Unregulated and Emerging Contaminants in Tribal Water

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Abstract: Emerging contaminants in Tribal water have been unexplored until implementation of the Unregulated Contaminant Monitoring Rule (UCMR) campaigns, which mandated the analysis of up to 30 new contaminants in drinking water every five years. As additions to the Safe Water Drinking Act (SDWA), the UCMR1 - 3 were created to assess contaminants which have not yet been assigned a maximum contaminant level (MCL) but may be regulated in the future to protect human health. While a handful of Tribes (n = 6) participated in UCMR1, public water systems (PWS) within reservation boundaries were intentionally included in representative nation-wide sampling beginning with UCMR2 after a period of Tribal consultation. Still, less than 3% of Tribal PWS were surveyed. The results from UCMR2 revealed that samples from all surveyed Tribal PWS fell below the method detection limits. Target analytes shifted to metals, perfluorinated chemicals, hormones, volatile organic compounds (VOCs), dioxane, and chlorate under UCMR3. Detectable levels of metals (chromium, hexavalent chromium, strontium, and vanadium), chlorate, and dioxane were observed, and in some cases, at concentrations greater than the U.S. Environmental Protection Agency's (EPA's) recommended health reference limit (HRL). The presence of elevated levels of vanadium, strontium, 1,4-dioxane, perfluorooctanesulfonate (PFOS), and chlorate defines a new set of emerging contaminants that needs to be considered with regards to risk, reporting and monitoring, and water treatment in Tribal drinking water.

Keywords: *Tribal Public Water Systems, Unregulated Contaminant Monitoring Rule, drinking water, emerging contaminants*

stablished in 1974, the Safe Drinking → Water Act (SDWA) regulates drinking water sources in the United States (EPA) 1986, 1999a). The SDWA enables the U.S. Environmental Protection Agency (EPA) to create primary and secondary contaminant standards that are then used by state and Tribal governments to implement water treatment practices. Primary drinking water standards set a maximum concentration level (MCL) for contaminants with regards to human health concerns and are enforceable by law. The SDWA includes National Primary Drinking Water Regulations which require monitoring and reporting results of drinking water systems and public notification in the case of a MCL or Treatment Technology (TT) violation.

In addition, the EPA created secondary standards for contaminants that are not considered to be a health risk but can result in unwanted aesthetic and cosmetic effects or become problematic to system equipment. Secondary standards are not enforced by the EPA, but some governments have independently chosen to regulate these contaminants. The SDWA sets these standards for both surface water and groundwater sources.

Tribal water quality within the United States follows the guidelines of the EPA's SDWA, where the sovereign nations must meet the MCL, TT, and subsequent ruled amendments when a water system serves greater than 25 consumers. Results are reported by the EPA, providing information on compliance, violations, and remedial actions taken, where necessary (EPA 2017a). Often, Tribal public water systems (PWS) are small facilities (<3,300 persons served), which may have issues in elevated violations for health-related requirements, monitoring, reporting, and notifications (Rubin 2013; Conroy-Ben and Richard 2018).

The Unregulated Contaminant Monitoring Rule (UCMR) was an amendment to the SDWA, which mandated the monitoring of up to 30 new contaminants every five years. There were four UCMR campaigns (UCMR1 - 4) as of 2019, covering metals, pathogens, and their associated toxins, and other emerging contaminants (Table 1). Each UCMR campaign is comprised of List 1 monitored contaminants and List 2 contaminants which are included in a screening survey. UCMR1 (2001 - 2005) List 1 chemicals were reserved for large facilities and select small facilities, while List 2 was for a subset of List 1 small facilities (EPA 1999b, 2019a). Under UMCR2 (2007 - 2011), all PWS serving greater than 10,000 people were required to participate, in addition to a select number of PWS serving less than 10,000 people (EPA 2007, 2019c). UCMR2 List 1 contained 10 chemicals for which there were established and well-adapted analytical methods. UCMR2 List 2 contaminants required the development of analytical methods. UCMR3 List 1 contaminants (2012 - 2016) were part of assessment monitoring, where samples from all large systems and a select number of facilities serving less than 10,000 people were analyzed for 21 chemicals (EPA 2012a, 2019d). UCMR3 List 2 included seven hormones to be monitored in all PWS greater than 100,000 customers, and select large and small facilities. Pre-screening (List 3) of select PWS was also conducted for two viruses (List 3), enterovirus and norovirus. As of October 2019, the UCMR4 campaign was on-going, where large groundwater systems were to monitor for non-cyanotoxin contaminants; groundwater and groundwater under the influence of surface water sources were to monitor additional contaminants (pesticides, alcohols, semivolatiles, metals, and brominated haloacetic acids) (EPA 2016b, 2019b).

Emerging contaminant monitoring and research in Tribal communities prior to and during the UCMR campaigns have been limited to a few published studies. Here, we discuss the major findings of the unregulated contaminant surveys in Tribal drinking water sources, pointing to the need to promote participation of PWS in Indian Country in UCMR campaigns and to target specific chemicals for future monitoring.

Methods

UCMR1 - 3 data were downloaded in October of 2019 (EPA 2012b, 2017c, 2017d). Data fields reported by the U.S. EPA included the PWS, facility, sampling point, water source (as surface water, groundwater, or groundwater under the influence of surface water), sampling event date, analytes, EPA analytical method, and other sample/ facility identifiers. Raw data (concentrations as µg/L) for each sampling point were averaged over the number of sampling events (up to four) during the respective UCMR. Tribal affiliations were assigned by matching the PWS identification number from the UCMR dataset to Tribal names and reservations listed in the EPA's Enforcement Compliance History Online (ECHO) (EPA 2017a). Public water systems and sampling points were de-identified, although these details are publicly available in downloaded data. Finally, surveyed Tribes may have more than one PWS, but only one to two PWS per Tribe were monitored under the UCMR.

Results and Discussion

The EPA selected a number of small (<3,300 customers) to large (>10,000 customers) PWS serving Indian Country under UCMR2 – 3 PWS to be tested for unregulated contaminants. As of October 2019, there were 1018 PWS within Tribal boundaries (EPA 2017a). Of these Tribal PWS, less than 2.9% were surveyed for the UCMR campaign (For UCMR1, n = 6 Tribal PWS or 0.6%; for UCMR2, n = 19 Tribal PWS or 1.9%; and for UCMR3, n = 30 Tribal PWS or 2.9%). The amount of non-Tribal PWS that participated in UCMR3 was 4%, pointing to Tribal underrepresentation during the UCMR campaign by at least ten systems.

Tribal PWS Size and Participation in UCMR1-3

Of the ~1000 Tribal PWS within Tribal boundaries, 26 were designated as large facilities

 Table 1. Contaminants monitored under each Unregulated Contaminant Monitoring Rule (UCMR) campaigns 1

 through 3. Lists under each UCMR specify contaminants targeted for select facility sizes. "Contaminants" refers to

 both chemicals and pathogens; UCMR1 and UCMR2 list chemicals only, while UCMR3 lists chemicals and viruses.

Rule	Class	Chemicals		
UCMR1				
List 1:	Herbicides	acetochlor, EPTC, molinate, terbacil; degradates: DCPA mono- and di-acid		
	Insecticide degradate	4,4'-DDE		
	Octane enhancer	MTBE		
	Organic precursors	2,4-dinitrotoluene, 2,6-dinitrotoluene		
	Oxygen additive	perchlorate		
List 2:	Combustion product	2,4,6-trichlorophenol, 2-methylphenol		
	Herbicide	diuron, linuron, prometon; by-product: 2,4-dichlorophenol		
	Insecticide	diazinon, disulfoton, fonofos, terbufos,		
	Organic precursor	1,2-diphenylhydrazine, nitrobenzene (List 1 & 2)		
	Industrial product	2,4-dinitrophenol		
UCMR2				
List 1:	Explosives	1,3-dinitrobenzene, 2,4,6-TNT, RDX		
	Flame retardants	2,2',4,4',5,5'-hexabromobiphenyl (HBB), 2,2',4,4',5,5'-hexabromodiphenyl ether (BDE-153), 2,2',4,4',5-pentabromodiphenyl ether (BDE-99), 2,2',4,4',6-pentabromodiphenyl ether (BDE-100), 2,2',4,4'-tetrabromodiphenyl ether (BDE-47)		
	Insecticides	dimethoate, terbufos sulfone		
List 2:	Acetanilides	acetochlor, alachlor, metolachlor; degradates: acetochlor ethane sulfonic acid, acetochlor oxanilic acid, alachlor ethane sulfonic acid, alachlor oxanilic acid, metolachlor ethane sulfonic acid, metolachlor oxanilic acid		
	Nitrosamines	N-nitroso-diethylamine (NDEA), N-nitroso-dimethylamine (NDMA), N-nitroso-di-n-butylamine (NDBA), N-nitroso-di-n-propylamine (NDPA), N-nitroso-methylethylamine (NMEA), N-nitroso-pyrrolidine (NPYR)		
UCMR3				
List 1:	Metals	Co, Cr, Cr6+, Mb, Sr, V		
	Oxyhalide anion	chlorate		
	PFCs	perfluorobutanesulfonic acid (PFBS), perfluoroheptanoic acid (PFHpA), perfluorohexanesulfonic acid (PFHxS), perfluorononanoic acid (PFNA), perfluorooctanesulfonic acid (PFOS), perfluorooctanoic acid (PFOA)		
	Synthetic organic	1,4-dioxane		
	VOCs	1,1-dichloroethane, 1,2,3-trichloropropane, 1,3-butadiene, bromochloromethane (halon 1011), methyl bromide, chlorodifluoromethane (HCFC-22), chloromethane		
List 2:	Hormones	androstenedione, equilin, estradiol, estriol, estrone, ethynylestradiol, testosterone		
List 3:	Viruses	enteroviruses, noroviruses		

(>10,000 individuals served), whereas the other 97.3% were small and medium facilities (Table 2). This information served two roles: first, each of the UCMRs listed and prioritized chemicals according to facility size and water source; second, large facilities were responsible for their own analyses, whereas the EPA covered the cost of analysis for small facilities, ranging from \$50 to \$470 per sample. Complimentary analyses can be beneficial for Tribes that are resource limited, but still wish to explore unregulated contaminants. Under UCMR1, only very small (25 - 500) to small (501 - 3,300) facilities were sampled (n = 6). For UCMR2, 5 out of 26 large Tribal PWS participated, with an additional three mediumsized (3,301 - 10,000) and 11 designated as small or very small PWS. Under UCMR3, 15 out of the 26 large facilities in Indian Country participated, with an additional 16 small Tribal PWS surveyed.

Frequency of Analysis and Detection of UCMR1–3 Contaminants

The objective of the UCMR Survey was to evaluate the frequency and levels of unregulated contaminants in PWS across the United States. With respect to Tribal drinking water, participation varied in each UCMR (Table 2), and surveyed contaminants were not analyzed in all participating PWS (Figure 1). A number of Tribal PWS were analyzed across two or more UCMRs: Gila River Indian Community, Manshantucket Pequot, Morongo Band of Cahuilla Mission Indians, Navajo Nation, Pechanga Band of Luiseño Mission Indians, Shakopee Mdewakanton Sioux Community, Turtle Mountain Band of Chippewa, and White Mountain Apache; Mescalero Apache participated in UCMR1 - 3. Results from the campaign highlighted insignificant and problematic unregulated contaminants in Tribal PWS.

Under UCMR1, six Tribal PWS were evaluated for List 1 contaminants. One facility was also evaluated for List 2 analyses. Results showed that all sampling point concentrations fell below the method detection limits for each analyte. With UCMR2, 39 Tribal drinking water facilities and/or sources from 19 different Tribal PWS were analyzed for List 1 and 2 contaminants (explosives, herbicides and herbicide degradates, insecticides, nitrosamines, and brominated flame retardants; see Table 1). Nearly 75% of samples were analyzed for List 1 contaminants, reflective of readily available analytical methods, with the remaining samples analyzed under List 2. As with UCMR1, all sample concentrations fell below the method detection limits.

Under UCMR3, samples from 76 Tribal drinking water treatment plants (85 sampling points) from 30 different Tribal PWS were analyzed for chlorate, metals, volatile organic compounds (VOCs), synthetic organics, and hormones. VOCs, metals, perfluorinated chemicals (PFCs), chlorate, and 1,4-dioxane were analyzed most frequently (80% of PWS, Figure 1) while the least frequently analyzed contaminants were the hormones (23% of Tribal PWS). Hormones were not detected in any Tribal samples, as concentrations fell below the method detection limit. The VOC Halon 1011 and PFCs (PFHpA, PfHxS, and PFOS) were each detected in separate samples, whereas the other VOCs and PFCs were not detected. With the exception of cobalt, metals were detected in 57 -80% of Tribal PWS, chlorate in 67% of PWS, and 1,4-dioxane in 13% of PWS.

As unregulated contaminants, MCLs had not yet been established and there were no enforceable actions imposed during this monitoring campaign. However, HRL or health reference levels provide guidance on the suggested maxima that should be present in drinking water due to potential adverse health or environmental effects. When comparing UCRM3 measured quantities to HRL, five contaminants were found in excess of HRL in Tribal drinking water (Figures 1 and 2): 1,4-dioxane, a probable human carcinogen, (health advisory concentration of $0.35 - 35 \mu g/L$, (EPA 2017b)) in 1 out of 30 Tribal PWS; PFOS, a probable endocrine disruptor, in 1 out of 30 Tribal PWS (health advisory concentration = $0.07 \mu g/L$, (EPA 2016a)); chlorate, a disinfection by-product, $(HLR = 210 \ \mu g/L, (EPA \ 2016c))$ in 12 out of 30 Tribal PWS; strontium (HRL = $1,500 \mu g/L$, (EPA 2017b)) in 1 out of 30 Tribal PWS; and vanadium $(HRL = 21 \ \mu g/L; (EPA \ 2016c))$ in 4 out of 30 Tribal PWS.

The drinking water source provided insight into the prevalence of contaminant type. All vanadium and strontium HRL exceedances arose from groundwater sources alone, though

Table 2. List of Tribal Public Water Systems (PWS) participating in Unregulated Contaminant Monitoring Rule Campaign, UCMR1 – 3, by Tribal PWS size and drinking water source. GU = groundwater under the influence of surface water. Beginning with UCMR3, Tribal PWS were identified as only small or large facilities. Small = < 3,300; medium = 3,310 – 10,000; and large = > 10,000 customers.

UCMR	Size	No.	Groundwater source	No.	Surface water source
UCMR1	Small	1	Blackfeet Tribe	5	Three Affiliated Tribes
		2	Fort McDowell Yavapai Nation	6	Kickapoo Tribe (Kansas)
		3	Mescalero Apache Tribe		
		4	Stockbridge Munsee Community		
UCMR2	Small	7	Mescalero Apache Tribe	23	Grindstone Indian Rancheria
		8	Minnesota Chippewa Tribe	24	Hoopa Valley Tribe
		9	Navajo Nation	25	Southern Ute Indian Tribe
		10	Paiute-Shoshone Indians of the Bishop Community		
		11	Rincon Band of Luiseno Mission Indians		
		12	San Carlos Apache Tribe		
		13	Sault Ste. Marie Tribe of Chippewa		
		14	Zia Pueblo		
	Medium	15	Gila River Indian Community		
		16	Little River Band of Ottawa Indians		
		17	Morongo Band of Cahuilla Mission Indians		
	Large	18	Mashantucket Pequot Tribe (GU)		
		19	Pechanga Band of Luiseño Mission Indians		
		20	Shakopee Mdewakanton Sioux Community		
		21	Turtle Mountain Band of Chippewa Indians		
		22	White Mountain Apache Tribe		
UCMR3	Small	26	Gila River Indian Community	51	Cow Creek Band of Umpqua Indians
		27	Navajo Nation	27	Navajo Nation
		28	Lac Courte Oreilles Band (Lake Superior Chippewa)	52	Oglala Sioux Tribe
		29	Lac du Flambeau Band (Lake Superior Chippewa)	53	Tulalip Tribes
		30	Muckleshoot Indian Tribe		
		31	Kaibab Band of Paiute Indians		
		32	Pueblo of Jemez		
		33	Pueblo of Laguna		
		34	Pueblo of San Ildefonso		
		35	Reno-Sparks		
		36	Soboba Band of Luiseño Indians		
		37	Tohono O'odham Nation		
	Large	38	Mashantucket Pequot Tribe (GU)	54	Mohegan Indian Tribe
		39	White Mountain Apache Tribe	39	White Mountain Apache Tribe
		40	Morongo Band of Cahuilla Mission Indians		
		41	Pala Band of Luiseño Mission Indians		
		42	Pechanga Band of Luiseño Mission Indians		
		43	Pueblo of Sandia		
		44	Rumsey Indian Rancheria of Wintun Indians		
		45	Saginaw Chippewa Indian Tribe		
		46	Salt River Pima-Maricopa Indian Community		
		47	Shakopee Mdewakanton Sioux Community		
		48	Stockbridge-Munsee Band of Mohicans		
		49	Turtle Mountain Band of Chippewa		
		50	Mescalero Apache Tribe		



Total Number of Tribal Public Water Systems

Figure 1. Thirty Tribal public water systems (PWS) sampled for Unregulated Contaminant Monitoring Rule Campaign 3 (UCMR3) contaminants are shown in bars. Number of Tribal PWS with non-detects is shown in gray. Number of Tribal PWS exceeding the method detection limit (MDL) is shown in yellow. Number of Tribal PWS exceeding the health reference limit (HRL) is shown in red. Hormones were analyzed in seven Tribal PWS; all were non-detects; the remaining contaminants were analyzed in 23 Tribal PWS.

metals (vanadium, strontium, and chromium/ hexavalent chromium) in general were detected in both surface and groundwater sources. Molybdenum was detected only in groundwater sources. Chlorate, a disinfection by-product, and dioxane were from both groundwater and surface water sources. The single perfluorinated sample (containing PFOS, PFHxS, and PFHpA) detected came from a groundwater source located near a major metropolitan area. Additional water parameters, including water treatment processes and disinfectant type, were not available in the UCMR dataset, nor in the ECHO.

Without this information, it is difficult to predict what actions will be needed to correct exceedances of the HRL in Tribal PWSs, should these contaminants become regulated. Five (out of 30) of the Tribal PWS exceeded the HRLs of two contaminants (1 – chlorate and 2 – dioxane, PFOS, strontium, or vanadium), the highest of the group surveyed. Nine additional Tribal PWS exceeded one HRL (chlorate or vanadium). Ten PWS will not require remedial actions, as UCMR contaminants were detected, but were measured less than all HRLs, while the other six PWS had no contaminants detected. The implications of the UCMR campaign on Tribal facilities are unknown, as the objective of the survey is to evaluate the prevalence of contaminants in drinking water, which are not yet regulated.

Tribal-specific analyses of emerging contaminants in environmental water samples



Figure 2. Concentration range in μ g/L of Unregulated Contaminant Monitoring Rule Campaign 3 (UCMR3) contaminants in Tribal Public Water Systems (PWS). The health reference limit (HRL) is shown in black arrow indicating the HRL value for the contaminant. Tribal PWS exceed the HRL for the contaminants 1,4-dioxane, chlorate, strontium, and vanadium.

have been previously reported, but in the context of monitoring of wastewater discharge to surface water. The U.S. Geological Survey (USGS) conducted an analysis of emerging contaminants with the collaboration of two Tribes, the Standing Rock Sioux and the Stillaguamish Tribe (Damschen and Lundgren 2009; Wagner et al. 2014). A screening of over 200 contaminants of water and riverbed sediment along the Missouri River on the Standing Rock Indian Reservation showed the antibiotic sulfamethoxazole above method detection limits. The USGS also coordinated with the Stillaguamish Tribe on an ongoing study of the Stillaguamish River basin that included samples from the main river and its tributaries. For several years following initial sampling, samples were taken from three wastewater treatment plants. The USGS plans to continue to monitor the sites. To date, this analysis has primarily detected pharmaceuticals, which have previously not been considered in any UMCR. Hormonal contaminants, listed in the UMCR, were also detected. Though the foci of emerging contaminant monitoring by the USGS and EPA differ, these studies show the potential for detection in Tribal water.

Conclusions

This is the first published review of unregulated contaminants in Tribal PWS providing drinking water to communities. Although better sampling efforts can be made to include additional Tribes, this snapshot revealed important priorities for the monitoring of emerging contaminants, risk assessment, and drinking water treatment. Metals continue to be a priority, and while the inclusion of strontium and vanadium in a regulated list would require drinking water treatment plant upgrades, the public would be protected against adverse health risks. Chlorate, a disinfection by-product, was detected most frequently as exceeding the HRL, in 12 out of 30 Tribal PWS analyzed. Single-point exceedances of 1,4-dioxane and PFOS suggest these emerging contaminants should continue to be monitored. Finally, the survey suggests that emerging contaminants, including hormones, nitrosamines, flame retardants, herbicides, and pesticides, among others, are not presently of concern in drinking water, but should not be neglected in future surveys.

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