	8.1 (1.0)	10 (1.3)	28 (3.9)	n.d.	19 (2.4)	n.d.	4.3 (0.9)	n.d.	10 (0.6)
Push well 3	n.m.	3.8 (1.6)	n.m.	25 (9.5)	n.m.	5.7 (3.8)	n.m.	7.3 (0.9)	n.m.	22 (2.7)	n.m.	13 (1.2)	n.m.	2.9 (0.3)	n.m.	6.2 (0.3)
Groundwater																
Well 1	n.d.	8.9 (0.7)	85 (8.7)	40 (3.4)	n.d.	2.9 (1.3)	n.d.	n.d.	14 (5.9)	12 (1.6)	n.d.	7.3 (0.8)	n.d.	2.2 (0.2)	26 (18)	n.d.
Well 2a	n.d.	8.9 (4.2)	82 (1.1)	26 (4.8)	n.d.	n.d.	n.d.	4.8 (2.9)	22 (1.1)	18 (5.7)	n.d.	8.6 (2.6)	n.d.	n.d.	n.d.	n.d.
Well 2c	11 (3.8)	17 (3.5)	192 (33)	87 (5.3)	n.d.	3.3 (1.8)	n.d.	2.4 (0.6)	10 (0.6)	12 (1.6)	n.d.	10 (0.9)	n.d.	3.7 (0.7)	n.d.	n.d.
Well 3	9.2 (1.4)	4.0 (0.3)	31 (6.0)	19 (3.1)	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

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[a] Mean ($n = 2$) concentrations for creek water, hyporheic water, and groundwater. Range is given in parentheses. PFNA and 6:2 FtS were also monitored but were not detected above detection limits of 4 and 10 ng/L in May 2006 and 10 and 4 ng/L in June 2007, respectively. Sites are depicted in Figure 3.1. Reprinted from Plumlee et al. (2008a) with permission from Elsevier.

Table 3.3. Summary of Perfluorochemicals (ng/L) Detected in Recycled Water in 2005–2007

San Jose/Santa Clara Water Pollution Control Plant Recycled Water[a]

Sample Date	PFHxS	PFOS	PFDS	PFHpA	PFOA	PFNA	PFDA	6:2 FtS	FOSA	*N*-EtFOSAA	Total PFCs
July 2005	20	341	7.7	13	113	15	4.6	n.d. (<4)	2.1	30	587
August 2005	8	258	6.1	12	103	14	4.5	5	1.7	21	488
November 2005	6.7	201	4.5	6.8	83	14	5	7.3	2.8	19	350
May 2006	n.d. (<4)	374	n.d. (<21)	5.4	120	9.5	n.d. (<21)	n.d. (<11)	n.d. (<21)	n.d. (<21)	508
June 2007	17	190	n.d. (<2)	13	180	32	7.5	n.d. (<4)	3.2	23	470

[a] tertiary treatment via dual media filtration and chloramination, followed by additional chloramination for reclaimed wastewater

3.4 CHARACTERIZATION OF WATER QUALITY—OTHER MICROCONTAMINANTS

3.4.1 Pharmaceuticals, Hormones, Plasticizers, and Fire Retardants

No hormones and few pharmaceuticals were detected in much of the baseline 2005 study. Two pharmaceuticals, carisoprodol and iminostilbene, were detected in the recycled water, and caffeine was detected in the creek water (Table 3.4). In a previous investigation, these same two pharmaceuticals were identified in the SJ/SC WPCP secondary effluent in June 2005 (data not shown). Note that all measurements reflect only the particular day and time sampled; pharmaceutical concentrations emitted in wastewater effluents may be quite variable even over a single day. Another reason for the absence of many targeted compounds may be that the final effluent is chlorinated, which can oxidize many organics.

Caffeine was detected at three creek sites in 2005, spanning both Upper Silver and Coyote creeks. Caffeine has been demonstrated for use as a marker for wastewater contamination of surface waters (Buerge et al., 2003).

NBBS, a plasticizer used in nylon production that is commonly found in U.S. water bodies and is reportedly neurotoxic (Duffield et al., 1994), was found in recycled water, creek water, and groundwater throughout the baseline 2005 study (Table 3.4). Creek concentrations were generally similar to recycled water concentrations, with the exception of May, when the creek levels at Sites 3, 4, 5, and 6 were higher than the recycled water.

A single detection of BPA, 18 ng/L, was found in the July 2005 groundwater Well 3. BPA is a plasticizer used in polycarbonate plastic and epoxy resins and is considered estrogenic.

Tris(3-chloropropyl)phosphate and tris(2,3-dichloropropyl)phosphate, which are organophosphates used as fire retardants, were also detected in the recycled water and creek water in 2005. Both are on the EU priority list for carcinogenic suspicion. Tris(3-chloropropyl)phosphate concentrations are much higher in the recycled water than in the natural waters and are also higher in the creek water than in the groundwater. Tris(2,3-dichloropropyl)phosphate was detected more sporadically.

The herbicide oxadiazon was added to the project analyte list after its discovery in preliminary analyses of the Coyote Creek surface water. It was not found in the recycled water or groundwater and was found in the surface water during the 2005 baseline study in only one month (July) at the three sites on Silver Creek.

As noted previously, a limited baseline water quality analysis was performed in May 2006 for the same 2005 sites plus additional push wells and groundwater wells (Table 3.5). Some pharmaceuticals and the hormones were omitted from the analysis (those belonging to a step in the analysis in which compounds are derivatized by silylation), because previous data showed few or no pharmaceutical and hormone detections. To save time and expense, the surface water samples were not analyzed for pharmaceuticals and other trace organics once it was determined that the augmentation would not occur in 2006, and instead, only the push and groundwater well samples were analyzed (as the 2005 data set for those sites was limited). The pharmaceutical compounds carisoprodol and iminostilbene, as well as NBBS, the organophosphates, NDMA, and perfluorochemicals, were detected in the recycled water, consistent with 2005 data.

3.4.2 APEMs

APEMs, nonionic surfactants frequently detected in wastewater, were detected in the recycled water each time it was sampled during the 2005 baseline study (Table 3.4). Among these APEMs were carboxylated APEMs (A+CAPECs; alkyl- and carboxyalkyl ethoxycarboxylates) and halogenated APEMs. Halogenated APEMs are chlorinated and brominated forms of the APEMs produced during wastewater disinfection. Halogenated APEMs made up 10, 19, and 5% of the total APEMs for May, July, and August 2005, respectively. No APEMs were detected in creek surface water or groundwater.

3.4.3 Herbicides, Pesticides, THMs, HAAs, VOCs, Metals, and Microbes

Herbicides, pesticides, THMs, HAAs, VOCs, metals, and microbes in the recycled water and at the site were also assessed by the District during some or all of the 2005–2007 summer monitoring campaigns. Herbicides and pesticides were monitored during the 2006–2007 campaigns and were not detected in the recycled water or at the site. THMs were monitored during 2005–2006 and were detected in the recycled water (total THMs ranged from 160 to 170 µg/L), and were not detected at the site with the exception of one incident at a relatively low concentration (Upper Silver Creek, August 2005, 0.5 µg of total THMs/L). HAAs were monitored over 2005–2007 and were detected in the recycled water (14 to 127 µg/L) but were not detected at the site with the exception of occasional detections ranging 1 to 3 µg/L in the surface water and groundwater. VOCs were monitored in the 2007 campaign and were not detected in the recycled water or in the creek. Metals were monitored over 2005–2007; detections of note included arsenic in the site surface water and groundwater (2 to 43 µg/L). *Escherichia coli (E. coli)*, fecal coliforms, and total coliforms were not detected in the recycled water when measured in 2007 but were detected in the site surface water in 2005 (not measured in other years). Maximum detected values in the site surface water were 3000, 3000, and >16,000 MPN/100 mL for *E. coli*, fecal coliforms, and total coliforms, respectively.

Table 3.4. Summary Report of Pharmaceuticals, Hormones, APEMs, and Other Compounds Monitored as Part of the 2005 Baseline Study of the Recycled Water (Yerba Buena Pump Station), Upper Silver and Coyote Creek Sites (SW 1–6), and Groundwater Monitoring Well No. 3 Near Coyote Creek (sample sites are shown in Figure 3.1)

Analyte	Yerba Buena Recycled Water			SW 1 (Silver Creek)			SW 2 (Silver Creek)			SW 3 (Silver Creek)			SW 4 (Coyote Creek)			SW 5 (Coyote Creek)			SW 6 (Coyote Creek)			Groundwater Well 3		
	May-05	Jul-05	Aug-05	May-05	Jul-05	Aug-05	May-05	Jul-05	Aug-05	May-05	Jul-05	Aug-05	May-05	Jul-05	Aug-05	May-05	Jul-05	Aug-05	May-05	Jul-05	Aug-05	May-05	Jul-05	Aug-05
Pharmaceuticals (ng/L)																								
Acetaminophen	n.d.	n.d.	n.m.	n.d.	n.d.	n.m.	n.d.	n.d.	n.m.	n.d.	n.d.	n.m.	n.d.	n.d.	n.m.	n.d.	n.d.	n.m.	n.d.	n.d.	n.m.	n.m.	n.d.	n.m.
Caffeine	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	**72**	n.d.	n.d.	**19**	n.d.	n.d.	**23**	n.d.	n.d.	n.d.	n.d.	n.m.	n.d.	n.d.
Carbamazepine	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.m.	n.d.	n.d.
Carisoprodol	n.d.	**217**	**195**	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.m.	n.d.	n.d.
Gemfibrozil	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.m.	n.d.	n.d.
Ibuprofen	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.m.	n.d.	n.d.
Iminostilbene	n.d.	**98**	**96**	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.m.	n.d.	n.d.
Ketoprofen	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.m.	n.d.	n.d.
Naproxen	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.m.	n.d.	n.d.
Primidone	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.m.	n.d.	n.d.
Propanolol	n.d.	n.d.	n.m.	n.d.	n.d.	n.m.	n.d.	n.d.	n.m.	n.d.	n.d.	n.m.	n.d.	n.d.	n.m.	n.d.	n.d.	n.m.	n.d.	n.d.	n.m.	n.m.	n.d.	n.m.
Hormones (ng/L)																								
Estradiol	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.m.	n.d.	n.d.
Estriol	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.m.	n.d.	n.d.
Estrone	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.m.	n.d.	n.d.
Ethynylestradiol	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.m.	n.d.	n.d.
APEOs[1] & APEMs[2] (ng/L)																								
APEOs	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.m.	n.d.	n.d.
Alkylphenols (nonyl-, octyl-)	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.m.	n.d.	n.d.
A+CAPECs[3]	**610**	**256**	**303**	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.m.	n.d.	n.d.
Halog. APEMs[4]	**60**	**48**	**17**	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.m.	n.d.	n.d.
Other (ng/L)																								
Bisphenol A	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.m.	**18**	n.d.
N-butyl benzenesulfonamide	**13**	**60**	**46**	**30**	**48**	**14**	**60**	**73**	**15**	**119**	**39**	**27**	**209**	**21**	**23**	**209**	**<d.l.**	**38**	**164**	**75**	**44**	n.m.	**19**	**<d.l.**
Tris(3-chloropropyl)phosphate	n.d.	**33**	**15**	**1.0**	**5.0**	**1.6**	**2.0**	**5.8**	**3.3**	**3.0**	**5.2**	**4.2**	n.d.	**2.6**	**1.5**	n.d.	**2.9**	**2.4**	n.d.	n.d.	**2.2**	n.m.	**1.0**	n.d.
Tris(2,3-dichloropropyl)phosphate	**244**	**13.4**	n.d.	**1.0E+04**	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.m.	**<d.l.**	n.d.
Oxadiazon	n.d.	n.d.	n.d.	n.d.	**12**	n.d.	n.d.	**12**	n.d.	n.d.	**3.4**	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.m.	n.d.	n.d.

[1] Alkylphenol polyethoxylates (AP1EO, AP2EO, AP3EO)

[2] Alkylphenol polyethoxylate metabolites

[3] Sum of alkylphenol ethoxycarboxylates and carboxyalkylphenol ethoxycarboxylates (both metabolites of APEOs).

[4] Sum of halogenated (chlorine or bromine) alkylphenols, APEOs, and A+CAPECs

Table 3.5. Summary Report of Pharmaceuticals, APEMs, and Other Compounds Monitored as Part of the May 2006 Baseline Study of the Recycled Water (Yerba Buena Pump Station), Upper Silver and Coyote Creek Sites (SW 1–6), Hyporheic Zone Wells (Push Wells, PW 1–2), and Groundwater Monitoring Wells (GW 1–3)[a]

Analyte	Recycled Water	PW1	PW2	GW1	GW2A	GW2C	GW3	SW1	SW2	SW3	SW4	SW5	SW6	Blank
Pharmaceuticals (ng/l)														
Caffeine	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.d.
Carisoprodol	**9**	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.d.
Gemfibrozil	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.d.
Ibuprofen	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.d.
Iminostilbene	**160**	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.d.
Ketoprofen	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.d.
Naproxen	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.d.
APEOs & APEMs (ng/l)														
Octylphenol	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.d.
Others (ng/l)														
NBBS	**103**	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.d.
NDMA	**26**	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.d.
Tris(2,3-dichloropropyl)phosphate	**36**	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.d.
Tris(3-chloropropyl)phosphate	**61**	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.d.
Oxadiazon	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.d.

[a] See Tables 3.2 and 3.3 for perfluorochemicals. Sample sites are shown in Figure 3.1.

3.5 PERFLUOROCHEMICALS IN WATER REUSE

Because of the persistence of perfluorochemicals in wastewater treatment (Boulanger et al., 2005; Schultz et al., 2006; Sinclair and Kannan, 2006) and their expected bioaccumulation, the occurrence of these compounds must be considered in wastewater and wastewater reclamation, especially where humans or wildlife may be exposed. To this end, a range of perfluorochemicals (Figure 3.2) was determined in three different reclaimed wastewaters in addition to the reclaimed wastewater intended for the stream flow augmentation and in a unique water recycling operation: a wetland constructed with wastewater for both treatment and habitat creation. Results were interpreted based on literature evaluations of perfluorochemical toxicity (Section 3.5) and were reported alongside data for the stream flow augmentation site in a study by Plumlee et al. (2008a).

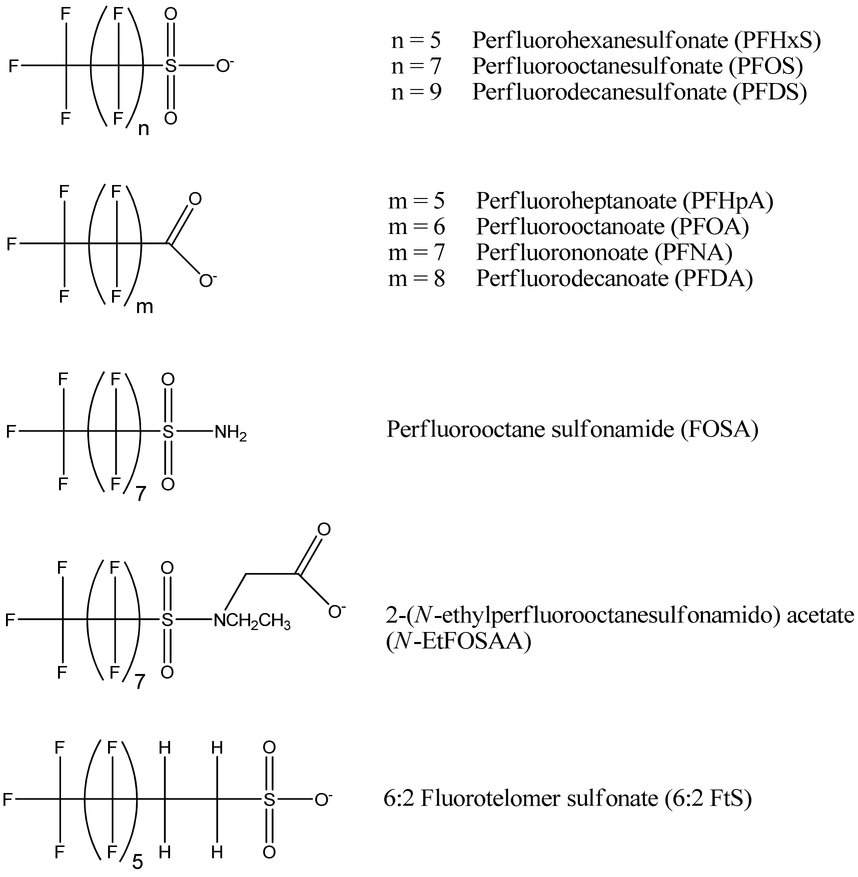

Figure 3.2. Perfluorochemicals monitored in the present study. Reprinted from Plumlee et al. (2008a) with permission from Elsevier.

3.5.1 Experimental Approach

Reclaimed wastewater was collected in June 2007 from four California wastewater treatment plants (WWTP 1, 2, 3, and 4) that produce tertiary treated effluent for landscape irrigation and other reuse purposes. Following primary and secondary treatment, the reclaimed wastewaters undergo the tertiary treatments listed in Table 3.6. Grab samples were collected following tertiary treatment.

Water samples also were collected from a constructed wetland (California) that receives primary treated wastewater (clarification and solid digestion) and discharges to the ocean. In addition to fulfilling treatment requirements for discharge, the wetland provides community recreation and wildlife habitat. Grab samples were taken in February 2006 from treatment stages, including the oxidation ponds, treatment marshes, and enhancement marshes. Chlorination and dechlorination occur prior to the enhancement marshes. The hydraulic retention time of each stage varies from 1 to 2 months for the oxidation ponds, is approximately 2 days for the treatment marshes, and is approximately 10 days for the enhancement marshes.

Samples and blanks were analyzed by direct, large-volume injection using LC-MS/MS (Higgins et al., 2005; Schultz et al., 2006).

3.5.2 Perfluorochemicals in Four Reclaimed Wastewaters

Nearly all of the perfluorochemicals monitored were detected in all wastewaters (Table 3.6). As evidenced by the detections, perfluorochemicals persisted beyond the tertiary treatment steps. Summing the 10 perfluorochemicals, the total concentration ranged from 90 to 470 ng/L across the effluents. PFOS and PFOA made the largest contributions to the total, at 7.6 to 46% and 13 to 68%, respectively. The perfluorochemical concentrations are consistent with reports for other municipal wastewaters (Table A2 of the Appendix), which vary between plants (Alzaga and Bayona, 2004; Boulanger et al., 2005; Schultz et al., 2006; Sinclair and Kannan, 2006).

3.5.3 Perfluorochemicals in a Constructed Wetland Receiving Primary Treated Wastewater

Perfluorochemicals were also measured at various treatment stages of a constructed wetland receiving wastewater. All 10 perfluorochemicals were detected (Table 3.6), with the exception of 6:2 FtS, which was not detected at any stage. No significant removal of the perfluorochemicals was observed across wetland treatment. Although PFOA and PFOS are often found in the highest concentrations compared to other perfluorochemicals in wastewaters, in this case PFDS and *N*-EtFOSAA were found at greater concentrations. From solely the biodegradation kinetics of *N*-EtFOSE, a precursor to *N*-EtFOSAA and PFOS that is used in protective paper coatings, higher concentrations of *N*-EtFOSAA than PFOS in wastewater effluent are expected, given the low rate of transformation from *N*-EtFOSAA to PFOS (Rhoads et al., 2008). However, there are additional sources of PFOS to wastewater, which may explain the higher concentrations of PFOS typically observed in monitoring studies than of other perfluorochemicals (Rhoads et al., 2008). For instance, because PFOS and PFOA are directly discharged to treatment plants (Prevedouros et al., 2006), their concentrations in most wastewaters may exceed precursors. Few monitoring studies include PFOS precursors like *N*-EtFOSAA; Boulanger et al. (2005) detected 3.6 ± 0.2 ng of *N*-EtFOSAA/L in WWTP effluent, compared to 26 ± 2.0 ng of PFOS/L.

Table 3.6. Perfluorochemicals (ng/L) in Reclaimed Wastewater from Four California Treatment Plants (June 2007) and in Consecutive Stages of a Constructed Wetland (February 2006) for Wastewater Treatment and Wildlife Habitat. (Values are the mean of duplicate samples. Mean percent difference between duplicate samples was 21%). Reprinted from Plumlee et al., 2008, with permission from Elsevier.

RECLAIMED WASTEWATER

Sample	PFHxS	PFOS	PFDS	PFHpA	PFOA	PFNA	PFDA	6:2 FtS	FOSA	EtFOSAA	Total PFCs
WWTP 1[a]	24	38	9.0	8.8	36	n.d. (<10)	11	11	2.8	11	150
WWTP 2[b]	17	190	n.d. (<2)	13	180	32	7.5	n.d. (<4)	3.2	23	470
WWTP 3[c]	6.5	20	n.d. (<2)	21	190	14	11	n.d. (<4)	4.8	5.5	270
WWTP 4[d]	8.0	42	3.3	5.6	12	n.d. (<10)	n.d.	n.d. (<4)	2.1	12	90

CONSTRUCTED WETLAND USING PRIMARY TREATED WASTEWATER

Sample	PFHxS	PFOS	PFDS	PFHpA	PFOA	PFNA	PFDA	6:2 FtS	FOSA	EtFOSAA	Total PFCs
Oxidation Pond Influent	3.4	23	36	n.d. (<4)	14	9.1	3.4	n.d. (<4)	8.8	48	150
Oxidation Pond Effluent	3.2	21	23	n.d. (<4)	13	7.8	n.d. (<2)	n.d. (<4)	6.9	69	140
Treatment Marsh Effluent	3.0	25	29	n.d. (<4)	12	5.4	n.d. (<2)	n.d. (<4)	6.9	59	140
Enhancement Marsh 1 Influent	3.2	23	14	n.d. (<4)	11	3.3	n.d. (<2)	n.d. (<4)	5.3	40	100
Enhancement Marsh 1 Effluent	3.3	19	10	16	9.1	3.0	n.d. (<2)	n.d. (<4)	4.5	41	110
Enhancement Marsh 3 Effluent	3.2	29	36	n.d. (<4)	11	3.5	n.d. (<2)	n.d. (<4)	7.4	85	170

[a] tertiary treatment via dual media filtration and chlorination, followed by polymer treatment and repeated filtration for reclaimed wastewater

[b] tertiary treatment via dual media filtration and chloramination, followed by additional chloramination for reclaimed wastewater

[c] tertiary treatment via dual media filtration and chlorination

[d] tertiary treatment via fixed growth reactor (ammonia removal), flocculation, dual media filtration, and chlorination, followed by additional flocculation, dual media filtration, and chlorination for reclaimed wastewater

3.6 ASSESSMENT OF PERFLUOROCHEMICAL OCCURRENCE AND TOXICITY IN WASTEWATER AND THE AQUATIC ENVIRONMENT

Following the detection of perfluorochemicals in the project recycled water as well as in the site stream and groundwater, potential toxicity was assessed based on a review of the available literature. The findings discussed here are also available in the resulting research publication (Plumlee et al., 2008a).

With regard to human health, the potential contribution of water reuse projects to perfluorochemical exposure depends on the nature of the application and existing perfluorochemical background concentrations at the reuse site. In general, no exposure to reclaimed wastewater is expected from drinking water, given that in the United States, recycled water is carried separately from potable water in clearly marked distribution systems. However, the possibility of perfluorinated compounds entering drinking water supplies cannot be excluded because surface waters bearing wastewater effluents contribute significantly to the replenishment of water resources, in some cases without much dilution.

Understanding the environmental risk requires analysis of perfluorochemical aquatic ecotoxicity at the levels of nanograms per liter typically observed in reclaimed wastewater or at application sites. Perfluorochemical toxicity research is currently limited and must be extrapolated from laboratory organisms to complex ecosystems; however, suggested reference values provide some insight. Lowest observed effect concentrations (LOECs) for both acute and subchronic/chronic toxicity laboratory studies are greater than typical environmental concentrations (Lange et al., 2006), namely, levels in the micrograms to milligrams per liter compared to levels of nanograms per liter found in surface water and wastewater and in water reuse sites characterized in the present study. A more conservative Tier II (potential risk) screening value of 1200 ng of PFOS/L ("aquatic chronic value") was determined by Beach et al. (2005) by using EPA methodology, namely, by adjusting the lowest available LOEC, which is 70 times greater than the calculated aquatic chronic value. None of the reclaimed wastewaters or sites surveyed in this study, including the wastewater intended for the stream flow augmentation (WWTP 2, Figure 3.3), exceeds this screening value.

For cases in which water recycling may expose organisms at upper trophic levels (namely, wetland or stream flow enhancement), the bioaccumulation of perfluorochemicals in aquatic and terrestrial organisms (Giesy and Kannan, 2002; Schultz et al., 2003; Kannan et al., 2005) is an additional issue that must be considered. The resulting tissue concentrations constitute an internal dose (Butenhoff et al., 2006), which may be more ecotoxicologically relevant than the aquatic perfluorochemical concentration. Taking into account bioaccumulation, Rostkowski et al. (2006) calculated a safe water concentration of 50 ng of PFOS/L that is protective of trophic level IV avian species ("avian wildlife value") that consume organisms in equilibrium with the water. When this value is compared to PFOS measured in the present study (Figure 3.3), one of five reclaimed wastewaters (WWTP 2) and two of six creek sites (2b and 3) exceed this threshold. The wastewater exceeding the threshold was the same water intended for the stream flow augmentation.

Assessment of the risk associated with recycled water projects is further complicated because perfluorochemicals are ubiquitous and thus are likely to be present at a site before application of reclaimed wastewater. This finding was in fact the case for the creek sites in the present study, making it more difficult to assess the contribution to and/or relevance of the potential risk from the augmentation of the stream with perfluorochemical-containing wastewater.

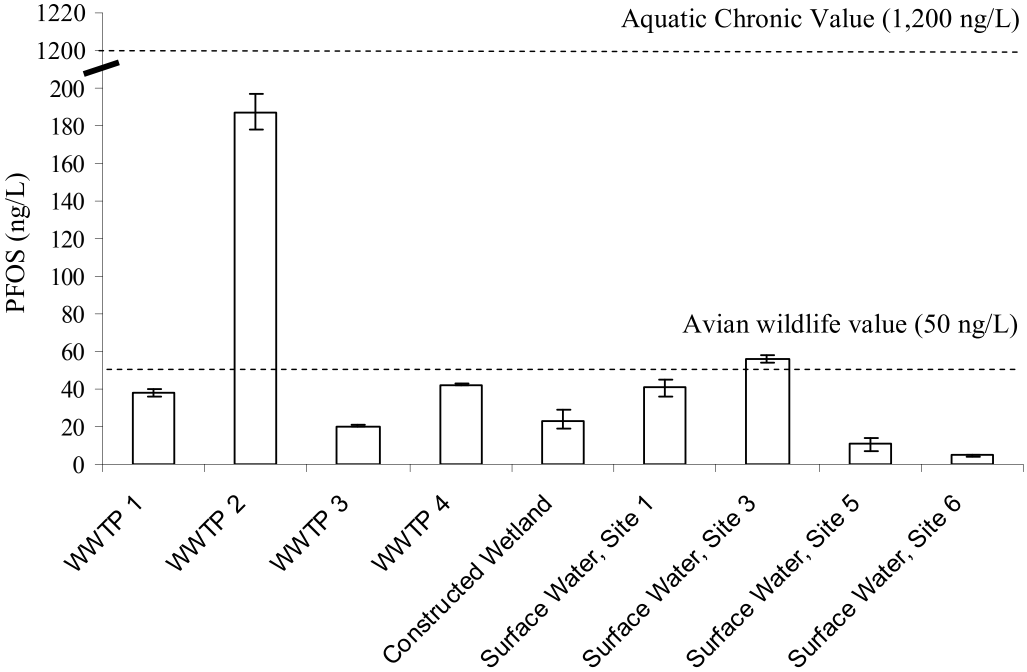

Figure 3.3. Mean concentrations of PFOS in reclaimed wastewater (WWTP 1–4; June 2007, *n* = 2), a treatment and habitat wetland constructed using primary treated wastewater (February 2006, mean of six treatment stages), and surface water samples from Upper Silver and Coyote creeks (June 2007, *n* = 2). Error bars of mean values indicate the range. Threshold concentrations considered protective of aquatic and avian life are shown (Beach et al., 2005; Rostkowski et al., 2006). Reprinted from Plumlee et al. (2008a) with permission from Elsevier.

CHAPTER 4

TECHNICAL CONCLUSIONS—IMPLICATIONS FOR STREAM AUGMENTATION WITH RECYCLED WATER

Presented in this section are the major technical conclusions of the water quality monitoring campaign and the supporting laboratory investigations.

Analysis of NDMA by SPE-LC-MS/MS

> The analytical method developed for NDMA in support of this project (Plumlee et al., 2008b) features a high extraction efficiency using SPE and accurate identification and quantification via LC-MS/MS at a reporting limit of 2 ng/L, below the 10-ng/L notification level specified by the California Department of Health Services. It may be applied for additional nitrosamine analyses.

Water Quality Comparison of Recycled Water and Site (Surface Water and Groundwater)

1. The assessment of the microconstituent risk associated with augmenting a semiurban stream with wastewater is complicated by the fact that different constituents may be present in different concentrations in the augmentation source (recycled water) and at the site. In this project, the recycled water quality was better than the site water with respect to metals and microbes. However, the recycled water also contained some constituents that were not present in the creek, such as NDMA and APEMs.
2. Some constituents were present in both waters (such as perfluorochemicals, organophosphates, and NBBS) at similar or different concentrations. The concentration in the wastewater or at the site is likely to vary with time, and thus a more detailed evaluation of microconstituent concentration over time scales of days to months may be required to fully assess the chemical impact of stream flow augmentation with recycled wastewater.

Perfluorochemicals in Water Reuse

1. As expected from their occurrence in wastewater and persistence during wastewater treatment, perfluorochemicals were detected in reclaimed wastewater from four California wastewater treatment plants that employ tertiary treatment (including the recycled water from the SJ/SC WPCP intended for the stream augmentation) and one that treats primary sewage in a wetland constructed for both treatment and wildlife habitat (Plumlee et al., 2008a). A range of 90 to 470 ng of total perfluorochemicals/L was detected in recycled water, typically dominated by PFOA and PFOS. Concentrations of total perfluorochemicals in the water intended for the stream flow augmentation ranged from 350 to 587 ng/L, and concentrations of PFOA and PFOS ranged from 83 to 180 and 190 to 374 ng/L, respectively.
2. Although many perfluorochemical monitoring studies focus on PFOA and PFOS, the results of the present study showed that inclusion of other perfluorochemicals in the monitoring program may identify several additional perfluorochemicals, resulting in a much greater total perfluorochemical concentration.

3 Although there was no known prior or ongoing wastewater discharge into Upper Silver and Coyote creeks, perfluorochemicals were found in the surface water and underlying groundwater at concentrations that were similar to the wastewater, highlighting the importance of baseline system characterization for decision making and risk evaluation in water reuse for environmental enhancement.

4 With respect to ecotoxicological effects, perfluorochemical release via recycled water into sensitive ecosystems requires evaluation. Perfluorochemicals bioaccumulate in aquatic and terrestrial organisms, and the resulting tissue concentrations constitute an internal dose that may be more ecotoxicologically relevant than the aquatic perfluorochemical concentration. One of five reclaimed wastewaters (the water intended for the augmentation in the present study) and two of the six creek sites exceeded a threshold concentration of 50 ng of PFOS/L that is viewed as protective of trophic level IV avian species that consume organisms in equilibrium with the water (Plumlee et al., 2008a).

Attenuation of NDMA and Other Nitrosamines in Surface Water

1 Results show that NDMA is poorly degradable biologically (Plumlee and Reinhard, 2007), a finding that was consistent with literature reports. Biotransformation of NDMA likely would not be a significant process during river and groundwater transport in the Upper Silver Creek and Coyote Creek system.

2 NDMA and six other *N*-nitrosamines were found to undergo direct photolysis when exposed to simulated sunlight (Plumlee and Reinhard, 2007).

3 Irradiations of 765 W/m^2, representing Southern California midsummer, midday sun, resulted in half-lives of 16 min for NDMA and 12 to 15 min for the other nitrosamines. The quantum yield for NDMA was determined to be $\Phi = 0.41$ and $\Phi = 0.43–0.61$ for the other nitrosamines (Plumlee and Reinhard, 2007).

4 Products of NDMA photolysis included methylamine, dimethylamine, nitrite, nitrate, and formate, with nitrogen and carbon balances exceeding 98 and 79%, respectively (Plumlee and Reinhard, 2007).

5 Because biodegradation is relatively slow and sorption to sediment is negligible, aquatic photolysis of NDMA is generally expected to be more significant even at relatively low levels of solar irradiation ($t_{1/2} = 8–38$ h at 244–855 W/m^2, 51° N latitude, 1 m depth).

Biotransformation of APEMs in Creek Sediment

1 Based on a laboratory biodegradation study using creek sediments (Montgomery-Brown et al., 2008), significant biotransformation of APEMs could be expected at the Coyote Creek site upon infiltration of water containing APEMs into the hyporheic and subsurface zones, particularly considering the long travel times of groundwater.

2 However, literature research suggests that under aerobic conditions, relatively stable APECs may be formed. Under anaerobic conditions, biodegradation may continue to form APs. Further degradation of APs under anaerobic conditions typically is not observed, but some biotransformation under aerobic conditions may occur.

3 Water quality monitoring of the surface water and groundwater following stream flow augmentation with recycled water would be required to fully assess whether

concentrations of APEMs, if detected, were significant following the expected attenuation and dilution with site water.

Hydroxyl Radical-Mediated Indirect Photolysis of Perfluoroalkanesulfonamides

1 Perfluorochemicals (selected perfluorooctanesulfonamides) were found to undergo indirect photolysis when irradiated in a solar simulator in aqueous hydrogen peroxide solutions. Indirect photolysis mediated by hydroxyl radical was observed for *N*-EtFOSE, *N*-EtFOSAA, *N*-EtFOSA, and FOSAA (Plumlee et al., 2009).

2 Final degradation products of the indirect photolysis of the perfluorooctanesulfonamides were PFOA and FOSA, which did not undergo additional degradation.

3 A proposed reaction pathway for degradation of the parent perfluorochemical, *N*-EtFOSE, to the other perfluoroalkanesulfonamides, FOSA, and PFOA was developed and includes oxidation and *N*-dealkylation steps.

4 Given the low rates expected for biodegradation and limited sorption, indirect photolysis of perfluorochemicals may be important in determining their environmental fate. However, the rates of indirect photolysis observed were quite low, and thus significant rates of transformation would not be expected over the Upper Silver and Coyote creeks' study reach. Some transformation may be possible during the additional travel time to San Francisco Bay, depending on the sunlight intensity and availability of reactive intermediates (photochemically produced radicals) to facilitate indirect photolysis of perfluorochemicals.

5 The laboratory study demonstrates that perfluorochemical (indirect) photolysis leads to formation of other perfluorochemicals via a transformation process and therefore does not constitute attenuation of perfluorochemicals in general.

General Conclusions

1 Supplying recycled water to ecosystems that provide essential service functions for humankind and the planet, such as food production, benefits to human health, regeneration of water resources, and biodiversity, is potentially feasible if concerns about the water quality of the recycled water can be alleviated.

2 Ecosystem support may require high-quality water that is protective of higher trophic level species.

3 There is regulatory, legal, and scientific uncertainty as to the contaminant levels that ecosystems can tolerate, in part because transport, fate, and toxicological impacts of most emerging contaminants are unknown.

4 To remove regulatory uncertainty, using treated wastewater for ecosystem support requires setting water quality standards that are protective of ecosystem health, especially with regard to the many newly discovered emerging contaminants (such as pharmaceuticals and personal care products).

5 Standards appropriate for wildlife protection may be lower than those adopted for drinking water. However, setting standards too conservatively may result in wasted resources and make water recycling impossible.

6 For compounds that are indestructible and poorly adsorbable by sediments, the ultimate sink is the ocean. Overreliance on natural attenuation exposes ecosystems to unacceptable levels of harmful compounds.

7 For persistent, bioaccumulative, and hazardous compounds that are not removed during conventional water treatment, such as the perfluorinated compounds, water reuse requires preventing these compounds from entering the aquatic environment.

Recommendations

1 To advance both the scientific and regulatory process, a study with similar objectives should be executed at a site where scientific benefits outweigh regulatory concerns. Such a study could be executed at a site where the practice of wastewater disposal into a creek has been in place for years.

2 Applicable toxicological information is needed to interpret water quality data. Only one perfluorochemical toxicological modeling study (Rostkowski et al., 2006) was available, and its use led to the significant outcome of project cancellation.

3 Source control appears to be the only feasible way to reduce the release of perfluorochemicals into the environment. Thus, steps should be taken to minimize the use of perfluorochemicals that find their way into the environment.

CHAPTER 5

LESSONS LEARNED

This section provides a brief history of the challenges the team faced initiating the project, reasons for the cancellation of the project, and summarizes "lessons learned." These experiences exemplify how unregulated (emerging) contaminants cause legal vulnerability and complicate the development of water reuse projects. This information may be useful to other water agencies that are considering the release of recycled water into ecosystems.

5.1 A BRIEF HISTORY OF THE PROJECT

To understand the eventual outcome—cancellation of the project due to regulatory uncertainty around perfluorochemicals—it is useful to review the sequence of the critical technical and ecological decision points and regulatory hurdles. The District is not the first agency to try stream flow augmentation with recycled water in San Jose. Starting in the late 1990s, the San Jose Environmental Services Department—an agency unrelated to the District—wanted to augment Coyote Creek with recycled water. The main motivation for the City was to improve habitat in Coyote Creek for anadromous fish (for example, trout and salmon), and biological concerns were brought to the fore throughout its project. The City met many important milestones including:

- Finding a suitable release location;
- Conducting environmental review;
- Receiving a National Pollutant Discharge Elimination System (NPDES) permit amendment from the Regional Water Quality Control Board to release recycled water to Coyote Creek; and
- Holding stakeholder review meetings.

Two developments conspired against the project. First, the City planned to enhance the creek for anadromous fish by chilling the recycled water before release to the creek. About 2001, California sank into an energy crisis caused by a botched deregulation of the electrical power markets. Energy prices soared, and consequently the cost of running such large units to chill up to 8 ft^3 of water/s over 20 ^{o}F grew substantially. The second difficulty was an outcome of advances in environmental research. As the City's plan was gaining momentum, studies were beginning to document the existence of endocrine disrupting compounds in wastewater. Stakeholders and the City became quite concerned that endocrine disruptors might be in the recycled water—a reasonable suspicion—and that these endocrine disruptors would negatively impact the very fish that the project was designed to help.

Perhaps the environmental dilemma of endocrine disruptors could have been addressed through monitoring, but with the huge energy requirements of the project and resolution of the power crisis nowhere in sight, the City decided to shelve the Coyote Creek augmentation project.

However, the District had been interested in the City's project throughout. Before the City abandoned the project, the District applied for a grant from the California Department of Water Resources to "piggyback" on the City's project. Whereas the City's focus was on fish, the District was interested in expanding the reuse of water. However, it was concerned about potential impacts on potable groundwater resources underneath the augmented stream. In 2003 the District received word that its grant application had been approved.

In late 2003, the District used the new grant award to hire Stanford University. Stanford's project objective was "*to assess the potential impact of large-scale augmentation of the Coyote Creek flow with tertiary treated water on the water quality of the river and the underlying groundwater. If results indicate adverse effects on groundwater or stream ecology, appropriate treatment methods will be evaluated. These treatment methods may include reverse osmosis treatment, soil treatment, or blending with higher quality water*" (SCVWD, 2004).

On the first visit to Coyote Creek in 2004, the District and Stanford staff were surprised to find that no infrastructure was in place to perform the critical task of the project: a pipe that actually delivered water from the recycled water pipeline to Coyote Creek. It became apparent that the project team would have to start from the beginning. If the District wanted to "assess the potential impact of large-scale augmentation" of a creek, then the District would have to go through the whole planning and building process to get recycled water into a creek.

At this point, the team now had a more realistic vision of the scope of this project—and the reality was that much more work and money would be required on the part of the District if it wanted this project to go forward. The team developed a flow chart of tasks required to achieve augmentation. Roughly, the tasks were as follows:

- Determine the location where augmentation would occur;
- Secure a budget to complete the expanded scope (beyond Stanford's scope);
- Secure all needed permits;
- Get required infrastructure built;and
- Solve water quality and other technical issues.

Soon, it became clear that direct release to Coyote Creek would require the construction of expensive infrastructure on land not owned by the District. A more suitable creek was a tributary of Coyote Creek, Upper Silver Creek. A release location was found directly adjacent to a recycled water pump station and District-owned land, minimizing the cost of infrastructure to be built.

In 2005, a consultant was hired to conduct the environmental review of the project as required for public agencies by the California Environmental Quality Act (CEQA). Baseline water quality monitoring was also initiated. The water quality studies are discussed in previous chapters of this report. The consultant's task was to complete an "Initial Study/Mitigated Negative Declaration," which is a declaration that the environmental impacts of the project can be mitigated to make the impacts less than significant. A draft Initial Study/Mitigated Negative Declaration was completed and issued for public comment in summer 2006, and a revised Declaration—incorporating responses to many public and regulatory agency comments—was completed in the final months of 2007. A summary of this Declaration is presented in the following section.

5.2 SUMMARY OF THE MITIGATED NEGATIVE DECLARATION

Although the project was cancelled before the Declaration was finalized, the resulting document from the CEQA review is a succinct summation of the project and the technical challenges faced by stream flow augmentation and also a snapshot of public and agency concerns about stream flow augmentation. As such, there is great value in making known the results of the CEQA review to other recycled water providers considering stream flow augmentation. The Project Objectives, Project Description, and Mitigation Measures sections below are verbatim quotes from the unpublished 2007 Mitigated Negative Declaration (SCVWD, 2007); these quotes give a sense of the potential impacts to the environment that were of such a concern that mitigation measures were considered necessary.

5.2.1 Project Objectives

The following is a verbatim quote from the unpublished 2007 Mitigated Negative Declaration.

> The objectives of the project are to determine whether augmenting stream flow with tertiary-treated recycled water in the Coyote Creek watershed is feasible within economic, environmental, and county-wide policy objectives for water supply management.
>
> In this grant-funded phase, the objectives are:
>
> 1. To evaluate the water quality and water temperature impacts to surface water and groundwater (the upper aquifer) from the release of tertiary-treated recycled water to augment stream flows;
> 2. To determine whether the chemical constituents in tertiary-treated recycled water are adequately filtered or degraded by natural processes, or whether further treatment of the recycled water is needed before it can be used for streamflow augmentation;
> 3. To evaluate the major issues that are barriers to implementing streamflow augmentation projects; and
> 4. To identify the potential solutions to these issues within existing policy and regulatory frameworks.

5.2.2 Project Description

The following is a verbatim quote from the unpublished 2007 Mitigated Negative Declaration.

> The proposed pilot research project will release up to 1 cubic foot per second (cfs)[1] of tertiary treated recycled water into a natural streambed to evaluate potential water quality impacts or benefits. The project entails using recycled water already available at the Yerba Buena Pump Station, removing residual chlorine (dechlorinating), and discharging the water to Upper Silver Creek at a sacked concrete-reinforced section of stream bank [Upper Silver Creek is a tributary of Coyote Creek]. The release of recycled water would occur during the low flow months from mid July through October. Depending on the temperature of Upper Silver Creek and of the recycled water, auxiliary evaporative cooling may be used. Water quality and temperature would be monitored throughout the study.

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[1] 1 cfs is approximately 450 gal per min, 646,000 gal per day, or 2 acre-ft per day.

5.2.3 Summary of Public Comments on the Mitigated Negative Declaration

One of the District's objectives for this project was to "to evaluate the major issues that are barriers to implementing stream flow augmentation projects." The comments received from the public and regulatory agencies during the CEQA review truly identified what the key barriers were for stream flow augmentation: temperature, emerging contaminants, and anadromous fish. Many of the comments correctly pointed out that these three factors are often interrelated. Brief summaries of select comments that altered the course of project planning are presented in the following.

California Regional Water Quality Control Board (RWQCB). The RWQCB commented that the Water Board recognizes the value of research to improve development of reclamation opportunities and was particularly interested in the fate and transport of unregulated emerging contaminants. Specifically, the Water Board commented that it wanted to know more about the fate of NDMA, as the concentrations in recycled water were greater than the California Office of Environmental Health Hazard Assessment public health goal but lower than action levels for drinking water. Furthermore, the Water Board was concerned that the addition of recycled water to Upper Silver Creek would raise receiving water temperatures by more than the 5 ^{o}F stipulated in the RWQCB Basin Plan (RWQCB, 2006).

South Valley Streams for Tomorrow. This local environmental organization provided substantial comments on the Mitigated Negative Declaration. This group was also concerned that temperatures in the receiving water would rise by more than 5 ^{o}F, specifically because such an increase would harm the creek ecology. In addition, the commentators requested that the District more closely evaluate impacts to salmonids in Coyote Creek, noting that spring and fall are sensitive times for these fish and that the stream flow augmentation should be protective of these fish. This group also identified what was ultimately given as the reason for project cancellation: that the ecological impacts of emerging contaminants were not fully assessed and that the existence of perfluorochemicals in Upper Silver Creek showed that the creek is already degraded and thus the District's imperative should be to prevent further degradation, not increase it by adding perfluorochemical-containing recycled water to the creek. The group concludes by saying, "It is our position that tertiary treated wastewater should not be used in stream flow augmentation programs because it contains too many contaminants and presents substantial ecological risks to the health of stream ecosystems. Any future for the use of recycled water in stream flow augmentation programs will rest on the ability to produce advanced treated recycled water that, through scientific demonstration, presents no significant ecological risk to the receiving streams."

US National Marine Fisheries Service. The Service commented that Coyote Creek contains salmonids at certain times of year and that the temperature increases from the addition of recycled water at these times of year—specifically starting in mid-September—could negatively impact these fish.

5.2.4 Mitigation Measures

The following is a verbatim quote from the unpublished 2007 Mitigated Negative Declaration.

> The principal mitigation incorporated in the project is the regulation or termination of the pilot program based on ongoing monitoring of water quality parameters.

Measure WQ-1: Groundwater Protection

A groundwater monitoring program is proposed to detect whether groundwater recharge occurs in Upper Silver Creek. Although there is reason to believe that the release into Upper Silver Creek will not enter groundwater used for water supplies, if monitored parameters compounds that have state or federal criteria for drinking water in Table 2 of the Initial Study are found above their respective drinking water standards (US Environmental Protection Agency website, 2007, CA Department of Health Services website, 2007), this will be construed as possible evidence that there is recharge and will lead to immediate suspension of the recycled water release. (See Appendix B. Groundwater Management Unit Memorandum, Santa Clara Valley Water District, SCVWD, Work Plan Section 1, Dec 2004).

Measure WQ-2: Surface Water Chemistry Protection

The surface water monitoring program is based on parameters tested in Table 2 of the Initial Study. Remedial measures will be taken if the monitoring program indicates adverse water quality impacts that the water quality in the creeks reaches or exceeds state or federal criteria for surface water standards, including immediate suspension of the recycled water release and discussion of appropriate treatment methods such as reverse osmosis treatment, soil treatment, or blending with higher quality water.

Measure WQ-3: Surface Water Temperature Protection

Temperature monitoring will show the magnitude of thermal effects on Upper Silver Creek and on Coyote Creek, to which it is a tributary. The temperature data will be used to regulate the volume of release and/or implement auxiliary cooling to keep temperature increases below permitted levels.

The project proposed for 2007 incorporates an auxiliary evaporative cooler, which will be used to cool the treated water prior to release during conditions when thermal criteria for the receiving water may be exceeded. Part of the purpose of this proposed mitigation is to measure the thermal capacity of the streambed, the effects of solar warming and natural evaporative cooling, and to determine the effectiveness of pre-cooling the release.

The District proposes to control the release into Upper Silver Creek based on the biotic standard of a warm-water fishery and respecting the tributary rule of the Basin Plan. Release volume and schedule will be adjusted based on the weekly collection of temperature data and the daily monitoring (when possible) of the release water temperature so as to prevent water temperature downstream of the release from rising above 75 ^{o}F or by more than 5 ^{o}F above the base temperature at the release. The measurement will be made at a point approximately 100 feet downstream of the release point to allow adequate mixing. In addition, The District will monitor the weather forecast, and in case of unseasonably hot or cool weather, the District will retrieve the stream temperature data daily when possible to avoid a substantial lag time in adjusting the chilled release temperature.

The last 1.2 miles of Upper Silver Creek before its confluence with Coyote Creek flows through an unshaded, open concrete channel subject to strong daytime heating, largely independent of the release water temperature upstream. Increased release into Upper Silver Creek during the afternoon will increase the flow of warm water into Coyote Creek. The proposed release is predicted to increase Coyote Creek temperature below the confluence by less than 2 ^{o}F above the modeled base temperature without the proposed project under most summer conditions. During the period from July 15 to September 15, the lower reach of Coyote Creek is normally warm and does not serve as cold water aquatic habitat; therefore, the project temperature increment is less than significant at that time.

After September 15, cold water species begin to move into Coyote Creek and are sensitive to even small temperature increases. After September 15, the project release volume and schedule will be re-calculated to prevent Coyote Creek temperature below the confluence from rising more than 1 ^{o}F above the modeled base temperature without the proposed project. The new release volume will be reduced during daytime hours when the concrete channel-warmed water in Upper Silver Creek has the most influence on the temperature in Coyote Creek.

Table 2. Water Quality Parameters to be Screened at Monitoring Sites
(Bold text denotes parameters that have state or federal criteria for surface and/or drinking water)

GENERAL WATER QUALITY	TRACE ORGANIC COMPOUNDS
Temperature	**NDMA (N-nitrosodimethylamine)**
Total dissolved solids (TDS)	**Organic Chemicals** (Volatile Organic Compounds, etc), **Trihalomethanes, Haloacetic Acids**
Conductivity	Pharmaceuticals, Endocrine Disrupting Compounds, and other Emerging Contaminants, including the following:
pH	Acetaminophen
Total Alkalinity	Caffeine
SAR (calculated parameter)	Carbamazepine
Cations and Anions	Carisoprodol
Sodium	Gemfibrozil
Potassium	Ibuprofen
Calcium	Iminostilbene
Magnesium	Ketoprofen
Sulfate	Naproxen
Chloride	Primidone
Bicarbonate	Propanolol
Nitrate as NO_3	Estradiol
Metals	Estriol
Aluminum	Estrone
Arsenic	Ethynylestradiol
Barium	Bisphenol A
Boron	Oxadiazon
Cadmium	Alkyl phenols (nonyl, octyl)
Total Chromium	Alkylphenol polyethoxylates (AP1EO, AP2EO, AP3EO)
Copper	Alkylphenol ethoxycarboxylates
Iron	Carboxylated alkylphenol ethoxycarboxylates
Lead	Tris(3-chloropropyl) phosphate
Mercury	Tri(2,3-dichloropropyl) phosphate
Manganese	N-butyl benzenesulfonamide
Nickel	Perfluorochemicals
Selenium	Microbes
Silver	**E. coli**
Zinc	**Fecal Coliforms**
	Total Coliforms

5.3 PROJECT CANCELLATION

Given the detections of perfluorochemicals in the recycled water, a literature review of perfluorochemical ecotoxicity was performed by Stanford University (Plumlee et al., 2008a) in an effort to assess the potential risks to the site. This exercise was difficult, given that perfluorochemical toxicity research is limited and that results from tests on selected laboratory organisms must be extrapolated to the more complex field setting. However, there were some reported reference values in the scientific literature that provided some insight.[2]

It is often the case that LOECs determined in laboratory studies for both acute and subchronic/chronic toxicity are greater than typical environmental concentrations (Lange et al., 2006), namely, LOECs in the milligrams to micrograms per liter compared to the levels of nanograms per liter found in surface water and wastewater. This finding is also true for perfluorochemicals. However, a more conservative Tier II (potential risk) screening value of 1200 ng of PFOS/L ("aquatic chronic value") was determined by Beach et al. (2005) by using EPA methodology. Beach et al. (2005) adjusted the lowest available LOEC, which is 70 times greater than the calculated aquatic chronic value. The recycled water intended for the stream flow augmentation did not exceed this screening value.

However, the recycled water did exceed an aquatic concentration reference value for PFOS suggested in another study. Taking into account bioaccumulation, Rostkowski et al. (2006) calculated a safe water concentration of 50 ng of PFOS/L that they considered protective of trophic level IV avian species ("avian wildlife value") that consume organisms in equilibrium with the water. In addition to the recycled water, some creek surface water sampled along the study reach also exceeded the avian wildlife value. Using a reference value that was developed recognizing that PFOS and other perfluorochemicals bioaccumulate (Giesy and Kannan, 2002; Schultz et al., 2003; Kannan et al., 2005) is reasonable, given that water recycling, particularly stream flow augmentation, may expose organisms at upper trophic levels. The resulting tissue concentration in affected wildlife constitutes an internal dose (Butenhoff et al., 2006).

Based on a review of this information and the recognition that knowingly discharging a potentially toxic effluent to a stream could make the District vulnerable to lawsuits from the public, environmental groups, or other organizations, the District decided to cancel the augmentation. The District is currently re-evaluating stream flow augmentation and reviewing alternative recycled water and stream sites.

5.4 DISCUSSION OF KEY CHALLENGES

As work progressed on this project, it became apparent that a valuable outcome would be to identify generally what technical issues could be expected by an organization considering stream flow augmentation with recycled water. This section discusses the major challenges encountered during project planning.

5.4.1 Adapting the Scope and Objectives

Because the basis of this project was essentially inherited from the City, the District has had to redefine the scope and objectives to reflect its own unique situation. From a technical

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[2] With regard to human health risks, some additional reference values for perfluorochemicals have recently come about (after the cancellation of the stream augmentation). These are the U.S. EPA Provisional Health Advisory Levels (PHALs) for PFOS and PFOA in drinking water, 200 and 400 ng/L, respectively.

standpoint, the most notable change in objectives was to shift the focus from assisting anadromous fish—the City's primary motivation—to understanding the fate of trace organic contaminants. The District recognized that fate and transport of microconstituents were a key area of research to facilitate further adoption of stream flow augmentation in other areas of the Santa Clara Valley, be it for environmental enhancement or source substitution for instream flow.

When the project team realized in the summer of 2004 that the project would entail many more steps than the grant proposal originally anticipated, the scope of the project grew. District management had to adapt to this new reality: either accept it and commit more resources to the project (possibly involving trade-offs with its other programs) or terminate the project. District management decided to continue the work and provide more funding. The grant given to the District stipulated that it partner with a research laboratory; because it was assumed the City would be researching the effects on fish, the grant did not place emphasis on finding biologists to study fish. And because the City project did not take off, the only actors left were those with a water quality core competency. However, as can be seen by the results of the CEQA review, the reality was that fish had to be considered in order to achieve the project objectives.

Furthermore, the District recognized that stream flow augmentation was a novel concept with an uncertain future. Thus, the project team added two more objectives: to learn the major issues that are barriers to implementing a stream flow augmentation project and to identify potential solutions to these issues.

5.4.2 Temperature

The impact of adding warmer recycled water to a colder creek was the most significant technical challenge for this project. In the late 1990s, the City had the stated goal of improving the cold-water habitat in Coyote Creek by chilling recycled water to 20 ^{o}F before releasing it to the instream flow. With much greater flow and much lower temperatures, the idea was that suitable habitat would bring back more anadromous fish. When the California power crisis hit, though, this idea proved fatally flawed.

Improving cold-water habitat was the de facto motivation when the District restarted the work, and equipment for chilling water to cold-water temperatures was investigated. Both mechanical chillers and evaporative cooling were considered. But the project team came to the same conclusion that the City did: that chilling water by 20 ^{o}F on a hot California day was not practical. The power demands were too great, and a rough cost–benefit analysis showed that this amount of chilling was not a wise use of resources.

Temperature regulations were also a key factor. The RWQCB for the San Francisco Bay region published the "Basin Plan," rules for water quality in the Bay and its tributaries (RWQCB, 2006). The Basin Plan generally limited temperature increases or decreases in a creek that were due to a discharge or release to ±5 ^{o}F. This guideline seemed responsible, considering that a greater change could cause permanent shifts in the creek ecology. With summertime temperatures of the recycled water in the low 80s and creek temperatures in the 60s, it became apparent with simple volumetric modeling that either, again chilling would be required or the volume of recycled water to be released to the creek would need to be limited (or both). And because the objective now was to study the fate of emerging contaminants, the danger would be that any identifiable contaminants in the recycled water would be diluted too rapidly to below detection limits, consequently diluting the quality of the study.

The CEQA review process yielded a workable solution (see the mitigation measure for temperature above). Warm-water conditions in Upper Silver Creek would be protected by using evaporative cooling (a technology that uses limited electricity), and the flow of the recycled water would be adjusted such that water temperatures were always below 75 ^{o}F, did not increase receiving water temperature by greater than 5 ^{o}F, or did not increase temperatures in Coyote Creek downstream of the confluence with Upper Silver Creek by greater than 2 ^{o}F during the summer months and by greater than 1 ^{o}F after September 15, when salmonids were expected to return to the area.

Note that the District's solution was not a positive impact on cold-water fish (as the City was intending) but rather solely a plan to mitigate any negative impacts. The circuitous route used to arrive at this plan shows the challenges of the temperature issue.

5.4.3 Dechlorination

The recycled water that was to be used for stream flow augmentation received tertiary treatment in the form of extra dosage of disinfectant. The recycled water would have to be dechlorinated prior to release to the creek. Unlike landscape watering or industrial uses, stream flow augmentation involves release of recycled water directly to an aquatic environment—an environment that would be immediately and significantly harmed by chlorine.

The recycled water would need to be dechlorinated prior to release to the creek. A system would have to be designed and installed that was redundant and fail-safe. There are multiple ways to design such a system, but given the consequences of chlorine in an aquatic environment, dechlorination is certainly an important technical challenge. The City had built a redundant dechlorination system that was stored in a shipping container.

5.4.4 Locating the Release Point and Impacts to Groundwater

So many other tasks depend heavily on finding a release location (installation of groundwater wells downstream, etc.)—indeed, it was a central task in this project. Once the project focus changed from improving habitat for anadromous fish to studying the fate and transport of emerging contaminants, more flexibility was available in choosing a release point: it was no longer necessary to add cold recycled water only where the salmonids were swimming.

Nonetheless, important questions regarding the release point had to be asked and answered, including:

- Would infiltration of recycled water potentially contaminate a valuable aquifer?
- How sensitive is the receiving water body ecosystem? Are endangered species present?
- Who owns the land at the release location? Is it feasible to locate dechlorination and pipeline infrastructure on this land?
- What is the proximity to the recycled water pipeline? How well does the location meet the goals?
- Will scientifically valid results be possible with this location and its consequent limitations?

5.4.5 Biological Impacts

The seasonal presence of cold-water fish in Coyote Creek, of which Upper Silver Creek is a tributary, constrained the decisions determining during which months augmentation could take place and the temperature of the release. As was said before, with the shifting of the project focus from improving habitat to researching the fate of trace organic contaminants, the planning also shifted from how to create better conditions for fish to how to minimize any negative impacts to fish while studying contaminant fate and transport. As the City showed, planning stream flow augmentation any other way when the temperature of the recycled water is above 80 ^{o}F is extremely difficult. In order to avoid biological impacts, the release was constrained to summer months when Coyote Creek was considered warm-water habitat, and the plan was to curtail flow of recycled water after September 15, when salmonids were potentially returning to Coyote Creek. Studying impacts to other parts of the ecosystem, such as benthic invertebrates or amphibians, was considered out of the scope of this project.

5.4.6 Emerging Contaminants

A lack of toxicological understanding leads to a lack of regulatory guidelines, and for this reason the District was forced to draw its own conclusions about the concentrations of perfluorochemicals detected in the recycled water. To avoid legal vulnerability, the District consequently adopted the most conservative approach: application of the lowest aquatic reference value available in the literature. Exceeding this criterion resulted in project termination.

The presence of microconstituents in recycled water is a significant barrier to full adoption of water reuse as a sustainable approach to water supply management. Clearly, regulatory guidelines for emerging contaminants (or applicable toxicological data and an accepted method to apply this information in decision making) are necessary to advance the sustainable reuse of water.

5.5 CONCLUSIONS

The City abandoned its stream flow augmentation project for reasons of temperature and the potential presence of emerging contaminants. The District also faced significant problems regarding temperature and emerging contaminants. Because of a scaled-back project objective—research into the fate and transport of emerging contaminants rather than habitat improvement for anadromous fish—the District was able to find a workable solution for the temperature issue. However, the existence of emerging contaminants in the recycled water as well as those pre-existing in the creek to be augmented proved once again to be a problem with no satisfactory resolution.

Given these lessons from both the City and the District, what would an ideal stream flow augmentation project look like? As a commentator on the Mitigated Negative Declaration stated, "Any future for the use of recycled water in stream flow augmentation programs will rest on the ability to produce advanced treated recycled water that, through scientific demonstration, presents no significant ecological risk to the receiving streams." It appears that without advanced treatment that removes the known emerging contaminants to nondetect levels, or without water quality criteria for emerging contaminants such as perfluorochemicals, any project where the ecosystem openly contacts recycled water would be subject to the charge of endangering the ecosystem with emerging contaminants. Stream flow augmentation likely has a brighter future if seen more as a matter of water supply and instream flow than of environmental enhancement. For example, during dry years on creeks that are fed by an upstream drinking water reservoir, there can be conflict between maintaining instream flow and conserving water in the reservoir. Indeed, this conflict can be acute in severe droughts. Recycled water could be used as a substitute to maintain instream flow—but, of course, such a project would likely come with substantial infrastructure needs of pipelines and pump stations and the sensitive needs of the entire creek ecology.

And last, it is unfortunate that although the presence of emerging contaminants in the recycled water provided the motivation for the more detailed occurrence and fate investigations presented in this work, it at the same time led to project termination. Somewhat ironically, billions of gallons of wastewater containing trace levels of organic contaminants are discharged every day into rivers across the United States and elsewhere. For this reason, and for the characterization of water reuse projects, it is imperative to understand the environmental fate and toxicological relevance of these compounds. However, the fields of analytical chemistry and environmental occurrence are far ahead of our understanding of microconstituent toxicity. In other words, the rapid advancement of analytical technology has led to the seemingly never-ending discovery of microconstituents of new varieties and in new places; decision-makers, however, are unable to accurately assess the relevance of these findings because they lack information on the toxicological significance of the typically low environmental concentrations. Many micropollutant researchers as well as water practitioners recognize this data gap. Further, toxicity research coupled with risk assessment/modeling is strongly needed to allow interpretation of the relevance of organic contaminants in the aquatic environment, wastewater, and/or drinking water to human or ecosystem health. Although there are many laboratory studies in which various animals and plants are exposed to chemicals, it remains difficult to extrapolate these types of studies to the environmental occurrence data produced by water quality analyses. Either a narrower, focused set of toxicological research is needed (namely, focused on particular environmental systems at concentrations that are relevant to environmental problems) or environmental risk assessment studies are required to allow environmental engineers and chemists to interpret and extrapolate the exposure data produced by toxicologists.

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APPENDIX

Table A1. Structures and Descriptions of Selected *N*-Nitrosamines

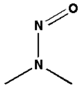
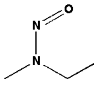
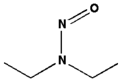
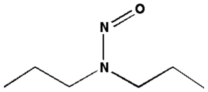
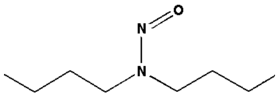
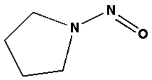
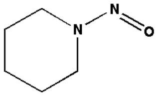
Nitrosamine	Structure	Sources and Reported Occurrence
N-Nitrosodimethylamine (NDMA)		May originate from reactions of nitrogen-containing precursors in the environment, foods, or during wastewater disinfection (Najm and Trussell, 2001; Choi et al., 2002; Mitch and Sedlak, 2002b). Typical concentrations range from 1–10 ng/L in drinking water (Grebel et al., 2006), 20–100 ng/L in wastewater effluent (Mitch et al., 2003; Plumlee et al., 2008b) and <10–35 ng/L in rivers receiving wastewater discharge (Pehlivanoglu-Mantas and Sedlak, 2006; Schreiber and Mitch, 2006). Increasing concentrations detected in a drinking water distribution system at 52–108 ng/L (Zhao et al., 2006).
N-Nitrosomethylethylamine (NMEA)		Found in tobacco smoke and food, not known to be produced commercially (HSDB, 2006).
N-Nitrosodiethylamine (NDEA)		Found in drinking water wells at 0.01 µg/L and DI water at 0.33 to 0.83 µg/L. Found in wastewater from chemical plants at 0.07 and 0.24 µg/L (U.S. Department of Health and Human Services).
N-Nitrosodi-*n*-propylamine (NDPA)		Detected in wastewater from chemical plants, rubber, cheese, alcohol, cigarette smoke, and herbicides including trifluralin (U.S. Department of Health and Human Services).
N-Nitrosodi-*n*-butylamine (NDBA)		Detected in a variety of products including soybean oil, cheese, smoked/cured meats, and cigarette smoke; also found in coke facility effluent water (U.S. Department of Health and Human Services).
N-Nitrosopyrrolidine (NPyr)		Found in nitrite-preserved or contaminated foods and associated vapors and tobacco smoke; reported in wastewater from chemical factories at 0.09–0.20 µg/L (U.S. Department of Health and Human Services). Increasing concentrations detected in a drinking water distribution system at 18–71 ng/L (Zhao et al., 2006).
N-Nitrosopiperidine (NPip)		Found in cigarettes, meats, and fish (because of use of sodium nitrite as a preservative) (U.S. Department of Health and Human Services). Increasing concentrations detected in a drinking water distribution system at 33–118 ng/L (Zhao et al., 2006).

Table A2. Summary of Perfluorochemical Occurrence in Wastewater, Freshwater, and Drinking Water

Site and Location	PFOA (ng/L)	PFOS (ng/L)	Other Perfluorochemicals Detected	Source of Perfluorochemicals[a]	Reference
Wastewater Effluent					
2 WWTPs (Catalonia, Spain)	<100-4300	n.m.	PFDA (50-8170)	domestic and industrial influents	Alzaga & Bayona, 2004
WWTP (Iowa City, Iowa, USA)	22	26	*N*-EtFOSAA (3.6 ng/l)	domestic influent (no known manufacturing or industrial perfluorochemical source)	Boulanger et al., 2005
10 WWTPs (USA)	3-97	1-130	PFBS, PFHxS, 6:2 FtS, PFHxA, PFNA, PFDA, FOSA	domestic, industrial, and commercial influents	Schultz et al., 2006
6 WWTPs (New York, USA)	58-1050	3-68	PFHxS, PFNA, PFDA, PFUnDA, 8:2 FTCA, 8:2 FTUCA	domestic, industrial, and commerical influents	Sinclair & Kannan, 2006
Reclaimed wastewater, 4 WWTPs (California, USA)	12-185	20-187	PFHxS, PFDS, PFHxA, PFHpA, PFNA, PFDA, 6:2 FtS, FOSA, *N*-EtFOSAA	domestic, industrial, and commercial influents	present study, 2011
Surface Water					
Tennessee River (Decatur, AL, USA) upstream and downstream of fluorochemical manufacturing facility	upstream: <25; downstream: <25-513	upstream: 17-53; downstream: 30-140	n.m.	fluorochemical manufacturing facility	Hansen et al., 2002
Etobicoke Creek (Toronto, Ontario, Canada) upstream and downstream of fluorochemical spill over time	upstream: n.d.-33; downstream: n.d.-10,600	upstream: n.d.; downstream: n.d.-995,000	PFHxS	accidental spill of aqueous film-forming foams (AFFFs)	Moody et al., 2002
Lake Erie and Lake Ontario (USA), urban and remote locations	27-50	21-70	*N*-EtFOSAA (4.2-11 ng/l), FOSA (0.6-1.3 ng/l), PFOSulfinate (n.d.-17 ng/l)	not stated	Boulanger et al., 2004
river (Iowa City, Iowa, USA)	8.7	23	*N*-EtFOSAA (1.2 ng/l)	wastewater effluent	Boulanger et al., 2005
"remote" lakes (Lake Superior, Minnesota, USA; Voyageurs National Park lakes, Canada)	0.1-0.7	n.d.-1.2	PFHxA, PFHpA, PFNA	atmospheric deposition	Simcik & Dorweiler, 2005
"urban" waters (3 lakes in Minneapolis and Minnesota River in Minnesota, USA)	0.5-19	2.4-47	PFHxA, PFHpA, PFNA, PFDA	urban location, runoff, and wastewater discharge	Simcik & Dorweiler, 2005
Lake Michigan (USA)	0.3-3.4	0.9-3.1	PFHpA	non-atmospheric sources	Simcik & Dorweiler, 2005
streams, lake in Shihwa and Banweol industrial areas, South Korea	0.9-62	2.2-651	PFBS, PFHxS, FOSA, PFHxA, PFHpA, PFDA	local industrial sources	Rostkowski et al., 2006

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