

Sources of Perfluoroalkyl Substances to San Francisco Bay

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Since the 1950s, perfluoroalkyl substances (PFAS) have been used in numerous applications including fire-fighting foams, stain-resistant coatings on textiles and carpets, and production of fluoropolymers, adhesives, electronics, electroplating, and insecticides. Due to their stability, excellent surface tension lowering properties, and ability to be both oleophobic (oil-repelling) and hydrophobic, significant volumes of these chemicals have been used and released to the environment, in the range of 3,200 to 7,300 tons worldwide for carboxylates (Prevedouros et al. 2006) and 96,000 tonnes for perfluorooctane sulfonate fluoride, precursors for the sulfonates (Paul et al. 2009). As a result, PFAS, most notably perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA), have been widely detected in the environment including in rainwater (Loewen et al. 2005, Scott et al. 2006), rivers (Murakami et al. 2008, Scott et al. 2009, Nakayama et al. 2010), oceans (So et al. 2004, Benskin et al. 2012) sediments (Higgins et al. 2005), and wastewater treatment plants (Schultz et al. 2005), as well as in biota including fish, bird eggs and seals throughout the world in both remote and urban areas (Giesy and Kannan 2001) (Houde et al. 2006, Holmstrom and Berger 2008, Houde et al. 2011)

PFAS, particularly PFOS, have been identified in San Francisco Bay seal and cormorant eggs at surprisingly high concentrations (Sedlak and Greig 2012); however, the sources of these compounds and the pathways by which they reach the Bay are not well understood. Prior research suggests that the presence of PFAS in the environment may come from releases from industries (Hansen et al. 2002), wastewater treatment facilities (Boulanger et al. 2005b, Schultz et al. 2006b, Sinclair and Kannan 2006), airports (Moody et al. 2002, Saito et al. 2004), and refineries (Vecitis et al. 2009). Pathways from these local and global sources to the environment likely include point sources, wastewater treatment effluent, stormwater runoff and tributary loading, groundwater seepage, and possibly precipitation.

Several studies have identified PFAS in San Francisco Bay area tributaries (Hoehn et al. 2007, Plumlee et al. 2008), wastewater treatment plants and sediments (Higgins et al. 2005). However, a concurrent study of loading from tributaries and wastewater effluent and ambient levels in sediment and surface waters has not been conducted to date. This study evaluated concentrations of PFAS in stormwater runoff, wastewater effluent, ambient surface waters, and sediments to assess the relative importance of these pathways of PFAS to the Bay ecosystem.

Materials and Methods

Sampling Design

Samples were collected from stormwater runoff (7 samples), wastewater treatment plant effluent (6 samples), Bay surface waters (10 samples), and surface sediments near the Bay margins (11 samples).

Stormwater

Between October 13th, 2009 and January 26th, 2010, stormwater samples were collected during precipitation events at four sampling locations on three tributaries to the Bay: the confluence of the San Joaquin and Sacramento Rivers (referred to as the Mallard Island station); the Guadalupe River (2 stations); and a storm drain located in Hayward (Figure 1, Table 1). As the major tributaries to the Bay, the San Joaquin and Sacramento Rivers collectively drain approximately 40% of California's land area. McKee et al. (2006) provide a more detailed description of the Mallard Island site. The Guadalupe River is the primary tributary in the southern portion of the estuary, draining both an undeveloped upper watershed (sampled by the Guadalupe (upper) site) as well as the highly developed City of San Jose (sampled by the Guadalupe (lower) site). The tributary in Hayward is an engineered channel that drains a very small, industrial, relatively impervious watershed. This watershed is representative of the many small, industrial or urban watersheds found in the Bay area that drain into the Bay.

Table 1. Watershed characteristics

Watershed	Size (sq km)	Impervious Surface Cover (%)	Land Use (%)				
			Ag.	Urban			Undeveloped
				Residential	Commercial	Industrial	
Sacramento/ San Joaquin	154,000	5-10	31	2			67
Guadalupe	445	25	-	46	11	11	26
Hayward	4.5	70	-	33	26	38	

At the Mallard Island and Guadalupe stations, two samples were collected during rainfall events to assess concentrations in rising stage and peak flow conditions. At the Hayward station, only one sample was collected during the rising stage.

At the Guadalupe River sites, grab samples were collected near the surface of the water column using a clean stainless steel bucket, which was poured into the one-liter high density polypropylene (HDPE) sample bottle. At the Mallard Island and Hayward sites, samples were collected directly into the one-liter HDPE samples bottle using a stainless steel pole equipped with a metal bottle cage to hold the HDPE bottle. All sample containers were rinsed three times with site water prior to sample collection.

Field blanks were collected at every site using water provided by the laboratory. Samples were transported on ice, and stored for a maximum of 12 days at 4°C prior to shipping on ice to AXYS Analytical (Sidney, BC, Canada) for analysis.

Wastewater Effluent

Grab samples of final effluent were collected and composited between October 26th, 2009 and January 21st, 2010 from six wastewater treatment facilities that discharge to the Bay. The facilities are located throughout the Bay and range in treatment capacities from

approximately 20 to 180 million gallons per day. Two of the facilities provide tertiary treatment; the remaining facilities provide secondary treatment.

Grab samples were collected post-chlorination and prior to discharge. Samples were either collected directly into a one-liter HDPE sample bottle from a port from the final effluent stream, or in absence of a sampling port, collected directly into the sampling container from the final effluent stream using a stainless steel pole equipped with a metal bottle cage. Bottles were rinsed three times with effluent prior to sample collection. Duplicates were collected at two sites. One field blank was collected using water that was provided by the laboratory. Samples were transported on ice, and stored for a maximum of 11 days at 4°C until being shipped on ice via overnight courier to AXYS Analytical.

Ambient Bay Surface Water

Surface water was sampled at five sites between August 25th and September 2nd, 2009 as part of the annual summer regional monitoring cruise (Suisun Bay, San Pablo Bay, Central Bay, South Bay, and Lower South Bay). Five additional nearshore sites were sampled December 10th, 2009 to January 13th, 2010 (Richmond, San Leandro Bay, Eden Landing, Foster City, and Cooley Landing). Sites were selected to provide good spatial coverage across the Bay (Figure 1). Grab samples were collected from the ship using a ten-foot stainless steel pole equipped with a metal bottle cage. Nearshore samples were collected by hand. Samples were rinsed with site water prior to collection. One field duplicate and one blank sample were collected on the cruise. Samples were transported on ice, and stored for a maximum of 14 days at 4°C until processing. One sample was received at AXYS Analytical Lab at a temperature of 11°C (San Pablo Bay); all others were 4°C or lower.

Surface Sediment

Surface sediment (top 1-5 cm) was collected into 250 mL HDPE jars at 11 nearshore sites around the Bay (Figure 1 and Table 2) during two time periods (December 10th, 2009 through January 13, 2010 and March 4th through July 23rd 2010). Samples were collected at low tide, by collecting the surface sediment either directly into the sample container or using a clean petite ponar grab and trowel. Samples were stored on ice after collection, and shipped frozen to AXYS Analytical in Sidney BC Canada for analysis.

Extraction

Aqueous samples were filtered through a 0.45 µm Nylon filter and the pH was adjusted to 7.0 using formic acid. The samples were spiked with isotope-labeled surrogate standards (¹³C₄PFBA, ¹³C₂PFHxA, ¹³C₂PFOA, ¹³C₅PFNA, ¹³C₂PFDA, ¹³C₂PFDaA and ¹³C₄PFOS). Samples were extracted using a weak anion SPE cartridge. Eluates were spiked with recovery standards (¹³C₂-2H-perfluoro-2-decenoic acid (¹³C₂-FOUEA) and ¹³C₄PFOA) prior to analysis. QA/QC samples were processed in a similar manner.

Analysis

Concentrations of PFAS were measured using a high performance liquid chromatograph (Waters 2795, Milford MA) with a triple quadrupole mass spectrometer (Micromass

Quattro Ultima, Manchester, UK) operating in the electrospray negative mode. Data were acquired using MassLynx v.4.1 software. A 15 uL sample was injected onto an Agilent Zorbax XDB reverse phase column (C18, 7.5 cm, 2.1mm id, 3.5 micron particle size column, Agilent, Santa Clara, CA). Flow rate was 0.15 ml per minute for the first minute and then set at 0.2 ml per minute for the remaining run time. The eluent consisted of varying amounts of acetonitrile and ammonium acetate to obtain optimal separation.

The following target compound transitions (parent mass to daughter mass) were monitored using Multiple Reaction Mode: perfluorobutanoate (PFBA, 213 to 169); perfluoropentanoate (PFPeA, 263 to 219); perfluorohexanoate (PFHxA, 313 to 269); perfluoroheptanoate (PFHpA, 363 to 319); perfluorooctanoate (PFOA, 413, to 369/219); perfluorononanoate (PFNA, 463 to 419); perfluorodecanoate (PFDA, 513 to 469); perfluoroundecanoate (PFUnA, 563 to 519); perfluorododecanoate (PFDoA, 613 to 569); perfluorobutanesulfonate (PFBS, 299 to 80/99); perfluorohexanesulfonate (PFHxS, 399 to 80/99), perfluorooctanesulfonate (PFOS, 499 to 80/99), and perfluorooctanesulfonamide (PFOSA, 498 to 78). Results were corrected for losses during extraction and cleanup through the use of internal standards. Solvents used were of HPLC grade or better and purchased from VWR International, Mississauga, ON. Isotope-labeled standards (¹³C₄PFBA, ¹³C₂PFHxA, ¹³C₂PFOA, ¹³C₅PFNA, ¹³C₂PFDA, ¹³C₂PFDoA, ¹³C₄PFOS, ¹⁸C₈PFOA and d7-N-Me-perfluoro-1-octanesulfonamide ethanol (d7-MeFOSE)) were purchased from Wellington Labs and Perkin Elmer. Native standards were purchased from Sigma Aldrich and Fluka.

Target analytes for all samples included PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnA, PFDoA, PFBS, PFHxS, PFOS, and PFOSA. The following PFAS precursors were analyzed for all samples but one (from the Guadalupe River): N-ethyl-perfluorooctanesulfonamide (N-Et FOSA), N-ethyl perfluorooctanesulfonamidoethanol (N-Et FOSE), N-methyl-perfluorooctanesulfonamide (N-Me FOSA), and N-methyl-perfluorooctanesulfonamidoethanol (N-Me FOSE). Precursors were not detected in any samples with one exception: N-Me FOSA (5.36 ng L⁻¹) was detected in a water sample.

Quality Control and Quality Assurance (QA/QC)

Data quality control and quality assurance samples included field blanks and replicates, matrix spikes and duplicates, and laboratory blanks, spikes, duplicates, and continuing calibration samples, all of which were analyzed in a manner similar to the samples. Method detection limits were developed in accordance with USEPA (2008) Part 136_Guidelines Establishing Test Procedures For The Analysis Of Pollutants. Appendix B to Part 136--Definition and Procedure for the Determination of the Method Detection Limit--Revision 1.11 B. Initial calibration occurred daily using a six-point calibration curve; midlevel calibration standards were run after every 20th sample.

PFAS were not detected in the field or laboratory blanks above the MDLs. Twelve laboratory spikes were run for the water samples; spike recoveries for the compounds detected varied between 75 and 124% recovery with an average recovery of 92%. Three batches of sediment spikes were performed with the samples, and recoveries on the seventeen compounds ranged from 39 to 145%, with an average recovery of 98%.

Relative percent difference (RPD) of three laboratory replicates for stormwater, effluent, and ambient Bay samples varied between 0.3 and 44.3% (PFHxS) and averaged 11.0%. RPDs for three field replicates varied between 0.5 and 42.9% (PFBS) with an average of 13.5%. Laboratory replicates were performed on two sediment samples, and relative percent differences ranged from 4 to 20% (PFNA), and averaged 10.4%.

Matrix spikes and matrix spike duplicates were conducted for one wastewater sample and one stormwater sample. Spike recoveries varied between 66.7 (PFPeA) to 128.6% (PFOSA); average spike recoveries were 96.6%. RPDs varied between 0.6 to 28.6% (PFBS) with an average of 6.1%.

Statistics

Because some compounds were below detection limits, summary statistics were calculated using the Regression on Order Statistics (ROS) method (Helsel 2005). This method uses sample data when possible, and assumes a log-normal distribution for samples below the detection limit. Analyses were performed in R version 2.12.2, using the NADA package developed by USGS (R Core Team, 2011 and Helsel, 2005.) Statistical comparisons of populations within the datasets were performed using paired and unpaired t-tests in Microsoft Excel.

Results

Table 2 presents a compilation of compounds detected in stormwater, effluent, ambient San Francisco Bay water samples, and sediment, along with means and standard deviation, calculated using the ROS method.

Table 2. PFAS concentrations in tributary flows, wastewater, Bay water, and Bay sediment. Blank cells indicate concentrations below detection.

Station Name (listed North to South)	Sample Date	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnA	PFDoA	PFBS	PFHxS	PFOS	PFOSA
Stormwater (ng L⁻¹)		nd: < 1									nd: < 2			nd: < 1
Mallard Island – Rise	1/23/10	1.6		1.9		2.4	1.1							
Mallard Island – Peak	1/26/10			1.7		1.5							2.1	
Hayward	10/13/09	16.6		23.7	22.3	69	23.5	21.4	4.7	1.2	6.5	10.2	5.8	
Guadalupe River (lower) - Rise	10/13/09	17.7	6.5	31.7	25.6	66	19	29.1	4.2	1.7	3.7	9.7	14.2	1.1
Guadalupe River (lower) - Peak	10/13/09	5.5	1.2	5.3	6.6	16.6	5.8	6.7	1.4			3.9	13.7	
Guadalupe River (upper) - Rise	1/20/10	3.9	1.7	3.7	2.8	7.6	1.9	1.4					4.6	
Guadalupe River (upper) - Peak	1/20/10	4.3	3.3	3.9	2.8	5.8	1.5					2.2	4.8	
Mean		7.2	2.1	10.3	8.7	24.1	7.6	8.4	1.7	0.8	2	4	6.6	
Standard Deviation		7	2.2	12.2	10.6	30.1	9.6	11.9	1.9	0.5	2.3	4.2	5.3	
Wastewater Effluent (ng L⁻¹)														
Mean		7.4	6.7	16.6	5.3	31.8	11.5	3.8	nd: < 1	nd: < 1	6	5.5	23.6	nd: < 1
Standard Deviation		4.7	7.6	4	1.2	30.1	5.6	1.8			6.5	5.5	32.2	
Ambient Bay Surface Water (ng L⁻¹)		nd: < 1									nd: < 2			nd: < 1
Suisun Bay	9/2/09					1.4	1							
San Pablo Bay	9/1/09													
Richmond (Breuner Marsh)	1/13/10		1	1.4		2								
Central Bay	8/31/09													
San Leandro Bay	12/28/09		1.4	1.8		3.7						2.1	2.4	
South Bay	8/27/09		1.3	1.6	1	3							2.9	
Eden Landing	12/28/09	2.6	1.7	3.1	1.7	6.8	1.4					2.3	6.5	
Foster City	12/10/09			2.5	1.5	4.2	1						5.7	
Lower South Bay	8/25/09	3	2.5	3.7	2.4	8.6	2.4						2.7	6.3
Cooley Landing	12/10/09	62.2	151	221	66.8	75.6	15.1	11.6	1.4		7.9	12.6	44.3	
Mean		6.8	15.9	23.5	7.3	10.6	2.2					2.1	7	
Standard Deviation		19.5	47.5	69.4	20.9	23	4.6					3.8	13.3	

Station Name (listed North to South)	Sample Date	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnA	PFDoA	PFBS	PFHxS	PFOS	PFOSA
Surface Sediment ($\mu\text{g Kg}^{-1} \text{ dw}$)		nd: < 0.1									nd: < 0.2		nd: < 0.1	
Reserve Fleet	6/3/10													
Richmond (Breuner Marsh)	1/13/10					0.1	0.2	0.1					0.8	
Hornet Field	7/23/10													
San Leandro Bay	12/28/09								0.2	0.1			0.7	
Oyster Bay Regional Shoreline	7/2/10					0.1	0.2	0.1		0.2			1.1	0.1
Oyster Point Marina	6/3/10						0.1			0.1			0.5	0.1
Eden Landing	12/28/09					0.2							0.7	
Foster City	12/10/09					0.1							0.4	
Cooley Landing	12/10/09			0.1	0.2	1.1	0.6	0.5	0.2	0.2			3.2	0.2
Palo Alto Landfill	4/29/10					0.7	0.4	0.5	0.2	0.3			2.3	0.2
Guadalupe Slough	3/4/10					0.2	0.1	0.1		0.5			3.2	0.3
Mean						0.2	0.1	0.1	0.1	0.2			1.2	0.1
Standard Deviation						0.3	0.2	0.2	0.1	0.1			1.1	0.1

Stormwater

Of the PFAS detected in stormwater, PFOA was detected in the highest concentrations (maximum of 69 ng L⁻¹) followed by PFHxA, PFDA, PFHpA, and PFNA (Figure 2). Concentrations of the remaining PFAS detected (PFBA, PFPeA, PFUnA, PFDoA, PFBS, PFHxS, PFOS, and PFOSA) were all less than 20 ng L⁻¹. PFOSA was detected at the lower Guadalupe River site on the rising stage at 1.1 ng L⁻¹, all other samples were below the detection limit of 1 ng L⁻¹. The concentrations of PFAS detected on the rising stage at the lower Guadalupe and Hayward sites were similar. Relatively few PFAS were detected at Mallard Island (only PFBA, PFHxA, PFOA, PFNA, and PFOS) and the concentrations were almost an order of magnitude lower. A pairwise t-test comparing the rise and peak at the Guadalupe and Mallard Island sites showed no statistical difference for PFOS or PFOA.

Wastewater Effluent

The wastewater results are aggregated so that individual dischargers remain anonymous. The average concentrations of PFAS observed in wastewater were similar to those measured in the tributaries (Table 2, Figure 3). On average, PFOA concentrations were the highest, followed by PFOS, PFHxA, and PFNA. Average concentrations of the remaining PFAS were all less than 10 ng L⁻¹, and PFOSA was not detected (detection limit 1 ng L⁻¹) in any of the effluent samples. Concentrations of PFOS and PFOA were highly variable (the standard deviations were 32 and 30 respectively); however, they were detected in all effluents sampled.

Ambient Bay Surface Water

Of the PFAS detected in Bay surface waters, PFOA was detected in the highest concentrations (1.38 to 75.6 ng L⁻¹) followed by PFOS (2.37 to 44.3 ng L⁻¹) (Table 2). The highest concentrations were observed in a Bay margin grab sample from Cooley Landing in the Lower South Bay. The concentrations of PFHxA, PFPeA, PFHpA, and PFBA at this site (220, 150, 66, and 62 ng L⁻¹, respectively) were an order of magnitude higher than those observed at the remaining sites. PFOS was only detected in the South Bay and Lower South Bay, and PFOSA was not detected (detection limit 1 ng L⁻¹) at any of the sites. In general, concentrations of the PFAS decreased from South to North with concentrations below detection limits in the Central Bay. With the exception of N-methyl perfluorooctane sulfonamide detected at the Eden Landing Bay margin site (5.36 ng L⁻¹), none of the precursors were detected in water. No statistical trends were detected: there was no significant difference for PFOA and PFOS between the samples collected in the open Bay and the near-shore samples, nor were the South Bay samples different from the Central and North Bay samples.

Surface Sediment

PFOS was detected at the highest concentrations (0.448 to 3.22 µg kg⁻¹), and was present in all samples except those from Hornet Field and the Reserve Fleet (PFAS were not detected in either sample). The highest concentrations detected were at the Cooley Landing and Palo Alto landfill sites. The sites where PFOA was detected were located almost exclusively in the South Bay and Lower South Bay, at concentrations ranging from 0.12 to 1.06 µg kg⁻¹. Longer-chain perfluorinated carboxylic acids (PFNA, PFDA,

PFUnA and PFDoA) were detected at low concentrations (up to 0.6, 0.5, 0.2 and 0.5 $\mu\text{g kg}^{-1}$, respectively) at a number of sites throughout the Bay. PFOSA was detected near the MDL at several sites in the South Bay, and all other samples were below the PFOSA detection limit of 0.1 $\mu\text{g kg}^{-1}$. As with ambient water, concentrations of all PFAS generally decreased from South to North.

Discussion

Stormwater

Concentrations of PFAS in the tributaries varied greatly among watersheds and between the rise and peak of the river hydrograph (Table 2).

The concentrations in samples collected from the upper portion of the Guadalupe watershed, which is primarily undeveloped, were lower than those collected in the lower, urbanized and industrialized portion of the watershed. Similarly, the Hayward tributary, which has a small, highly urbanized and impervious watershed (Table 1), had concentrations that exhibited patterns like to the rising stage on the lower Guadalupe River. Low concentrations were detected in the Sacramento and San Joaquin rivers, which drain watersheds that are largely agricultural and open space.

This association between PFAS concentrations and urban land use has also been observed in other studies. Urban lakes in New York state had higher concentrations of PFOA, PFHpA, PFDA and PFOS compared with lakes located in rural areas, and higher concentrations of PFOA in tributaries located in close proximity to parking lots and areas with heavy traffic (Kim and Kannan 2007). In a study of 18 Japanese rivers, Murakami identified a strong correlation between population density and PFOS, PFHpA and PFNA levels (Murakami et al. 2008). A similar association was observed in a study of 59 Canadian rivers (Scott et al. 2009).

At the lower Guadalupe site, concentrations of many of the PFAS detected in the rising stage of the storm event were substantially higher than the peak flow concentrations. For example, the PFOA concentration from the lower Guadalupe River site collected during the rising stage was 66 ng L^{-1} compared to 16.6 ng L^{-1} at peak flow. In contrast, concentrations of PFOS at the lower Guadalupe site remained relatively constant (rising stage concentration of 14.2 ng L^{-1} versus peak flow concentration of 13.7 ng L^{-1}). PFOA has a lower sorption coefficient than PFOS (Higgins and Luthy 2006); these results support the hypothesis that PFOA is more rapidly transported in the watershed due to its higher solubility. After the mobilization during the rising stage, concentrations of PFOA and PFOS were similar (e.g., 16.6 ng L^{-1} and 13.7 ng L^{-1} , respectively, at the lower Guadalupe River) and were higher than most other compounds (Figure 2). Concentrations of PFOA at Mallard Island remained relatively constant through the hydrograph (rise versus peak). This may be a result of the high dilution of urban runoff in the San Joaquin and Sacramento rivers and the low proportion of urban land use in the watershed. While the samples collected on the rise were higher in general, a pair-wise t-test on the sample sets indicated that there was no statistical difference between the rise and peak samples.

Concentrations observed in this study are similar to ambient concentrations observed in rivers in the Upper Mississippi River basin (Nakayama et al. 2010), in Canadian rivers (Scott et al. 2009), in European rivers (McLachlan et al. 2007, Kwadijk et al. 2010), in Japan (Murakami et al. 2008) and in the Guadalupe River watershed (Hoehn et al. 2007, Plumlee et al. 2008) (Table 3). Much higher concentrations of these compounds, particularly PFOS and PFOA, have been reported at sites where spills or direct releases have occurred such as Etobicoke Creek where a direct release of aqueous film-forming foams (AFFFs) from an airport occurred, with concentrations ranging from below detection to 11,300 ng L⁻¹ PFOA (Moody et al. 2002), the Tennessee River in the vicinity of a fluorochemical manufacturer, ranging from 140 to 598 ng L⁻¹ PFOA (Hansen et al. 2002), and the Conasauga River, Dalton, GA in the vicinity of a wastewater treatment plant responsible for treating wastewater from a carpet manufacturing area, with concentrations ranging from 1,110 to 1,280 ng L⁻¹ PFOA (Konwick et al. 2008). Very high concentrations of PFAS were observed in a study of Taiwanese rivers receiving effluent from semiconductor and electronics industries. The highest concentration detected were of PFOS at 5400 ng L⁻¹ (Lin et al. 2009).

PFOA is typically the primary PFAS observed in tributaries, an observation supported by this study, although a study of 88 sampling sites in the Upper Mississippi River basin identified perfluorobutanoic acid (PFBA) as the most abundant compound with median concentrations exceeding PFOA (2.7 ng L⁻¹ vs 2.1 ng L⁻¹, respectively) (Nakayama et al. 2010), attributed to the use of PFBA as a replacement for PFOA. Concentrations of PFOS in Bay Area studies were almost double those of PFOA in a tributary to the South Bay (Hoehn et al. 2007, Plumlee et al. 2008).

These results indicate that urban sources strongly influence PFAS concentrations in tributaries to the Bay, while watersheds dominated by open areas or agricultural uses have lower PFAS. The levels detected in this study are similar to concentrations seen in comparable locations around the world. PFOA, and to a lesser extent PFOS, were the dominant compounds, and the more soluble PFOA appears to be more rapidly mobilized into the water column during a storm event.

Table 3. PFOA and PFOS concentrations (ng L⁻¹) in Rivers and Stormwater from other studies

Location	Description	PFOA	PFOS	Source
Altamaha River, GA	Pristine River	3 - 3.1	2.6 - 2.7	(Konwick et al. 2008)
Albany, NY	Rain stormwater runoff	2.8 - 13.35	0.36 - 5.64	(Kim and Kannan 2007)
Upper Silver Creek, CA	Rivers	<0.4 - 15	14 - 38	(Hoehn et al. 2007)
Upper Silver and Coyote Creek, CA	Rivers	8-36	5-56	(Plumlee et al. 2008)
Canada	Rivers	0.044-9.9	0.91-34.64	(Scott et al. 2009)
Netherlands	Rivers	6.5 - 43	4.7 - 32	(Kwadijk et al. 2010)
Tennessee River, AL	Upstream of fluorochemical manufacturing plant	<25	16.8 - 54.1	(Hansen et al. 2002)
Upper Mississippi River Basin	Rivers	<1 - 125	<1 - 245	(Nakayama et al. 2010)
Japan	Rivers	0.76 - 192	<0.1 - 191	(Murakami et al. 2008)
Europe	Rivers	<0.65 - 200	-	(McLachlan et al. 2007)
Tennessee River, AL	Downstream of fluorochemical manufacturing plant	140 - 598	5 - 98	(Hansen et al. 2002)
Conasauga River, GA	Downstream of discharge from WWTP receiving water from carpet manufacturing plant	226 - 1280	0.2 - 368	(Konwick et al. 2008)
Etobicoke Creek, Toronto, ON	Downstream of AFFF release	<9 - 11300	<17 - 995000	(Moody et al. 2002)

Wastewater Effluent

Concentrations of PFOS and PFOA among the individual wastewater treatment plants (WWTPs) were extremely variable, reflecting the variation in contributions from individual sources within the treatment catchment area (Table 2). WWTPs have been

identified as significant environmental sources of PFAS as a result of the industrial uses of PFAS and its precursors, the loss of fluoropolymers from consumer and industrial products, and the low removal rates of PFAS in the wastewater treatment process (Boulanger et al. 2005a, McLachlan et al. 2007). A mass flow study in Switzerland indicated that wastewater treatment plant effluent is the principal contributor of fluorochemicals to the Glatt River (Huset et al. 2008). The average concentrations of PFOS and PFOA observed in the present study (23.6 and 31.8 ng L⁻¹, respectively) are similar to concentrations observed in municipal effluents in the USA and around the world (Table 4), although significantly higher concentrations of PFOA and PFOS in industrial wastewater have been observed (Sinclair and Kannan 2006, Bossi et al. 2008, Yu et al. 2009). Nonetheless, high concentrations of PFOA have also been observed in effluent from facilities that do not receive industrial wastewater (e.g., 663 and 697 ng L⁻¹ for two facilities in New York) suggesting that even domestic and commercial wastewater can be quite variable (Sinclair and Kannan 2006).

The sources of PFAS to wastewater effluent are not known with certainty. Numerous researchers have identified biodegradation of precursors as a potentially significant source (Dinglasan-Panlilio and Mabury 2006, Schultz et al. 2006b, Rhoads et al. 2008), as well as direct use of products (Boulanger et al. 2005a) and or spills of materials such as aqueous film-forming foams that are used in fire suppression (Moody et al. 2002, Nakayama et al. 2010). Fluorotelomer stain resistant coatings used in food-packaging materials and cookware can contain PFOS as an impurity, and fluorotelomer mixtures can migrate from the coatings into food (Begley et al. 2005). Industrial and commercial products can also be a significant source of fluorinated materials to the environment, with 0.04 to 3.8% (dry weight) residual fluorinated alcohols found in carpet treatments, windshield fluids, and industrial products incorporated into caulks, paints, coatings, adhesives, and floor waxes (Dinglasan-Panlilio and Mabury 2006). In one study, the source of PFAS to a WWTP was identified as effluent from a facility that used an “organic fluorosulfonate” as a mist suppressant in chrome-plating operations (Nakayama et al. 2010).

In WWTPs, precursors can undergo aerobic biodegradation to various PFAS (Wang et al. 2005, Rhoads et al. 2008), and studies have reported an increase in PFOS and PFOA concentrations from wastewater treatment facility influent to effluent (Schultz et al. 2006a, Loganathan et al. 2007). Numerous precursors, such as perfluorooctane sulfonamidoacetate (FOSAA) and N-ethyl and N-methyl derivatives as well as N-methyl perfluorooctane sulfonamido ethanol, N-ethyl perfluorooctane sulfonamido ethanol, N-methyl perfluorooctane sulfonamide ethyl acrylate and fluorotelomer alcohols, can be metabolized to PFOS and PFOA during wastewater treatment (Sinclair and Kannan 2006, Bossi et al. 2008). In a national study of ten WWTPs, PFOA and PFOS concentrations increased between 9 to 352% from influent to effluent (Schultz et al. 2005). A recent study by Ma and Shih (2010) showed higher concentrations of even-chain length perfluorinated carboxylic acids in wastewater treatment plant effluent, supporting the theory that the degradation of FTOHs contributes to carboxylic acid concentrations in effluent.

Table 4. Concentrations of PFOA and PFOS in effluent (ng L⁻¹) in other studies

Location	Type of Wastewater	PFOA	PFOS	Source
United States	Domestic and Commercial	30.3	23.4	(Schultz et al. 2006a)
Iowa City	Domestic and Commercial	22 (±2)	26 (±2)	(Boulanger et al. 2005b)
Denmark	Domestic and Commercial	<2.0 - 17.55	<1.5 - 12.75	(Bossi et al. 2008)
Singapore	Domestic and Commercial	11.2 - 138.7	5.3 - 29.8	(Yu et al. 2009)
Switzerland	Domestic, Commercial and Industrial	12 - 35	16 - 303	(Huset et al. 2008)
New York State	Domestic, Commercial and Industrial	58 - 1050	3 - 68	(Sinclair and Kannan 2006)
California	Domestic, Commercial and Industrial	12-185	20-187	(Plumlee et al. 2008)
Denmark	Industrial	<2.0 - 115.4	<1.5 - 1115	(Bossi et al. 2008)
Singapore	Industrial	31.8 - 1057.1	48.1 - 560.9	(Yu et al. 2009)

Bay Surface Water

In general, much lower PFAS concentrations were observed in Bay water than in tributaries and WWTP effluent, reflecting the large dilution capacity of the tidally influenced Bay (Table 2). The range of concentrations of PFOS and PFOA in this study were generally lower than other urban water bodies (Table 5) such as Tokyo Bay (Boulanger et al. 2005a, Yamashita et al. 2005) and Lake Ontario (Furdui et al. 2008). Concentrations of PFOS and PFOA in the remaining Great Lakes (e.g., Superior, Huron and Erie) and Narragansett Bay were of a similar range to that observed in San Francisco Bay. Hong Kong coastal waters (So et al. 2004) and open ocean (Yamashita et al. 2005) were generally even lower. The next most frequently detected compound in Bay surface waters was PFHxA, ranging in concentration from <1 to 3.7 ng L⁻¹, with the exception of the detection of 221 ng L⁻¹ at the Cooley Landing site. Concentrations of all PFAS were elevated at the Cooley Landing site, at levels similar to the highest tributary concentrations. At all other sites, the remaining PFAS were detected in concentrations less than 3.0 ng L⁻¹.

Table 5. PFOA and PFOS concentrations (ng L⁻¹) in surface water reported in other studies.

Location	PFOA	PFOS	Source
Tokyo Bay	1.8 – 192	0.338 - 57.7	(Yamashita et al. 2005)
Lake Superior	0.07-1.2	<0.15-0.41	(Scott et al. 2010)
Lake Ontario	1.8-6.7	3.6- 37.6	(Furdui et al. 2008)
Lake Ontario (average)	2.5	5.0	(Myers et al. 2012)
Lake Huron	<LOQ	1.2-3.2	(Furdui et al. 2008)
Lake Erie	1.6-2.2	4.0-5.3	(Furdui et al. 2008)
Narragansett Bay	5.8*	ND	(Benskin et al. 2012)
Hong Kong coastal waters	0.73 - 5.5	0.09 - 3.2	(So et al. 2004)
Eastern Pacific Ocean	0.015 - 0.062	0.0011 - 0.02	(Yamashita et al. 2005)

*This number is a sum of PFOA, PFHxA and PFHpA.

Bay Surface Sediment

The PFOS and PFOA concentrations detected in this study were comparable to prior studies of San Francisco Bay and other world-wide studies. A previous survey of San Francisco Bay sediment found PFOS at 0.3 to 3.1 $\mu\text{g kg}^{-1}$ dw and PFOA at 0.1 to 0.6 $\mu\text{g kg}^{-1}$ dw (Higgins et al. 2005). The highest concentration of PFOS observed in this study (3.2 $\mu\text{g kg}^{-1}$) was detected in the samples from both Cooley Landing and Guadalupe Slough, and was very close to the highest concentration detected by Higgins et al, at the San Francisquito Creek site (3.1 $\mu\text{g kg}^{-1}$). The PFOA concentration at Cooley Landing (1.1 $\mu\text{g kg}^{-1}$) was much higher than the highest PFOA level seen by Higgins et al. (0.6 $\mu\text{g kg}^{-1}$, Hayward Marsh). Within the US, sediment concentrations in urban estuaries appear to bracket those observed in San Francisco Bay. Baltimore Harbor sediments were lower, with PFOS and PFOA concentrations of 0.8 and 0.4 $\mu\text{g kg}^{-1}$ dw, respectively (Higgins et al. 2005). Concentrations from Lake Ontario were slightly higher on average, 26 ± 16 ng g⁻¹ PFOS and 2.6 ± 2.2 ng g⁻¹ PFOA (Myers et al. 2012). PFOS and PFOA concentrations in Dutch sediments were slightly higher than the levels seen in this study, ranging in concentration from 0.5 to 8.7 $\mu\text{g kg}^{-1}$ dw PFOS and 0.3 to 6.3 $\mu\text{g kg}^{-1}$ dw PFOA (Kwadijk et al. 2010). Concentrations of PFOS and PFOA in sediment from rivers around Europe varied from <0.5 to 14.0 $\mu\text{g kg}^{-1}$ PFOS and <1.2 to 16.8 $\mu\text{g kg}^{-1}$ PFOA dw (de Voogt et al. 2006).

PFAS Sources and Pathways

Nguyen et al. (2011) proposed four pathways for PFAS and PFAS precursor transport from their sources to the aquatic environment: 1) precipitation containing photochemically-oxidized compounds released into the atmosphere (Ellis et al. 2004); 2) discharge from WWTPs (Schultz et al. 2006a, Sinclair and Kannan 2006, Bossi et al. 2008, Yu et al. 2009) ; 3) runoff of stormwater from urban areas influenced by point or

non-point sources (Kim and Kannan 2007); and 4) seepage from groundwater affected by landfill leachate or spills (Moody et al. 2003). These pathways are generally difficult to track back to the original sources, largely because of the ubiquitous use of PFAS and the ready transformation and degradation of precursors. However, environmental PFAS concentrations are generally greatly influenced by their proximity to the source (Hansen et al. 2002, Moody et al. 2003, Konwick et al. 2008).

For the Bay Area, there is no information on the concentrations of PFAS in local precipitation. Work by Scott and colleagues (Scott et al. 2006) suggest that concentrations of PFOA in precipitation can be significant particularly in urban areas. Concentrations of PFOA in rain water from the Northern Toronto area ranged from 1.0 to 11 ng L⁻¹. Concentrations of PFOA in rain collected near urban areas in Delaware were even higher 0.6 to 89 ng L⁻¹, although sampling the following year indicated much lower concentrations <0.1 to 2.7 ng L⁻¹. Although this study did not evaluate groundwater, based on the work by Plumlee et al. (2008), concentrations of PFOS in groundwater may be significant, ranging from 19 to 195 ng L⁻¹ for a San Jose site. Data from the Plumlee et al. study suggest that in the Bay Area, WWTP effluent, stormwater, and groundwater may be sources of similar magnitude.

While the tributary and WWTP data indicated variation in source loads to the Bay, only one of the sites appeared to contain anomalously high concentrations or point sources. The water collected at Cooley Landing revealed very high concentrations of PFAS, over an order of magnitude higher than all of the other surface water samples, and similar to or higher than the tributary samples for many compounds. This likely indicates a discrete source to this area. The vicinity of this sampling location includes a former landfill, a former hazardous waste management facility, and concentrated industrial activities. Higgins et al. (2005) associated high levels of PFAS in South Bay sediment with inputs from domestic sewage. In that study, San Francisquito Creek, located about 1 km south of Cooley Landing, had significantly higher PFAS concentrations than other Bay sediments. They noted that while there are no WWTPs directly discharging into San Francisquito Creek, it has received periodic release of sewage from sewer overflows (Higgins et al. 2005). While a discrete source is suggested by the high concentrations detected at Cooley Landing, further investigations would be required to identify it.

The use of PFAS in aqueous film-forming foams (AFFFs) may represent a significant source to the Bay because of the abundance of airports, present and former military facilities, and refineries. Little information on this topic is available to date, however. After release, AFFFs may enter the Bay either directly or via stormwater runoff or WWTPs. AFFFs have been in use at airports and airbases since the 1960s. Fluorotelomer sulfonates, as well as fluoroalkyl sulfonates and fluoroalkyl carboxylates at lower levels, were detected in the groundwater at Wurtsmith Air Force Base, MI and Tyndall Air Force Base, FL, suggesting that AFFFs produced by fluorotelomerization were used at the Wurtsmith and Tyndall fire-training pads (Schultz et al. 2004). High concentrations of PFBS, perfluoropentasilulfonate (PFPeS), PFHxS and PFOS were measured in the groundwater near Naval Air Station Fallon, NV, however no fluorotelomer sulfonates were detected, suggesting that no fluorotelomer based AFFFs

were in use at this site (Schultz et al. 2004). However, PFBS and PFHxS are impurities in certain formulations of AFFF (Taniyasu et al. 2003). Detections of PFOS and PFOA in tributaries and groundwater near military bases, fire departments, and airports up to 10 years after the cessation of use of AFFFs suggest that they can continue to contaminate nearby water and soil long after their use ceases (Moody et al. 2003, Taniyasu et al. 2003, Saito et al. 2004, Nakayama et al. 2010, Nguyen et al. 2011, Myers et al. 2012). In the present study, a few sediment sites may have been influenced by nearby airports, including Guadalupe Slough, Palo Alto Landfill, and Oyster Bay Regional Shoreline, which were all within 2 miles of nearby airports. The highest PFOS sediment concentrations were seen at these locations, along with Cooley Landing. These sites also had PFOA, PFNA, and PFDoA concentrations between 0.1 and 0.7 $\mu\text{g kg}^{-1}$. The higher concentrations of PFOS is suggestive of contamination from AFFF (Saito et al. 2004).

The Bay water and surface sediment results also suggest a trend of decreasing concentrations from the South Bay to the North Bay, consistent with the spatial trends seen in seals and cormorant eggs (Sedlak and Greig 2012), and with spatial trends in other organic contaminants (San Francisco Estuary Institute 2010). This may be related to higher contaminant loads into the South Bay, as well as longer water residence time. In this study, PFOS concentrations were generally higher than PFOA concentrations in sediment, while the reverse was true in water. In general, the perfluorinated sulfonic acids (e.g., PFOS, PFDS) have higher sediment-water partitioning coefficients than the corresponding carboxylic acids (e.g., PFOA, PFDA) (de Voogt et al. 2006, Higgins and Luthy 2006). In addition, the PFAS water concentrations detected at sites located near the margins of the Bay (Richmond, San Leandro Bay, Eden Landing, Foster City, and Cooley Landing) were generally higher than those from sites in the open waters (Figure 1, Table 2), suggesting that the sources of PFAS to the Bay through stormwater, wastewater effluent, and nearshore groundwater seepage are large enough and frequent enough to cause elevated concentrations near the shorelines despite Bay mixing processes.

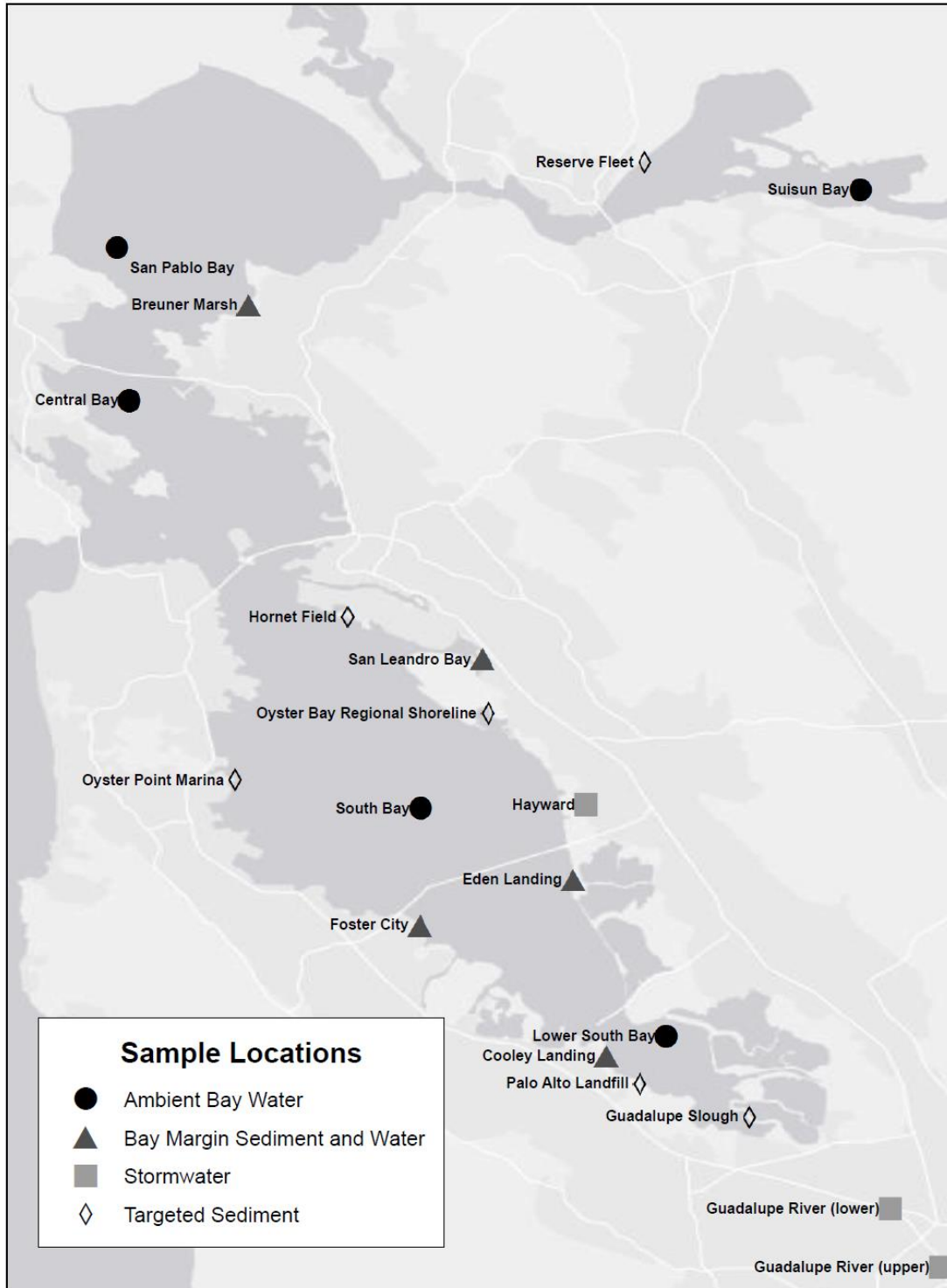
The concentrations of PFOS detected in South San Francisco Bay seals and cormorant eggs (Sedlak and Greig 2012) are higher than seen in other urban estuaries. However, the concentrations detected in Bay water and sediment as well as inputs from effluent and tributaries suggest that Bay levels are similar to those detected around the world, and few indications of dominant sources were detected. While the spatial gradient of decreasing concentrations from the Lower South Bay through the North Bay is consistent with the trends seen in biota, the linkage between the moderate concentrations in these abiotic matrices and the high concentrations in aquatic apex predators remains a major gap in understanding of PFAS in San Francisco Bay.

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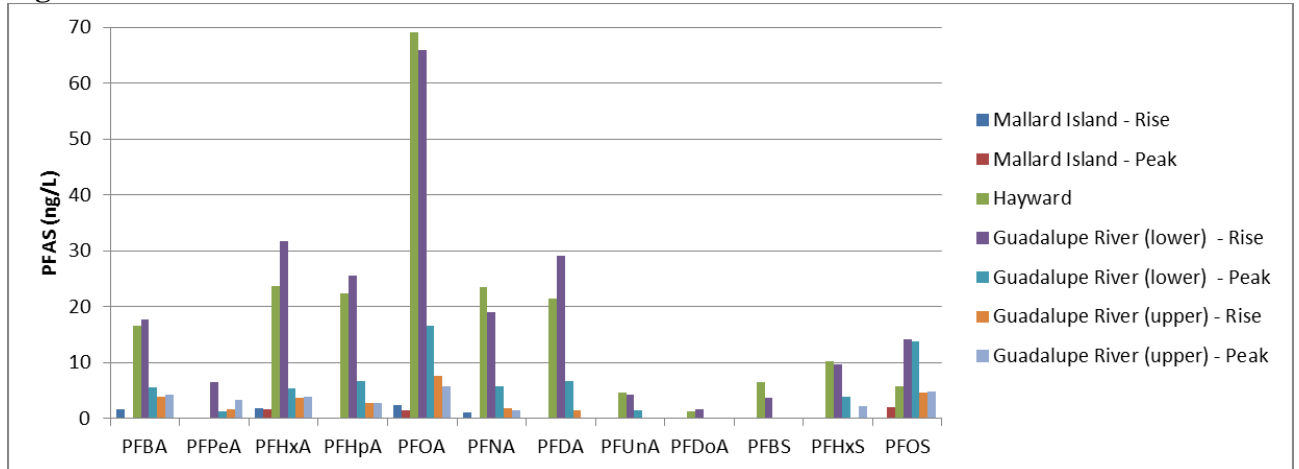
FIGURES

Figure 1. Locations of sampling sites. Wastewater effluent sample locations not shown



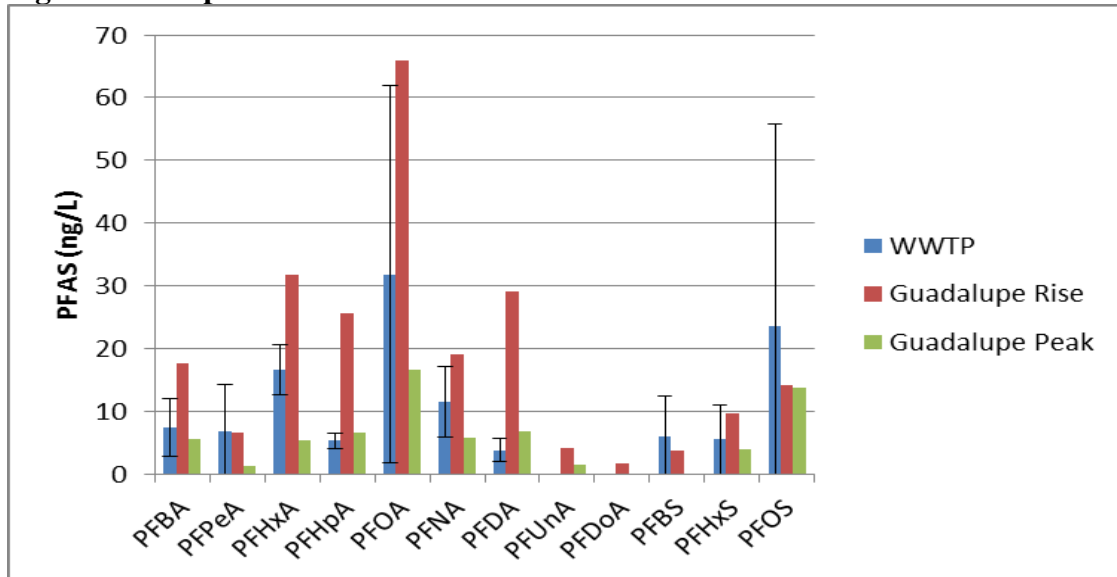
One sample was collected between August 25th 2009 and July 23rd 2010 at each of the locations shown, except for the stormwater sites, where two samples were collected at both Guadalupe River sites and the Mallard Island site.

Figure 2. PFAS Detected in Tributaries



Concentrations of PFAS in stormwater at the Guadalupe River sites and the Hayward site. The highest concentrations were seen at Hayward and at the lower Guadalupe site on the rising stage, suggesting that these compounds are associated with urban, industrial areas and are rapidly mobilized.

Figure 3. Comparison of PFAS Detected in WWTPs and Tributaries



Concentrations of PFAS in wastewater treatment plant effluent compared with stormwater from a large industrial watershed. The WWTP effluent concentrations are averaged across the six participating facilities. While there was high variability among the different facilities, average concentrations were on the same order as concentrations entering the Bay from the urban Guadalupe River watershed.

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