

## Assessment of Emerging Polar Organic Pollutants Linked to Contaminant Pathways within an Urban Estuary using Non-targeted Analysis

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### SUPPORTING INFORMATION

#### Additional Information on Site Selection

Local water quality manager expertise and past water quality assessment efforts informed selection of three ambient SF Bay sites, each predominantly influenced by a specific pathway of interest. Site selection factors included land use information in the upstream watershed (Table SI-1), as well as the discharge of treated wastewater effluent in the vicinity, with additional site-specific information summarized below.

**San Leandro Bay:** While the streams discharging to San Leandro Bay are not gauged to provide storm-specific flow data, the estimated annual stormwater runoff volume is 5.3 Mm<sup>3</sup> (A. Gilbreath, personal communication). In addition to urban stormwater runoff, San Leandro Bay also receives intermittent discharges from a wastewater treatment plant wet weather outfall, consisting primarily of stormwater and groundwater inflow and infiltration to the wastewater collection system, which are subjected to primary treatment followed by disinfection and dechlorination prior to release. This outfall is located in the East Creek Slough, a tributary to San Leandro Bay located 2 km north of the deployment site.

**Napa River:** The local WWTP discharges a mean of 30 million liters of secondary-treated effluent per day, but is only permitted to discharge to the Napa River during the wet season, between November and April (Napa Sanitation District); septic tanks are also employed in the region.

**Coyote Creek:** The Coyote Creek site is particularly influenced by upstream mean wastewater effluent discharges of over 300 million liters per day from the San José-Santa Clara Regional Wastewater Facility, the largest advanced secondary WWTP in the western United States. This facility serves 1.4 million residents and over 17,000 businesses in eight cities in the Lower South Bay region, and discharges to the nearby Artesian Slough. The site is also influenced by stormwater discharges from the watershed, which features primarily open space (52%) and urban (43%) land uses (Table SI-1).

**Wastewater Treatment Plants:** The four facilities included one or more discharging to the Central Bay (which contains the San Leandro Bay site), the North Bay (which receives Napa River discharges), and the Lower South Bay (which includes the Coyote Creek site).

**Table SI-1.** Watershed characteristics of sample sites.

Sample site	San Leandro Bay	Napa River	Coyote Creek
Latitude	37.743212	38.297537	37.46384444
Longitude	-122.208368	-122.283146	-122.0241694
Watershed size (km <sup>2</sup> )	25.7	520	400

Population density (per km <sup>2</sup> )	2996	148	1303
Land use (%)			
Agricultural	0	42	5
Open space	12	44	52
Industrial	13	1	4
Commercial	11	1	7
Residential	42	8	21
Transportation	22	3	11

**Table SI-2.** Measured recoveries of surrogate standards used in targeted analysis quantitation

Compound	% Recovery
Atrazine-d5	92 ± 3
DEET-d7	73 ± 9
Imidacloprid-d4	101 ± 4
Metalaxyl	138 ± 9
Prometon-d14	99 ± 6
Propanolol-d7	59 ± 6
Thiophanate-methyl-d6	14 ± 4

**Table SI-3.** Sampling rates from literature used for POCIS time-weighted average concentration calculations. Asterisk values indicate values measured in coastal/estuary conditions; all other values were measured in freshwater conditions. All values were measured under flow conditions rather than quiescent conditions.

Compound Name	Chemical Formula	Rs value (L/day)	Literature source for Rs value
Atrazine	C <sub>8</sub> H <sub>14</sub> ClN <sub>5</sub>	0.214*	(Bueno, Hernando et al. 2009)
Azoxystrobin	C <sub>22</sub> H <sub>17</sub> N <sub>3</sub> O <sub>5</sub>	0.336	(Poulier, Lissalde et al. 2014)
Benzotriazole	C <sub>6</sub> H <sub>5</sub> N <sub>3</sub>	0.134	(Carpinteiro, Schopfer et al. 2016)
Carbamazepine	C <sub>15</sub> H <sub>12</sub> N <sub>2</sub> O	0.398*	(Togola and Budzinski 2007)
Carbaryl	C <sub>12</sub> H <sub>11</sub> NO <sub>2</sub>	0.013*	(Bueno, Hernando et al. 2009)
Carbendazim	C <sub>9</sub> H <sub>9</sub> N <sub>3</sub> O <sub>2</sub>	0.304	(Poulier, Lissalde et al. 2014)
Citalopram	C <sub>20</sub> H <sub>21</sub> FN <sub>2</sub> O	1.224	(Bayen, Segovia et al. 2014)
DEET	C <sub>12</sub> H <sub>17</sub> NO	0.19	(Harman, Allan et al. 2012)
Diphenhydramine	C <sub>17</sub> H <sub>21</sub> NO	1.317	(Bayen, Segovia et al. 2014)
Metalaxyl	C <sub>15</sub> H <sub>21</sub> NO <sub>4</sub>	0.264	(Ibrahim, Togola et al. 2013)
Prometon	C <sub>10</sub> H <sub>19</sub> N <sub>5</sub> O	0.459	(Harman, Allan et al. 2012)
Propanolol	C <sub>16</sub> H <sub>21</sub> NO <sub>2</sub>	0.98*	(Macleod, McClure et al. 2007)
Simazine	C <sub>7</sub> H <sub>12</sub> ClN <sub>5</sub>	0.223*	(Bueno, Hernando et al. 2009)
Sulfapyridine	C <sub>11</sub> H <sub>11</sub> N <sub>3</sub> O <sub>2</sub> S	0.051*	(Macleod, McClure et al. 2007)
Terbutylazine-desethyl	C <sub>7</sub> H <sub>12</sub> ClN <sub>5</sub>	0.29	(Poulier, Lissalde et al. 2014)

Propiconazole	$C_{15}H_{17}Cl_2N_3O_2$	0.3	(Alvarez, Huckins et al. 2007)
Trimethoprim	$C_{14}H_{18}N_4O_3$	0.36*	(Macleod, McClure et al. 2007)
Trimethoprim	$C_{14}H_{18}N_4O_3$	0.36*	(Macleod, McClure et al. 2007)

**Tables SI-4 – SI-6.** Individual concentration values plotted for each sampling site in Figure 2. POCIS accumulations are shown both in raw values (ng/POCIS) and in time-weighted average concentrations (ng/L) calculated using the sampling rates in Table SI-3.

**Table SI-4.** Coyote Creek concentration values plotted in Fig. 2.

Compound Name	POCIS TWA (ng/L)	Deployment (ng/L)	Retrieval (ng/L)
Benzotriazole	214.98 ± 26	346 ± 40	792 ± 9
Carbamazepine	7.87 ± 2.0	--	35 ± 0.6
Carbendazim	3.86 ± 1.6	15 ± 0.6	21 ± 7
Citalopram	0.32 ± 0.1	0.65 ± 0.06	1.3 ± 0.1
DEET	5.01 ± 1.2	4.9 ± 0.2	13 ± 1
Diphenhydramine	0.51 ± 0.2	0.46 ± 0.1	0.91 ± 0.2
Propanolol	0.08 ± 0.01	0.78 ± 0.1	2.1 ± 0.1
Simazine	0.16 ± 0.1	0.82 ± 0.1	0.79 ± 0.1
Sulfapyridine	4.51 ± 0.05	2.3 ± 0.2	6.2 ± 2
Tertbutylazin-desethyl	0.06 ± 0.1	0.83 ± 0.1	0.77 ± 0.1
Propiconazole	0.01 ± 0.005	0.64 ± 0.3	1.5 ± 1

**Table SI-5.** Napa River concentration values plotted in Fig. 2.

Compound Name	POCIS TWA (ng/L)	Deployment (ng/L)	Retrieval (ng/L)
Atrazine	8.69 ± 2.9	--	2.2 ± 0.1
Azoxystrobin	0.612 ± 0.3	3.5	4.3 ± 0.1
Benzotriazole	9.151 ± 4.6	4.300	17 ± 2
Carbamazepine	0.691 ± 0.1	--	1.5 ± 0.02
Carbendazim	0.638 ± 0.04	1.6	1.4 ± 0.7
Citalopram	0.047	0.115	0.079 ± 0.0
DEET	6.231 ± 1.3	--	3.4 ± 0.0
Prometon	0.527 ± 0.2	--	0.18 ± 0.03
Simazine	6.022 ± 1.6	11	9.8 ± 0.7
Tertbutylazin-desethyl	4.63 ± 1.2	10.8	9.8 ± 0.7

**Table SI-6.** San Leandro Bay concentration values plotted in Fig. 2.

Compound Name	POCIS TWA (ng/L)	Deployment (ng/L)	Retrieval (ng/L)
Atrazine	0.030	0.23 ± 0.1	1.2 ± 0.1
Benzotriazole	10.033 ± 1.94	38 ± 2	31 ± 4
Carbamazepine	1.157 ± 0.34	2.6 ± 0.5	2.2 ± 0.07
Carbendazim	1.369 ± 0.55	8.4 ± 0.7	3.8 ± 1
Citalopram	0.035	0.29 ± 0.31	--
DEET	4.101 ± 0.82	8.1 ± 0.6	11 ± 1.
Metalaxyl	0.028 ± 0.01	0.58 ± 0.5	--
Prometon	0.135 ± 0.02	1.9 ± 0.2	1.4 ± 0.01
Propanolol	0.006 ± 0.01	0.198	--
Simazine	0.601 ± 0.17	1.9 ± 0.2	1.8 ± 0.08
Tertbutylazin-desethyl	0.462 ± 0.13	1.9 ± 0.2	1.8 ± 0.08
Propiconazole	0.127 ± 0.06	11 ± 3	26 ± 1
Trimethoprim	0.034	0.90 ± 0.8	--

**Table SI-7.** Full list of compounds annotated at the probable structure level from non-targeted analysis of San Francisco Bay water and wastewater samples. (see Excel Spreadsheet)

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