Fate of 17β-estradiol and 4-nonylphenol in the Redwood River of Minnesota

Jeffrey H. Writer, Joseph N. Ryan, Steffanie H. Keefe, and Larry B. Barber

Supporting Information (5 pages)

Supporting Information Figures

Figure S1 Molecular structure of the compounds evaluated.

Supporting Information

Reagents and chemicals. 17β-estradiol, 17α-ethynylestradiol, estrone, 4-nonylphenol, 4-nonylphenolmonoethoxylate, and 4-nonylphenoldiethoxylate were purchased from Sigma Aldrich (St. Louis, MO). Deuterated (d_4) 17β-estradiol, 4-*n*-nonylphenolmonoethoylate, and 4-*n*-nonlyphenoldiethoxylate were obtained from Cambridge Isotope Laboratories (Andover, MA), and 4-*n*-nonylphenol were obtained from Dr. Ehrenstorfer GmbH (Augsburg, Germany).

Analytical Procedures. Organic contaminants in water samples were extracted using three different procedures[1]. Steroidal hormones were isolated from unfiltered water samples by octadecyl silica solid-phase extraction (C_{18}-SPE) followed by elution with methanol, Florisil™ cleanup, and target compound derivatization with N-methyl-N-trimethylsilyltrifluoroacetamide (MSTFA, Sigma Aldrich, St. Louis, MO). 4-nonylphenol, 4-nonyphenolpolyethoxylates (NPEOs), and other organic wastewater contaminants were isolated from unfiltered water samples using continuous liquid-liquid extraction (CLLE) with methylene chloride at pH 2 following ionic strength adjustment. Samples for 4-nonylphenolpolyethoxycarboxylates (NPECs) and EDTA analyses were evaporated to dryness and derivatized with an acetyl chloride/propanol mixture to form propyl esters. The derivatized C_{18}-SPE samples were analyzed by gas chromatography/tandem mass spectrometry (GC/MS/MS; Agilent 6890 GC and Waters QuattroMicro QqQ MS/MS). The CLLE and evaporated extracts were analyzed by electron impact gas chromatography/mass spectrometry (GC/MS; Hewlett Packard 6890 GC and Hewlett Packard 6973 MS). Target compounds in the sediment and stream biofilm samples were isolated by accelerated solvent extraction (ACE) with isopropyl alcohol and cleaned on a Fluorocil™ column[2]. Extracts from the sediment and stream biofilm samples were prepared and analyzed as described above.

Indirect Photolysis Calculations for 17β-estradiol. An indirect photolysis decay coefficient of 0.1 d^{-1} was calculated using methods outlined in Schwarzenbach et al.[3], based on a rate constant ($k'_{OH\cdot,E2} = 1\times10^{10}$ M^{-1} s^{-1}, ref. 4) for the reaction between 17β-estradiol and the photochemically produced hydroxyl radical ([OH●], M), using a DOC concentration of 8 mg L^{-1}, a NO_3^- concentration of 10 mg L^{-1}, a NO_2^{-1} concentration of 0.1 mg L^{-1}, a HCO_3^{-1} concentration of 60 mg L^{-1}, and a CO_3^{-2} concentration of 0.6 mg L^{-1}.

$$[OH\bullet]_{noon} = \frac{1.4\times10^{-7}[NO_3^-]+1.7\times10^{-5}[NO_2^-]}{2.5\times10^{4}[DOC]+1.0\times10^{7}[HCO_3^-]+4.0\times10^{8}[CO_3^{-2}]} = \frac{6\times10^{-11}}{2.1\times10^{5}} = 2.9\times10^{-16}\,M$$

$$[OH\bullet]_{24} = [OH\bullet]_{noon}\times 0.44 \text{ (correction based on 40°N latitude, ref. 3)}$$

$$k_{E2} = k'_{\mathrm{E2,OH}}.[OH\bullet]_{(24\mathrm{h})} = 1.3\times10^{-6}\,s^{-1} = 0.11\ \mathrm{d}^{-1}$$

Volatilization of 4-nonylphenol calculations. A volatilization first-order decay coefficient (k_{vol}) of 0.07 d^{-1} was calculated by applying the boundary layer model developed by Deacon[5]:

$$k_{vol} = \frac{1}{h_{mix}}\left(\frac{1}{v_{water}}+\frac{1}{v_{air}K_H}\right)^{-1} = 0.07\ \mathrm{d}^{-1}$$

$$K_H = \frac{P}{C_w RT}$$

$$D_{air}^{H_2O}(20°\mathrm{C}) = 0.26\ \mathrm{cm}^2 s^{-1}; D_{air}^{NP} = D_{air}^{H_2O}\left(\frac{\text{mol wt } H_2O}{\text{mol wt NP}}\right)^{0.5}$$

$$v_{air}^{H_2O} = 0.3+0.2u_{10}\ ;\ v_{air}^{H_2O} = 1.1\ \mathrm{cm\ s^{-1}}\ ;\ v_{air}^{NP} = v_{air}^{H_2O}\left(\frac{D_{air}^{NP}}{D_{air}^{H_2O}}\right)^{.67}$$

$$D_{water}^{CO_2}(20°\mathrm{C}) = 1.68\times10^{-5}\,\mathrm{cm}^2 s^{-1}; D_{water}^{NP} = D_{water}^{CO_2}\left(\frac{\text{mol wt } CO_2}{\text{mol wt NP}}\right)^{0.5}$$

$$v_{water}^{CO_2} = 0.65\times10^{-3}\,\mathrm{cm\ s^{-1}}; v_{water}^{NP} = v_{water}^{CO_2}\left(\frac{D_{water}^{NP}}{D_{water}^{CO2}}\right)^{.67}$$

assuming the average depth of well-mixed water (h_{mix}) was 100 cm, a wind speed of 4 ms^{-1}, a temperature of the air and water (20°C), using the kinematic viscosity of air (v_{air}), kinematic viscosity of water (v_{water}) defined by the molecular diffusivity (D) of the compound (e.g. H_2O) through the medium (e.g air), and a dimensionless Henry's Law constant (K_H) for 4-nonylphenol (NP, $10^{-3.7}$) calculated from water solubility (C_w, 2.45×10^{-5} M, ref. 6) and vapor pressure data (P, 10^{-7} bar, ref. 7).

Supporting Information References

1. Writer, J.H.; Barber, L.B.; Brown G.K.; Taylor, H.E.; Kiesling R.L.; Ferrey, M.L.; Jahns, N.D.; Bartell, S.E.; Schoenfuss, H.L. Anthropogenic tracers, endocrine disrupting chemicals, and endocrine disruption in Minnesota lakes. *Sci. Total Environ.* **2010***,* 409, 100-111.

2. Burkhardt, M.R.; ReVello, R.C.; Smith, S.G.; Zaugg, S.D. Pressurized liquid extraction using water/isopropanol coupled with solid-phase extraction cleanup for industrial and anthropogenic waste-indicator compounds in sediment. *Anal. Chim. Acta* **2005**, *534,* 89-100.

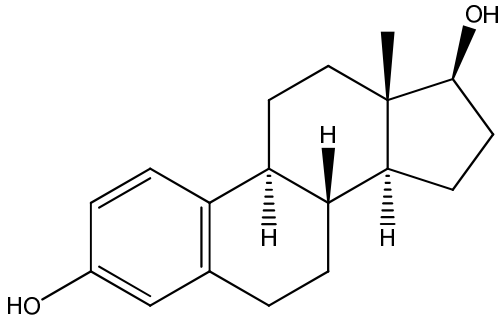
3. Schwarzenbach, R.P.; Gschwend, P.M.; Imboden, D.M. *Environmental Organic Chemistry.* Wiley Interscience: New York, **2003**; 681 pp.

4. Rosenfeldt, E.J.; Linden, K.G. Degradation of endocrine disrupting chemicals bisphenol A, ethynylestradiol, and estradiol during UV photolysis and advanced oxidation processes. *Environ. Sci. Technol.* **2004**, *38,* 5476-5483.

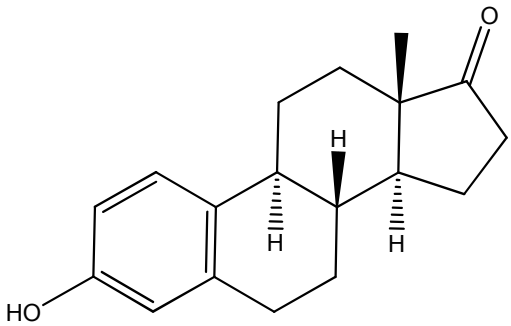
5. Deacon, E.L. Gas transfer to and across an air/water interface. *Tellus* **1977**, *29,* 363-374.

6. Ahel, M.; Giger, W.; Schaffner, C. Behaviour of alkylphenol polyethoxylate surfactants in the aquatic environment - II: Occurrence and transformation in rivers. *Water Res.* **1994c**, *28,* 1143-1152.

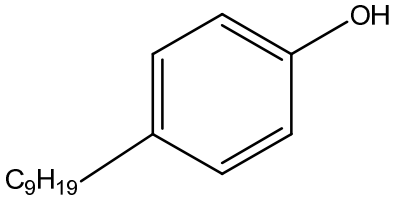
7. Xie, Z.; Le Calvé, S.; Feigenbrugel, V.; Preuß, T.G.; Vinken, R.; Ebinghaus, R.; Ruck, W. Henry's Law constants measurements of the nonylphenol isomer 4(3′,5′-dimethyl-3′-heptyl)-phenol, tertiary octylphenol and hexachlorocyclohexane between 278 and 298 K. *Atmos. Environ.* **2004**, *38,* 4859-4868.



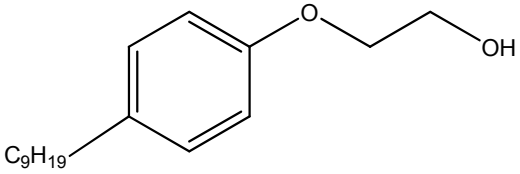
17β-estradiol



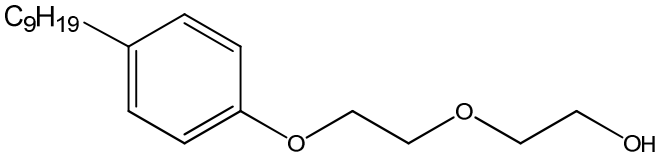
estrone



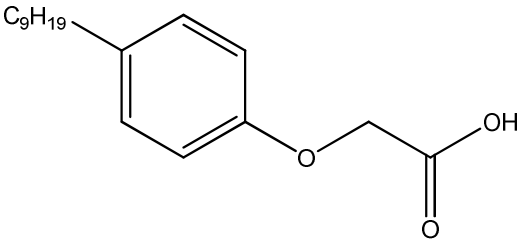
4-nonylphenol



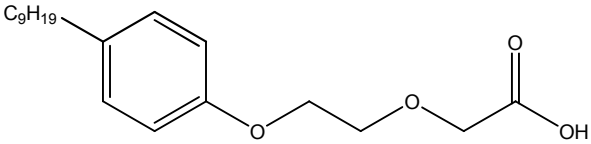
4-nonylphenolmonoethoxylate



4-nonylphenoldiethoxylate



4-nonylphenol-
monoethoxycarboxylate



4-nonylphenoldiethoxycarboxylate

Figure S1 Molecular structure of some of the compounds evaluated.