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Organic Wastewater Contaminant Levels in Canal Waters Entering Biscayne National Park and the Potential for Concordant Endocrine Disruption in the Resident Biota

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ABSTRACT

A component of the Comprehensive Everglades Restoration Plan is rehydration of the coastal wetlands adjacent to Biscayne Bay (Bay). The plan was to simply divert water from adjacent canals into the wetlands, but it was determined that the canals had an insufficient water volume to adequately rehydrate the wetlands throughout the year. As a result, water managers are planning to use treated wastewater from the South District Wastewater Treatment Plant (WWTP) to supplement the canal waters. However, treated wastewater could adversely impact biota in the coastal wetlands and in the Bay. Even though treatment of water entering the WWTP reduces organic wastewater contaminant (OWC) concentrations in the effluent, it still contains detectable OWC concentrations. Before the planned rehydration of the wetlands begins (~2012), Biscayne National Park (Park) wants to understand the existing threats to its resources from OWCs. During September of 2009, passive samplers (Polar Organic Chemical Integrative Sampler [POCIS] and Semi-Permeable Membrane Devices [SPMD]) were deployed at the mouths of nine different canals where they enter into the Bay and at three locations within the Bay for the purpose of determining OWC introduction into and presence within the Bay prior to the planned wetland rehydration. Those samplers were retrieved approximately 30 days after deployment and analyzed for OWCs. In addition, extracts from a subset of the POCIS from each location were subjected to the Yeast Estrogen Screen to determine the estrogenicity of the chemical mixture in the aquatic system. Data from this pilot study will give an indication of the background OWC levels in the Bay and Park as well as the potential for adverse impacts to the aquatic organisms due to any detected contamination.

METHODS

- Twelve passive samplers (Polar Organic Chemical Integrative Sampler [POCIS] and Semi-Permeable Membrane Devices [SPMD]) were deployed between September 21 and 25 (interior bay locations) of 2010 at the locations shown in **Figure 1** and then retrieved approximately 30 day later.
- **Figure 2** shows the canister in which the SPMDs (**Figure 3**) and POCIS (**Figure 4**) are inserted. **Figure 5** shows an deployed canister containing POCIS and SPMD.
- Extracts from the SPMDs were analyzed for polynuclear aromatic hydrocarbons (PAHs) and organochlorines, PCBS, and polybrominated diphenyl ethers (PBDEs) while extracts from the POCIS were analyzed for wastewater chemicals and agrochemicals (**Table 1**).
- Extracts from one of the POCIS samplers at each location were subjected to the Yeast Estrogen Screen (YES) to assess the estrogenicity of the chemical mixture extracted from the surface waters by the POCIS (Alvarez et al. 2008).

Figure 2

Figure 3

Figure 4

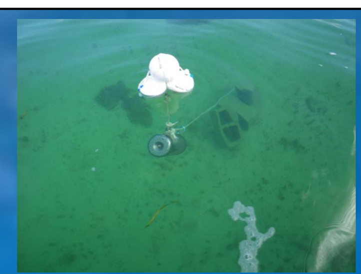

Figure 5

Table 1. Analyte List and Method Detection Limits (pg/L) for the Different Analyses Performed on the SPMD and POCIS Extracts.

Waste Water Chemicals	MDL	Polynuclear Aromatic Hydrocarbons	MDL	Organochlorines, PCBs, PBDEs	MDL	Agrochemicals	MDL
Tetrachloroethylene	0.8	Naphthalene	2200	Trifluralin	19.0	EPTC	1.10
Bromoform	0.7	Acenaphthylene	150	Hexachlorobenzene (HCB)	1.8	Desisopropylatrazine	0.63
Isopropylbenzene (cumene)	0.9	Acenaphthene	230	Pentachloroanisole (PCA)	8.1	Desethylatrazine	1.50
Phenol	2.0	Fluorene	85	Tefluthrin	32.0	Trifluralin	1.40
1,4-Dichlorobenzene	3.6	Phenanthrene	140	alpha-Benzenehexachloride (a-BHC)	4.8	Atraton	0.48
d-Limonene	1.0	Anthracene	68	Lindane	6.9	Simazine	0.33
Acetophenone	42.0	Fluoranthene		beta-Benzenehexachloride (b-BHC)	68.0	Prometon	0.11
para-Cresol	20.0	Pyrene		Heptachlor	1.0	Atrazine	0.29
Isophorone	0.3	Benz[a]anthracene	10	delta-Benzenehexachloride (d-BHC)	2.8	Propazine	0.30
Triethyl phosphate	11.0	Chrysene	9	Dacthal	38.0	Terbuthylazine	0.25
Camphor	1.0	Benzo[b]fluoranthene	10	Chlorpyrifos	88.0	Fonofos	1.20
Menthol	1.1	Benzo[k]fluoranthene	11	Oxychlordane	0.9	Diazinon	0.16
Methyl salicylate	0.9	Benzo[a]pyrene	11	Heptachlor Epoxide	26.0	Metribuzin	3.50
Dichlorvos	3.3	Indeno[i,2,3-c,d]pyrene	44	trans-Chlordane	0.0	Acetochlor	0.17
Isoquinoline	4.2	Dibenz[a,h]anthracene	37	trans-Nonachlor	18.0	Methyl Parathion	0.57
Indole	0.8	Benzo[g,h,i]perylene	41	o,p'-DDE	9.1	Simetryn	1.60
Cashmeran (DPMI)	92.0	Benzo[b]thiophene	530	cis-Chlordane	1.2	Alachlor	0.20
N,N-diethyltoluamide (DEET)	160.0	2-methylnaphthalene	280	Endosulfan	22.0	Ametryn	0.82
Diethyl phthalate	450.0	1-methylnaphthalene	200	p,p'-DDE	34.0	Prometryn	0.52
p-tert-Octylphenol	1.4	Biphenyl	44	Dieldrin	33.0	Terbutryn	0.41
Benzophenone	20.0	1-ethylnaphthalene	18	o,p'-DDD	3.7	Malathion	28.00
Tributyl phosphate	1.3	1,2-dimethylnaphthalene	22	Endrin	28.0	Metolachlor	0.16
Ethyl citrate	2.6	4-methylbiphenyl	230	cis-Nonachlor	14.0	Chlorpyrifos	1.30
Cotinine	1.0	2,3,5-trimethylnaphthalene	22	o,p'-DDT	0.9	Dacthal	1.20
Celestolide (ADBI)	1.3	1-methylfluorene	150	p,p'-DDD	17.0	Pendimethalin	1.30
Prometon	0.2	Dibenzothiophene	34	Endosulfan-II	160.0	Fipronil	1.20
Phantolide (AHMI)	1.5	2-methylphenanthrene	72	p,p'-DDT	57.0		
4-Octylphenol	8.6	9-methylanthracene	10	Endosulfan Sulfate	32.0		
Tri(2-chloroethyl) phosphate	0.2	3,6-dimethylphenanthrene	25	p,p'-Methoxychlor	14.0		
N-butyl benzenesulfonamide	1.1	2-methylfluoranthene	9	Mirex	130.0		
Tris-(2-chloropropyl)phosphate	6.5	Benzo[b]naphtho[2,1-d]thiophene	10	cis-Permethrin	61.0		
Diazinon	0.2	Benzo[e]pyrene	12	trans-Permethrin	17.0		
Tris-(1,3-dichloro-2-propyl)phosphate	6.8	Perylene	10	Total PCBs	23.0		
Musk Ambrette	6.0	3-methylcholanthrene	18	PBDE-28	54.0		
Carbazole	1.0			PBDE-47	64.0		
Caffeine	1.7			PBDE-99	44.0		
Traseolide (ATII)	1.4			PBDE-100	31.0		
Galaxolide (HHCB)	0.3			PBDE-153	26.0		
Tonalide (AHTN)	0.3						
Musk Xylene	1.2						
Carbaryl	5.1						
Metalaxyl	6.5						
Bromacil	5.2						
Anthraquinone	5.2						
Musk Ketone	6.4						
Chlorpyrifos	1.3						
Triclosan	5.7						
methyl triclosan	1.2						
Tri(dichloroisopropyl) phosphate	6.8						
Tri(butoxyethyl) phosphate	3.1						
Triphenyl phosphate	1.4						
Tris-(2-ethylhexyl)phosphate	93.0						
Diethylhexylphthalate (DEHP)	2700						
Cholesterol	68.0						

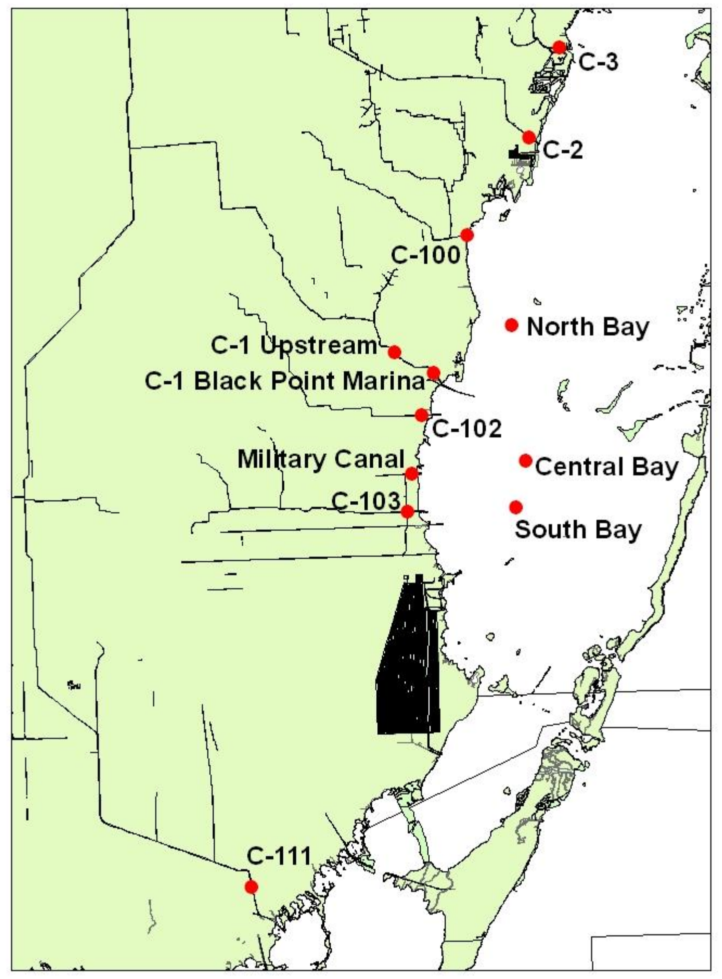

Figure 1

RESULTS / DISCUSSION

- Based on the total number of detected contaminants, waters in the C-111 canal were the most contaminated while the least contaminated locations were the Central and North Bay locations (**Table 2**). The South Bay location was more contaminated relative to the Central and North Bay locations.
- Majority of agricultural chemicals detected by the POCIS are herbicides registered for use in agriculture, horticulture, and turf.
- Very few waste water chemicals were detected indicating low waste water contribution to Biscayne Bay. The C-1 canal, which passes the South Dade Wastewater Treatment Plant, did not have a considerable wastewater contaminant load relative to the other canals. The wastewater chemicals detected were primarily synthetic fragrances and flame retardants.
- No contaminant concentrations exceeded water quality criteria (WQC) (Florida or USEPA), if WQC were available for the contaminant. No WQC are available for many contaminants.
- **Figure 2** shows the number of contaminants detected at each location. The locations in Figure 2 have been arranged to separate the canals that either pass through or are adjacent to agricultural areas (C-111, C-103, Military, C-12, C-1) from those that do not (C-100, C-2, C-3). There is a greater pesticide presence in waters of the "agricultural" canals.
- Results from the YES indicated estrogenicity at every location at which the POCIS were deployed (**Figure 3**). The estrogen equivalence (as ng 17β-estradiol per liter) for the POCIS extracts ranged from 1 to 17.4 ng/L. Superimposed on the figure are effect levels (dotted lines) for fish as reported in the literature for synthetic (ethynylestradiol) and natural estrogens (17β-estradiol). Estrogenicity at all locations exceeded the PNEC reported by Young et al. (2002), while estrogenicity at six and two of the locations exceeded the effect levels reported by Lange et al. (2001) and Seki et al. (2005), respectively. Based on these data, endocrine disruption in fish is likely. Not shown are YES results for the field blanks, which were negative for estrogenicity.
- **Figure 4** shows contaminant prevalence at each location in relation to estrogenicity. No relationship was evident between estrogenicity and the contaminants assayed in the POCIS extracts. The greatest estrogenicity was for samples from the Central and North Bay locations where contaminant detections were least. Analytes that were not assessed for the POCIS were the steroid hormones, which may be responsible for the detected estrogenicity.
- Overall aquatic contamination is quite low (parts per trillion to parts per quadrillion) and is below any regulatory levels. However, estrogenicity of the contaminant mixture from the POCIS deployed at all of the locations indicates the possibility of endocrine disruption in fish in these areas.

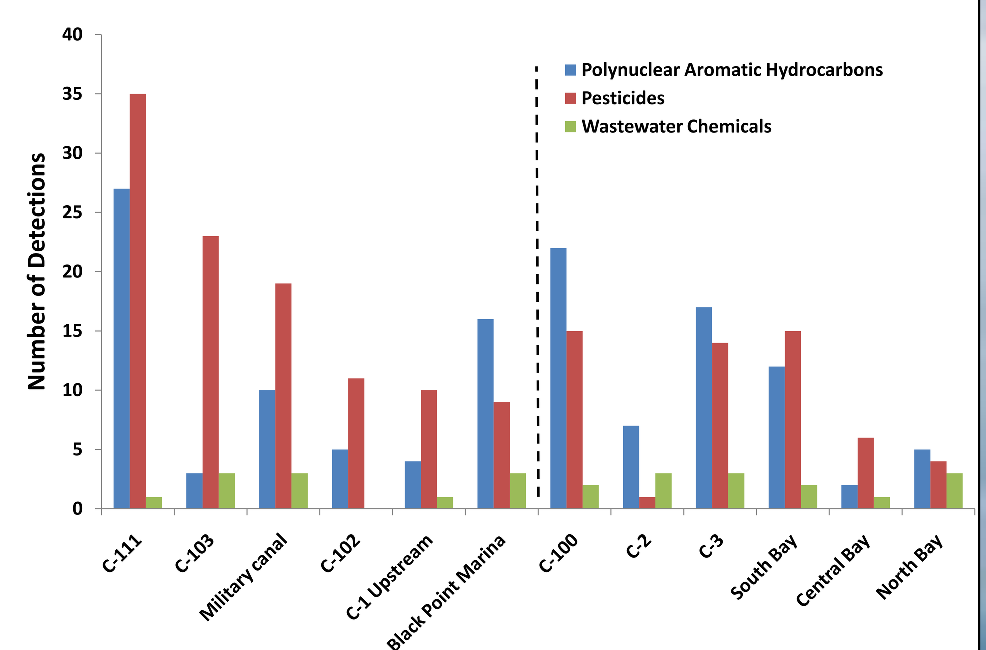

Figure 2

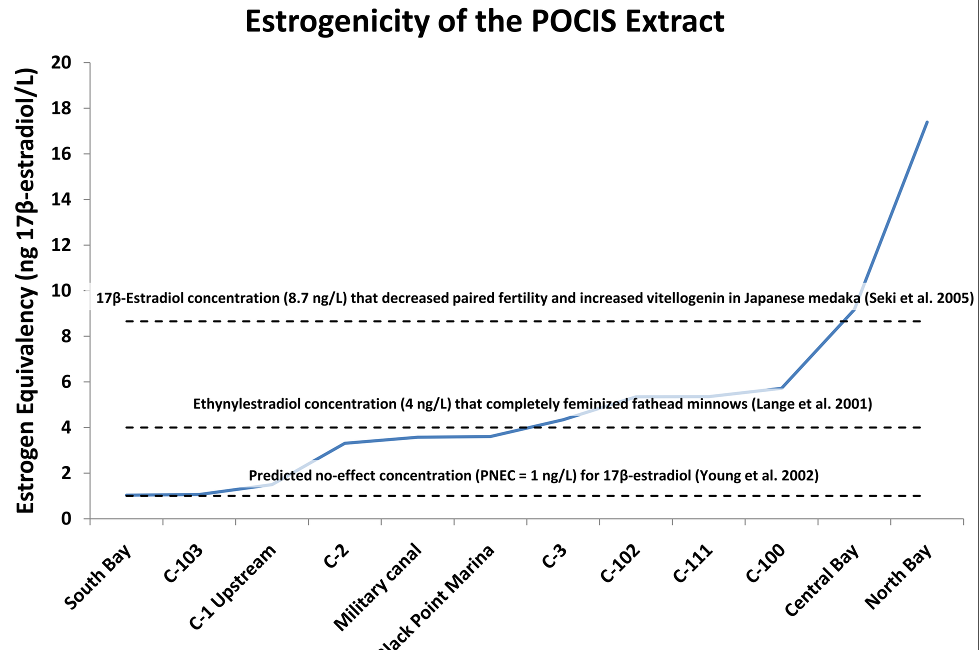

Figure 3

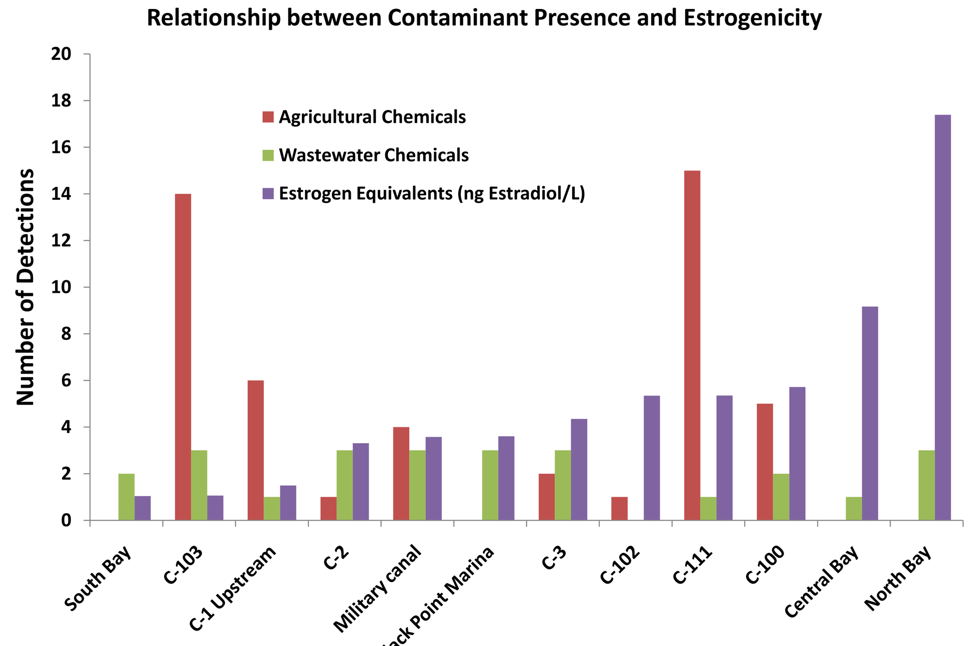

Figure 4

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Table 2. Analyte concentrations* (pg/L - parts per quadrillion) detected by the SPMD and POCIS samplers.

	South Bay	C-103	C-1 upstream	C-2	Military canal	C-1 Black Point Marina	C-3	C-102	C-111	C-100	Central Bay	North Bay
Polynuclear Aromatic Hydrocarbons												
1,2-dimethylnaphthalene	**210**	-	-	-	-	**1400**	-	-	-	50	-	-
1-ethylnaphthalene	-	-	-	-	-	**310**	-	-	-	-	-	-
1-methylfluorene	390	-	-	-	-	-	-	-	180	-	-	-
1-methylnaphthalene	400	-	-	-	**790**	**1400**	-	-	320	280	-	-
2,3,5-trimethylnaphthalene	**620**	-	-	-	**240**	**3800**	-	-	**350**	46	-	-
2-methylfluoranthene	-	-	-	-	-	-	**65**	-	**280**	**170**	-	-
2-methylnaphthalene	630	-	-	-	**780**	**2100**	-	340	540	420	-	320
2-methylphenanthrene	**1100**	-	-	-	**4900**	**6100**	140	-	**320**	160	-	-
3,6-dimethylphenanthrene	**320**	-	-	-	**480**	**1500**	62	-	**200**	59	-	-
4-methylbiphenyl	-	-	-	-	-	**1100**	-	-	290	-	-	-
9-methylanthracene	-	-	-	-	-	-	-	-	-	14	-	-
Acenaphthene	-	-	-	-	-	-	-	-	530	-	-	-
Anthracene	-	-	-	-	-	**3500**	110	-	**470**	-	-	-
Benz[a]anthracene	-	-	-	-	-	**330**	**101**	-	**360**	**290**	-	-
Benzo[a]pyrene	-	-	-	12	-	-	**130**	-	**220**	**190**	-	-
Benzo[b]fluoranthene	-	-	-	23	-	-	**230**	-	**650**	**710**	-	-
Benzo[b]naphtho[2,1-d]thiophene	-	-	-	-	-	-	19	-	**190**	**140**	-	-
Benzo[e]pyrene	-	-	-	16	-	-	**190**	-	**740**	**710**	-	-
Benzo[g,h,i]perylene	-	-	-	-	-	-	**130**	-	**220**	**240**	-	-
Benzo[k]fluoranthene	-	-	-	18	-	-	**210**	-	**490**	**460**	-	-
Biphenyl	-	-	-	-	160	**450**	52	-	140	46	-	-
Chrysene	**260**	37	31	30	**610**	**1700**	**330**	45	**1600**	**1400**	-	**58**
Dibenz[a,h]anthracene	-	-	-	-	-	-	-	-	38	-	-	-
Dibenzothiophene	**260**	-	37	-	-	**2500**	-	-	**140**	35	-	-
Fluoranthene	**780**	100	**150**	61	**1200**	**3400**	**1000**	**200**	**4400**	**2500**	**160**	**200**
Fluorene	-	-	-	-	-	-	-	-	**440**	-	-	-
Indeno[i,2,3-c,d]pyrene	-	-	-	-	-	-	95	-	**220**	**190**	-	-
Perylene	-	-	-	-	-	-	-	-	**120**	-	-	-
Phenanthrene	**1200**	-	-	-	**3800**	**6400**	230	150	**1000**	**470**	-	190
Pyrene	**510**	73	110	63	**680**	**3100**	**1000**	120	**3500**	**2700**	65	110
Organochlorine Pesticides, PCBs, PBDEs												
Chlorpyrifos	-	-	-	-	-	-	120	-	**280**	100	-	-
cis-Chlordane	-	**14**	1.7	-	**22**	**11**	**35**	**15**	**39**	-	-	**3.9**
cis-Nonachlor	**120**	-	-	-	16	-	-	-	28	19	-	-
delta-Benzenehexachloride (d-BHC)	-	-	-	-	-	-	-	-	-	**35**	-	-
Dieldrin	-	34	-	-	-	-	79	56	95	-	-	-
Endosulfan	**130**	103	**230**	-	110	**290**	-	**490**	**720**	-	100	-
Endosulfan Sulfate	**450**	-	-	-	**300**	-	-	-	-	-	**420**	-
Endosulfan-II	-	-	310	-	-	250	-	370	**620**	**1800**	-	-
Endrin	-	-	-	-	74	-	-	-	-	-	-	-
Heptachlor	-	4.1	-	-	**12**	**8.0**	1.8	3.1	**13**	**6.7**	-	-
Heptachlor Epoxide	-	-	-	-	-	-	34	-	-	-	-	-
Hexachlorobenzene (HCB)	**14**	-	-	-	4.8	**5.1**	3.1	-	**22**	-	**4.9**	-
Lindane	**130**	-	-	-	-	-	-	-	-	-	**150**	-
Mirex	-	-	-	-	**550**	-	-	-	-	-	-	-
o,p'-DDD	**17**	**14**	-	-	-	11	-	-	**100**	**46**	-	-
o,p'-DDT	-	**32**	-	-	**80**	**54**	**38**	**33**	-	**17**	-	**52**
Oxychlordane	2.1	-	-	-	-	-	-	-	-	-	2.0	-
p,p'-DDD	20	-	-	-	20	-	-	-	31	-	-	-
p,p'-DDE	-	60	-	-	-	-	**61**	**62**	**170**	-	-	-
p,p'-DDT	-	-	-	-	**99**	-	-	69	**140**	61	-	-
p,p'-Methoxychlor	34	-	-	-	-	-	-	-	-	-	-	-
Pentachloroanisole (PCA)	**31**	-	-	-	9.9	-	**34**	-	**25**	-	12	-
trans-Chlordane	-	**10**	**1.0**	-	**6.9**	**8.7**	**12**	**8.5**	-	-	-	**23**
trans-Nonachlor	-	25	-	-	-	-	-	19	**67**	-	-	-
Trifluralin	-	-	-	-	-	-	-	-	22	-	-	-
Total PCBs	500	-	-	-	**600**	280	**960**	-	**880**	**1400**	-	-
PBDE-28	-	-	-	-	-	-	-	-	67	-	-	-
PBDE-47	**320**	-	-	-	75	-	-	-	**160**	-	-	**320**
PBDE-99	**130**	-	-	-	-	-	51	-	**150**	81	-	-
PBDE-100	34	-	-	-	-	-	-	-	38	-	-	-
PBDE-153	**87**	-	-	-	-	-	-	-	-	-	-	-
Agricultural Chemicals												
Ametryn	-	**2.4**	-	-	-	-	-	-	**2.8**	1.7	-	-
Atraton	-	**2.4**	0.52	-	0.8	-	-	-	**2.2**	0.91	-	-
Atrazine	-	**7.3**	**8.2**	**3.9**	**2.5**	-	-	-	**2.0**	-	-	-
Chlorpyrifos	-	-	-	-	-	-	-	-	-	-	-	-
Dacthal	-	**12**	-	-	-	-	2.6	-	2.6	-	-	-
Desethylatrazine	-	**4.6**	**4.7**	-	-	-	-	-	3.2	-	-	-
Desisopropylatrazine	-	**5.2**	1.5	-	-	-	-	-	**3.1**	-	-	-
Metolachlor	-	**2.8**	**0.85**	-	-	-	0.76	-	**1.7**	**0.83**	-	-
Metribuzin	-	4.5	-	-	-	-	-	**16**	5.6	-	-	-
Prometon	-	**3.3**	**0.96**	-	**1.0**	-	-	-	**1.6**	**1.2**	-	-
Prometryn	-	**3.0**	-	-	-	-	-	-	**3.5**	1.1	-	-
Propazine	-	**2.7**	-	-	-	-	-	-	0.83	-	-	-
Simazine	-	**3.9**	-	-	-	-	-	-	**3.0**	-	-	-
Simetryn	-	-	-	-	-	-	-	-	2.6	-	-	-
Terbuthylazine	-	**3.0**	-	-	-	-	-	-	0.72	-	-	-
Terbutryn	-	**2.4**	-	-	0.7	-	-	-	**2.8**	-	-	-
Waste Water Chemicals												
Bromoform	**69**	**41**	-	-	-	-	-	-	**26**	-	**43**	**89**
Cashmeran (DPMI)	-	-	-	-	170	**350**	-	-	-	-	-	-
Cholesterol	79	**360**	-	-	-	74	83	-	-	-	-	**360**
d-Limonene	-	-	-	-	**26**	-	-	-	-	-	-	-
Galaxolide (HHCB)	-	**4.5**	**5.2**	**3.7**	0.95	-	**3.2**	-	-	1.3	-	**2.6**
Indole	-	-	-	-	-	**41**	-	-	-	**9.6**	-	-
Tris-(1,3-dichloro-2-propyl)phosphate	-	-	-	**150**	-	-	-	-	-	-	-	-
Tris-(2-chloropropyl)phosphate	-	-	-	**41**	-	-	26	-	-	-	-	-

* **Bolded numbers** reflect quantifiable concentrations whereas underlined numbers reflect detections between the MDL and the practical quantification limit.