Evaluation of Drinking Water Treatment Technologies for Removal of Endocrine Disrupting Chemicals

上水道における内分泌かく乱化学物質の除去技術

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Evaluation of Drinking Water Treatment Technologies for Removal of Endocrine Disrupting Chemicals

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Endocrine disrupting chemicals (EDCs) are exogenous agents that interfere with the synthesis, secretion, transport, binding, action, or elimination of natural hormones in the body that are responsible for the maintenance of homeostasis, reproduction, development, and/or behavior.

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Legislation Associated with Endocrine Disrupting Chemicals

- Food Quality Protection Act of 1996
- Safe Drinking Water Act Amendments of 1996

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Many of the compounds identified as potential endocrine disrupting chemicals (EDCs) may be present in surface or ground waters used as drinking water sources due to their introduction from:

- Domestic and industrial sewage treatment systems.
- Wet-weather runoff.

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Occurrence of EDCs in U.S. streams

Compound	Number of samples	Reporting limit µg/L	Freq. of detection %	Maximum conc. µg/L	Median detectable conc. µg/L
estradiol	70	0.005	10.0	0.093	0.009
ethynyl-estradiol	70	0.005	5.7	0.273	0.094
testosterone	70	0.005	2.8	0.214	0.116
nonylphenol	85	0.50	50.6	40[a]	0.8[a]

a: concentration estimated – reference standard from technical mixture

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Environ. Sci. Technol. 36,4007 – 4008, 2002

Basic strategies to decrease the potential risk of adverse health effects associated with the presence of EDCs in drinking water:

- Protect drinking water sources from contamination by EDCs.
- Remove EDCs, that may be present in source waters, during drinking water treatment.

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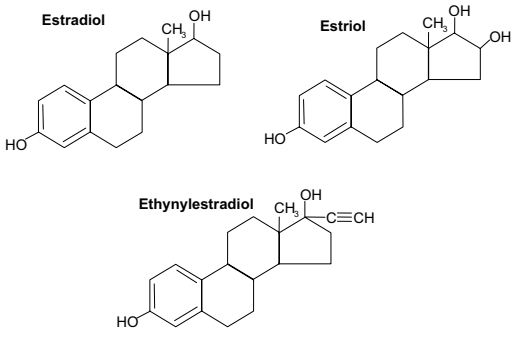
Compounds to be evaluated



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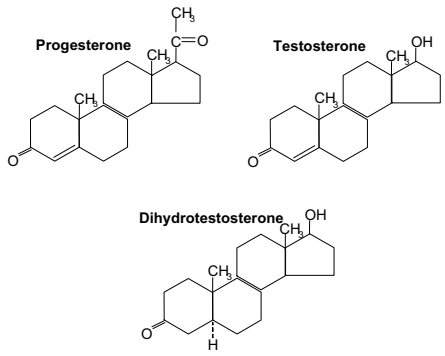


Technical approach

❖Develop analytical methods to identify and quantify the target compounds. The approach includes concentration by solid-phase extraction, followed by LC/MS.

Analytical method for steroid compounds

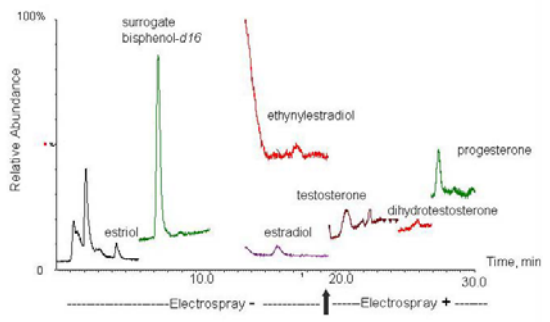
Solid phase extraction:

❖Baker C18 XF speed disks eluted with methanol

Quantitation:

❖Waters ZQ LC/MS, electrospray
❖Xterra C18 column
❖Single step gradient, 50 – 65% methanol in ammonium hydroxide in water
❖Single ion mode

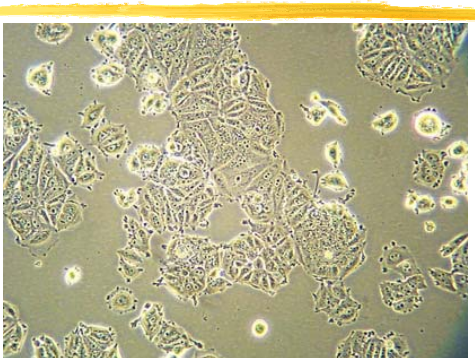
Single ion chromatograms of reagent water fortified at 1ng/L



Technical approach (cont.)

❖Evaluate the use of a reporter gene assay, the MVLN assay, to detect the presence/removal of estrogenic activity. This assay uses a human breast cell line (MCF-7) which has been stably transfected with the firefly luciferase gene.

MVLN Cells

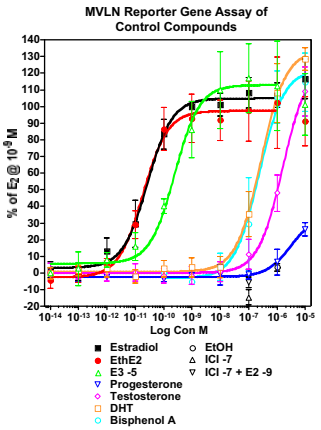


MVLN Assay

❖MVLN cells, previously withdrawn from estrogens, are seeded into 96 well plates (day 1).
❖Media is removed from wells and replaced with media containing treatments (samples, and positive and negative controls) in ethanol carrier solvent. All treatments are done in quadruplicate (day 2).
❖Treatment media is removed and replaced with fresh treatments (day 3).

MVLN Assay (cont.)

❖Treatment media is removed, the cells are washed, and lysed. The luciferase activity (light production) is then determined using a luminometer. (day 4)
❖Estrogenic activity is determined by comparing the average luciferase activity for each treatment group to the activity of estradiol or the dose-response curve of the analyte used.



Technical approach (cont.)

- Conduct bench-scale evaluations of various drinking water treatment technologies, including granular activated carbon (GAC), conventional treatment, softening and nanofiltration.
- Pilot-scale evaluations may be conducted on the treatment technologies that appear promising at bench-scale.

Modeling Requirements

- Carbon Information
- Isotherms
- Film Transfer Coefficient
- Internal Diffusion Coefficient

Carbon Information

	Norit 1240	Hydrodarco 4000	Superdarco
Bulk Density (g/ml)	0.48	0.40	0.33
Apparent Density (g/ml)	0.66	0.59	0.41
Bed Void Fraction	0.26	0.32	0.21
Particle Diameter (mm)	1.04	1.14	1.00

Granular activated carbon (GAC) isotherm studies

- Organic–free filter sterilized water buffered to pH 7 with phosphate buffer (0.005 M)
- Target compound (100 µg/L) added to buffer and mixed for approximately 24 hours
- Solution added to isotherm bottles containing various amounts of GAC
- After various treatment times, solution is pumped out through a 0.22 µm filter
- Initial and final concentration data used to determine adsorption capacity of GAC

Adsorption of Ethynylestradiol (EE2) on Norit GAC 1240

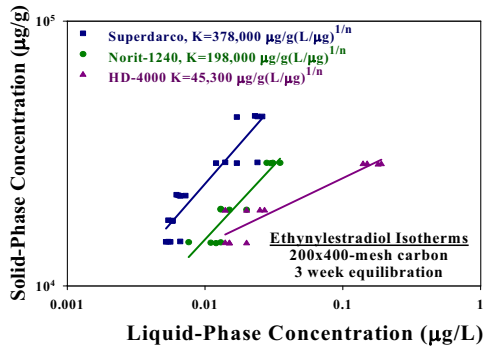
	Liquid-Phase Concentration µg/L	Capacity µg/g[b]
100-200 Mesh		
Week 1	0.57 ± 0.039[a]	13400 ± 43
Week 2	0.14 ± 0.014	13500 ± 40
Week 3	0.060 ± 0.011	13500 ± 33
200-400 Mesh		
Week 1	0.076 ± 0.0042	13500 ± 72
Week 2	0.034 ± 0.0066	13500 ± 46
Week 3	0.011 ± 0.0015	13500 ± 50

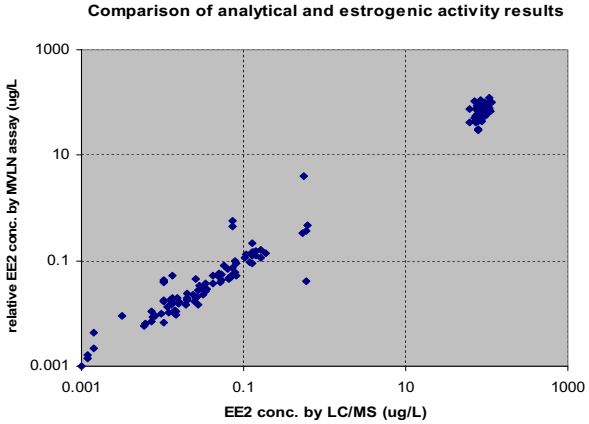
[a] Mean ± standard deviation of four replicate treatment samples (N=4)
[b] C_0 was determined by averaging the untreated samples (N=44)

Adsorption of Ethynylestradiol (EE2) on Hydrodarco 4000 GAC

	Liquid-Phase Concentration µg/L	Capacity µg/g[b]
100-200 Mesh		
Week 1	0.12 ± 0.013[a]	15700 ± 480
Week 2	0.022 ± 0.0052	16000 ± 13
Week 3	0.011 ± 0.0054	16000 ± 58
200-400 Mesh		
Week 1	0.091 ± 0.066	16000 ± 46
Week 2	0.019 ± 0.0074	16000 ± 14
Week 3	0.0076 ± 0.0029	16000 ± 0

[a] Mean ± standard deviation of four replicate treatment samples (N=4)
[b] C_0 was determined by averaging the untreated samples (N=44)





Short-Bed Adsorber Studies

- Influent: 100 µg/L ethynylestradiol in organic free water buffered to pH 7 with phosphate buffer (0.005 M)
- Column: 44g or 88g of granular activated carbon
- Flow rate: 350 ml/min
- Length of run: 10 hrs (210 L)
- Sampling: Influent samples were collected at 0 min, 1, 2, 4, 6, 8 and 10 hrs. Effluent samples were collected at 10, 20, 30, 40 and 50 min; 1, 2, 4, 6, 8, and10 hrs.

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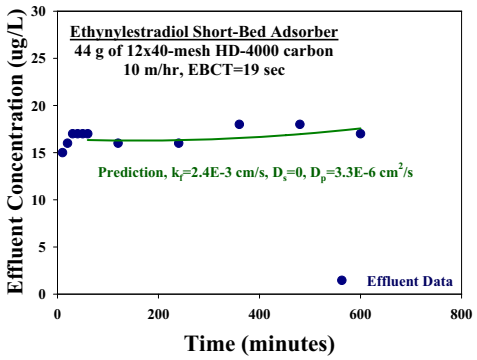

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Average Film Transfer Determination

Carbon	k_{film} (cm/sec) Data	k_{film} (cm/sec) Gnielinski Correlation
Superdarco	3.4×10^{-3}	2.6×10^{-3}
Hydrodarco 4000	2.1×10^{-3}	1.8×10^{-3}
Norit 1240	2.4×10^{-3}	2.2×10^{-3}

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Future Study Options

- Run batch-recirculating study to determine internal diffusion
- Run RSSCT
- Run pilot columns

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This study will provide information on:

- Currently available drinking water treatment technologies that can remove EDCs, specifically the steroid hormones.
- Approaches to optimize these treatment technologies for EDC removal.

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