

# Compounds of Emerging Concern Monitoring Program

# Water Quality Department

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, pesticides, and other compounds of concern 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 (partners) are the cities of Boulder, Broomfield, Fort Collins, Greeley, Longmont, and Loveland, 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 existing and potential regulations.
- 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. The partners will evaluate and agree on studies and/or initiatives to inform and improve the program.



## FUNDING

The CEC Program was launched as a collaborative effort in 2008. The program is managed by Northern Water and co-funded by Boulder, Broomfield, Estes Park, Fort Collins, Greeley, Longmont, Loveland, and Northern Water. During monitoring years, funding is determined by who has an interest in each monitoring site and costs are shared accordingly. During special study years, funding is determined based on the percentage of each partner's contribution during monitoring years for monitoring locations where there are multiple funders. The total amount spent in a special study year is not to exceed what would be spent in a monitoring year unless the exceedance is approved by all partners. This keeps the annual budget consistent from year to year.

## **MONITORING LOCATIONS**

Table 1 - CEC monitoring sites.

Station	Description	Lat.	Long.	C-BT
AT-EP	Adams Tunnel East Portal near Estes Park	40.3278	-105.5782	Х
BT-FRD	Big Thompson below confluence with Fall River	40.3757	-105.5212	Х
OLY	Olympus Tunnel at Lake Estes	40.3764	-105.4858	Х
BT-UTD	Big Thompson dwnstr. of Upper Thompson Sanitation District	40.3805	-105.4776	Х
BT-DLU	Big Thompson upstream of Dille Tunnel	40.4200	-105.2828	Х
LWTP-GRGR	Loveland WTP Raw Water Green Ridge Glade Reservoir	40.4258	-105.2082	
LWTP-BT	Loveland WTP Raw Water Big Thompson River	40.4258	-105.2082	
LWTP-FIN	Loveland WTP finished water	40.4258	-105.2082	
BT-LWWU	Big Thompson upstream of Loveland WRF	40.3832	-105.0540	
BT-LWWD	Big Thompson downstream of Loveland WRF	40.2857	-105.0500	
LWW-INF	Loveland WRF inflow	40.3865	-105.0537	
BB-LOV	Big Barnes Ditch to Lake Loveland/Boyd Lake	40.4056	-105.1427	
HFC-HT	Hansen Feeder Canal at inlet to Horsetooth	40.5056	-105.1970	Х
CL-DAM1	Carter Lake Dam #1	40.3253	-105.2152	Х
HT-SOL	Horsetooth Reservoir at Soldier Canyon Dam	40.5888	-105.1649	Х
HT-SPR	Horsetooth Reservoir at Spring Canyon Dam	40.5292	-105.1456	Х
SVSC-SV	Saint Vrain Supply Canal at Saint Vrain Creek	40.2182	-105.2582	Х
SV-LD	South Saint Vrain River at the Longmont Diversion	40.2139	-105.2772	
NFWTP-CL	Nelson Flanders WTP at Carter Lake Connecting Pipeline	40.2142	-105.2289	Х
NFWTP-SV	Nelson Flanders WTP at North Saint Vrain	40.2142	-105.2289	
NFWTP-HD	Nelson Flanders WTP at Highland Ditch	40.2144	-105.2283	
BFC-BR	Boulder Feeder Canal at Star Turnout upstr. of Boulder Res.	40.0947	-105.2209	Х
<b>BRWTF-FIN</b>	Boulder Reservoir WTP finished water	40.0768	-105.2087	Х
NF-PRU	North Fork upstream of the Poudre River	40.7039	-105.2277	
PR-NFU	Poudre River upstream of the North Fork	40.7007	-105.2421	
PR-MWWU	Poudre River at Lincoln Ave upstream of Mulberry WWTP	40.5879	-105.0693	
BET-FIN	Betasso WTP Plant finished water	40.0118	-105.3348	
BET-BAR	Betasso WTP Raw Water – Barker R	40.0118	-105.3348	
BET-LAK	Betasso WTP Raw Water - Lakewood	40.0118	-105.3348	

# Map of Monitoring Locations

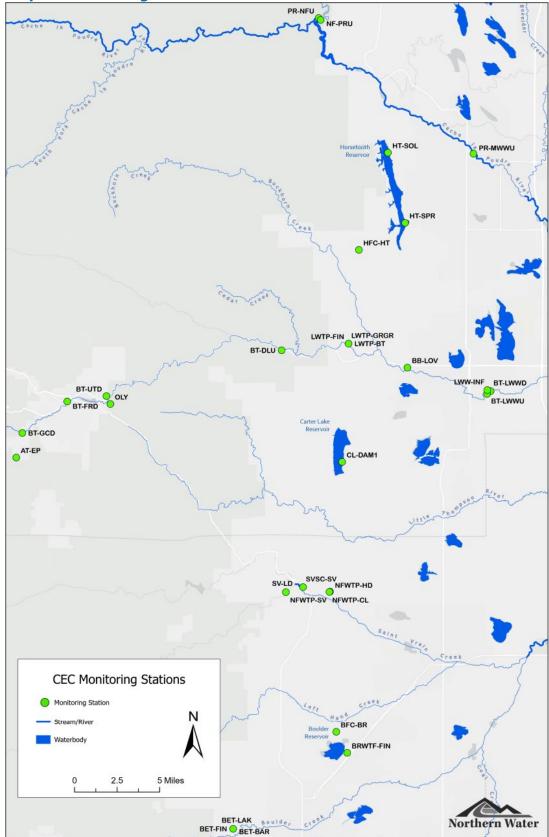


Figure 1. Map of Compounds of Emerging Concern Monitoring Locations

## SAMPLING SCHEDULE AND COLLECTION FOR ROUTINE MONITOIRNG YEARS

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

The participants of the monitoring program share the responsibility of sampling. Each participating entity is assigned a sampling site(s) 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 2*.

Station	Nov	Feb	Jun	Aug	Sampling Entity
AT-EP		х	х	х	Northern Water
BT-FRD		x	х	х	Estes
OLY		х	х	х	Northern Water
BT-UTD		х		х	Northern Water
BT-DLU		х	х	х	Loveland
LWTP-GRGR				х	Loveland
LWTP-BT				х	Loveland
LWTP-FIN				х	Loveland
BT-LWWU				х	Loveland
BT-LWWD				х	Loveland
LWW-INF				х	Loveland
BB-LOV			х	х	Greeley
HFC-HT	x		х	х	Northern Water
CL-DAM1	х		х	х	Northern Water
HT-SOL	х		х	х	Northern Water
HT-SPR	х		х	х	Northern Water
SVSC-SV			х	х	Longmont
SV-LD		х	х	х	Longmont
NFWTP-CL		х	х	х	Longmont
NFWTP-SV		х	х	х	Longmont
NFWTP-HD			х	х	Longmont
BFC-BR			х	х	Northern Water
BRWTF-FIN	x		х	х	Boulder
NF-PRU		х	х	х	Fort Collins
PR-NFU		х	х	х	Fort Collins
PR-MWWU		х	х	х	Northern Water
BET-FIN		х	х	х	Boulder
BET-BAR		х	х	х	Boulder
BET-LAK		х	х	х	Boulder

Table 2 - Routine CEC Monitoring Schedule

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.

# **QUALITY ASSURANCE AND CONTROL**

Samples are collected per guidelines provided by the CEMS standard operating procedure (SOP) dated March 2021, found in *Appendix F – CEMS SOP*. Precautions taken during collection to prevent contamination of the sample include:

- Using disposable gloves to prevent personal care products from contaminating the sample and sample bottle.
- Refraining from any use of DEET by the sampler during the day of sampling.
- Refraining from caffeine consumption and the use of tobacco products during the sampling period.

## **Field Quality Control Sampling**

Quality Control (QC) samples are used to measure and maintain data quality, limit error, and ensure that data quality objectives are met. Field QC samples include several types of blank and duplicate samples, which are listed in Table 3 and described in this section. Approximately 10 percent of all samples collected are QC samples. To meet this target, eight QC samples are collected throughout the sampling season, two for each sampling event. Four of these samples are blank samples, and four are duplicate samples. QC sampling rotates between entities on a yearly basis, with each entity collecting at least one blank or duplicate during a normal sampling year, except for Northern Water, which collects both a blank and a duplicate yearly.

#### Table 3 - Field QC sample types.

QC Sample	Data Quality Indicator	Field QC Sample Type	% Collected	Acceptance Criteria	Corrective Action
Blank Samples	Bias due to sample contamination	Trip Blanks (TB) Field Blanks (FB) Field Equipment Blanks (FEB)	5% of all samples collected	≤ Reporting Limit (RL)	Investigate & eliminate source of contamination: improperly cleaned sample bottles, contamination of sample bottles, contamination of the blank water, lab error; flag suspect data.
Duplicate Samples	Precision	Sequential Sample (SQR)	5% of all samples collected	For concentrations > RL: Relative Percent Difference (RPD) ≤ 25%	Investigate cause: natural variability in space and/or time, inconsistent field techniques & sample processing, lab error; request re-analysis of sample; flag suspect data.

#### **Blank Samples**

Blank QC samples provide an estimate of bias due to sample contamination that could occur during sample collection. Blank samples are used to demonstrate that contamination of the environmental samples has not occurred or, if it did, where in the sampling process it occurred. Blank samples are made up of de-ionized (D.I.) water free of the analytes of interest. D.I. water is tap water treated by filtering through a standard de-ionizing resin column filter.

Routine blank samples collected for the CEC Program include lab D.I. trip blanks (TB), field equipment blanks (FEB), and field blanks (FB). If chronic sample contamination is suspected, additional blank samples can be collected at additional points in the sample collection and processing sequence to help determine exactly

where the contamination is occurring. Blank samples constitute approximately 5 percent of the total sample load.

#### Field blanks (FB)

Field blank samples are collected to determine if contaminants are introduced to the sample in the field during sample collection. Field blanks are collected by pouring D.I. water directly into a sample bottle in the field. D.I. water for all field blanks is provided by CEMS.

### Trip blanks (TB)

Trip blanks are used to narrow down any possible contamination sources if a field blank detects target compounds. Trip blanks are pre-filled D.I. samples carried into the field alongside the sampling container for the environmental sample. The cap of the prepared trip blank is opened when the environmental sample is collected. D.I. water for all trip blanks is provided by CEMS.

#### Field equipment blanks (FEB)

Field equipment blank samples are collected to determine if contaminants are introduced to the sample in the field or through sampling equipment during the collection of reservoir samples. Field equipment blanks are collected by taking D.I. water into the field and processing it as if it were a sample. Northern Water collects the only field equipment blank each season during reservoir sampling using a Kemmerer sampler according to Northern Water's Standard Operating Procedures. The Kemmerer is decontaminated prior to entering the field at Northern Water's laboratory. D.I. water for field equipment blanks is provided by Northern Water's lab.

## **Duplicate Samples**

Duplicate samples are used to assess precision and random error. Precision is a measure of how well repeated measurements agree, and how consistent and reproducible the field and lab measurements are. Imprecision is the result of inconsistent field techniques or laboratory analysis. Field duplicate samples are two samples collected and processed together that should produce essentially identical results when analyzed. However, because many CEC compounds have historically been found in very low concentrations, identical results are unlikely for this program.

Field duplicates are collected randomly at different sites throughout the sampling season, except for the duplicate collected by Northern Water at the BT-UTD sampling location, which remains consistent. The BT-UTD sampling site has the highest and most frequent detections of CECs which will provide the best data for assessing the QC program's effectiveness.

All field duplicate samples collected by the CEC Program are sequential samples (SQR). Sequential samples are two samples collected consecutively at the same location to determine variability in the collection, processing, and analysis of samples. Field duplicate samples constitute approximately 5 percent of the total sample load.

# **ANALYSIS AND COUMPOUNDS FOR ROUTINE MONITORING YEARS**

Dr. Imma Ferrer and Dr. Michael Thurman with CEMS conduct the laboratory analyses for routine monitoring years. The instruments used are Agilent HPLC Model Infinity II and Agilent Model 6546. The analytical method is an ultra-high performance liquid chromatography/quadrupole-time of flight-mass spectrometry (LC/Q-TOF-MS).

The methods provide qualitative concentrations for over 135 compounds and low-level quantification for over 30 compounds. Additional analysis (positive and negative ion analysis) is needed for 8 hormones and hormone-mimicking compounds (endocrine disruptors). The compounds analyzed include herbicides, pharmaceuticals and personal care products, endocrine disrupting compounds (EDC), opioids, fracking related compounds, fire related compounds, industrial and benzotriazoles.

Since the suite of EDCs requires a separate analysis, it is included only during the August sampling event. During the month of August sampling is conducted at all the sites in the program and it represents low flow conditions. For the remaining sampling events (November, February, and June), only estrone is analyzed since baseline data have shown that it is the most frequently detected EDC. If estrone is detected, follow-up analysis is done on the remaining 7 EDCs.

The full list of compounds can be found in Appendix E – Compounds Analyzed.

## SUPPLEMENTAL SAMPLING

Supplemental sampling is sometimes conducted at a variety of locations based on the needs of the CEC Collaborative. A history of supplemental sampling can be found in *Appendix D – Supplemental Monitoring*.

# **APPENDIX A – SPECIAL STUDIES**

Year	Study
2019	<ul> <li>Literature review conducted that informed an updated comound list which was adopted</li> <li>Outreach materials created fro stakeholders connected to the CEC Collaborative</li> <li>Microplastics study conducted</li> <li>Gylyphosate analysis conducted</li> </ul>
2021	Due to fires in 2020, the CEC 2021 Special Study investigated ash and fire related compounds including method development, source water sampling and treatment effectiveness.
2023	The Collaborative contracted with Hazen and Sawyer to complete a Comprehensive Assessment of all the CEC Data collected to date and to provide analysis, trends, dashboarding and recommendations for future monitoring.

# **APPENDIX B – CHANGES TO ROUTINE MONITORING**

Year	Description of Change		
2008	AT-EP, CL-DAM, HT-SOL, and BR-SDT sites added to routine monitoring plan.		
2009	BFC, BRWTF-BFC, BRWTF-BR, BRWTF-FIN, PR-NFU, and NF-PRU added to routine monitoring plan.		
2010	BET-BAR, BET-LAK, BET-FIN, SVSC-SV, BB-LOV, and HT-SPR sites added to routine monitoring plan.		
2010	The Center for Environmental Mass Spectrometry provided a Standard Operating Procedure for the CEC Partners. This method was adopted for CEC sampling.		
2011	OLY, BT-UTD, BT-DLU, and HFDC-HT sites added to routine monitoring plan.		
2013	SV-LD, NFWTP-CL, NFWTP-HD, NFWTP-SV, and BT-FRD sites added to routine monitoring plan.		
2013	A large flood in September 2013 affected the source waters of all the participants of the Emerging Contaminants Program. The regularly scheduled monitoring in November 2013 was moved up to September/October 2013 to capture the effects of the flood event. Additionally, some sites that are not typically part of the monitoring program and were not scheduled to be sampled in November 2013 were added the floodwater sampling in September/October of 2013.		
2015	In 2015 the site WG-DAM located on Windy Gap Reservoir was discontinued from monitoring as it was determined that water from Windy Gap is diluted significantly before it is transported to the East Slope and compounds detected at WG-DAM did not persist as water is moved from the West Slope to the East Slope. A better indicator is the AT-EP site that remains part of the routine monitoring.		
2016	In 2016, analytical costs increased. To offset the costs, the CEC participants opted to reduce the frequency of analysis for the suite of the 8 endocrine disrupting compounds. Other than estrone, these compounds are generally not detected above the method detection limit, especially during high flows. The full suite of 8 endocrine disrupting compounds are only included during the August sampling event at low flow conditions. Estrone was added to the list of compounds analyzed at all other sampling events.		
2018	The City of Boulder did not collect samples at any of the Betasso Water Treatment Plant sites. The City of Boulder also only collected samples of raw and finished water at the Boulder Reservoir Water Treatment Plant, sampling of alternate source water was discontinued.		
2018	The CEC Partners agreed to reduce the sampling frequency from annual to bi-annual. Annual sampling was performed from 2008 to 2018 which established a good baseline of data. In addition, the data show that there is not significant variation in concentrations from year-to-year. In years where routine sampling is not done, the CEC Partners will choose a special study or project to dedicate funding that will enhance the program or develop best management practices for CECs. There is flexibility in the program to add special monitoring events in years when sampling is not scheduled.		
2020	The City of Boulder resumed collecting routine samples at the Betasso Water Treatment Plant sites.		
2020	In 2020 the location for the NISP diversion in the Poudre River was selected. The CEC site PR- MWWU, which represents conditions at the diversion, was maintained and incorporated into regular monitoring. The following sites that were being monitored to determine baseline data for NISP alternatives were discontinued: PR-MWWD and PR-NCD		
2020	Because of the completion and operation of the Southern Water Supply Project II pipeline in April 2020, the final water delivery from the Boulder Feeder Canal is now upstream of Boulder Reservoir, at the Star Headgate. This eliminated the need for some monitoring along the canal. The following changes were made:		

Year	Description of Change	
	<ul> <li>BRWTP-BR: removed from routine monitoring</li> <li>Sampling at BFC-BR site moved upstream to the Star turnout. BFC-STAR renamed BFC-BR</li> <li>BRWTP-BFC: removed from routine monitoring, replaced with a site upstream (BFC-BR, previously BFC-STAR)</li> </ul>	
2024	A more robust QA/QC program was implemented for the 2024 sampling season and beyond. Replicate samples were introduced along with Field Blanks. Two QA/QC samples are now collecte during each sampling event.	

# **APPENDIX C – CHANGES TO COMPOUND LIST AND ANALYSIS**

Year	Description of Change	
2012	In 2012 the Collaborative switched all its lab analysis to CEMS. Before this, analysis for hormone compounds was done at the Underwriters Laboratory (UL) using a USGS-approved method. In 2011, CEMS finalized a method for hormone analysis (endocrine disruptors). During this sampling season, duplicate samples were collected and analyzed at both CEMS and UL. Comparative results showed no significant difference, so the decision was made to shift all analyses to CEMS.	
2013	<ul> <li>The herbicide Triclopyr was added to the list of compounds using the low-level method. Northern Water began using this product instead of 2,4-D on the south end of the C-BT canal system (Saint Vrain Supply and Boulder Feeder Canals).</li> <li>Four hormones were also added to the hormone suite: <ul> <li>4-Androstene-3</li> <li>17-dion</li> <li>Equilin</li> <li>Estroil</li> </ul> </li> </ul>	
2014	Two compounds were added to the low-level method list: dextrorphan (a metabolite of dextromethorphan, the active ingredient in cough syrup) and gabapentin (a pain medication and anti-epileptic). These compounds had been regularly detected as present with the TOF method and were added to the LC/MS/MS method to quantify the concentrations.	
2016	Three herbicides were added to both the TOF and low-level method compound lists: imazamox, topramezone, and penoxsulam. The earthen-lined Boulder Feeder Canal is prone to excessive weed growth. In 2016, Northern Water added herbicides containing these three compounds to their weed management plan to help control weed growth in this section of the canal system.	
2017		
2019	<ul> <li>Extensive review of the compound list was completed. This included a literature review that informed what compounds should be added to or removed from the list. In summary, the following changes were made: <ul> <li>Removal of herbicides that were never detected and either banned or not used in study area.</li> <li>Addition of opioids</li> <li>Addition of benzotriazoles (organic compounds used as correction inhibitors)</li> <li>Addition of compounds of concern from the EU, CCL-4 and California watchlists</li> <li>Addition of fracking family compounds</li> <li>Addition of GBD and THC</li> <li>Removal of compounds from the low-level list that were either never detected or always detected. These were replaced with compounds of greater concern. The following changes were made: <ul> <li>Removed: acetaminophen, caffeine, gabapentin, and sucralose. These compounds remain on the qualitative list.</li> <li>Added: fexofenadine, tramadol and EDDP (methadone metabolite)</li> </ul> </li> </ul></li></ul>	

Year	Description of Change	
2020	CEMS acquired new instrumentation that resulted in a change in methodology. In previous years sample analysis was 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 EDCs. The screening method will continue to be used moving forward, but the two low-level methods will be replaced with Liquid Chromatography/Quadrupole Time-Of-Flight Mass Spectrometry (LC/Q-TOF-MS)	
	New methods and calibration curves were developed using the new Q-TOF-MS instrument. For QAQC purposes, stored samples that were analyzed in previous year were reanalyzed with the new method and the data from both analyses were compared. The data compared well, and the new instrument proved to have good accuracy. For some compounds, the detection limit changed.	

# **APPENDIX D – SUPPLEMENTAL MONITORING**

Year	Description of Change		
2016- present	<ul> <li>Boulder Feeder Canal – because of aquatic nuisance and invasive weed species in the canal herbicides are applied in the fall after the canal is shut down for the season. Additional samples are collected at the BFC-BR site where Northern Water's herbicide applications end. The samples are collected in late March/early April to look at concentrations of imazamox, fluridone, topramezone and penoxsulam – ingredients in herbicide products used by Northern Water. The sampling schedule is: <ol> <li>Sample of the water that has pooled over the winter before any C-BT water is released for the season;</li> <li>A sample collected of the first water released into the canal for delivery to Boulder;</li> <li>A sample collected when the canal begins normal operations;</li> <li>Frequent samples are collected through May to track the decrease in concentrations of the detected compounds.</li> </ol> </li> </ul>		
2016- 2020	Additional monitoring on the Poudre River was conducted to establish a baseline of emerging contaminants data to assist in evaluating water quality in the Poudre River for assessment of various NISP alternative locations. Monitoring was completed in 2020 as the location for NISP diversion in the Poudre River was selected.		
2017- 2024	The City of Loveland began sampling at six additional sites in 2017 at the City of Loveland Water Treatment Plant and Water Reclamation Facility. In 2024 these six sites were added to the routine monitoring program.		
2020- Present	5 1		

# **APPENDIX E – COMPOUNDS ANALYZED**

Table 4 - LC/Q-TOF-MS analyzed compounds

Compound Type	Compounds Analyzed
Herbicides	Acetamiprid, Acetochlor, Alachlor, Azoxystrobin, Bromuconazole, Buprofezin, Carbaryl, Carbendazim, Carbofuran, Chlorpyrifos-methyl, Cyproconazole, Cyromazine, Deethylatrazine, Deisopropylatrazine, Dichlorvos, Difenoconazole, Diflubenzuron, Dimethenamide, Dimethoate, Dimethomorph, Ethoprop, Flufenacet, Fluroxypyr, Hydroxyatrazine, Imazapyr, Imidacloprid, Iprodione, Isoproturon, Isoxaben, Isoxaflutole, Malathion, Metalaxyl, Methidathion, Methiocarb, Methiocarb sulfone, Methomyl, Metolachlor, Metribuzin, Nicosulfuron, Oxyfluorfen, Parathion-methyl, Pendimethalin, Phosmet, Piperonyl butoxide, Profenofos, Prometon, Propazine, Propiconazole, Propoxur, Prosulfuron, Simazine, Spinosyn A, Spinosyn D, Tebuconazole, Tebufenozide, Terbuthylazine, Thiacloprid, Thiophanate-methyl, and Triflumizole.
Benzotriazoles	4-methyl benzotriazole, 5-methyl benzotriazole, Benzothiazole, and Benzotriazole.
Manufacturing	Melamine, Tributyl phosphate, Triphenylphospate, and Tris(2-chloroethyl) phosphate.
Opiod	Codeine, Desmethyl-tramadol, Dihydrocodeine, Fentanyl, Hydrocodone, Methadone, and Oxycodone.
Rx	1,7 Dimethylxanthine, 10-Hydroxycarbamazepine, Acetaminophen, Albuterol, Amphetamine, Atorvastatin, Azithromycin, Caffeine, Cannabidiol, Cimetidine, Dehydronifedipine, Desmethyl-venlafaxine, Dextromethorphan, Diazepam, Diclofenac, Erthyromycin Anhydrate, Erythrohydro-bupropion, Fluoxetine, Gabapentin, Ibuprofen, Iopromide, Lamotrigine Glucuronide, Meprobamate, Metformin, Miconazole, Naproxen, Ranitidine, Sulfadimethoxine, THC, Triclocarban, and Warfarin.
Other	Sucralose and Thiabendazole.

#### Table 5 - Low level LC/Q-TOF-MS analyzed compounds.

Compound Type	Compounds Analyzed
Herbicide	2,4-D, Atrazine, Diazinon, Diuron, Fluridone, Imazamox, Penoxsulam, Topramezone, and Triclopyr.
Manufacturing	Bisphenol A
Personal Care Product	Deet and Triclosan
Opiod	EDDP and Tramadol
Rx	Atenolol, Bupropion, Carbamazepine, Clarithromycin, Cotinine, Dextrorphan, Diltiazem, Diphenhydramine, Erthyromycin, Fexofenadine, Gemfibrozil, Lamotrigine, Metoprolol, Propranolol, Sulfamethoxazole, Trimethoprim, and Venlafaxine.

Table 6 - LC/Q-TOF-MS (positive/negative ion) hormone compounds.

Compound Type	Compounds Analyzed
Endocirne Disruptor	17-a-Ethinylestradiol, 17-b-Estradiol, 4-Androstene-3,17-dione, Equilin, Estriol, Estrone, Progesterone, and Testosterone

#### Table 7 - LC/Q-TOF-MS fracking family compounds.

Compound Type	Compounds Analyzed
Polypropylene Glycol	PEG-EO7, PEG-EO8, PEG-EO9, PEG-EO10, PEG-EO11, PPG-EO5, PPG-EO6, PPG-EO7, PPG-EO8, PPG-EO9, C10-EO4, C10-EO5, C10-EO6, C10-EO7, and C10-EO8

## **APPENDIX F – CEMS SOP**

#### **CEMS Sampling Protocol – Updated March 2021**

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 March 2021

#### **Sampling Procedures for Soil and Ash Samples:**

All samples will be collected in baked (or new) glass jars of approximately 250 mL volume with Teflon lined capes to ensure sample purity. Because of the occurrence of surfactants on plastic gloves, it is preferred that they not be used. Rather a spatula or similar device is used to take the soil sample and transfer into the glass jar without touching the sample with ones' hands. Fill the jar to the top and replace lid. Do not freeze the samples.

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  $\pm 4^{\circ}$ 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.

#### **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  $\pounds$ 4°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.

