

APPENDIX O

Unregulated Contaminants Information

Wastewater Emerging Contaminants Report

Traditionally, water quality is evaluated by comparing the measured concentration of a particular substance with the respective benchmark values based on drinking water standards (MCL's). There are many chemicals for which no regulated standards in drinking water have been set. California along with other water regulating entities (EPA) are researching non-regulated chemicals, and developing some methods for monitoring the chemicals of emerging concern.

Non-regulated chemicals have been detected in the Wichita Falls wastewater effluent, through our extensive testing on regulated and non-regulated analytes. (See Table 1) The City of Wichita Falls wastewater effluent has detected 44 analytes out of numerous compounds tested. The following paragraphs are descriptions of the non-regulated chemicals that were detected.

- N-acetyl-p-aminophenol (acetaminophen), also known as Tylenol, is a widely used over the counter pain reliever. A 1999 U.S. Geological Survey of 139 streams in thirty states found at least one pharmaceutical in 80 percent of the streams tested, and Acetaminophen (aspirin) was found in 23.8 percent of streams tested. (10) N-acetyl-p-aminophenol is a hydrophilic, uncharged molecule.
- Antipyrine (phenazone) is a compound formerly used as an analgesic (pain reliever) and antipyretic (fever reducer).
- Atenolol is a drug belonging to the group of beta blockers (sometimes written β -blockers), a class of drugs used primarily in cardiovascular diseases.
- Azithromycin (Zithromax, Azithrocin, Zmax, Azin) is an azalide, a subclass of macrolide antibiotics.
- Bezafibrate is a fibrate drug used for the treatment of hyperlipidaemia. It helps to lower LDL cholesterol and triglyceride in the blood, and increase HDL.
- Carbamazepine is an anticonvulsant and mood-stabilizing drug used primarily in the treatment of epilepsy and bipolar disorder, as well as trigeminal neuralgia. Carbamazepine is a hydrophilic, uncharged molecule. It has an excellent removal in RO treatments according to research done from a full-scale application of RO membranes (15).
- Chromium (total & hex) Trivalent chromium (Cr(III) or Cr³⁺) occurs in trace amounts in foods and waters, and appears to be benign. (21) In contrast, hexavalent chromium (Cr(VI) or Cr⁶⁺) is very toxic and mutagenic when inhaled. Cr(VI) has not been established as a carcinogen when in solution, although it may cause allergic contact dermatitis (ACD). (22)
- Cotinine is a by-product of nicotine metabolism in the liver.
- DEET (N,N-Diethyl-meta-toluamide), the most common active ingredient in insect repellents.
- Diazepam is a benzodiazepine drug known as Valium.
- Diclofenac is a nonsteroidal anti-inflammatory drug (NSAID) taken to reduce inflammation and as an analgesic reducing pain in certain conditions

- Dilantin (Phenytoin) is a commonly used antiepileptic.
- Diltiazem a nondihydropyridine (non-DHP) member of the class of drugs known as calcium channel blockers, used in the treatment of hypertension, angina pectoris, and some types of arrhythmia.
- DCMU (3-(3,4-dichlorophenyl)-1,1-dimethylurea)(Diuron) is an herbicide that inhibits photosynthesis. The RO membranes within our facility (ESPA2) has a 97% rejection rate for Diuron, which is most likely due to the molecular size.
- Estrone is an estrogenic hormone secreted by the ovary as well as adipose tissue with the chemical name of 3-hydroxyestra-1,3,5(10)-triene-17-one. Estrone is one of several natural estrogens, which also include estriol and estradiol.
- Fluoxetine (Prozac) is an antidepressant.
- Galaxolide a polycyclic musk that's used in some perfumes as a fragrance. It is also used in soaps, cosmetics and detergents.
- Gemfibrozil is an oral drug used to lower lipid levels. Is considered moderately hydrophobic in its neutral form.
- Meprobamate is a carbamate derivative which is used as an anxiolytic drug; anti-anxiety and muscle relaxant.
- Naproxen is a nonsteroidal anti-inflammatory drug.
- Nicotine is a potent parasympathomimetic alkaloid found in cigarettes.
- N-Nitrosodimethylamine (NDMA) a semi-volatile organic chemical an industrial by-product or waste product of several industrial processes. Research has proven that NDMA has been reduced approximately 50% through the reverse osmosis treatment. (9)
- N-Nitrosopyrrolidine (NPYR) is a nitrosamine that may be formed from preservatives in meats during their preparation or in the liver during metabolism.
- Paraxanthine (1,7 – Dimethylxanthine) a psychoactive central nervous system (CNS) stimulant
- Perchlorate is the salts derived from perchloric acid.
- Perfluorooctanoic acid (PFOA) is a synthetic perfluorinated carboxylic acid and fluorosurfactant.
- Perfluoroheptanoic acid (PFHpA) is a breakdown product of stain- and grease-proof coatings on food packaging, couches, carpets.
- Primidone is an anticonvulsant drug. Research has found that Primidone was completely removed through the reverse osmosis treatment. (8)
- Progesterone is a C-21 steroid hormone involved in the female menstrual cycle, pregnancy, and embryogenesis.

- Salicylic acid is a plant hormone and is also a component of Asprin.
- Sucralose is an artificial sweetener.
- Sulfamethizole is a sulfonamide antibiotic.
- Sulfamethoxazole is a sulfonamide bacteriostatic antibiotic. Sulfamethoxazole possesses two ionisable amine groups and it can carry a positive, neutral, or negative charge.
- Sulfasalazine is an oral drug to treat rheumatoid arthritis
- Testosterone (trans) is a steroid hormone from the androgen group. Approximately 7% of testosterone is reduced to 5 α -dihydrotestosterone (DHT) by the cytochrome P450 enzyme 5 α -reductase,(19) an enzyme highly expressed in male accessory sex organs and hair follicles.(18)
- Tetracycline is a broad spectrum polyketide antibiotic
- Theobromine (Xantheose) is an alkaloid found in chocolate.
- Theophylline is a methylxanthine drug used in therapy for respiratory diseases.
- Tonalide (1-(5,6,7,8-Tetrahydro-3,5,5,6,8,8-hexamethyl-2-naphthalenyl)ethanone) is a very powerful, warm, and radiant musk odor.
- Triclocarban (TCC) (3, 4,4' – trichlorocarbanilide) is an anti-bacterial and anti-fungal that is used in disinfectants, soaps, and other household products. Existing environmental data submitted to EPA under the HPV program shows that TCC is inherently biodegradable and extensively removed during wastewater treatment. This datum indicated that up to 98% of TCC is removed by wastewater treatment plants and the remainder undergoes rapidly photodegradation. TCC that enters wastewater treatment plants is predominantly sequestered into sludge. The degree of degradation in sludge depends on the type of sludge treatment, with greater degradation occurring under aerobic conditions compared to anaerobic conditions. Researchers reported TCC levels in the ppm range for both anaerobically digested sludge (median levels: 27.6 $\pm$ 7.2 ppm) and aerobically digested sludge (mean: 18 ppm). (14)
- Trimethoprim is a bacteriostatic antibiotic mainly used in the prophylaxis and treatment of urinary tract infections.
- 17 β -estradiol a sex hormone. Approximately 0.3% of testosterone is converted into estradiol by aromatase (CYP19A1) (20) an enzyme expressed in the brain, liver, and adipose tissues.(18)
- 2, 4, 6 – Trichlorophenol (TCP, phenaclor, Dowicide 2S, Dowicide 2S, omal) is a chlorinated phenol that has been used as a fungicide, herbicide, insecticide, antiseptic, defoliant, and glue preservative.

Calculation of ADI

Through extensive research these non-regulated compounds, can be classified using calculations that the EPA and the state of California has adopted as guidelines for various chemicals. The acceptable daily intake (ADI) is a calculated health based guidance value and is defined as a daily oral exposure to the human population (including sensitive subgroups) that is likely to be free of appreciable health risks over a lifetime.

$$\text{ADI (mg/kg-d)} = \text{NOAEL or LOAEL/UF's}$$

- NOAEL – the highest exposure level at which there is no biologically significant increases in the frequency or severity of adverse effect between the exposed population and its appropriate control. Some effects may be produced at this level, but they are not considered adverse or precursors of adverse effects.
- LOAEL – The lowest exposure level at which there is biologically significant increase in frequency or severity of adverse effects between the exposed population and the appropriate control group.
- UF's – Uncertainty factors, which account for differences in human response to toxicity, uncertainties in the extrapolation of the toxicity data between humans and animals (if animal data are used), as well as other uncertainties associated with data extrapolation.

The Table 2 was created using the non-regulated chemicals found within the wastewater effluent including the following: $\log K_{ow}$, molecular weight, and the ADI calculated by EPA or from cited sources.

Removal Rates based on RO, MF

Speciation of molecules, i.e. changing of their charge as a function of pH, will significantly influence their rejection on the membranes. Charge for most of the thin layer composite RO membranes in neutral solutions is negative, due to the dissociation of sulfonic and carboxylic groups on the membrane's skin. Therefore, increased rejection of negatively charged solutes could be expected due to electrostatic repulsion with the membrane surface (16). Rejections of sulfamethoxazole through RO membranes were high with approximately 95% removal, probably a result of the combination of size exclusion mechanisms (molecular cut off rate) and the repellent electric force between the solutes and the membrane ($\log K_{ow}$). (17)

Physicochemical properties of the chemicals are used to characterize their behavior, molecular weight and octanol-water partition coefficient. Size exclusions based on molecular weight cut off values for RO membranes will remove molecules with molecular weights larger than the cut off rate. The current membranes within our facility are ESPA2 and ESPA4, and have the molecular cut off rates of 54 with a 99.6% removal of NaCl and the ESPA4 have a slightly higher molecular cut off rate with a 99.2% removal of NaCl. (23)

Octanol-water partition coefficient ($\log K_{ow}$) is a coefficient representing the ratio of the solubility of a compound in octanol (a non-polar solvent) to its solubility in water (a polar solvent, hydrophobic and hydrophilic). The higher the K_{ow} value, the more non-polar the compound, thus indicating that they readily adsorb to hydrophobic materials such as membrane surfaces under favorable conditions. Adsorption is driven by hydrophobic interactions, and other physicochemical parameters including dipole moment and dielectric constant.

Within a RO removal rate study, research has shown that RO removal of NDMA is approximately 50%. (9) NDMA has a $\log K_{ow}$ value of -0.57, and having the 50% removal rate.

Research has shown that Primidone is completely removed by the RO (8) The log K_{ow} value for Primidone is 0.91 and a molecular weight of 218.25, thus suggesting that any analytes having a molecular weight and a log K_{ow} value equal to or larger than Primidone should also be completely removed by the RO.

Removal Rates based on Dilution

Removal calculations based on dilutions and comparisons to the calculated ADI guidelines have not been projected because of removal rates from the RO have not been verified. However, dilutions of 50% will further reduce the amounts of an unregulated analytes through the process.

Removal Rates based on Conventional Treatment Processes

The conventional water treatment process (coagulation/flocculation sedimentation/filtration) had very low removal efficiencies (0 to 7%) for all the Endocrine Disrupting Chemical's except Di(2-ethylhexyl) phthalate (DEHP), DBP, and DEP that were removed by 53%, 49%, and 46%, respectively. (12) Very little research has been done on the affects of lime softening/pH change on unregulated chemicals. Also, the affects of the chloramines to the compounds hasn't been researched enough to see the breakdown of the chemicals that could possible occur. The verification test will give us the information here to fill in this gap of research.

The removal efficiencies of the different parts to the treatment process: microfiliterers, reverse osmosis, 50% dilutions, and then the conventional are important along with the half-life and the chemical makeup of the compounds also. The chemical breakdown of the pharmaceuticals is well known within the human body, but little information is known about the half-life within water. There are many things that can cause breakdown within the environment such as photodegradation, chemical reactions, and just time. The verification test will account for the "unknown" through the plant: the reactions we cannot project, the removal rates we cannot project, the half-life time in the environment, etc.

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UNREGULATED CONTAMINANTS DETECTED

Classification	MIN	MAX	AVG	ADI	Also Found		Reference
Pharmaceuticals				mg/kg - d	Tap	Raw	
Acetaminophen (ug/L)	0	0.011	0.0052	0.34			1, 4
Antipyrine (ug/L)	0	0.004	0.001	0.0284			1, 5
Atenolol (ug/L)	0	0.22	0.13	0.002			1, 2
Azithromycin (ug/L)	0	0.25	0.058	0.011			5
Bezafibrate (ug/L)	0	0.0006	0.00012	0.0086			5
Carbamazepine (ug/L)	0.05	0.35	0.18	0.0028/0.00034			1, 5, 2, 6
Diazepam (ug/L)	0	0.002	0.0006	0.000071/0.001			1, 2, 5
Diclofenac (ug/L)	0	0.077	0.019	0.0005/0.067			1, 2, 5
Dilantin (ug/L)	0.19	0.51	0.41	0.00019			1, 2
Diltiazem (ug/L)	0	0.088	0.017	0.014/0.0017			1, 4, 5
Fluoxetine (Prozac) (ug/L)	0.007	0.035	0.018	0.00097/0.00028/0.0029			1, 2, 4, 5
Gemfibrozil (ug/L)	0	0.3	0.069	0.0013/0.017/0.055			1, 2, 4, 5
Meprobamate (ug/L)	0.41	0.78	0.53	0.0075			1, 2
Naproxen (ug/L)	0	0.036	0.011	0.0063/0.57			1, 2, 5
Paraxanthine (ug/L)	0.026	0.21	0.08			X	
Primidone (ug/L)	0.32	1.1	0.64				
Salicylic acid (ug/L)	0	0.19	0.11		X	X	
Sulfamethizole (ug/L)	0	1	0.2	0.01			1, 5
Sulfamethoxazole (ug/L)	0	1.5	0.27	0.51/0.13/0.01/0.13			1, 2, 4, 5, 6
Sulfasalazine (ug/L)	0	0.042	0.011				
Tetracycline (ug/L)	0	0.93	0.23	0.3			1, 4, 5
Theophylline (ug/L)	0	0.12	0.053	0.006			13
Triclocarban (ug/L)	0.07	0.22	0.12			X	
Trimethoprim (ug/L)	0	0.64	0.16	0.19/0.02/0.0042			1, 2, 4, 5
Personal Care Products							
DEET (ug/L)	0.035	0.197	0.094	0.75/1.8	X	X	1, 6
Galaxolide (ug/L)	0.27	1.2	0.66	0.5			1, 5
Tonalid (ug/L)	0.042	0.13	0.089				
Waste Water Indicators							
Cotinine (ug/L)	0	0.025	0.017	0.00028		X	1, 5
Nicotine (ug/L)	0	0.1	0.043			X	
Sucralose (ug/L)	43	43	43				
Theobromine (ug/L)	0.24	0.86	0.61		X	X	
Endocrine Disrupters							
17beta-Estradiol (ng/L)	0	2.9	0.72	0.00005			1, 2, 3, 5
Estrone (ng/L)	0	30	8.7				
Progesterone (ng/L)	0	0.4	0.18	0.03	X	X	1, 5
trans-Testosterone (ng/L)	0	0.4	0.1	0.002			1, 2
Household Use							
Perfluorooctanoic acid (PFOA) (ng/L)	20	28	22.83	0.0015			1, 3, 6
Perfluoroheptanoic acid (PFHpA) (ng/L)	0	10	2.5			X	
2,4,6-Trichlorophenol (ug/L)	0	0.5	0.13				
Diuron (ug/L)	0.21	0.21	0.21	0.003/0.002			1, 2, 3
Disinfection by-products							
N-Nitrosodimethylamine (NDMA) (ng/L)	0	18	10.25	0.000008		X	1, 3, 6
N-Nitrosopyrrolidine (NPYR) (ng/L)	0	2	0.5				
Perchlorate (ug/L)	0.11	0.21	0.1625	0.007		X	1, 3
Metals							
Chromium (Hex) (ug/L)	0.025	0.08	0.052			X	
Nickel (ug/L)	5	5.5	5.25				

UNREGULATED CONTAMINANTS MOLECULAR WEIGHT

Classification	Molecular Weight	K _{ow}	ADI	Reference
Pharmaceuticals			mg/kg - d	
Acetaminophen	151.17	0.46	0.34	1, 4
Antipyrine	188.226	0.38	0.0284	1, 5
Atenolol	266.336	0.16	0.002	1, 2
Azithromycin	748.984	4.02	0.011	5
Bezafibrate	361.819	4.25	0.0086	5
Carbamazepine	236.269	2.45	0.0028/0.00034	1, 5, 2, 6
Diazepam	284.7	2.82	0.000071/0.001	1, 2, 5
Diclofenac	296.148	4.6	0.0005/0.067	1, 2, 5
Dilantin	252.268	2.47	0.00019	1, 2
Diltiazem	414.519	2.7	0.014/0.0017	1, 4, 5
Fluoxetine (Prozac)	309.33	4.05	0.00097/0.00028/0.0029	1, 2, 4, 5
Gemfibrozil	250.333	4.77	0.0013/0.017/0.055	1, 2, 4, 5
Meprobamate	218.25	0.7	0.0075	1, 2
Naproxen	230.259	3.18	0.0063/0.57	1, 2, 5
Paraxanthine	180.16	-0.22		
Primidone	218.25	0.91		
Salicylic acid	138.12	2.26		
Sulfamethizole	270.333	0.54	0.01	1, 5
Sulfamethoxazole	253.28	0.89	0.51/0.13/0.01/0.13	1, 2, 4, 5, 6
Sulfasalazine	398.394	3.81		
Tetracycline	444.44	-1.3	0.3	1, 4, 5
Theophylline	180.17	-0.02	0.006	13
Triclocarban	315.58	4.9		
Trimethoprim	290.32	0.91	0.19/0.02/0.0042	1, 2, 4, 5
Personal Care Products				
DEET	191.27	2.18	0.75/1.8	1, 6
Galaxolide	258.4	5.43	0.5	1, 5
Tonalide	258.4	5.8		
Waste Water Indicators				
Cotinine	176.22	0.34	0.00028	1, 5
Nicotine	162.23	1		
Sucralose	397.64	-1		
Theobromine	180.16	-0.78		
Endocrine Disrupters				
17beta-Estradiol	272.38	4.01	0.00005	1, 2, 3, 5
Estrone	270.366	3.43		
Progesterone	314.46	4.63	0.03	1, 5
trans-Testosterone	288.42	3.84	0.002	1, 2
Household Use				
Perfluorooctanoic acid (PFOA)	414.07	6.3	0.0015	1, 3, 6
Perfluoroheptanoic acid (PFHpA)	364.06	5.33		
2,4,6-Trichlorophenol	197.445	3.69		
Diuron	233.09	2.68	0.003/0.002	1, 2, 3
Disinfection by-products				
N-Nitrosodimethylamine (NDMA)	74.08	-0.57	0.000008	1, 3, 6
N-Nitrosopyrrolidine (NPYR)	100.12	-0.104		
Perchlorate	301.4	-4.63	0.007	1, 3