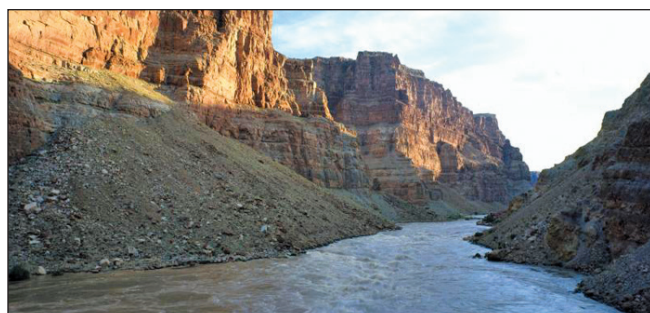




Screening for Contaminants of Emerging Concern in the Northern Colorado Plateau Network, 2013

Natural Resource Technical Report NPS/NCPN/NRTR—2014/923



ON THE COVER

Downward from top left: Colorado River at Big Drops, Canyonlands National Park; Yampa River, Dinosaur National Monument; Fremont River, Capitol Reef National Park; Hansen Cave Lake, Timpanogos Cave National Monument. NPS photos.

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The National Park Service Natural Resource Stewardship and Science office in Fort Collins, Colorado, publishes a range of reports that address natural resource topics. These reports are of interest and applicability to a broad audience in the National Park Service and others in natural resource management, including scientists, conservation and environmental constituencies, and the public.

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All manuscripts in the series receive the appropriate level of peer review to ensure that the information is scientifically credible, technically accurate, appropriately written for the intended audience, and designed and published in a professional manner. This report received informal peer review by subject-matter experts who were not directly involved in the collection, analysis, or reporting of the data.

Views, statements, findings, conclusions, recommendations, and data in this report do not necessarily reflect views and policies of the National Park Service, U.S. Department of the Interior. Mention of trade names or commercial products does not constitute endorsement or recommendation for use by the U.S. Government.

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Executive Summary

After three years of sampling for pesticides and wastewater indicators and two years of sampling for pharmaceutical and personal care products (PPCPs), patterns of contamination are beginning to emerge in selected locations in Northern Colorado Plateau Network park units. The Colorado River at the Potash boat ramp, just upstream of Canyonlands National Park, has frequent (>30% of sample visits) detections of the herbicide 2,4-D; caffeine; the insect repellent, DEET; the pesticide degradation product, Metolachlor ESA; and the prescription antibiotic, sulfamethoxazole. A highly visited area in Middle Cave, at Timpanogos Cave National Monument, also has frequent detections of caffeine and DEET, although sample contamination has not been ruled out for this site. The Yampa River, at Deerlodge Park upstream of Dinosaur National Monument, continues to have a wide variety of contaminants of emerging concern detected, although no contaminants have yet been shown to frequently occur. The Fremont River, at the Hickman Bridge trailhead inside Capitol Reef National Park, has relatively few detections. Several PPCPs added to the analytical suite in 2013 occurred frequently at multiple sites, including the prescription drugs, gabapentin (used to treat seizure disorders and bipolar disorders) and metformin (used to treat diabetes). Sampling will continue in 2014 and 2015, with the continuation of surface water sampling and the addition of bed sediment sampling in coordination with the U.S. Geological Survey. A final report is expected in 2016.

Acknowledgements

Many thanks to Kristen Keteles, of the U.S. Environmental Protection Agency (EPA), Region 8, and Colleen Flanagan, of the National Park Service Air Resources Division, for coordinating support for this project. Ken Dahlin, EPA Region 8 laboratory manager, provided invaluable expertise in analyzing samples and interpreting quality assurance results. Andy Armstrong (Timpanogos Cave National Monument), Carolyn Hackbarth (Northern Colorado Plateau Network), Cami McKinney (Timpanogos Cave National Monument), Mary Moran (Canyonlands National Park), and Tamara Naumann (Dinosaur National Monument) organized sample collection.

1 Introduction

1.1 Background

The Northern Colorado Plateau Network (NCPN) provides long-term monitoring and other natural resource data to 16 national park units throughout Utah, western Colorado, southern Wyoming, and northern Arizona. In 2010, in cooperation with the Environmental Protection Agency (EPA) Region 8, NCPN began screening selected surface waters in NCPN parks for pesticides, pesticide degradation products, and wastewater indicators. After a sampling hiatus in 2011, pharmaceuticals and personal care products (PPCPs) were added to the analytical suite in 2012. These analytes, collectively known as contaminants of emerging concern (CECs), have been detected in a variety of NCPN waters (Weissinger et al. 2013). Contaminants of emerging concern are trace organic compounds that are not commonly tested for during routine water quality monitoring but may have adverse effects on aquatic and terrestrial life at very low (sub part per billion) concentrations (Battaglin and Kolok 2014).

This is an interim report. For more details on the background of this project, see Weissinger and others (2013).

1.2 Sampling locations

In 2013, four sites that had previously shown high numbers of CECs or detection levels of concern (Weissinger et al. 2013) were targeted for additional sampling: the Colorado River near Canyonlands National Park (NP), the Fremont River in Capitol Reef NP, the Yampa River near Dinosaur National Monument (NM), and Middle Cave Lake in Timpanogos Cave NM (Table 1-1; Figure 1-1). A more remote location in Timpanogos Cave NM, Hansen Cave spring, was sampled in 2013 as a comparison for the high visitor-use area sampled in Middle Cave.

Sites were typically sampled by park personnel on a monthly or bi-monthly basis, depending on the availability of sample allocations from the EPA Region 8 laboratory. No sampling occurred in October 2013 due to a shutdown of the federal government.

Table 1-1. Northern Colorado Plateau Network waters sampled in 2013 for pesticides, pesticide degradation products, pharmaceuticals and personal care products, and wastewater indicators.

Park unit	Site	STORET ID	Datum	Latitude	Longitude
Canyonlands NP	Colorado River at Potash boat ramp	4956290	NAD83	38.50553859	-109.6595616
Capitol Reef NP	Fremont River at Hickman Bridge trailhead	4954360	NAD83	38.28859102	-111.2348913
Dinosaur NM	Yampa River at Deerlodge Park	09260050	NAD83	40.45163387	-108.525101
Timpanogos Cave NM	Middle Cave Lake Bridge	NA	NAD83	40.43796018	-111.7105406
	Hansen Cave Spring in TICA	4994970	NAD83	40.437639	-111.710778

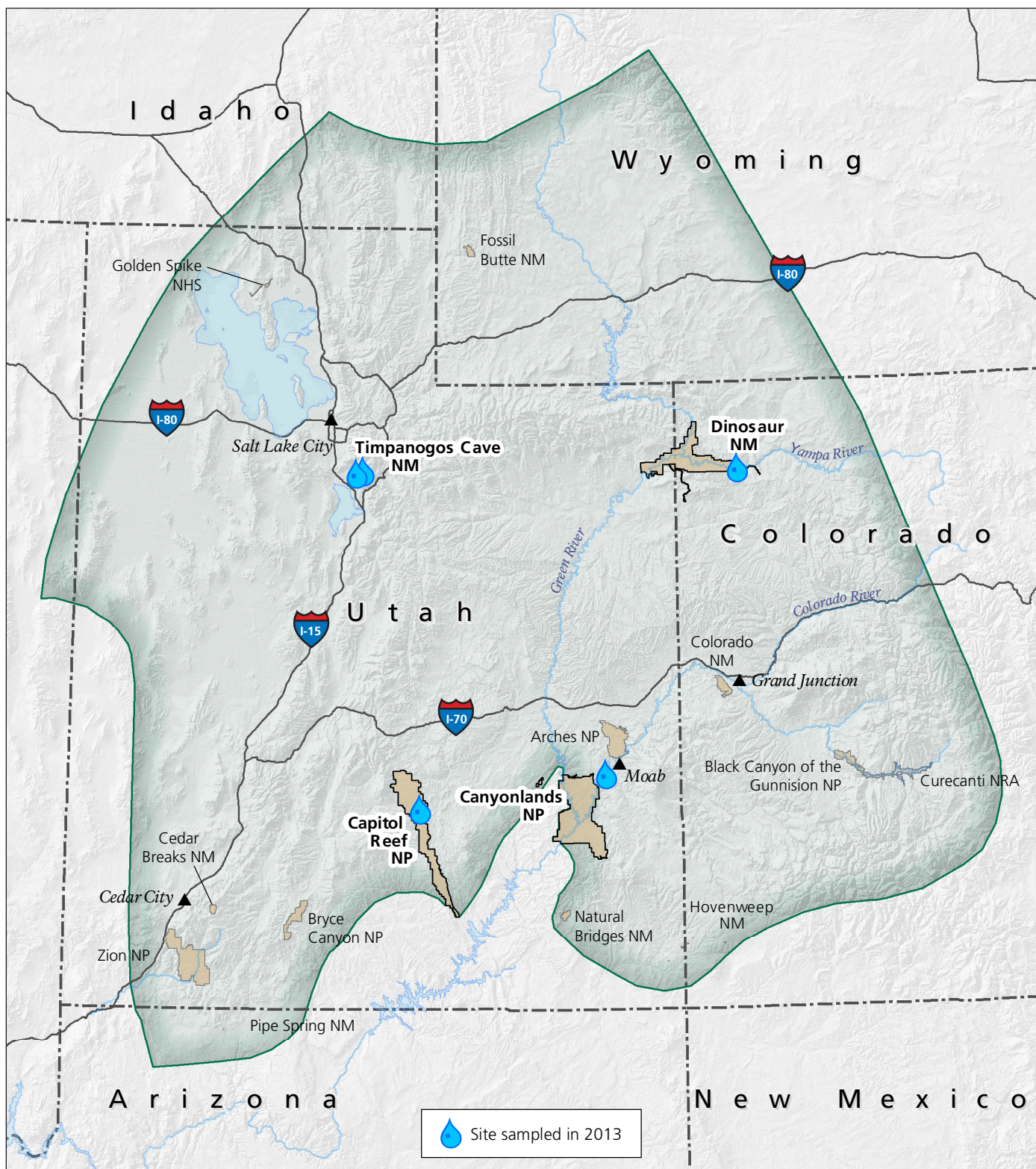


Figure 1-1. Park units in the Northern Colorado Plateau Network, with parks sampled in 2013 highlighted.

2 Methods

2.1 Sampling

Sample bottles and coolers were provided by the EPA laboratory. Park personnel put on clean gloves for each sample, dipped and rinsed the sample bottles in source water twice, then collected grab samples of the source water. Sample bottles were labeled and immediately placed on ice. Samples were packed in ice and shipped overnight to the EPA lab as soon as possible after sampling (maximum hold time of five days).

Laboratory analysis methods used are shown in Table 2-1. Pesticide and PPCP samples were filtered at the laboratory, and the dissolved fraction was analyzed. Wastewater samples were not filtered, and the total sample was analyzed. Water samples were analyzed for 69 pesticides and pesticide-degradation products, 143 PPCPs, and 53 wastewater-indicator compounds. A table of all analytes and the lowest concentration at which they are reported (the laboratory reporting limit, usually 2–10 times the method detection limit) is provided in Appendix A. Results that fall between the method detection limit and the laboratory reporting limit are not available for analysis.

PPCP samples collected in May, June, and July were analyzed outside of their desired holding time due to processing limitations at the laboratory. PPCPs are considered robust to holding-time exceedances, and the data are presented as estimated, with a J-flag.

2.2 Quality assurance

Quality assurance was performed through the use of blank and replicate samples in the field and additional procedures conducted in the laboratory.

2.2.1 Field blanks

Field-blank samples, which use “blank water” (water known to be analyte-free) provided by the EPA, are processed at the field site in the same manner and using the same equipment as the environmental samples. The purpose of a field blank is to determine whether contamination is being introduced during sample collection and handling; ideally, the results from field blanks should be analyte-free. Field blanks are evaluated with the benchmark of no detection for every parameter.

If a field blank has a detected level of an analyte, then the field blank is compared to source-water samples. If the level of an analyte in the source water is detected at 0–2× the level detected in the field blank, then the source-water samples are considered to be contaminated and recorded as Not Detected in the database. If the level of an analyte in the source water is detected at 2–5× the level detected in the field blank, then the results are reported as Detected, without an estimated value. If the level of an analyte in the source water is detected at more than 5× the level detected in the field blank, then the detection is considered robust to contamination and the results are retained.

Table 2-1. Analysis methods and sample requirements for the EPA Region 8 laboratory.

Parameter	Analytical method	Sample volume	Container size and type	Preservation	Maximum holding time
Pesticides and pesticide degradation products	Liquid Chromatography–Mass Spectrometry. EPA Method 8321A, EPA R8 Laboratory SOP ORGM-550 (2013a)	40 ml	Sterile 40-ml amber glass volatile organic analysis (VOA) vials	Ice to 2–6°C	7 days
PPCPs	Liquid Chromatography–Mass Spectrometry. EPA Method 1694 EPA R8 Laboratory SOP ORGM-001 (2013b)	40 ml	Sterile 40-ml amber glass VOA vials	Ice to 2–6°C	7 days
Wastewater Indicator Compounds	Gas Chromatography–Mass Spectrometry. EPA R8 Laboratory SOP ORGM-006 (2011)	250 ml	Sterile 250-ml amber glass vials	Ice to 2–6°C	7 days to extraction

Field blanks were submitted for 5 of 23 (22%) sampling visits for pesticides, PPCPs, and wastewater-indicator samples. Each individual who regularly collected samples submitted at least one set of field blanks. Field blanks for pesticides, PPCPs, and wastewater indicators submitted by Dinosaur NM in May 2013 met the quality assurance/quality control (QA/QC) goal of having no detections. Field blanks submitted by Canyonlands NP in August 2013 had a positive detection for the PPCP, caffeine. Caffeine was also detected in the source-water sample and replicate (see Section 2.2.2) within 2× the level detected in the field blank. The source-water and replicate sample detections were changed to Not Detected in the database and not reported.

Field blanks submitted by the NCPN on behalf of Capitol Reef NP in June and November 2013 had positive detections of the PPCPs, methylparaben (both occasions) and caffeine (Nov.), and the wastewater indicators, Bisphenol A (June) and acetophenone (Nov.). The same bottle of blank water was used on both occasions. Methylparaben was detected in a source-water sample in June at roughly 10× the amount detected in the field blank, but it was not detected in a replicate source-water sample in June or in the source water sample in November. The source-water detection in June was retained and flagged as Estimated. Bisphenol A was detected at similar levels to the field blank in the source-water sample but was not detected in the replicate source-water sample. The source-water sample was recorded as Not Detected for Bisphenol A. In November, caffeine was detected in the source-water sample at a level within 2× the level detected in the field blank, and it was recorded as Not Detected. Acetophenone was not detected in the source-water sample in November.

Field blanks submitted by Timpanogos Cave NM in September 2013 used commercial distilled water rather than blank water provided by the EPA. Twenty-one analytes were detected in the field blanks: 1 pesticide, 5 PPCPs, and 15 wastewater indicators. DEET was reported in source-water and replicate samples for that month, and caffeine was reported near the reporting limit in one source-water sample. All three detections were well below the amounts reported for

the field blank, and they were changed to Not Detected and not reported.

Field blanks continue to be a source of concern. Commercial distilled water is clearly not suitable for use, as was shown in 2012 (Weissinger et al. 2013) and again in 2013.

2.2.2 Replicate samples

Replicate samples are collected concurrently with environmental samples and processed in the same lab. The purpose of a replicate is to determine the variability introduced from collection, processing, shipping, and laboratory handling; ideally, the results from replicate samples should be identical to those from concurrently collected environmental samples. Replicate samples are evaluated with the benchmark that all detected parameters are within 30% relative percent difference (RPD) of those detected in the environmental sample. RPD is calculated as the percent difference between the detected amounts, divided by the average of the amounts: $(A-B)/((A+B)/2)*100$.

A non-detected parameter in the environmental sample should also be non-detected in the replicate sample. If a parameter is detected in one sample, but not the other, then the detected result should be within 30% of the reporting limit. When original samples and their replicates are entirely composed of non-detects, it is assumed that the analyses are falling within the desired precision.

Replicate samples were submitted for 5 of 23 (22%) sampling visits for pesticides, PPCPs, and wastewater indicator samples, for a total of 1,274 comparisons. Each individual who regularly collected samples submitted at least one set of replicates. In 1,251 of 1,274 comparisons (98%), both the environmental and the replicate samples were non-detects and were assumed to meet precision goals.

Analytes that were detected in both the environmental and the replicate samples were compared to determine whether the analysis met the precision goal (12 comparisons). Analytes in which one replicate had a detected amount and the other replicate was a non-detect were compared by adding 30% to the reporting limit and seeing if the detected amount fell within this range (11 compari-

sons). Following these criteria, 4 of 23 comparisons (17%) had an RPD of >30%. In all these cases, the analyte was detected in one sample but not the other. These analytes are reported with a note indicating the RPD was higher than the desired range.

2.2.3 Laboratory measures

Laboratory QA/QC measures include laboratory (1) blanks that test for contamination during the analysis process, (2) spikes in which an analyte of known concentration is analyzed, and the percent recovery of the known amount is recorded*, and (3) duplicates that test for precision. For pesticides and pesticide degradation products, the acceptance criteria are +/- 20% of the matrix spikes, duplicates, and blanks. For PPCPs and wastewater indicators, the acceptance criteria are +/- 30% of the matrix spikes, duplicates, and blanks. Analytes may be flagged for any single or combination of reasons.

Thirty-six of 173 detected analytes were flagged for analytical reasons. Of those, 20 were analyzed in the same batch as a contaminated laboratory blank. For these analytes, the detected amount was compared to the amount reported for the laboratory blank.

If the detected amount in the source-water sample was within 2× the amount reported for the blank, then the data were not reported (i.e., set to Not Detected). A source-water detection 2–5× the field-blank detection was reported as Detected without an estimated value. If the amount in the source water was more than 5× the amount reported for the contaminated blank, then the data were reported as estimated, with a J-flag.

In 19 cases, analytes were flagged as having greater than 120–130% recovery of a spike. If the detected amount in the source-water sample was within 200% of the reporting limit, then data were reported as Detected without an estimated value. If the source-water detection was more than 200% of the reporting limit, then the data were reported as estimated with a J-flag. The remaining analytically flagged data were reported as estimated, with a J-flag. In two cases, analytes were flagged for low recovery (<70–80%). One analyte was detected outside the calibrated range for the test and should be considered as reported at the lower boundary of its actual concentration.

*For example, if 50 ng/L of caffeine was added to a sample and the analyzed result said 52.3 ng/L, then the “percent recovery” would be 104.6%.

3 Results

All data for this project are publicly accessible through the EPA Storage and Retrieval database, available at <http://www.epa.gov/storet/>. To access the data, select the Organization Name: 11NPSWRD_WQX and the Project Name: NPS_3P EPA/NPS Emerging Contaminants Program (3P).

3.1 Canyonlands National Park

The Colorado River at the Potash boat ramp was sampled four times in 2013: in April, June, August, and November. Twenty-seven unique CECs have been detected in the Colorado River at the Potash boat ramp since sampling began in 2010, twenty-three of which were detected at least once in 2013 (Table 3-1, Figure 3-1, pages 8–9). Replicate samples were collected in August. Several CECs continue to be detected on a regular basis (>30% of samples for CECs sampled at least 8 times from 2010 to 2013; Figure 3-2), including 2,4-D (9 of 10 samples), caffeine (5 of 10), DEET (3 of 8), Metolachlor ESA (5 of 10), and sulfamethoxazole (6 of 8). Several PPCPs newly added to the analysis suite frequently occurred in 2013: desmethylvenlafaxine (2 of 4 samples in 2013), gabapentin (4 of 4), lamotrigine (3 of 4), and metformin (4 of 4).

3.2 Capitol Reef National Park

The Fremont River at the Hickman Bridge trailhead was sampled five times in 2013: in April, June, July, September, and November. Nine unique CECs have been detected at this site since sampling began in 2010, seven of which were detected at least once in 2013 (Table 3-2, Figure 3-3, page 10). Replicate samples were collected in June. None of the CECs has been detected on a regular basis (>30% of samples for CECs with at least 8 samples). As in past years, the majority of detections occurred in June or July (3 unique analytes in each month, none of which overlapped between months, Figure 3-4).

3.3 Dinosaur National Monument

The Yampa River at Deerlodge Park was sampled seven times in 2013: in April, May, June, July, August, September, and November. Thirty-seven unique CECs have been detected at this site since sampling began in 2010, twelve of which were detected at least once in 2013

(Table 3-3; Figure 3-5, pages 11–12). Replicate samples were collected in April and May. Of CECs with at least 8 samples from 2010 to 2013, none was present on more than 30% of sampling occasions, although 2,4-D, Bisphe-nol A, and caffeine approached this number (5 of 19 samples since 2010). Two new PPCPs frequently occurred in 2013: gabapentin (6 of 7 samples in 2013) and metformin (7 of 7, Figure 3-6).

3.4 Timpanogos Cave National Monument

Middle Cave Lake at the visitors' bridge was sampled four times in 2013: in May, July, September, and November. Thirteen unique CECs have been detected at this site since sampling began in 2010, nine of which were detected at least once in 2013 (Table 3-4; Figure 3-7, pages 13–14). Replicate samples were collected in September. Caffeine and DEET continue to be detected on a regular basis (>30% of samples for CECs with at least 8 samples from 2010 to 2013; 7 of 13, and 5 of 8 samples, respectively; Figure 3-7). Three new PPCPs occurred in 2 of 4 samples in 2013: methylparaben, theobromine, and theophylline (Figure 3-8).

Hansen Cave spring was added to CEC sampling this year as a more remote contrast to the heavily visited area in Middle Cave. Previously, a less-visited area of Middle Cave Lake was sampled to compare to the visitor area, but overlap in contaminants during sampling in 2010 and 2012 raised questions as to whether the sites were independent (Weissinger et al. 2013). The hydrology of the Timpanogos Cave system is largely unknown. It is hoped that by sampling the more remote site in Hansen Cave, visitor impacts in Middle Cave can be better assessed.

Seven unique CECs were detected in Hansen Cave spring in 2013, over three sampling visits in May, July, and November (Table 3-5). CEC detections in Hansen Cave closely tracked CECs found at the Middle Cave Lake visitor area, as was the case for previous years of data in comparing the highly visited site with a less-visited site in Middle Cave (Weissinger et al. 2013). In conjunction with a heavily contaminated field blank submitted in September 2013 (see Section 2.2.1), contamination cannot be ruled out for the results at Timpanogos Cave NM.

Table 3-1. Contaminants of emerging concern detected in the Colorado River at the Potash boat ramp, Canyonlands National Park, 2013.

Analyte	Sample type	Concentration (ng/L)			
		Apr	Jun	Aug	Nov
Atenolol	Environmental	16.8	ND	ND	ND
2,4-D	Environmental	ND	63.8	74.2	51.5
	Replicate	-	-	79.4	-
Benzophenone	Environmental	66.3	ND	ND	ND
Bisphenol A	Environmental	ND	Detected	70.7 ^a	ND
	Replicate	-	-	<50.0 ^a	-
Caffeine	Environmental	96.3	ND	ND	ND
	Replicate	95	-	-	-
DEET	Environmental	ND	ND	16 ^a	16.6
	Replicate	-	-	23.7 ^a	-
Desmethylvenlafaxine	Environmental	13.4	10.2	ND	ND
Gabapentin	Environmental	509	124	161	82.6
	Replicate	-	-	153	-
Hydrochlorothiazide	Environmental	ND	ND	11	ND
	Replicate	-	-	<10	-
Hydroxybupropion	Environmental	12.8	ND	ND	ND
Lamotrigine	Environmental	34.3	ND	11.5	11.4
Levorphanol	Environmental	11.1	ND	ND	ND
Metformin	Environmental	210	39.1	53.1	35.9
	Replicate	-	-	51	-
Metolachlor ESA	Environmental	ND	ND	26.2	ND
	Replicate	-	-	30.5	-
Paraxanthine	Environmental	26.1	ND	ND	ND
Pregabalin	Environmental	12.1	ND	ND	ND
Sulfamethoxazole	Environmental	41.9	ND	12.8	ND
	Replicate	-	-	15	-
Theobromine	Environmental	146 J ¹	ND	ND	ND
Theophylline	Environmental	30.3	ND	ND	ND
Tri(2-butoxyethyl) phosphate	Environmental	ND	1140 J ²	ND	ND
Tri(2-chloroethyl) phosphate	Environmental	ND	ND	ND	138 J ²
Tri(dichloroisopropyl) phosphate	Environmental	ND	ND	ND	Detected
Triphenyl phosphate	Environmental	ND	ND	ND	73.8

^a Replicate samples not within 30% RPD. ng = nanogram

J¹ matrix spike acceptance criteria not met (low)

J² control sample acceptance criteria not met (high); detected value is >200% of recovery

Table 3-2. Contaminants of emerging concern detected in the Fremont River at the Hickman Bridge trailhead, Capitol Reef National Park, 2013.

Analyte	Sample type	Concentration (ng/L)				
		Apr	Jun	Jul	Sep	Nov
2,4-D	Environmental	ND	ND	19.1	ND	ND
Bisphenol A	Environmental	ND	67.1	ND	ND	ND
	Replicate	-	<50.0	-	-	-
Caffeine	Environmental	ND	ND	49.9 J	ND	ND
DEET	Environmental	ND	23.9 J ^a	ND	ND	ND
	Replicate	-	<10 J ^a	-	-	-
Methylparaben	Environmental	ND	223 ^a	ND	ND	ND
	Replicate	-	<10.0 ^a	-	-	-
p-Cresol	Environmental	123	ND	ND	ND	ND
Tri(2-butoxyethyl) phosphate	Environmental	ND	ND	Detected	ND	ND

^a Replicate samples not within 30% RPD.

J Analyzed outside of holding time.

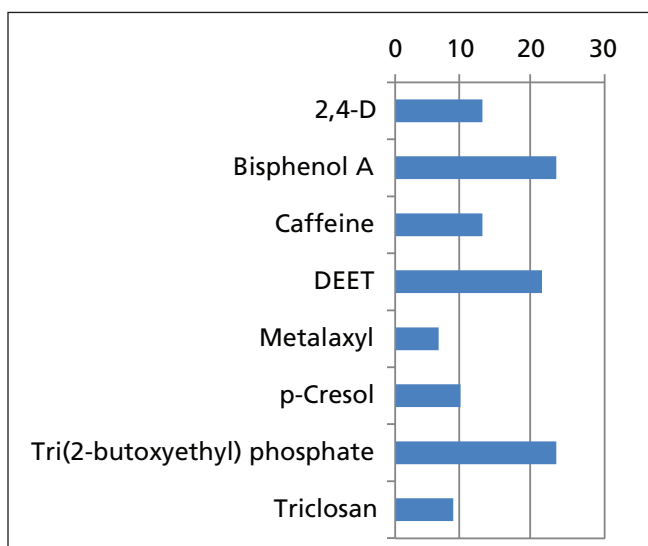


Figure 3-3. Frequency of detections for all detected CECs with more than 8 sample visits since 2010 in the Fremont River at the Hickman Bridge trailhead, Capitol Reef National Park.

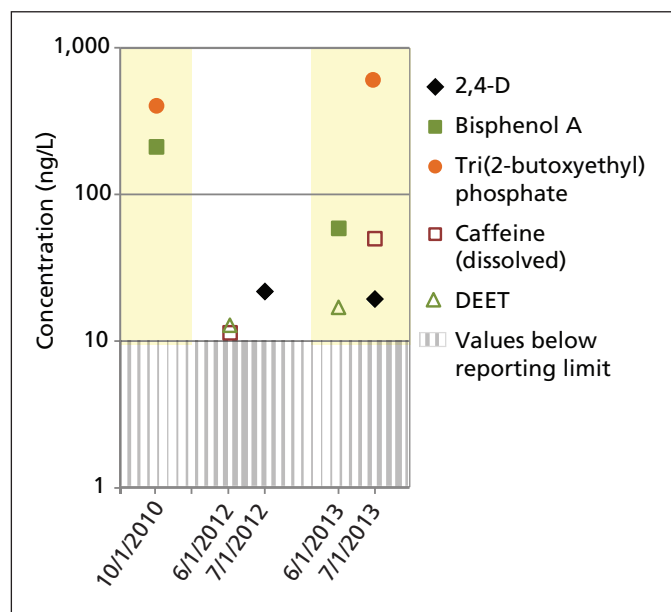


Figure 3-4. Concentrations of CECs with more than one detection since 2010, Capitol Reef National Park. Filled markers represent CECs that have been analyzed since 2010, hollow markers since 2012. Estimated data are included in the figure.

Table 3-3. Contaminants of emerging concern detected in the Yampa River at Deerlodge Park, Dinosaur National Monument, 2013.

Analyte	Sample type	Concentration (ng/L)						
		Apr	May	Jun	Jul	Aug	Sep	Nov
2,4-D	Environmental	ND	ND	ND	22.3	ND	ND	ND
Bisphenol A	Environmental	ND	ND	ND	55.6	ND	ND	ND
Bromacil	Environmental	ND	ND	ND	ND	ND	ND	142 J ²
Caffeine	Environmental	ND	ND	ND	63.2 J ¹	41	ND	18.6
Camphor	Environmental	ND	ND	ND	ND	ND	174	ND
DEET	Environmental	ND	ND	ND	26.2 J ¹	12.4	ND	ND
Gabapentin	Environmental	55.1	10.5 J ¹	ND	75.2 J ¹	28.5	56.2	42.6
	<i>Replicate</i>	52	<10.0 J ¹	-	-	-	-	-
Lamotrigine	Environmental	10.9	ND	ND	ND	ND	17.3	ND
	<i>Replicate</i>	<10.0	ND	-	-	-	-	-
Metformin	Environmental	86.9	15.3 J ¹	17.0 J ¹	40.8 J ¹	56.8	42.4	31.5
	<i>Replicate</i>	88.2	13.4 J ¹	-	-	-	-	-
Sulfamethoxazole	Environmental	ND	ND	ND	ND	ND	10.5	ND
Theobromine	Environmental	ND	ND	12.9 J ¹	ND	ND	ND	ND
Tri(dichloroisopropyl) phosphate	Environmental	ND	ND	ND	ND	70.4	ND	ND

J¹ Analyzed outside of holding time.

J² Calibration criteria not met (high); detected value >200% of reporting limit

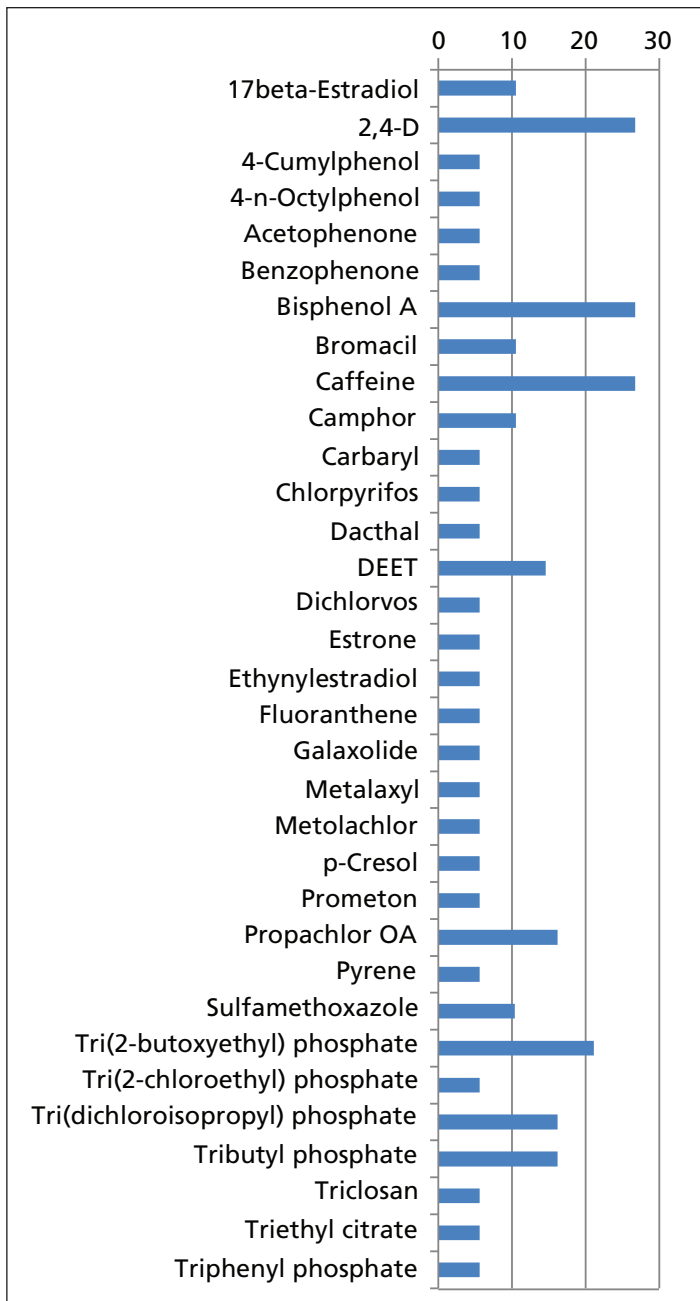


Figure 3-5. Frequency of detections for all detected CECs with more than 8 sample visits since 2010 in the Yampa River at Deerlodge Park, Dinosaur National Monument.

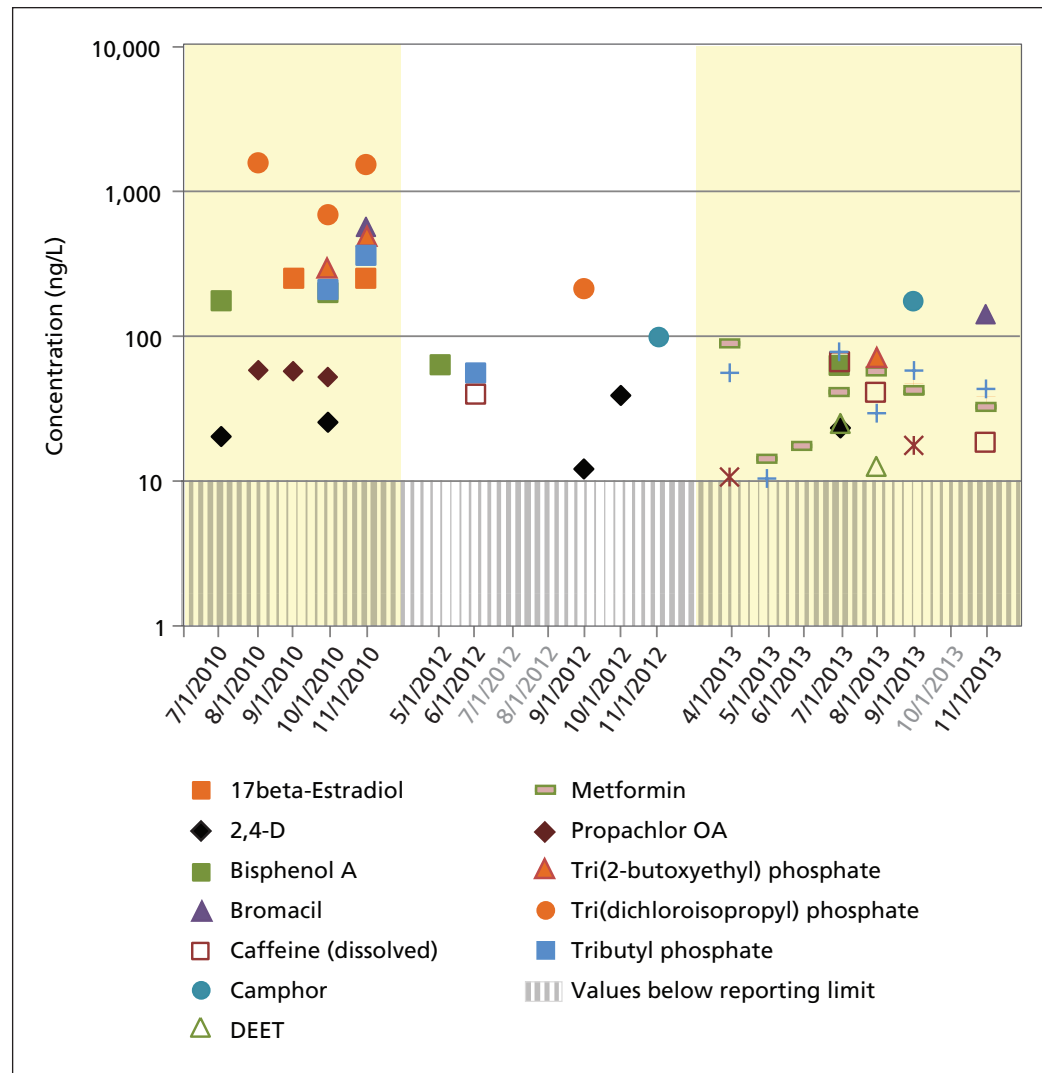


Figure 3-6. Concentrations of CECs with more than one detection since 2010, Dinosaur National Monument. Filled markers represent CECs that have been analyzed since 2010, hollow markers represent CECs added since 2012, and line markers represent CECs added in 2013. Estimated data are included in the figure.

Table 3-4. Contaminants of emerging concern detected in Middle Cave Lake at the visitors' bridge, Timpanogos Cave National Monument, 2013.

Analyte	Sample type	Concentration (ng/L)			
		May	Jul	Sep	Nov
Acetaminophen	Environmental	ND	17.2	ND	ND
Caffeine	Environmental	411	52.1	ND	20.4 ^a
	<i>Replicate</i>	-	-	-	129 ^b
DEET	Environmental	44.1	62.9	ND	ND
Galaxolide	Environmental	ND	76.8	ND	132
Methylparaben	Environmental	50.8	14.4	ND	ND
Paraxanthine	Environmental	172	ND	ND	ND
Theobromine	Environmental	543	109	ND	ND
Theophylline	Environmental	187	13.2	ND	ND
Tri(2-butoxyethyl) phosphate	Environmental	ND	ND	ND	Detected

^a Dissolved fraction

^b Total

Table 3-5. Contaminants of emerging concern detected in Hansen Cave spring, Timpanogos Cave National Monument, 2013.

Analyte	Concentration (ng/L)		
	May	Jul	Nov
Methylparaben	2,810 J ¹	14.1	ND
Caffeine	159	83.0	87.2 J ²
DEET	14.6	11.4	ND
Ethinylestradiol	ND	ND	119
Paraxanthine	45.9	ND	11.6 J ³
Theobromine	277	135	85.3
Theophylline	47.0	14.3	20.4

No replicate samples taken.

J¹ Result outside of quantitation range; detected value is lower bound of true value

J² Matrix spike duplicate criteria not met (high); detected value >200% of reporting limit

J³ Matrix spike duplicate criteria not met (low)

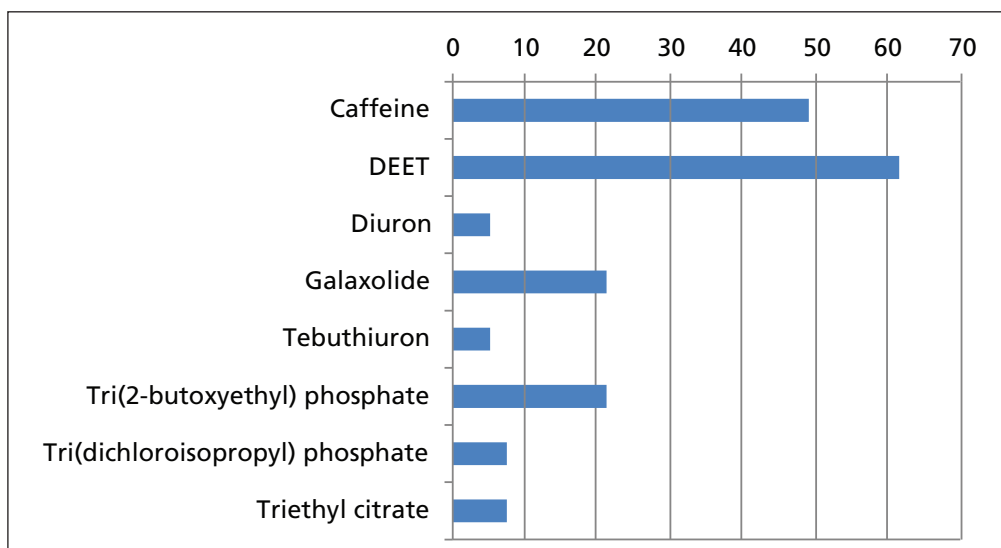


Figure 3-7. Frequency of detections for all detected CECs with more than 8 sample visits since 2010 in Middle Cave Lake at the visitors' bridge, Timpanogos Cave National Monument. CECs detected at more than 30% of visits are potentially chronic contaminants at the site.

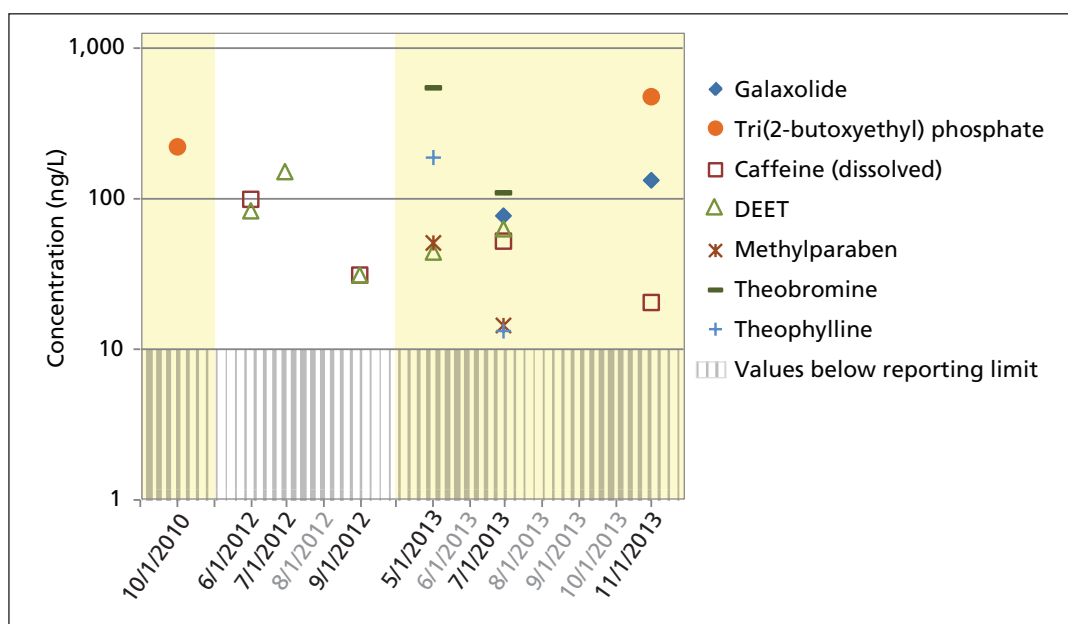


Figure 3-8. Concentrations of CECs with more than one detection since 2010, Timpanogos Cave National Monument. Filled markers represent CECs that have been analyzed since 2010, hollow markers since 2012, and line markers represent CECs added in 2013. Estimated data are included in the figure.

4 Discussion

CEC sampling of NCPN surface waters will continue in 2014 and 2015, in conjunction with EPA Region 8. In addition, a separately funded project to analyze bed sediments for endocrine-disrupting hormones was initiated with the U.S. Geological Survey in 2014. Surface-water and bed-sediment samples will be co-sampled in 2014 and 2015 to provide a more complete understanding of how CECs accumulate and are transported in NCPN aquatic systems.

In addition to the sites featured in this report, sampling locations will be added in Arches, Bryce

Canyon, and Canyonlands NPs, Dinosaur NM, and Zion NP in 2014 and 2015. To provide a survey of CECs and endocrine-disrupting hormones in NCPN waters, sampling will occur during conditions of high and low flow, and periods of high and low visitation, at a broad array of sites—from isolated springs to inter-regional rivers. Several new sites will be sampled along the Green River to improve our understanding of the distribution of CECs in the major tributaries to the Colorado River. Bioassay and tissue sampling will be done using a subsample of sites in 2015, to determine the bioactivity of some sampled source water. A final report is expected in 2016.

5 Literature Cited

- Battaglin, W. A., and A. Kolok. 2014. Featured collection introduction: Contaminants of emerging concern II. *Journal of the American Water Resources Association* 50(2):261–265.
- EPA Region 8 Laboratory. 2011. Technical standard operating procedure ORGM-006 v.1.0. Determination of waste indicator compounds in water by GC/MS. Golden, Colorado.
- EPA Region 8 Laboratory. 2013a. Technical standard operating procedure ORGM-550 v.1.0. Determination of pesticides and herbicides in water by direct aqueous injection LC/MS/MS. Golden, Colorado.
- EPA Region 8 Laboratory. 2013b. Technical Standard Operating Procedure ORGM-001 v.1.0. Determination of pharmaceuticals and personal care products (PPCPs) in water by direct aqueous injection LC/MS/MS. Golden, Colorado.
- Weissinger, R., D. Thoma, K. Dahlin, and K. Keteles. 2013. Screening for contaminants of emerging concern in the Northern Colorado Plateau Network, 2010 and 2012. Natural Resource Technical Report NPS/NCPN/NRTR—2013/802. National Park Service, Fort Collins, Colorado.

Appendix A (All Analytes and the Lowest Concentration at Which They Are Reported)
is available as an .xls attachment to the electronic version of this document.

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