

# COMPOUNDS OF EMERGING CONCERN MONITORING PROGRAM WATER YEAR 2018

The Northern Colorado Compounds of Emerging Concern Program (CEC Program) is a collaborative monitoring effort designed to take a cost-effective and proactive approach to determine if pharmaceuticals, personal care products, hormones, and pesticides are present in the Colorado Big-Thompson (C-BT) and Windy Gap projects and other source waters of interest associated with drinking water supplies in Northern Colorado. The collaborative partners are the cities of Boulder, Broomfield, Fort Collins, Greeley, Longmont, and Loveland, and the Town of Estes Park and Northern Water.

The objectives of this program are to:

- Maintain a baseline of data that monitors current conditions, trends, and changes in water quality
- Assess impacts from adverse events such as floods and wildfires
- Collect data to support the assessment of regulatory issues
- Develop source water protection measures to maintain a high-quality water supply
- Maintain a robust and evolving list of compounds

Sampling for the CEC Program is conducted bi-annually. In years where monitoring does not occur, the focus is on program development, special studies, and/or other activities that inform the partners.

## *Monitoring Locations*

The CEC Program includes monitoring sites in canals, streams, reservoirs, and raw and finished water from water treatment plants (Table 1). While most of the sites are within the C-BT system, some sites in the program are in tributaries, reservoirs or ditches that serve as drinking water sources for the municipalities that participate in the program. Each year, the participants review the monitoring locations and during this review sites can be added or discontinued from the program. A map of the sites is in Appendix 1.

Table 1 – CEC Monitoring Locations

Station	Description	Latitude	Longitude	C-BT
AT-EP	Adams Tunnel at East Portal	40.3278	-105.5782	Y
BT-FRD	Big Thompson below confluence with Fall River	40.3757	-105.5212	Y
OLY	Olympus Tunnel	40.3764	-105.4858	Y
BT-UTD	Big Thompson Downstream of Upper Thompson Sanitation District	40.3805	-105.4776	Y
BT-DLU	Big Thompson Upstream of Dille	40.4200	-105.2828	Y
BB-LOV	Big Barnes Ditch to Lake Loveland/Boyd	40.4056	-105.1427	N
HFC-HT	Hansen Feeder Canal Upstream of Horsetooth	40.5056	-105.1970	Y
CL-DAM1	Carter Lake	40.3253	-105.2152	Y
HT-SPR	Horsetooth Reservoir Spring Canyon Dam	40.5292	-105.1456	Y
HT-SOL	Horsetooth Reservoir Soldier Canyon Dam	40.5888	-105.1649	Y
SVSC-SV	Saint Vrain Supply Canal at Saint Vrain crossing	40.2220	-105.2483	Y
SV-LD	South Saint Vrain River at the Longmont Diversion	40.2139	-105.2772	N
NFWTP-CL	Nelson Flanders WTP at Carter Lake Connecting Pipeline	40.2142	-105.2289	Y
NFWTP-SV	Nelson Flanders WTP at North Saint Vrain	40.2142	-105.2289	N
NFWTP-HD	Nelson Flanders WTP at Highland Ditch	40.2144	-105.2283	N
BRWTF-RAW	Boulder Raw Water (BR-SDT or BFC is source water)	40.0768	-105.2087	Y
BRWTF-FIN	Boulder Finished Water	40.0768	-105.2087	Y
NF-PRU	North Fork of the Cache La Poudre River	40.7039	-105.2277	N
PR-NFU	Cache La Poudre River upstream of North Fork	40.7007	-105.2421	N
BET-FIN	Betasso Plant Finished Water	40.0118	-105.3348	N
BET-BAR	Betasso Plant Barker	40.0118	-105.3348	N
BET-LAK	Betasso Plant Lakewood	40.0118	-105.3348	N

### Changes to Monitoring Locations

In 2018, the City of Boulder did not collect samples at any of the Betasso Water Treatment Plant sites. It is not certain at this time if sampling will resume in 2020.

Historically, the City of Boulder collected three samples at the Boulder Reservoir Water Treatment Plant: raw water, finished water and alternate source water. In 2018, samples were collected for the raw and finished water only; sampling of the alternate source water was discontinued.

### Funding

The CEC Program was launched as a collaborative effort in 2008. The program is co-funded by Northern Water and Boulder, Broomfield, Fort Collins, Greeley, Longmont, Loveland, and Estes Park. Funding for the sites is determined by who has an interest in each site. Cost is shared by all participants at the sites that are located at the headwaters of the C-BT system

(AT-EP, BT-FRD, and OLY). Other sites may only be of interest to and funded by a sole participant or a few participants (Table 2).

Table 2 - Funders for Monitoring Locations

Station	Northern Water	Boulder	Broom-field	Estes Park	Fort Collins	Greeley	Long-mont	Loveland
AT-EP	X	X	X	X	X	X	X	X
BT-FRD	X	X	X	X	X	X	X	X
OLY	X	X	X	X	X	X	X	X
BT-UTD	X	X	X	X	X	X	X	X
BT-DLU	X				X	X		X
HFC-HT	X				X	X		
NF-PRU					X	X		
PR-NFU					X	X		
SVSC-SV	X	X					X	
SV-LD							X	
NFWTP-CL							X	
NFWTP-SV							X	
NFWTP-HD							X	
BRWTF-RAW	X	X						
BRWTF-FIN		X						
CL-DAM1	X	X	X				X	
HT-SOL	X				X	X		
HT-SPR	X				X	X		
BB-LOV						X		X

### *Sampling Schedule and Sample Collection*

The sampling schedule has evolved since 2008 to include more sampling events to capture seasonal influences of spring runoff, recreational activities, herbicide applications, reservoir stratification and turnover, and fall/winter low stream flow conditions. For funding purposes, the sampling schedule follows the Northern Water fiscal year: October 1st to September 30th.

The participants of the monitoring program share the responsibility of sampling. Each participating entity is assigned a sampling site(s) that is of interest to them. The sampling is coordinated to occur during the same week of the month to make the data comparable. The sampling schedule and sampling entity is shown in Table 3.

Table 3 - Sampling Schedule and Sampling Entity

Station	Nov-17	Feb-18	Jun-18	Aug-18	Sampling Entity
AT-EP		X	X	X	Northern Water
BT-FRD		X	X	X	Estes Park
OLY		X	X	X	Northern Water
BT-UTD		X		X	Northern Water
BT-DLU		X	X	X	Loveland
HFC-HT	X		X	X	Northern Water
NF-PRU		X	X	X	Fort Collins
PR-NFU		X	X	X	Fort Collins
SVSC-SV			X	X	Longmont
SV-LD		X	X	X	Longmont
NFWTP-CL		X	X	X	Longmont
NFWTP-SV		X	X	X	Longmont
NFWTP-HD			X	X	Longmont
BRWTF-RAW	X		X	X	Boulder
BRWTF-FIN	X		X	X	Boulder
CL-DAM1	X		X	X	Northern Water
HT-SOL	X		X	X	Northern Water
HT-SPR	X		X	X	Northern Water
BB-LOV			X	X	Greeley

All samples (except for the lake samples collected at a specific depth) are grab samples collected directly into a sampling bottle prepared by Center for Environmental Mass Spectrometry at the University of Colorado (CEMS). The lake samples collected at a specific depth are collected with a Kemmerer sampler.

### Changes to the Sampling Schedule

In 2018, the CEC Program partners reduced the sampling frequency from annual to bi-annual. Annual data collection has been ongoing since 2008 and a good baseline of data has been established. In addition, the data show that there is not significant variation in concentrations from year-to-year. In the years where sampling is not done, program funding will be dedicated to special studies and projects that will enhance the program, investigate treatment options and support development of best management practices for CECs.

There is flexibility in the program to add special monitoring events in the years when sampling is not scheduled to capture impacts of adverse events such as floods or wildfires.

## Quality Control and Assurance

Samples are collected per guidelines provided by the CEMS standard operating procedure (SOP) dated January 1, 2010, found in Appendix 2. Precautions taken during collection to prevent contamination of the sample include:

- Use of disposable gloves to prevent personal care products from contaminating the sample and sample bottle
- DEET should not be used by the sampler
- Coffee should not be consumed during the sampling period
- Cigarettes should not be used during the sampling period

For each scheduled sampling event, one blank sample is collected. There are two types of blank samples:

- Trip blank - A prepared sample bottle is filled with de-ionized water and carried into the field alongside the sampling container for the environmental sample. The blank sample bottle is opened in the field when the environmental sample is collected.
- Equipment blank - This is collected alongside of the lake samples collected at a specific depth. The de-ionized water is processed through the Kemmerer sampler.

The blank samples help ensure that there is no contamination due to sample collection processes. Blank sample collection is alternated between the sampling entities.

## *Analysis and Parameters*

CEMS conducts all the laboratory analyses. Sample analysis is done using three different methods: a presence/absence screening method (Liquid Chromatography/Time-Of-Flight Mass Spectrometry, LC/TOF-MS) and two low-level quantification methods (Liquid Chromatography/Mass Spectrometry/Mass Spectrometry, LC/MS/MS) for pharmaceuticals and endocrine disruptors.

The presence/absence screening method using LC/TOF-MS allows detection of constituents above the method reporting limits but does not allow a precise quantification of the concentration. In 2018, the list of compounds tested with this method includes 114 compounds: 43 commonly used personal care products/pharmaceuticals and 71 herbicides/pesticides.

The low-level method using LC/MS/MS began in 2010. This method allows actual quantification of the concentrations of the detected compounds and is used for a subset of compounds that are of particular interest. The list of compounds tested with this method is reviewed by the participants each year and compounds can be added or discontinued at this time. The 2018 list of compounds analyzed by LC/MS/MS includes 32 herbicides/pesticides and personal care products/pharmaceuticals (subset from the

LC/TOF-MS method) and 8 endocrine disrupting compounds (hormones and hormone-mimicking compounds).

The suite of endocrine disrupting compounds is included only during the August sampling event; all the sites are sampled in August and it is low flow conditions. For the remaining sampling events (November, February and June), the endocrine disrupting compound estrone is analyzed with the low-level LC/MS/MS method. If estrone is detected, follow-up analysis is done on the remaining 7 endocrine disrupting compounds.

The full list of compounds and their typical reporting limits can be found in Appendix 3.

### *Supplemental Sampling on the Boulder Feeder Canal*

Northern Water maintains the East Slope C-BT canal systems, which includes control of nuisance and invasive weed species. The Boulder Feeder Canal (BFC), which runs south to Boulder Reservoir, is an earthen lined canal that is prone to excessive weed growth. Herbicides are applied to the Boulder Feeder Canal in the fall, after the canal is shut down for the season. The City of Boulder’s Boulder Reservoir Water Treatment Facility (BRWTF) uses water that comes from the canal for a drinking water source. Therefore, monitoring concentrations of compounds related to Northern Water’s herbicide applications is important.

Additional samples are collected on the Boulder Feeder Canal, at the Star Turnout, approximately 0.8 miles upstream of Boulder Reservoir (BFC-STAR). This site is the point where Northern Water’s herbicide applications end; there will not be herbicide applied to the 0.8-mile section of canal between the Star Turnout and the Boulder Reservoir.

Table 4 - Boulder Feeder Canal Sampling Site

Station	Description	Latitude	Longitude	C-BT
<b>BFC-STAR</b>	Boulder Feeder Canal at Star Turnout on Monarch Road	40.0947	-105.2209	Y

Samples collected at this site assess the impact of Northern Water’s herbicide applications. A minimum of three additional samples are collected in late March/early April to look at concentrations of imazamox, fluridone, topramezone and penoxsulam which are active ingredients in herbicide products used by Northern. The sampling schedule is:

1. A sample of the water that has pooled over the winter before any C-BT water is released for the season;
2. A sample collected of the first water released into the canal for delivery to Boulder;
3. A sample collected when the canal begins normal operations;
4. Frequent samples are collected through May to track the decrease in concentrations of the detected compounds.

Additional samples will be collected if the data show that there are elevated concentrations for any of the compounds related to that year’s application. This site is sampled and funded by Northern Water.

### *Supplemental Sampling on the Poudre River for NISP Water Quality Analysis*

Northern Water continued monitoring three sites on the Poudre River in 2018 (Table 5). The purpose of these sites is to establish a baseline of CEC data to assist in evaluating water quality in the Poudre River for assessment of various Northern Integrated Supply Project (NISP) alternatives. Samples are collected in February, June and August at all three locations. These sites are sampled and funded by Northern Water and the NISP participants.

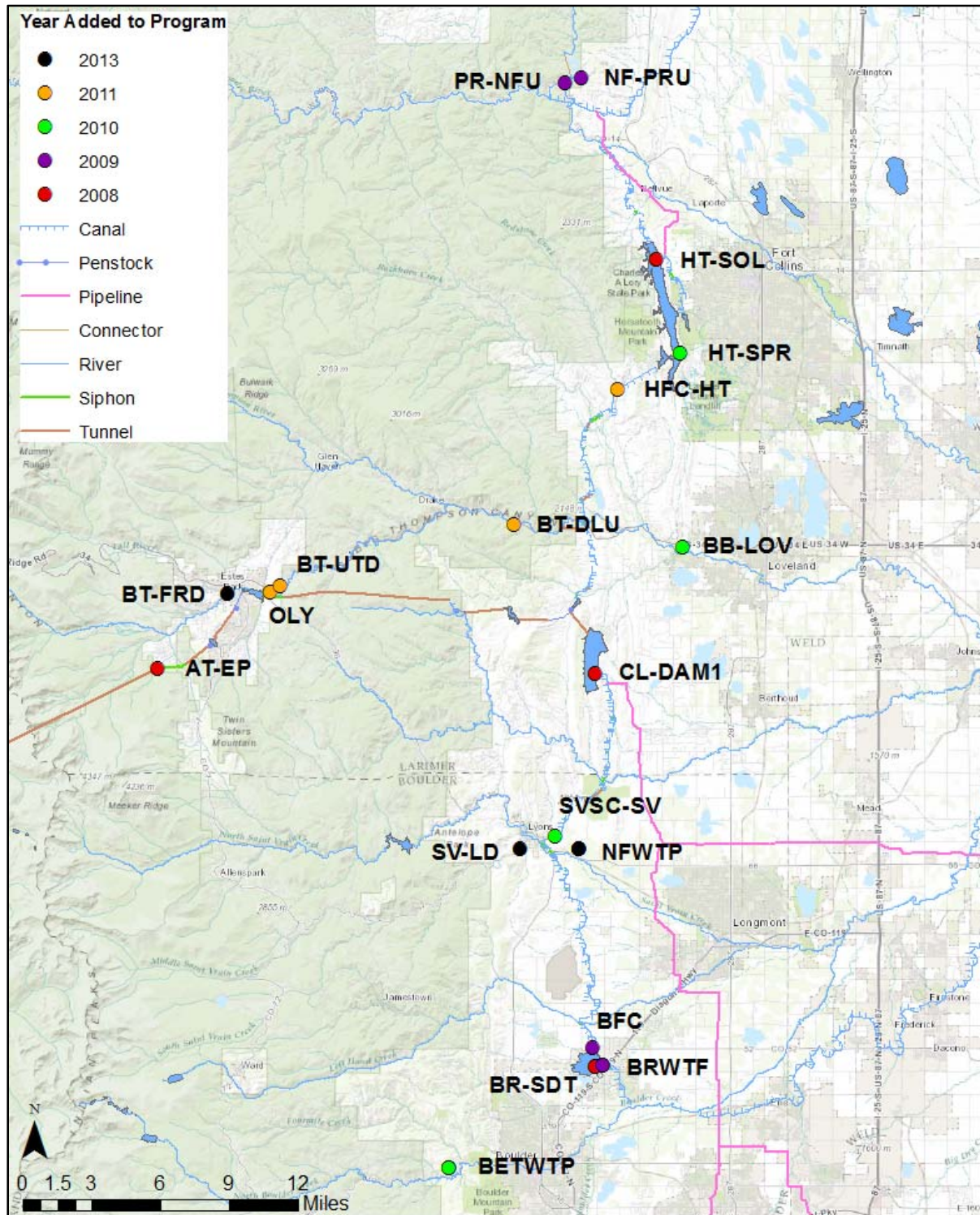
Table 5 - Monitoring Sites on the Poudre River

Station	Description	Latitude	Longitude	C-BT
PR-MWWU	Poudre River at Lincoln Ave upstream of Mulberry WWTP	40.5879	-105.0693	N
PR-MWWD	Poudre River at Timberline Ave downstream of Mulberry WWTP	40.5786	-105.0355	N
PR-NCD	Poudre River downstream of Fossil Creek and New Cache Ditch	40.5008	-104.9673	N

### *Map of Sampling Locations*

The map in Appendix 1 shows the location of the routine sites included in the monitoring program as well as the year they were added to the program. The supplemental sampling sites are not included on the map.

## 2018 Sampling Sites



### Note on Map

*NFWTP is the location of three sampling sites: NFWTP-CL, NFWTP-HD, and NFWTP-SV*

*BRWTF is the location of three sampling sites: BRWTF-BFC, BRWTF-BR, and BRWTF-FIN*

*BETWTP is the location of three sampling sites: BET-BAR, BET-LAK and BET-FIN*



## CEMS Sampling Protocol

*January 1, 2010*

The University of Colorado, Center for Environmental Mass Spectrometry, CEMS, is committed to a rigorous program of quality assurance and quality control for all phases of research and analysis, including sample collection, sample storage, physical and chemical analyses, and evaluation of the resulting data. The following sampling procedures are taken from our most recent SOP Manual, dated January 1, 2010.

### *Sampling Procedures for Water Samples:*

All samples will be collected in baked, glass, 1-liter, amber bottles complete with Teflon lined caps to ensure sample integrity. In addition, a concerted effort will be made to keep bottle head space to a minimum by filling the bottles to the top. The bottles will be rinsed in the field three times with sample and filled to the top on the fourth sampling. Disposable gloves will be used by the sampler to prevent any personal care products from contaminating the sample bottles. No use of insect repellent (i.e. DEET) is allowed, and no smoking or coffee should be consumed during the sampling period.

Any unusual conditions concerning each sample will be noted in a field notebook and copies of these field notes will be sent along with the samples in a waterproof envelope. All samples will be kept refrigerated at  $\leq 4^{\circ}\text{C}$  from the time of collection until sample extraction has taken place. This is accomplished by placing all samples in an appropriate ice-chest filled with blue ice packets or regular ice. The sample bottles will be labeled clearly with an indelible black pen and covered with cellophane tape for name protection. The bottle will be wrapped with bubble wrap and taped to prevent banging and breakage of the bottles.

Finally, All details related to sample collection and preservation will be recorded in a notebook. This notebook will contain all relevant information including time and date of sampling, retrieval method, initials of sampler, sample identification number, and any other data deemed necessary. This notebook will also contain any deviations that may occur during the sampling process.

### *River and Lake Water Sampling:*

Proper integrated sampling of river and water is necessary for quantitative results. This may follow standard USGS protocol and be taken by integrating sampling across the river or profile depth sampling of a lake. If this is not available, a grab sample may be taken. Grab samples are not quantitative but may be useful for early surveys. Grab samples should be taken from the rapid area of the stream or river where the majority of flow is occurring. Care is taken that the sample is not contaminated by the sampler during this process.

## 2018 List of Compounds Analyzed

### Pesticides Suite (LC/TOF-MS)

Compound	MRL (ng/L)
Acetamidrid	3
Acetochlor	2
Alachlor	3
Aldicarb	5
Atrazine	5
Azoxystrobin	1
Bromacil	5
Bromoxnil	20
Bromuconazole	1
Buprofezin	1
Captan	15
Carbaryl	3
Carbendazim	1
Carbofuran	4
Chlorpyrifos-ethyl	30
Chlorpyrifos methyl	30
Cyanazine	2
Cyproconazole	1
Cyromazine	9
Deethylatrazine	2
Deisopropylatrazine	2
Diazinon	1
Dichlorvos	1
Difenoconazole	1
Diflubenzuron	12
Dimethenamide	1
Dimethoate	1.5
Dimethipin	20
Dimethomorph	4
Diuron	15
Ethoprop	20
Flufenacet	3
Fluridone	5
Fluroxypyr	45
Hexaflumuron	8
Hydroxyatrazine	1
Imazalil	1
Imazapyr	5
Imidacloprid	2
Iprodione	4
Isoxaben	5
Isoxaflutole	5
Malathion	1.5
Metalaxyl	1
Methidathion	15
Methiocarb	1
Methiocarb sulfone	9
Methomyl	2
Metolachlor	1
Metribuzin	1
Nicosulfuron	1
Oxyfluorfen	20
Parathion-methyl	17
Pendimethalin	11
Phosmet	1
Profenofos	20
Prometon	1
Propachlor	1
Propazine	1
Propiconazole	1

### Pesticides Suite (LC/TOF-MS) Continued

Compound	MRL (ng/L)
Propoxur	5
Prosulfuron	5
Simazine	5
Spinosyn A	1
Spinosyn D	6
Terbutylazine	5
Terbutylazine	5
Thiabendazole	5
Thiacloprid	1.5
Tribufos	20
Triflumizole	3
<b># of Pesticides</b>	<b>71</b>

### PPCPs Suite (LC/TOF-MS)

Compound	MRL (ng/L)
1,7 Dimethylxanthine	100
Acetaminophen	50
Albuterol	10
Atenolol	5
Azithromycin	10
Bupropion	10
Bupropion Metabolite	10
Caffeine	20
Carbamazepine	5
Carbamazepine Metabolite	5
Cimetidine	10
Ciprofloxacin	5
Clarithromycin	10
Codeine	10
Cotinine	20
DEET	20
Dehydronifedipine	2
Dextromethorphan	10
Dextrorphan	10
Diclofenac	20
Diltiazem	15
Diphenhydramine	2
Erythromycin	5
Erythromycin Anhydrate	5
Fentanyl	10
Fluoxetine	10
Hydrocodone	10
Ibuprofen	50
Lamotrigine	5
Lamotrigine Glucuronide	10
Metformin	50
Metoprolol	5
Naproxen	50
Norvenlafaxine Metabolite	20
Oxycodone	20
Propranolol	5
Ranitidine	10
Sulfadimethoxine	5
Sulfamethoxazole	50
Triclocarban	20
Trimethoprim	5
Venlafaxine	10
Warfarin	10
<b># of PPCPs</b>	<b>43</b>

### Low Level Suite (LC/MS-MS)

Compound	MRL (ng/L)
2,4-D	5
Acetaminophen	5
Atenolol	5
Atrazine	2
Bisphenol A	20
Bupropion	1
Caffeine	10
Carbamazepine	2
Clarithromycin	2
Cotinine	5
DEET	20
Dextrorphan	5
Diazinon	1
Diltiazem	5
Diphenhydramine	5
Diuron	5
Erythromycin	10
Fluridone	5
Gabapentin	15
Gemfibrozil	5
Imazamox	5
Lamotrigine	5
Metoprolol	1
Penoxsulam	10
Propranolol	1
Sucralose	15
Sulfamethoxazole	5
Topramezone	20
Triclopyr	10
Triclosan	20
Trimethoprim	5
Venlafaxine	1
<b># of Low Level</b>	<b>32</b>

### Hormone Suite (LC/MS-MS)

Compound	MRL (ng/L)
17-a-Ethinylestradiol	10
17-b-Estradiol	5
4-Androstene-3,17-dione	2
Equilin	5
Estriol	10
Estrone	5
Progesterone	1
Testosterone	1
<b># of Hormones</b>	<b>8</b>